CHEMICAL THERMODYNAMICS

VOLUME 14

# SECOND UPDATE ON THE CHEMICAL THERMODYNAMICS OF URANIUM, NEPTUNIUM, PLUTONIUM, AMERICIUM AND TECHNETIUM

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# SECOND UPDATE ON THE CHEMICAL THERMODYNAMICS OF URANIUM, NEPTUNIUM, PLUTONIUM, AMERICIUM AND TECHNETIUM


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# CHEMICAL THERMODYNAMICS

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# Foreword

This volume is dedicated to the memory of our dear colleague and friend Professor Ingmar Grenthe, who passed away in January 2020, a few months before completing the editorial work of this book. His motivation, endless energy, and outstanding knowledge of solution chemistry and thermodynamics of the actinides have been essential for the successful completion of this book.

Ingmar was one of the founders of the Nuclear Energy Agency (NEA) Thermochemical Database (TDB) project. He was the chairman of the first volume of the *Chemical Thermodynamic Series* on Uranium [1992GRE/FUG], scientific editor and contributor of the *Modelling in Aquatic Chemistry* book [1997ALL/BAN], reviewer of Volumes 5 (*Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, [2003GUI/FAN]) and 11 (*Chemical thermodynamics of Thorium*, [2008RAN/FUG]), and finally co-chair of Volume 14 (*2nd Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, [2020GRE/GAO]). He made many key contributions in the field of nuclear waste disposal, including as a member of the team that developed the KBS-3 repository concept for the disposal of high-level radioactive waste in Sweden.

The broad research interests of Ingmar went way beyond thermodynamics and extended to coordination chemistry, environmental aquatic chemistry and materials science, among others. He was passionate about the enormous potential of quantum computational chemistry, and was deeply convinced of its ground-breaking impact in a diversity of technology fields. Among many of the honours he received during his career for his scientific achievements, his membership of the Nobel Committee for Chemistry from 1992 to 2001 deserves special mention.

Professor Ingmar Grenthe has made a lasting contribution in the field of actinide chemistry and thermodynamics. He will be fondly remembered by the colleagues fortunate to have worked with him, and the excellence of his work will continually be recognised by future researchers in this field.

Xavier Gaona

Co-chair, on behalf of the NEA-TDB *2nd Update* team

Karlsruhe, April 2020

# Preface

This volume is the fourteenth of the series "Chemical Thermodynamics" edited by the OECD Nuclear Energy Agency (NEA). It is the second update of the critical reviews published, successively, in 1992 as *Chemical Thermodynamics of Uranium* [1992GRE/FUG], in 1995 as *Chemical Thermodynamics of Americium* [1995SIL/BID], in 1999 as *Chemical Thermodynamics of Technetium* [1999RAR/RAN], in 2001 as *Chemical Thermodynamics of Neptunium and Plutonium* [2001LEM/FUG] and in 2003 as the first *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium* [2003GUI/FAN]. The review is mostly based on the literature from 2001 (cut-off date of the first update volume) up to 2015, but with some publications up to 2017. Focus is given to literature that contained new information, but in some cases material already analysed was re-examined in order to include all the data referring to a specific system/problem. In all cases, the arguments leading to a necessary change in previously selected values were carefully considered. There are several differences from the previous reviews:

- The Russian literature is covered much more extensively and includes publications dating back to the 1950s.
- The section on uranium minerals is more extensive than in previous reviews.
- Thermodynamic and structure data obtained by quantum chemical methods are discussed in some detail in order to provide the reader with information on the developments in this rapidly expanding field. No critical review of the pros and cons of the different methods has been made and thermodynamic data based on theory have not been included among the selected values.
- A large number of thermodynamic data for uranium phosphate, arsenate, silicate, vanadate and borate compounds, both anhydrous and hydrated, have been studied by dissolution calorimetry and calorimetric measurements of isobaric heat capacity, $C^{\circ}_{p,\mathrm{m}}(T)$, which makes it possible to compare Gibbs energies of formation obtained from calorimetric and solubility data. Most of these data originate from the same research group at Nizhny Novgorod State University. Data of this type are sensitive towards errors in the water content and the papers rarely report analytical data, and for this reason we found it necessary to provide a detailed discussion of their consistency by using entropy estimates (a method not used in [1992GRE/FUG] and [2003GUI/FAN]) when selecting the thermodynamic data.
- Appendix B has been updated with information on the method to be used for correction of enthalpies of reaction to zero ionic strength. We have also pointed out potential problems with the calculation of ion-interaction

parameters from data in mixed $MClO_4/MCl/MNO_3$ ionic media and in pure MCl and $MNO_3$ media.

- Appendix C has been updated with an introductory text on uncertainty estimates.
- An Appendix D has been added with information on the Latimer method for estimation of entropies.
- New selected thermodynamic data and revisions of previous selected values in Tables 3.1 to 7.3 are denoted with an asterisk "*".

This review was initiated in January 2014 with the appointment of the chairpersons that prepared an initiation report including a literature review in July 2014. The kick-off meeting including all team members was held in February 2015 (at KIT-INE in Karlsruhe, Germany), followed by two plenary meetings in March 2016 (at NEA headquarters in Paris, France) and November 2016 (at JRC in Karlsruhe, Germany).

The review team was composed of scientists with different scientific backgrounds and this is reflected in their review assignments: The solution chemical parts of the uranium chapter was authored by Drs. Linfeng Rao, Andrey Plyasunov and Ingmar Grenthe; the corresponding sections in the neptunium, plutonium and americium chapters by Drs. Xavier Gaona, Linfeng Rao, Wolfgang Runde and Ingmar Grenthe; the technetium chapter by Dr. Bernd Grambow and the various solid state sections by Drs. Rudy Konings, Anna Smith and Emily Moore. It should be noted, however, that all texts have been scrutinised and accepted by the entire review team.

The scientific editing was done by the chairpersons and the technical editing by Drs. Maria-Eleni Ragoussi, Jesus S. Martinez and Davide Costa at the NEA. We acknowledge the participation of Dr. Andrew Felmy, who contributed to an initial draft of the americium chapter, but then left the review team.

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The authors wish to thank the TDB V Management Board, Executive Group and the staff at the OECD Nuclear Energy Agency Data Bank for guidance and help in the completion of this volume. In particular, we are grateful for the assistance of Drs. Maria-Eleni Ragoussi (project co-ordinator and series editor), Jesus S. Martinez (junior expert and volume editor) and Davide Costa (junior expert and volume editor). Dr. Kastriot Spahiu from SKB, Sweden has always been most helpful in dealing with technical and administrative problems that have appeared during our work. We also wish to thank several authors who have contributed with clarifications, both technical and scientific, on questions posed by the review team.

The entire manuscript has undergone a peer review by an independent, international group of reviewers, according to the procedures in the TDB-6 Guidelines, developed by the NEA. The peer-reviewers have seen and approved the modifications made by the authors in response to their comments. The peer review comment records may be obtained on request from the NEA. The peer reviewers were:

Dr. Wolfgang Hummel, Paul Scherrer Institute (PSI), Villigen, Switzerland

Dr. Thomas Vercouter, Atomic Energy and Alternative Energies Commission (CEA), Gif-sur-Yvette, France

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Dr. Christine Guéneau, Atomic Energy and Alternative Energies Commission (CEA), Gif-sur-Yvette, France.

Their valuable contributions to this review are gratefully acknowledged.

# Editor's note

This is Volume 14 of a series of expert reviews of the chemical thermodynamics of key chemical elements in nuclear technology and waste management. This volume is devoted to updating the previously published *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, [2003GUI/FAN]. The tables contained in Chapters 3 to 8 list the currently selected thermodynamic values within the NEA TDB Project. The database system developed at the NEA Data Bank assures consistency among all the selected and auxiliary data sets.

The recommended thermodynamic data are the result of a critical assessment of published information. The values in the auxiliary data set (see Tables 8-1 and 8-2) have been adopted from CODATA key values or have been critically reviewed in this or earlier volumes of the series.

**How to contact the NEA TDB Project**

Information on the NEA and the TDB Project is available at www.oecd-nea.org/dbtdb. Selected data, as well as many documents in electronic format, can also be found on the NEA website.

To contact the TDB Project co-ordinator and the authors of the review reports, send comments on the TDB reviews, or to request further information, please send e-mails to tdb@oecd-nea.org or write to:

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# Part I

# Introductory material

# Chapter 1

# Introduction

## 1.1 Background

In the field of radioactive waste management, hazardous material consists to a large extent of actinides, fission products and activation products from nuclear reactors, in addition to lesser amounts from other sources such as waste from medicine, industry and research facilities. The scientific literature on thermodynamic data, mainly on equilibrium constants and redox potentials in aqueous solution, has been contradictory in a number of cases, especially in actinide chemistry. A critical and comprehensive review of the available literature is necessary to establish a reliable thermochemical database that fulfils the requirements for proper modelling of the behaviour of actinides and fission products in the environment.

Between 1963 and 1967, the International Atomic Energy Agency (IAEA) published three technical reports with thermochemical assessments of the nuclear fuel systems: U-C and Pu-C [1963IAE], $UO_2$ and related phases [1965IAE], and Pu-O and U-Pu-O [1967IAE]. These reports were followed by nine special issues of Atomic Energy Review with compilations of physicochemical properties of compounds and alloys of elements important in reactor technology: Pu, Nb, Ta, Be, Th, Zr, Mo, Hf and Ti. In 1976, the IAEA also started to publish the series "The Chemical Thermodynamics of Actinide Elements and Compounds", oriented towards nuclear engineers and scientists. This international effort resulted in the publication of ten volumes, each concerning the thermodynamic properties of a given type of compounds for the entire actinide series. It should be noted that these volumes only list literature data but do not provide critical reviews of these data. These reviews cover the literature up to about 1984, although the last volume published in this series, Part 12: The Actinide Aqueous Inorganic Complexes [1992FUG/KHO], did not appear until 1992. Unfortunately, four of the reviews planned for inclusion in the IAEA series, reviews of importance for radioactive waste management, were never published (for example, Part 10: The Actinide Oxides and Part 14: Aqueous Organic Complexes).

The Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency (NEA) recognised the need for an internationally acknowledged, high quality thermochemical database for application in the safety assessment of radioactive waste disposal, and undertook the development of the NEA Thermochemical

Data Base (TDB) project [1988WAN], [2003MOM/WAN], [2015RAG/BRA], [2019RAG/COS]. The RWMC assigned high priority to the critical review of relevant chemical thermodynamic data of compounds and complexes containing the actinides uranium, neptunium, plutonium or americium, or the fission product technetium. The first four books in this series on the chemical thermodynamics of uranium [1992GRE/FUG], americium [1995SIL/BID], technetium [1999RAR/RAN] and neptunium and plutonium [2001LEM/FUG] originated from this initiative. In addition a separate text, Modelling in Aquatic chemistry [1997ALL/BAN], was produced that contains the chemical background for the modelling of reactions in aqueous systems and details on methods used to obtain information on the thermodynamics of compounds and complexes. The book also contains examples of transport modelling of radionuclides in surface and ground water systems.

In 1998, Phase II of the TDB Project (TDB-II) was started to meet the requirements of radioactive waste management programmes by updating the existing database and applying the TDB review methodology to other elements (nickel, selenium, zirconium) and to simple organic compounds and complexes. In TDB-II the overall objectives were set by a Management Board, including the representatives of 17 organisations from the field of radioactive waste management. These participating organisations, together with the NEA, provided financial support for TDB-II. The TDB-II Management Board was assisted in technical matters by a group of experts in chemical thermodynamics (the Executive Group). The NEA acted in this phase as Project Co-ordinator ensuring the implementation of the Project Guidelines and liaising with the Review Teams. Five publications resulted from TDB-II: the update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium [2003GUI/FAN], the books on chemical thermodynamics of nickel [2005GAM/BUG], selenium [2005OLI/NOL] and zirconium [2005BRO/CUR] and the volume discussing compounds and complexes of the above mentioned metals with selected organic ligands [2005HUM/AND].

In 2003 TDB-III, the third phase of the Project, began, and it was organised in a way similar to that used for TDB-II. An expert group was constituted to prepare a state-of-the-art report on the chemical thermodynamics of solid solutions of interest in radioactive waste management. That report [2007BRU/BOS] was published as volume 10 of the Chemical Thermodynamics Series. Additionally, three Review Teams were established to focus on the elements thorium, tin and iron. The volumes devoted to inorganic species and compounds of thorium [2008RAN/FUG] and tin [2012GAM/GAJ] have been published as volumes 11 and 12 of the Chemical Thermodynamics Series. However, it was recognised early in Phase III that assessment of the chemical thermodynamics of inorganic species and complexes of iron was too large an endeavour for a single book. Therefore, in 2008 the NEA RWMC and the Executive Group endorsed deferral of the assessment of data for some iron species to Phase IV of the Project. The first of two volumes on iron species and compounds, was the final deliverable from

TDB III, and was published as volume 13a in the Chemical Thermodynamics Series. The fourth phase (2008-2013), included in its programme of work three reviews concerning iron (part 2), molybdenum and ancillary data as well as the initiation of two state-of-the-art reports on cement minerals and high ionic strength solutions. The fifth phase of the TDB project entered into force in 2014. The work programme of TDB-V consisted of the completion of the reviews and state-of-the-art reports initiated in the fourth phase, and the preparation of an update of the phase II actinide volumes, including technetium (this review). The present volume, the fourteenth in the Series, is the second published within TDB-V after the recent release of the *Chemical Thermodynamics of Iron, Part 2* (Volume 13b).

The earlier volumes of the series are listed in the frontispiece of this volume; all of them (including the companion volume on the Modelling in Aquatic Chemistry [1997ALL/BAN]) are available for free on the NEA website: www.oecd-nea.org/dbtdb/info/publications.

Simultaneously with the NEA TDB project, other reviews on the physical and chemical properties of actinides have appeared, including the book by Cordfunke *et al.* [1990COR/KON], the series edited by Freeman *et al.* [1984FRE/LAN], [1985FRE/LAN], [1985FRE/KEL], [1986FRE/KEL], [1987FRE/LAN], and [1991FRE/KEL], Part 12 of the IAEA review series by Fuger *et al.* [1992FUG/KHO] mentioned above and the two comprehensive books by Katz *et al.* [1986KAT/SEA] and Morss *et al.* [2006MOR/EDE] (particularly Chapter 19 [2006KON/MOR]). All the compilations mentioned, although much less detailed than the NEA reviews (particularly with regard to documentation and discussion of published data), are important sources of information, and complement the thermodynamic data contained in the TDB volumes (though only with due regard to consistency).

## 1.2 Focus of the review

This second NEA TDB Update is within the scope and the spirit of previous reviews aimed at helping to model the chemical behaviour of actinides and fission products in the near and far field of a radioactive waste repository using consistent data. The present critical review deals with U, Np, Pu, Am (Cm) and Tc. The data discussed and selected in some cases complement those of the previous reviews and in other cases revise them; they cover both solid compounds and soluble species of these elements. There has been a rapid development both in experimental techniques and theoretical methods to study actinides and other elements both in solution and in the solid state since the start of the NEA TDB project. This is reflected in the current update containing more extensive chemical discussions than in [1992GRE/FUG] and [2003GUI/FAN], which often result in an improved knowledge of the stoichiometry and structure of complexes in solution. However, this information does not always allow the determination of thermodynamic data at zero ionic strength and is therefore not listed in the tables of selected

thermodynamic data. It is very important to be aware of this when using the information in the update for modelling of speciation in models for radionuclide transport in ground and surface water systems, but also in other technical systems. To give an example: the quantitative characterisation of the formation of weak complexes like $UO_2Cl_n^{(2-n)}$ and $UO_2(NO_3)_n^{(2-n)}$ is not straightforward using "traditional" solution chemical methods, but the inclusion of these complexes in chemical models might be very important. This can be assessed by using the equilibrium constants as a "free" parameter to judge under which conditions these complexes are important. To neglect the formation of the complexes may result in a biased and erroneous model.

The literature has been surveyed since the last review [2003GUI/FAN] and contains information until 2015, with some additional references up to 2017. In addition, a large number of Russian studies that were not reviewed in [2003GUI/FAN] have been included. There has been a rapid development in quantum chemical methods and these are able to make accurate predictions of structures of actinide compounds and complexes that often are more detailed than current experimental data. In addition, quantum chemical methods have been used to calculate reaction energies and other thermodynamic data. However, these methods are not accurate enough to compete with experimental information. The present review has found it important to provide information on the development in the quantum chemical field, but the literature survey is not complete and we have had no ambition to make an in-depth analysis of the pros and cons of different quantum chemical methods and models.

Although the focus of the review is on actinides and Tc, it is necessary to use data on a number of other elements during the evaluation process that leads to selected data. These auxiliary data are taken both from the publication of CODATA key values [1989COX/WAG] and from the evaluation of additional auxiliary data in the series of volumes entitled "Chemical Thermodynamics", and their use is recommended by this review. We have also included thermodynamic data from the compilations by Glushko *et al.* in Chapter 14 ([1965GLU/MED]–[1982GLU/GUR]). Care has been taken that all the selected thermodynamic data at standard state and conditions (*cf.* Section 2.3) and 298.15 K are internally consistent. In order to maintain consistency in the application of the values selected by this review, it is essential to use these auxiliary data when calculating equilibrium constants involving actinide compounds and complexes.

This review does not include any compounds and complexes containing organic ligands.

## 1.3 Review procedure and results

The objective of the present review is to update the database for the inorganic species of U, Np, Pu, Am (Cm) and Tc. This aim is achieved by an assessment of the new sources of thermodynamic data published since the cut-off dates for the literature searches in the

earlier volumes of the series. This assessment is performed in order to decide on the most reliable values that can be recommended. Experimental measurements published in the scientific literature are the main source for the selection of recommended data. Previous reviews are not neglected, but form a valuable source of critical information on the quality of primary publications. When necessary, experimental source data are re-evaluated by using chemical models that are either found to be more realistic than those used by the original author, or are consistent with side-reactions discussed in another section of the review (for example, data on carbonate complex formation might need to be re-interpreted to take into account consistent values for hydrolysis reactions). Re-evaluation of literature values might be also necessary to correct for known systematic errors (for example, if the junction potentials are neglected in the original publication) or to make extrapolations to standard state conditions ($I = 0$) by using the specific ion interaction (SIT) equations (*cf.* Appendix B). For convenience, these SIT equations are referred to in some places in the text as "the SIT". In order to ensure that consistent procedures are used for the evaluation of primary data, a number of guidelines have been developed. They have been updated and improved since 1987, and their most recent versions can be downloaded free of charge from the NEA website [2000OST/WAN], [1999WAN/OST], [2000WAN/OST], [1999WAN], [2013GRE/MOM]. Some of these procedures are also outlined in this volume, *cf.* Chapter 2, Appendix B, and Appendix C. Parts of these sections, which were also published in earlier volumes have been revised in this review. Appendix D deals with an empirical method of estimating entropies of solid compounds. The method presented in [1992GRE/FUG] is extended in the present review to cover additional chemical elements.

During the review process, we have identified reactions and their corresponding thermodynamic data for which the experimental information is not sufficient to allow them to be included among the selected values. We have discussed the reasons in the Appendix A section and listed the thermodynamic data in the main text as "for information only"; this information is of interest because it may provide a basis for additional experimental work.

Once the critical review process in the NEA TDB project is completed, the resulting manuscript is reviewed independently by qualified experts nominated by the NEA. The independent peer review is performed according to the procedures outlined in the TDB-6 guideline [1999WAN]. The purpose of the additional peer review is to receive an independent view of the judgements and assessments made by the primary reviewers, to verify assumptions, results and conclusions, and to check whether the relevant literature has been exhaustively considered. The independent peer review is performed by persons having technical expertise in the subject matter to be reviewed, to a degree at least equivalent to that needed for the original review. The thermodynamic data selected in the present review (see Chapters 3, 4, 5, 6, 7, 8 and 14) refer to the reference temperature of 298.15 K and to standard conditions, *cf.* Section 2.3. For the modelling of real systems it is, in general, necessary to recalculate the standard thermodynamic data to

non-standard state conditions. For aqueous species a procedure for the calculation of the activity factors is thus required. This review uses the approximate specific ion interaction method (SIT) for the extrapolation of experimental data to the standard state in the data evaluation process, and in some cases this requires the re-evaluation of original experimental values (solubilities, emf data, *etc.*). For maximum consistency, this method, as described in Appendix B, should always be used in conjunction with the selected data presented in this review. The thermodynamic data selected in this review are provided with uncertainties representing the 95 % confidence level. As discussed in Appendix C, there is no unique way to assign uncertainties, and the assignments made in this review are to a large extent based on the subjective choice by the reviewers, supported by their scientific and technical experience in the corresponding area. The quality of thermodynamic models cannot be better than the quality of the data on which they are based. The quality aspect includes both the numerical values of the thermodynamic data used in the model and the "completeness" of the chemical model used, *e.g.*, the inclusion of all the relevant dissolved chemical species and solid phases. For the user it is important to consider that the selected data set presented in this review (Chapters 3 to 8) is certainly not "complete" with respect to all the conceivable systems and conditions; there are gaps in the information. The gaps are pointed out in the various sections of the present review, and this information may be used as a basis for the assignment of research priorities.

# Chapter 2

# Standards, conventions and contents of the tables

This chapter outlines and lists the symbols, terminology and nomenclature, the units and conversion factors, the order of formulae, the standard conditions, and the fundamental physical constants used in this volume. They are derived from international standards and have been specially adjusted for the Thermochemical Database (TDB) publications.

## 2.1 Symbols, terminology and nomenclature

### 2.1.1 Abbreviations

Abbreviations are mainly used in tables where space is limited. Abbreviations for methods of measurement are listed in Table 2-1.

Table 2-1: Abbreviations for experimental methods.

| | |
|---|---|
| aix | Anion exchange |
| AES | Atomic Emission Spectroscopy |
| BET | Brunauer-Emmett-Teller specific surface area measurement |
| cal | Calorimetry |
| CE | Capillary electrophoresis |
| CZE | Capillary zone-electrophoresis |
| chr | Chromatography |
| cix | Cation exchange |
| col | Colorimetry |
| con | Conductivity |
| cou | Coulometry |
| cry | Cryoscopy |
| dis | Distribution between two phases |
| DSC | Differential Scanning Calorimetry |
| DTA | Differential Thermal Analysis |
| EDS | Energy Dispersive Spectroscopy |
| em | Electromigration |
| $E_{cell}$ | Potential difference of an electrochemical cell |

(Continued on next page)

Table 2-1 (continued)

| | |
|---|---|
| EPMA | Electron Probe Micro Analysis |
| ESR | Electron Spin Resonance Spectroscopy |
| EXAFS | Extended X-ray Absorption Fine Structure |
| FTIR | Fourier Transform Infra Red |
| gl | Glass electrode |
| HEXS | High Intensity X-ray Scattering |
| ICP | Inductively Coupled Plasma |
| IDMS | Isotope Dilution Mass–Spectroscopy |
| IR | Infrared |
| ise–x | Ion selective electrode with ion X stated |
| isop | Isopiestic |
| ix | Ion exchange |
| kin | Rate of reaction |
| LDA | Local Density Approximation |
| LIBD | Laser Induced Breakdown Detection |
| MS | Mass Spectrometry |
| MVD | Molar Volume Determination |
| NMR | Nuclear Magnetic Resonance |
| PAS | Photo Acoustic Spectroscopy |
| pol | Polarography |
| pot | Potentiometry |
| prx | Proton relaxation |
| qh | Quinhydrone electrode |
| red | $E_{cell}$ with redox electrode |
| rin | Refractometry (refractive index measurements) |
| SEM | Scanning Electron Microscopy |
| sp | Spectrophotometry |
| sol | Solubility |
| TC | Transient Conductivity |
| TEM | Transmission Electron Microscopy |
| TGA | Thermo Gravimetric Analysis |
| TLS | Thermal Lensing Spectrophotometry |
| Tj | Temperature jump |
| TRLFS | Time Resolved Laser Fluorescence Spectroscopy |
| UV | Ultraviolet |
| vlt | Voltammetry |
| XANES | X-ray Absorption Near Edge Structure |
| XRD | X-ray Diffraction |
| ? | Method unknown to the reviewers |

Other abbreviations may also be used in tables, such as SHE for the standard hydrogen electrode or SCE for the saturated calomel electrode. The abbreviation NHE has been widely used for the “normal hydrogen electrode”, which is by definition identical to the SHE. It should nevertheless be noted that NHE customarily refers to a standard state pressure of 1 atm, whereas SHE always refers to a standard state pressure of 0.1 MPa (1 bar) in this review.

## 2.1.2 Symbols and terminology

The symbols for physical and chemical quantities used in the TDB review follow the recommendations of the International Union of Pure and Applied Chemistry, IUPAC [1979WHI], [1993MIL/CVI], [2007COH/CVI]. They are summarised in Table 2-2.

Table 2-2: Symbols and terminology.

| Symbols and terminology | |
|---|---|
| length | $l$ |
| height | $h$ |
| radius | $r$ |
| diameter | $d$ |
| volume | $V$ |
| mass | $m$ |
| relative atomic mass | $A_r$ |
| molar mass | $M$ |
| density (mass divided by volume) | $\rho$ |
| molar surface area | $\mathcal{A}$ |
| time | $t$ |
| frequency | $\nu$ |
| wavelength | $\lambda$ |
| internal transmittance (transmittance of the medium itself, disregarding boundary or container influence) | $T$ |
| internal transmission density, (decadic absorbance): $\log_{10}(1/T_i)$ | $A$ |
| molar (decadic) absorption coefficient: $A / c_n l$ | $\varepsilon$ |
| relaxation time | $\tau$ |
| Avogadro constant | $N_A$ |
| relative molecular mass of a substance[(a)] | $M_r$ |
| thermodynamic temperature, absolute temperature | $T$ |
| Celsius temperature | $t$ |
| room temperature | $rt$ |
| (molar) gas constant | $R$ |
| Boltzmann constant | $k_B$ |
| Faraday constant | $F$ |
| (molar) entropy | $S_m$ |
| (molar) heat capacity at constant pressure | $C_{p,m}$ |
| (molar) enthalpy | $H_m$ |
| (molar) Gibbs energy | $G_m$ |
| chemical potential of substance B | $\mu_B$ |
| pressure | $p$ |
| partial pressure of substance B: $x_B p$ | $p_B$ |
| fugacity of substance B | $f_B$ |
| fugacity coefficient: $f_B/p_B$ | $\gamma_{f_B}$ |
| amount of substance[(b)] | $n$ |
| mole fraction of substance B: | $x_B$ |
| molarity or concentration of a solute substance B (amount of B divided by the volume of the solution) [(c)] | $c_B$, [B] |
| molality of a solute substance B (amount of B divided by the mass of the solvent) [(d)] | $m_B$ |
| factor for the conversion of molarity to molality of a solution: $m_B / c_B$ | $\xi$ |

(Continued on next page)

Table 2-2 (continued)

| Symbols and terminology | |
|---|---|
| mean ionic molality [(e)], $m_{\pm}^{(\nu_+ + \nu_-)} = m_+^{\nu_+} m_-^{\nu_-}$ | $m_{\pm}$ |
| activity of substance B [(*)] | $a_B$ |
| activity coefficient, molality basis: $a_B / m_B$ | $\gamma_B$ |
| activity coefficient, concentration basis: $a_B / c_B$ | $y_B$ |
| mean ionic activity [(e)], $a_{\pm}^{(\nu_+ + \nu_-)} = a_B = a_+^{\nu_+} a_-^{\nu_-}$ | $a_{\pm}$ |
| mean ionic activity coefficient [(e)], $\gamma_{\pm}^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$ | $y_{\pm}$ |
| osmotic coefficient, molality basis | $\phi$ |
| ionic strength: $I_m = \frac{1}{2}\sum_i m_i z_i^2$ or $I_c = \frac{1}{2}\sum_i c_i z_i^2$ | $I$ |
| SIT ion interaction coefficient between substance $B_1$ and substance $B_2$) | $\varepsilon(B_1, B_2)$ |
| stoichiometric coefficient of substance B (negative for reactants, positive for products | $\nu_B$ |
| general equation for a chemical reaction | $0 = \sum_B \nu_B B$ |
| equilibrium constant [(f)] | $K$ |
| charge number of an ion B (positive for cations, negative for anions) | $z_B$ |
| charge number of a cell reaction | $n$ |
| Potential difference of an electrochemical cell | $E$ |
| $pH = -\log_{10}[a_{H^+} / (\text{mol}\cdot\text{kg}^{-1})]$ | pH |
| molar conductivity | $\Lambda$ |
| molar conductivity at $I = 0$ | $\Lambda_0$ |
| superscript for standard state [(g)] | $^\circ$ |

(a) Ratio of the average mass per formula unit of a substance to $\frac{1}{12}$ of the mass of an atom of nuclide $^{12}C$.

(b) *cf.* Sections 1.2 and 3.6 of the IUPAC manual [1979WHI].

(c) This quantity is called "amount-of-substance concentration" in the IUPAC manual [1979WHI]. A solution with a concentration equal to 0.1 $\text{mol}\cdot\text{dm}^{-3}$ is called a 0.1 molar solution or a 0.1 M solution.

(d) A solution having a molality equal to 0.1 moles of solute per kg solvent is called a 0.1 molal solution or a 0.1 m solution.

(e) For an electrolyte $N_{\nu_+} X_{\nu_-}$ which dissociates into $\nu_{\pm}$ $(= \nu_+ + \nu_-)$ ions, in an aqueous solution with molality $m$, the individual cationic molality and activity coefficient are $m_+ (= \nu_+ m)$ and $\gamma_+ (= a_+ / m_+)$. A similar definition is used for the anionic symbols. Electrical neutrality requires that $\nu_+ z_+ = \nu_- z_-$.

(f) Special notations for equilibrium constants are outlined in Section 2.1.7. In some cases, $K_c$ is used to indicate a concentration constant in molar units, and $K_m$ a constant in molal units.

(g) See Section 2.3.1.

(*) In many places in this volume $a_W$ has been used as synonym for $a_{H_2O}$.

## 2.1.3 Chemical formulae and nomenclature

This review follows the recommendations made by IUPAC [1971JEN], [1977FER], [1990LEI] on the nomenclature of inorganic compounds and complexes, except for the following items:

- The formulae of co-ordination compounds and complexes are not enclosed in square brackets [1971JEN] (Rule 7.21). Exceptions are made in cases where square brackets are required to distinguish between co-ordinated and unco-ordinated ligands.
- The prefixes "oxy-" and "hydroxy-" are retained if used in a general way, *e.g.*, "gaseous uranium oxyfluorides". For specific formula names, however, the

IUPAC recommended citation [1971JEN] (Rule 6.42) is used, *e.g.*, "uranium(IV) difluoride oxide" for $UF_2O$(cr).

An IUPAC rule that is often not followed by many authors [1971JEN] (Rules 2.163 and 7.21) is recalled here: the order of arranging ligands in co-ordination compounds and complexes is the following: central atom first, followed by ionic ligands and then by the neutral ligands. If there is more than one ionic or neutral ligand, the alphabetical order of the symbols of the ligands determines the sequence of the ligands. For example, $(UO_2)_2CO_3(OH)_3^-$ is standard, $(UO_2)_2(OH)_3CO_3^-$ is not recommended.

It is convenient to have a shorthand method of referring to an ionic medium where the anion concentration is kept constant, but the cation concentrations vary, since such solutions are often used to minimise changes in interionic attractions. For this we enclose the major cation in parentheses. For example, a solution described as "3.00 M (Na)$ClO_4$" could be a mixture of 0.01 M $Th(ClO_4)_4$ and 2.96 M $NaClO_4$ with a total perchlorate concentration of 3.00 M.

Abbreviations of names for organic ligands appear sometimes in formulae. Following the recommendations by IUPAC, lower case letters are used, and if necessary, the ligand abbreviation is enclosed within parentheses. Hydrogen atoms that can be replaced by the metal atom are shown in the abbreviation with an upper case "H", for example: $H_3edta^-$, Am(Hedta)(s) (where edta stands for ethylenediaminetetraacetate).

### 2.1.4 Phase designators

Chemical formulae may refer to different chemical species and are often required to be specified more clearly in order to avoid ambiguities. For example, $UF_4$ occurs as a gas, a solid, and an aqueous complex. The distinction between the different phases is made by phase designators that immediately follow the chemical formula and appear in parentheses. The only formulae that are not provided with a phase designator are aqueous ions. They are the only charged species in this review since charged gases are not considered. The use of the phase designators is described below.

- The designator (l) is used for pure liquid substances, *e.g.*, $H_2O$(l).
- The designator (aq) is used for undissociated, uncharged aqueous species, *e.g.*, $U(OH)_4$(aq), $CO_2$(aq). Since ionic gases are not considered in this review, all ions may be assumed to be aqueous and are not designed with (aq). If a chemical reaction refers to a medium other than $H_2O$ (*e.g.*, $D_2O$, 90% ethanol/10% $H_2O$), then (aq) is replaced by a more explicit designator, *e.g.*, "(in $D_2O$)" or "(sln)". In the case of (sln), the composition of the solution is described in the text.
- The designator (sln) is used for substances in solution without specifying the actual equilibrium composition of the substance in the solution. Note the

difference in the designation of $H_2O$ in Eqs. (2.2) and (2.3). $H_2O(l)$ in Reaction (2.2) indicates that $H_2O$ is present as a pure liquid, *i.e.*, no solutes are present, whereas Reaction (2.3) involves an HCl solution, in which the thermodynamic properties of $H_2O$(sln) may not be the same as those of the pure liquid $H_2O$(l). In dilute solutions, however, this difference in the thermodynamic properties of $H_2O$ can be neglected, and $H_2O$(sln) may be regarded as pure $H_2O$(l).

Example:

$$UO_2Cl_2(cr) + 2\,HBr(sln) \rightleftharpoons UO_2Br_2(cr) + 2\,HCl(sln) \quad (2.1)$$

$$UO_2Cl_2{\cdot}3H_2O(cr) \rightleftharpoons UO_2Cl_2{\cdot}H_2O(cr) + 2\,H_2O(l) \quad (2.2)$$

$$UO_3(\gamma) + 2\,HCl(sln) \rightleftharpoons UO_2Cl_2(cr) + H_2O(sln) \quad (2.3)$$

- The designators (cr), (am), (vit), and (s) are used for solid substances. (cr) is used when it is known that the compound is crystalline, (am) when it is known that it is amorphous, and (vit) for glassy substances. Otherwise, (s) is used.
- In some cases, more than one crystalline form of the same chemical composition may exist. In such a case, the different forms are distinguished by separate designators that describe the forms more precisely. If the crystal has a mineral name, the designator (cr) is replaced by the first four characters of the mineral name in parentheses. If there is no mineral name, the designator (cr) is replaced by a Greek letter preceding the formula and indicating the structural phase, *e.g.*, $\alpha$-$UF_5$, $\beta$-$UF_5$.

Phase designators are also used in conjunction with thermodynamic symbols to define the state of aggregation of a compound to which a thermodynamic quantity refers. The notation is in this case the same as outlined above. In an extended notation (*cf.* [1982LAF]) the reference temperature is usually given in addition to the state of aggregation of the composition of a mixture.

Example:

| | |
|---|---|
| $\Delta_f G_m^o(Na^+, 298.15\ K)$ | standard molar Gibbs energy of formation of aqueous $Na^+$ at 298.15 K |
| $S_m^o(UO_2(SO_4){\cdot}2.5H_2O, cr, 298.15\ K)$ | standard molar entropy of $UO_2(SO_4){\cdot}2.5H_2O$(cr) at 298.15 K |
| $C_{p,m}^o(UO_3, \alpha, 298.15\ K)$ | standard molar heat capacity of $\alpha$-$UO_3$ at 298.15 K |
| $\Delta_f H_m(HF, sln, HF{\cdot}7.8H_2O)$ | enthalpy of formation of HF diluted 1:7.8 with water. |

### 2.1.5 Processes

Chemical processes are denoted by the operator Δ, written before the symbol for a property, as recommended by IUPAC [1982LAF]. An exception to this rule is the equilibrium constant, *cf.* Section 2.1.7. The nature of the process is denoted by annotation of the Δ, *e.g.*, the Gibbs energy of formation, $\Delta_f G_m$, the enthalpy of sublimation, $\Delta_{sub} H_m$, *etc.* The abbreviations of chemical processes are summarised in Table 2-3.

Table 2-3: Abbreviations used as subscripts of Δ to denote the type of chemical process.

| Subscript of Δ | Chemical process |
|---|---|
| at | separation of a substance into its constituent gaseous atoms (atomisation) |
| dehyd | elimination of water of hydration (dehydration) |
| dil | dilution of a solution |
| f | formation of a compound from its constituent elements |
| fus | melting (fusion) of a solid |
| hyd | addition of water of hydration to an unhydrated compound |
| mix | mixing of fluids |
| r | chemical reaction (general) |
| sol | process of dissolution |
| sub | sublimation (evaporation) of a solid |
| tr | transfer from one solution or liquid phase to another |
| trs | transition of one solid phase to another |
| vap | vaporisation (evaporation) of a liquid |

The most frequently used symbols for processes are $\Delta_f G$ and $\Delta_f H$, the Gibbs energy and the enthalpy of formation of a compound or complex from the elements in their reference states (*cf.* Table 2-6).

### 2.1.6 Nomenclature in log terms

It is of course clear that the arguments used in log functions must be dimensionless, and this practice has been used in writing pressures, usually as $\log_{10} p$/bar. However, since the units of the equilibrium constants, $K_m$ and $K_c$, are frequently quite cumbersome, they have been omitted in the log terms of these ( $\log_{10} K_m$ and $\log_{10} K_c$ ) to facilitate reading of the text.

### 2.1.7 Equilibrium constants

IUPAC has not explicitly defined the symbols and terminology for equilibrium constants of reactions in aqueous solution. The NEA TDB Project has therefore adopted the conventions that have been used in the work *Stability Constants of Metal Ion Complexes* by Sillén and Martell [1964SIL/MAR], [1971SIL/MAR]. An outline is given in the paragraphs below. Note that, for some simple reactions, there may be different correct ways to index an equilibrium constant. It may sometimes be preferable

to indicate the number of the reaction to which the data refer, especially in cases where several ligands are discussed that might be confused. For example, for the equilibrium:

$$m\,\mathrm{M} + q\,\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q \tag{2.4}$$

both $\beta_{q,m}$ and $\beta$ (2.4) would be appropriate, and $\beta_{q,m}$ (2.4) is accepted, too. Note that, in general, $K$ is used for the consecutive or stepwise formation constant, and $\beta$ is used for the cumulative or overall formation constant. In the following outline, charges are only given for actual chemical species, but are omitted for species containing general symbols (M, L).

The expressions in sub-Sections 2.1.7.1 through 2.1.7.5 are expressed in terms of (amount substance) concentrations (*i.e.*, $[\mathrm{X}] \equiv c_\mathrm{X}$ and the constants are $K_c$; *cf.* footnote *f* to Table 2-2), but parallel nomenclature has been used in the rest of the review for equilibria expressed using molalities ($K_m$) or using activities in thermodynamic equilibrium constants ($K^\circ$). The units here for

$$K_c = \prod_\mathrm{B} c^{\nu_\mathrm{B}}$$

are $(\mathrm{mol}\cdot\mathrm{dm}^{-3})^{\Sigma_\mathrm{B}\nu_\mathrm{B}}$.

### 2.1.7.1 Protonation of a ligand

$$\mathrm{H}^+ + \mathrm{H}_{r-1}\mathrm{L} \rightleftharpoons \mathrm{H}_r\mathrm{L} \qquad K_{1,r} = \frac{\left[\mathrm{H}_r\mathrm{L}\right]}{\left[\mathrm{H}^+\right]\left[\mathrm{H}_{r-1}\mathrm{L}\right]} \tag{2.5}$$

$$r\,\mathrm{H}^+ + \mathrm{L} \rightleftharpoons \mathrm{H}_r\mathrm{L} \qquad \beta_{1,r} = \frac{\left[\mathrm{H}_r\mathrm{L}\right]}{\left[\mathrm{H}^+\right]^r\left[\mathrm{L}\right]} \tag{2.6}$$

This notation has been proposed and used by Sillén and Martell [1964SIL/MAR], but it has been simplified later by the same authors [1971SIL/MAR] from $K_{1,r}$ to $K_r$.

For the addition of a ligand, the notation shown in Eq. (2.7) is used.

$$\mathrm{HL}_{q-1} + \mathrm{L} \rightleftharpoons \mathrm{HL}_q \qquad K_q = \frac{\left[\mathrm{HL}_q\right]}{\left[\mathrm{HL}_{q-1}\right]\left[\mathrm{L}\right]} \tag{2.7}$$

Eq. (2.8) refers to the overall formation constant of the species $\mathrm{H}_r\mathrm{L}_q$.

$$r\,\mathrm{H}^+ + q\,\mathrm{L} \rightleftharpoons \mathrm{H}_r\mathrm{L}_q \qquad \beta_{q,r} = \frac{\left[\mathrm{H}_r\mathrm{L}_q\right]}{\left[\mathrm{H}^+\right]^r\left[\mathrm{L}\right]^q} \tag{2.8}$$

In Eqs. (2.5), (2.6) and (2.8), the second subscript *r* can be omitted if *r* = 1, as shown in Eq. (2.7).

Example:

$$H^+ + PO_4^{3-} \rightleftharpoons HPO_4^{2-} \qquad \beta_{1,1} = \beta_1 = \frac{[HPO_4^{2-}]}{[H^+][PO_4^{3-}]}$$

$$2\,H^+ + PO_4^{3-} \rightleftharpoons H_2PO_4^- \qquad \beta_{1,2} = \frac{[H_2PO_4^-]}{[H^+]^2[PO_4^{3-}]}$$

#### 2.1.7.2 Formation of metal complexes

$$ML_{q-1} + L \rightleftharpoons ML_q \qquad K_q = \frac{[ML_q]}{[ML_{q-1}][L]} \tag{2.9}$$

$$M + q\,L \rightleftharpoons ML_q \qquad \beta_q = \frac{[ML_q]}{[M][L]^q} \tag{2.10}$$

For the addition of a metal ion, *i.e.*, the formation of polynuclear complexes, the following notation is used, analogous to Eq. (2.5):

$$M + M_{m-1}L \rightleftharpoons M_mL \qquad K_{1,m} = \frac{[M_mL]}{[M][M_{m-1}L]} \tag{2.11}$$

Eq. (2.12) refers to the overall formation constant of a complex $M_mL_q$.

$$m\,M + q\,L \rightleftharpoons M_mL_q \qquad \beta_{q,m} = \frac{[M_mL_q]}{[M]^m[L]^q} \tag{2.12}$$

The second index can be omitted if it is equal to 1, *i.e.*, $\beta_{q,m}$ becomes $\beta_q$ if $m = 1$. The formation constants of mixed ligand complexes are not indexed. In this case, it is necessary to list the chemical reactions considered and to refer the constants to the corresponding reaction numbers.

It has sometimes been customary to use negative values for the indices of the protons to indicate complexation with hydroxide ions, $OH^-$. This practice is not adopted in this review. If $OH^-$ occurs as a reactant in the notation of the equilibrium, it is treated like a normal ligand L, but in general formulae the index variable $n$ is used instead of $q$. If $H_2O$ occurs as a reactant to form hydroxide complexes, $H_2O$ is considered as a protonated ligand, HL, so that the reaction is treated as described below in Eqs. (2.13) to (2.15) using $n$ as the index variable. For convenience, no general form is used for the stepwise constants for the formation of the complex $M_mL_qH_r$. In many experiments, the formation constants of metal ion complexes are determined by adding a ligand in its protonated form to a metal ion solution. The complex formation reactions

thus involve a deprotonation reaction of the ligand. If this is the case, the equilibrium constant is supplied with an asterisk, as shown in Eqs. (2.13) and (2.14) for mononuclear and in Eq. (2.15) for polynuclear complexes.

$$\mathrm{ML}_{q-1} + \mathrm{HL} \rightleftharpoons \mathrm{ML}_q + \mathrm{H}^+ \qquad {}^*K_q = \frac{[\mathrm{ML}_q][\mathrm{H}^+]}{[\mathrm{ML}_{q-1}][\mathrm{HL}]} \tag{2.13}$$

$$\mathrm{M} + q\,\mathrm{HL} \rightleftharpoons \mathrm{ML}_q + q\mathrm{H}^+ \qquad {}^*\beta_q = \frac{[\mathrm{ML}_q][\mathrm{H}^+]^q}{[\mathrm{M}][\mathrm{HL}]^q} \tag{2.14}$$

$$m\,\mathrm{M} + q\,\mathrm{HL} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q + q\mathrm{H}^+ \qquad {}^*\beta_{q,m} = \frac{[\mathrm{M}_m\mathrm{L}_q][\mathrm{H}^+]^q}{[\mathrm{M}]^m[\mathrm{HL}]^q} \tag{2.15}$$

Example:

$$\mathrm{UO_2^{2+}} + \mathrm{HF(aq)} \rightleftharpoons \mathrm{UO_2F^+} + \mathrm{H^+} \qquad {}^*K_1 = {}^*\beta_1 = \frac{[\mathrm{UO_2F^+}][\mathrm{H^+}]}{[\mathrm{UO_2^{2+}}][\mathrm{HF(aq)}]}$$

$$3\,\mathrm{UO_2^{2+}} + 5\,\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{UO_2})_3(\mathrm{OH})_5^+ + 5\,\mathrm{H^+} \qquad {}^*\beta_{5,3} = \frac{[(\mathrm{UO_2})_3(\mathrm{OH})_5^+][\mathrm{H^+}]^5}{[\mathrm{UO_2^{2+}}]^3}$$

Note that an asterisk is only assigned to the formation constant if the protonated ligand that is added is deprotonated during the reaction. If a protonated ligand is added and co-ordinated as such to the metal ion, the asterisk is to be omitted, as shown in Eq. (2.16).

$$\mathrm{M} + q\,\mathrm{H}_r\mathrm{L} \rightleftharpoons \mathrm{M(H}_r\mathrm{L)}_q \qquad \beta_q = \frac{[\mathrm{M(H}_r\mathrm{L)}_q]}{[\mathrm{M}][\mathrm{H}_r\mathrm{L}]^q} \tag{2.16}$$

Example:

$$\mathrm{UO_2^{2+}} + 3\,\mathrm{H_2PO_4^-} \rightleftharpoons \mathrm{UO_2(H_2PO_4)_3^-} \qquad \beta_3 = \frac{[\mathrm{UO_2(H_2PO_4)_3^-}]}{[\mathrm{UO_2^{2+}}][\mathrm{H_2PO_4^-}]^3}$$

#### 2.1.7.3 Solubility constants

Conventionally, equilibrium constants involving a solid compound are denoted as "solubility constants" rather than as formation constants of the solid. An index "s" to the equilibrium constant indicates that the constant refers to a solubility process, as shown in Eqs. (2.17) to (2.19).

$$\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) \rightleftharpoons a\,\mathrm{M} + b\,\mathrm{L} \qquad K_{\mathrm{s},0} = [\mathrm{M}]^a[\mathrm{L}]^b \tag{2.17}$$

$K_{s,0}$ is the conventional solubility product, and the subscript "0" indicates that the equilibrium reaction involves only uncomplexed aqueous species. If the solubility constant includes the formation of aqueous complexes, a notation analogous to that of Eq. (2.12) is used:

$$\frac{m}{a}\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) \rightleftharpoons \mathrm{M}_m\mathrm{L}_q + \left(\frac{mb}{a} - q\right)\mathrm{L} \qquad K_{s,q,m} = \left[\mathrm{M}_m\mathrm{L}_q\right]\left[\mathrm{L}\right]^{\left(\frac{mb}{a}-q\right)} \tag{2.18}$$

Example:

$$\mathrm{UO_2F_2(cr)} \rightleftharpoons \mathrm{UO_2F^+ + F^-} \qquad K_{s,1,1} = K_{s,1} = \left[\mathrm{UO_2F^+}\right]\left[\mathrm{F^-}\right] \ .$$

Similarly, an asterisk is added to the solubility constant if it simultaneously involves a protonation equilibrium:

$$\frac{m}{a}\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) + \left(\frac{mb}{a} - q\right)\mathrm{H^+} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q + \left(\frac{mb}{a} - q\right)\mathrm{HL}$$

$$^{*}K_{s,q,m} = \frac{\left[\mathrm{M}_m\mathrm{L}_q\right]\left[\mathrm{HL}\right]^{\left(\frac{mb}{a}-q\right)}}{\left[\mathrm{H^+}\right]^{\left(\frac{mb}{a}-q\right)}} \tag{2.19}$$

Example:

$$\mathrm{U(HPO_4)_2{\cdot}4H_2O(cr) + H^+ \rightleftharpoons UHPO_4^{2+} + H_2PO_4^- + 4\,H_2O(l)}$$

$$^{*}K_{s,1,1} = {}^{*}K_{s,1} = \frac{\left[\mathrm{UHPO_4^{2+}}\right]\left[\mathrm{H_2PO_4^-}\right]}{\left[\mathrm{H^+}\right]}.$$

#### 2.1.7.4 Equilibria involving the addition of a gaseous ligand

A special notation is used for constants describing equilibria that involve the addition of a gaseous ligand, as outlined in Eq. (2.20).

$$\mathrm{ML}_{q-1} + \mathrm{L(g)} \rightleftharpoons \mathrm{ML}_q \qquad K_{p,q} = \frac{\left[\mathrm{ML}_q\right]}{\left[\mathrm{ML}_{q-1}\right]p_{\mathrm{L}}} \tag{2.20}$$

The subscript "$p$" can be combined with any other notations given above.

Example:

$$\mathrm{CO_2(g) \rightleftharpoons CO_2(aq)} \qquad K_p = \frac{\left[\mathrm{CO_2(aq)}\right]}{p_{\mathrm{CO_2}}}$$

$$\mathrm{3\,UO_2^{2+} + 6\,CO_2(g) + 6\,H_2O(l) \rightleftharpoons (UO_2)_3(CO_3)_6^{6-} + 12\,H^+}$$

$$ {}^{*}\beta_{p,6,3} = \frac{\left[(UO_2)_3(CO_3)_6^{6-}\right]\left[H^+\right]^{12}}{\left[UO_2^{2+}\right]^3 \; p_{CO_2}^6} $$

$$ UO_2CO_3(cr) + CO_2(g) + H_2O(l) \rightleftharpoons UO_2(CO_3)_2^{2-} + 2H^+ $$

$$ {}^{*}K_{p,s,2} = \frac{\left[UO_2(CO_3)_2^{2-}\right]\left[H^+\right]^2}{p_{CO_2}} $$

In cases where the subscripts become complicated, it is recommended that $K$ or $\beta$ be used with or without subscripts, but always followed by the equation number of the equilibrium to which it refers.

#### 2.1.7.5 Redox equilibria

Redox reactions are usually quantified in terms of their electrode (half cell) potential, $E$, which is identical to the potential difference of a galvanic cell in which the electrode on the left is the standard hydrogen electrode, SHE[1], in accordance with the "1953 Stockholm Convention" [1993MIL/CVI]. Therefore, electrode potentials are given as reduction potentials relative to the standard hydrogen electrode, which acts as an electron donor. In the standard hydrogen electrode, $H_2(g)$ is at unit fugacity (an ideal gas at unit pressure, 0.1 MPa), and $H^+$ is at unit activity. The sign of the electrode potential, $E$, is that of the observed sign of its polarity when coupled with the standard hydrogen electrode. The standard electrode potential, $E^\circ$, *i.e.*, the potential of a standard galvanic cell relative to the standard hydrogen electrode (all components in their standard state, *cf.* Section 2.3.1, and with no liquid junction potential) is related to the standard Gibbs energy change $\Delta_r G_m^\circ$ and the standard (or thermodynamic) equilibrium constant $K^\circ$ as outlined in Eq. (2.21):

$$ E^\circ = -\frac{1}{nF}\Delta_r G_m^\circ = \frac{RT}{nF}\ln K^\circ \tag{2.21} $$

and the potential, $E$, is related to $E^\circ$ by:

$$ E = E^\circ - (RT/nF)\sum \nu_i \ln a_i . \tag{2.22} $$

For example, for the hypothetical galvanic cell:

$$ \mathrm{Pt} \;\vert\; H_2(g, p = 1\ \mathrm{bar}) \;\vert\; \mathrm{HCl}(aq, a_{H^+} = 1,\ f_{H_2} = 1) \;\vdots\; \begin{matrix} Fe(ClO_4)_2\,(aq, a_{Fe^{2+}} = 1) \\ Fe(ClO_4)_3\,(aq, a_{Fe^{3+}} = 1) \end{matrix} \;\vert\; \mathrm{Pt} \tag{2.23} $$

where $\vdots$ denotes a liquid junction and $\vert$ a phase boundary, the reaction is:

[1] The definitions of SHE and NHE are given in Section 2.1.1.

$$Fe^{3+} + 1/2\,H_2(g) \rightleftharpoons Fe^{2+} + 2\,H^+ \tag{2.24}$$

Formally Reaction (2.24) can be represented by two half cell reactions, each involving an equal number of electrons, (designated "$e^-$"), as shown in the following equations:

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \tag{2.25}$$

$$1/2\,H_2(g) \rightleftharpoons H^+ + e^- \tag{2.26}$$

The terminology is useful, although it must be emphasised "$e^-$" here does not represent the hydrated electron.

Equilibrium (2.26) and Nernst law can be used to introduce $a_{e^-}$:

$$E = E^o(2.26) + \frac{RT}{F}\ln(\sqrt{f_{H_2}} / (a_{H^+} a_{e^-})) \tag{2.27}$$

According to the SHE convention $E^o(2.26) = 0$, $f_{H_2} = 1$, $a_{H^+} = 1$, hence

$$E = -\frac{RT}{F}\ln a_{e^-} \tag{2.28}$$

This equation is used to calculate a numerical value of $a_{e^-}$ from potential-difference measurements *vs.* the SHE; hence, as for the value of $E$ (V *vs.* the SHE), the numerical value of $a_{e^-}$ depends on the SHE convention. Equilibrium constants may be written for these half cell reactions in the following way:

$$K^o(2.25) = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}} \cdot a_{e^-}} \tag{2.29}$$

$$K^o(2.26) = \frac{a_{H^+} \cdot a_{e^-}}{\sqrt{f_{H_2}}} = 1 \quad \text{(by definition)} \tag{2.30}$$

In addition, $\Delta_r G_m^o(2.26) = 0$, $\Delta_r H_m^o(2.26) = 0$, $\Delta_r S_m^o(2.26) = 0$ by definition, at all temperatures, and therefore $\Delta_r G_m^o(2.25) = \Delta_r G_m^o(2.24)$. From $\Delta_r G_m^o(2.26)$ and the values given at 298.15 K in selected auxiliary data for $H_2(g)$ and $H^+$, the corresponding values for $e^-$ can be calculated to be used in thermodynamic cycles involving half cell reactions. The following equations describe the change in the redox potential of Reaction (2.24), if $p_{H_2}$ and $a_{H^+}$ are equal to unity *(cf.* Eq. (2.22)):

$$E(2.24) = E^o(2.24) - RT\ln\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right) \tag{2.31}$$

For the standard hydrogen electrode $a_{e^-} = 1$ (by the convention expressed in Eq. (2.30)), while rearrangement of Eq. (2.29) for the half cell containing the iron perchlorates in cell (2.23) gives:

$$-\log_{10} a_{e^-} = \log_{10} K^{o}(2.25) - \log_{10}\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right)$$

and from Eq. (2.27):

$$-\log_{10} a_{e^-} = \log_{10} K^{o}(2.24) - \log_{10}\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right) \tag{2.32}$$

and

$$-\log_{10} a_{e^-} = \frac{F}{RT\ln(10)} E(2.24) \tag{2.33}$$

which is a specific case of the general Equation (2.28).

The splitting of redox reactions into two half cell reactions by introducing the symbol "$e^-$", which according to Eq. (2.27) is related to the standard electrode potential, is arbitrary, but useful. When calculating the equilibrium composition of a chemical system, both "$e^-$", and $H^+$ can be chosen as components and they can be treated numerically in a similar way: equilibrium constants, mass balance, *etc.* may be defined for both. However, while $H^+$ represents the hydrated proton in aqueous solution, the above equations use only the activity of "$e^-$", and never the concentration of "$e^-$". Concentration to activity conversions (or activity coefficients) are never needed for the electron (*cf.* Appendix B, Example B.3).

In the literature on geochemical modelling of natural waters, it is customary to represent the "electron activity" of an aqueous solution with the symbol "pe" or "p$\varepsilon$" ($=-\log_{10} a_{e^-}$) by analogy with pH ($=-\log_{10} a_{H^+}$), and the redox potential of an aqueous solution relative to the standard hydrogen electrode is usually denoted by either "Eh" or "$E_H$" (see for example [1981STU/MOR], [1982DRE], [1984HOS], [1986NOR/MUN]).

In this review, the symbol $E'^{o}$ is used to denote the so-called "formal potential" [1974PAR]. The formal (or "conditional") potential can be regarded as a standard potential for a particular medium in which the activity coefficients are independent (or approximately so) of the reactant concentrations [1985BAR/PAR] (the definition of $E'^{o}$ parallels that of "concentration quotients" for equilibria). Therefore, from

$$E = E'^{o} - \frac{RT}{nF}\sum \nu_i \ln c_i \tag{2.34}$$

$E'^{o}$ is the potential $E$ for a cell when the ratio of the *concentrations* (not the activities) on the right-hand side and the left-hand side of the cell reaction is equal to unity, and

$$E_c'^{o} = E_c^{o} - \frac{RT}{nF}\sum \nu_i \ln \gamma_{c,i} \tag{2.35}$$

$$E_c^{'o} = E_c^o - \frac{RT}{nF} \sum \nu_i \ln(\xi \cdot \gamma_{m,i} \cdot \rho^*_{H_2O}) \quad (2.36)$$

$$\gamma_{c,i} = \left( \frac{m_i / m^o}{c_i / c^o} \right) (\rho^*_{H_2O} / \rho^o) \gamma_{m,i} \quad (2.37)^1$$

where the $\gamma_{c,i}$ and $\gamma_{m,i}$ are the activity coefficients on amount concentration and molality basis, respectively [2008GAM/LOR], related by Eq. (2.37), $\rho^*_{H_2O}$ is the density of pure water, and $\xi$ is $(m_i/c_i)$, the ratio of molality to molarity (*cf.* Section 2.2). The medium must be specified. Equation (2.37) has been derived most elegantly by [1959ROB/STO].

## 2.1.8 pH

Because of the importance that potentiometric methods have in the determination of equilibrium constants in aqueous solutions, a short discussion on the definition of "pH" and a simplified description of the experimental techniques used to measure pH will be given here. For a comprehensive account, see [2002BUC/RON].

The acidity of aqueous solutions is often expressed in a logarithmic scale of the hydrogen ion activity. The definition of pH as:

$$\text{pH} = -\log_{10} a_{H^+} = -\log_{10} (m_{H^+} \gamma_{H^+})$$

can only be strictly used in the range of the limiting Debye-Hückel equation (that is, in extremely dilute solutions). In practice the use of pH values requires extra assumptions as to the values for single ion activities. In this review, values of pH are used to describe qualitatively the ranges of acidity of experimental studies, and the assumptions described in Appendix B are used to calculate single ion activity coefficients.

The determination of pH is often performed by potential-difference measurements of galvanic cells involving liquid junctions [1969ROS], [1973BAT]. A common setup is a cell made up of a reference half cell (*e.g.*, Ag(s)|AgCl(s) in a solution of constant chloride concentration), a salt bridge, the test solution, and a glass electrode (which encloses a solution of constant acidity and an internal reference half cell):

| Pt(s) | Ag(s) | AgCl(s) | KCl(sln) | salt bridge | test solution | KCl(sln) | AgCl(s) | Ag(s) | Pt(s) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | *a* | *b* | | | | |

(2.38)

where ||| stands for a glass membrane (permeable to hydrogen ions).

---

1 $\rho^*_{H_2O}$ is a variable depending on $T$, $m^o$ = 1 mol·kg$^{-1}$, $c^o$ = 1 mol·dm$^{-3}$.

The potential difference of such a cell is given by:

$$E = E^* - \frac{RT}{nF} \ln a_{H^+} + E_j$$

where $E^*$ is a constant, and $E_j$ is the liquid junction potential. The purpose of the salt bridge is to minimise the junction potential in junction "*b*", while keeping constant the junction potential for junction "*a*". Two methods are most often used to reduce and control the value of $E_j$. An electrolyte solution of *high* concentration (the "salt bridge") is a requirement of both methods. In the first method, the salt bridge is a saturated (or nearly saturated) solution of potassium chloride. A problem with a bridge of high potassium concentration is that potassium perchlorate might precipitate[1] inside the liquid junction when the test solution contains a high concentration of perchlorate ions.

In the other method the salt bridge contains the same *high* concentration of the same inert electrolyte as the test solution (for example, 3 M $NaClO_4$). However, if the concentration of the background electrolyte in the salt bridge and test solutions is reduced, the values of $E_j$ are dramatically increased. For example, if both the bridge and the test solution have $[ClO_4^-]$ = 0.1 M as background electrolyte, the dependence of the liquid junction at "*b*" on acidity is $E_j \approx -440\,[H^+]$ mV·dm$^3$·mol$^{-1}$ at 25 °C [1969ROS] (p.110), which corresponds to an error of ≥ 0.07 in pH at a pH value of 2.

Because of the problems in eliminating the liquid junction potentials and in defining individual ionic activity coefficients, an "operational" definition of pH is given by IUPAC [1993MIL/CVI]. This definition involves the measurement of pH differences between the test solution and standard solutions of known pH and similar ionic strength (in this way similar values of $\gamma_{H^+}$ and $E_j$ cancel each other when potential-difference values are subtracted).

Another method of determining the molal $H^+$ concentration, $\log_{10} m_{H^+}$, in chloride solutions up to high ionic strength was proposed by Knauss *et al.* [1990KNA/WOL]. The activity of HCl ($a_{HCl}$) can be measured with a liquid junction free cell consisting of a $H^+$ sensitive glass electrode and a chloride sensitive electrode from the relation:

$$\log_{10} a_{HCl} = ½ (\log_{10} m_{H^+} + \log_{10} m_{Cl^-} + \log_{10} \gamma_{H^+} + \log_{10} \gamma_{Cl^-}) \qquad (2.39)$$

The value of $\log_{10} m_{H^+}$ in the test solution can then be derived from the measured value of $\log_{10} a_{HCl}$, the given chloride concentration $\log_{10} m_{Cl^-}$ and the activity coefficients $\log_{10} \gamma_{H^+}$ and $\log_{10} \gamma_{Cl^-}$ which can be calculated either with the SIT or, for higher chloride concentrations, with the Pitzer equations as proposed by [1990KNA/WOL].

The measurement and use of pH in equilibrium analytical investigations creates many problems that have not always been taken into account by the

[1] $KClO_4$(cr) has a solubility of ≈ 0.15 M in pure water at 25 °C.

investigators, as discussed in many reviews in Appendix A. In order to deduce the stoichiometry and equilibrium constants of complex formation reactions and other equilibria, it is necessary to vary the concentrations of reactants and products over fairly large concentration ranges under conditions where the activity coefficients of the species are either known, or constant. Only in this manner is it possible to use the mass balance equations for the various components together with the measurement of one or more free concentrations to obtain the information desired [1961ROS/ROS], [1990BEC/NAG], [1997ALL/BAN], pp. 326–327. For equilibria involving hydrogen ions, it is necessary to use concentration units, rather than hydrogen ion activity. For experiments in an ionic medium, where the concentration of an "inert" electrolyte is much larger than the concentration of reactants and products we can ensure that, as a first approximation, their trace activity coefficients remain constant even for moderate variations of the corresponding total concentrations. Under these conditions of fixed ionic strength the free proton concentration may be measured directly, thereby defining it in terms of $-\log_{10}[H^+]$ (also often referred to as $pC_H$, $p[H^+]$ or $pH_c$, and correspondingly $pH_m$ for $\log_{10} m_{H^+}$) rather than on the activity scale as pH, and the value of $-\log_{10}[H^+]$ and pH will differ by a constant term, *i.e.*, $\log_{10} \gamma_{H^+}$. Equilibrium constants deduced from measurements in such ionic media are therefore *conditional* constants, because they refer to the given medium, not to the standard state. In order to compare the magnitude of equilibrium constants obtained in different ionic media it is necessary to have a method for estimating activity coefficients of ionic species in mixed electrolyte systems to a *common* standard state. Such procedures are discussed in Appendix B.

Note that the precision of the measurement of $-\log_{10}[H^+]$ and pH is virtually the same, in very good experiments, $\pm 0.001$. However, the accuracy is generally considerably poorer, depending in the case of glass electrodes largely on the response of the electrode (linearity, age, pH range, *etc.*), and to a lesser extent on the calibration method employed, although the stoichiometric $-\log_{10}[H^+]$ calibration standards can be prepared far more accurately than the commercial pH standards.

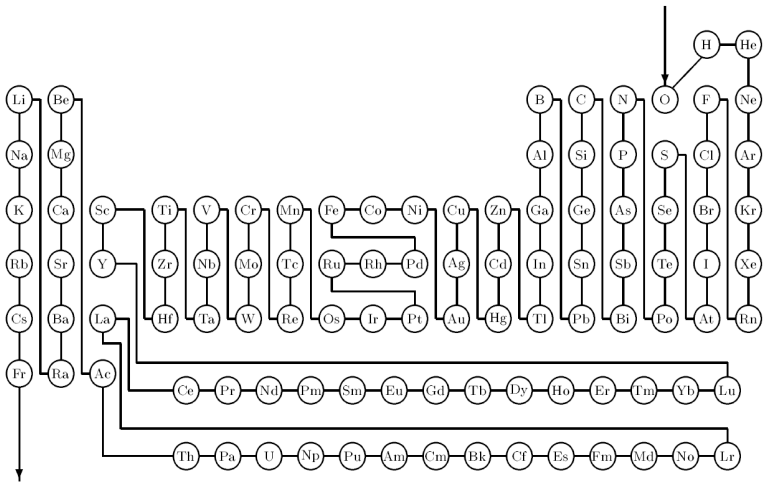
### 2.1.9 Order of formulae

To be consistent with CODATA, the data tables are given in "*Standard Order of Arrangement*" [1982WAG/EVA]. This scheme is presented in Figure 2-1 below, and shows the sequence of the ranks of the elements in this convention. The order follows the ranks of the elements.

For example, for uranium, this means that, after elemental uranium and its monoatomic ions (*e.g.*, $U^{4+}$), the uranium compounds and complexes with oxygen would be listed, then those with hydrogen, then those with oxygen and hydrogen, and so on, with decreasing rank of the element and combinations of the elements. Within a class, increasing coefficients of the higher rank elements go before increasing

coefficients of the lower rank elements. For example, in the U-O-F class of compounds and complexes, a typical sequence would be $UOF_2$(cr), $UOF_4$(cr), $UOF_4$(g), $UO_2F$(aq), $UO_2F^+$, $UO_2F_2$(aq), $UO_2F_2$(cr), $UO_2F_2$(g), $UO_2F_3^-$, $UO_2F_4^{2-}$, $U_2O_3F_6$(cr), *etc.* [1992GRE/FUG]. Formulae with identical stoichiometry are in alphabetical order of their designators.

Figure 2-1: Standard order of arrangement of the elements and compounds based on the periodic classification of the elements (from [1982WAG/EVA]).




### 2.1.10 Reference codes

The references cited in the review are ordered chronologically and alphabetically by the first two authors within each year, as described by CODATA [1987GAR/PAR]. A reference code is made up of the four digits of the year of appearance, followed by the first three letters of the surnames of the first two authors, separated by a slash.

If there are multiple reference codes, a "2" will be added to the second one, a "3" to the third one, and so forth. Reference codes are always enclosed in square brackets.

## 2.2 Units and conversion factors

Thermodynamic data are given according to the *Système International d'unités* (SI units). The unit of energy is the joule. Some basic conversion factors, also for non-thermodynamic units, are given in Table 2-4.

Table 2-4: Unit conversion factors.

| To convert from (non–SI unit symbol) | to (SI unit symbol) | multiply by |
|---|---|---|
| ångström (Å) | metre (m) | $1\times10^{-10}$ (exactly) |
| standard atmosphere (atm) | pascal (Pa) | $1.01325\times10^{5}$ (exactly) |
| bar (bar) | pascal (Pa) | $1\times10^{5}$ (exactly) |
| thermochemical calorie (cal) | joule (J) | 4.184 (exactly) |
| entropy unit e.u. $\triangleq$ cal·K$^{-1}$·mol$^{-1}$ | J·K·mol$^{-1}$ | 4.184 (exactly) |

Since a large part of the NEA TDB Project deals with the thermodynamics of aqueous solutions, the units describing the amount of dissolved substance are used very frequently. For convenience, this review uses "M" as an abbreviation of "mol·dm$^{-3}$" for molarity, $c$, and, in Appendices B and C, "m" as an abbreviation of "mol·kg$^{-1}$" for molality, $m$. It is often necessary to convert data from molarity to molality and *vice versa*. This conversion is used for the correction and extrapolation of equilibrium data to zero ionic strength by the specific ion interaction treatment, which works on molality basis (*cf.* Appendix B). This conversion is made in the following way.

Molality[1], $m_B$, is defined as the amount of substance, $n_B$ dissolved in the mass of pure solvent, $m_A$, which in most cases is pure water

$$m_B = n_B / m_A .$$

Molarity (concentration), $c_B$, is defined as the amount of substance, $n_B$, dissolved in the volume, $V$, of solution

$$c_B = n_B / V.$$

Density of solution, $\rho$, is given by mass of solution divided by its volume,

$$\rho = ( n_B M_B + m_A )/V$$

where $M$ is the molar mass of the solute.

From this it follows that:

$$m_B = \frac{c_B}{\rho - c_B M_B} .$$

When the ionic strength is kept high and constant by an inert electrolyte, I, the ratio $m_B/c_B$ can be approximated by

$$\frac{m_B}{c_B} = \frac{1}{\rho - c_I M_I}$$

where $c_I$ is the concentration of the inert electrolyte and $M_I$ its molar mass.

[1] In this derivation the symbol $m$ is used with two different meanings: $m_B$ denotes the *molality* of solute B and $m_A$ denotes the *mass* of solvent A.

Baes and Mesmer [1976BAE/MES], (*p*.439) give a table with conversion factors (from molarity to molality) for nine electrolytes at various ionic strengths. Conversion factors at 298.15 K for twenty one electrolytes, calculated using the density equations reported by Söhnel and Novotný [1985SOH/NOV], are reported in Table 2-5.

Example:

$$1.00\ \text{M}\ NaClO_4 \triangleq 1.05\ \text{m}\ NaClO_4$$
$$1.00\ \text{M}\ NaCl \triangleq 1.02\ \text{m}\ NaCl$$
$$4.00\ \text{M}\ NaClO_4 \triangleq 4.95\ \text{m}\ NaClO_4$$
$$6.00\ \text{M}\ NaNO_3 \triangleq 7.55\ \text{m}\ NaNO_3$$

It should be noted that equilibrium constants need also to be converted if the concentration scale is changed from molarity to molality or *vice versa*. For a general equilibrium reaction, $0 = \sum_B \nu_B B$, the equilibrium constants can be expressed either in molarity or molality units, $K_c$ or $K_m$, respectively:

$$\log_{10} K_c = \sum_B \nu_B \log_{10} c_B$$
$$\log_{10} K_m = \sum_B \nu_B \log_{10} m_B$$

With $(m_B/c_B) = \xi$, or $(\log_{10} m_B - \log_{10} c_B) = \log_{10} \xi$, the relationship between $K_c$ and $K_m$ becomes very simple, as shown in Eq. (2.40).

$$\log_{10} K_m = \log_{10} K_c + \sum_B \nu_B \log_{10} \xi \qquad (2.40)$$

$\sum_B \nu_B$ is the sum of the stoichiometric coefficients of the solutes and the values of $\xi$ are the factors for the conversion of molarity to molality as tabulated in Table 2-5 for several electrolyte media at 298.15 K. The differences between the values in Table 2-5 and the values listed in the uranium NEA TDB review [1992GRE/FUG] (*p*.23) are found at the highest concentrations, and are no larger than ± 0.003 $dm^3 \cdot kg^{-1}$, reflecting the accuracy expected in this type of conversion. The uncertainty introduced by the use of Eq. (2.40) in the values of $\log_{10} K_m$ will be no larger than ± 0.001 $\sum_B \nu_B$.

Table 2-5: Factors $\xi$ for the conversion of molarity, $c_B$, to molality, $m_B$, of a substance B, in various media at 298.15 K (calculated from densities in [1985SOH/NOV]).

| | $\xi = m_B / c_B$ ($dm^3$ of solution per kg of $H_2O$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $c$ (M) | $HClO_4$ | $NaClO_4$ | $LiClO_4$ | $NH_4ClO_4$ | $Ba(ClO_4)_2$ | HCl | NaCl | LiCl |
| 0.10 | 1.0077 | 1.0075 | 1.0074 | 1.0091 | 1.0108 | 1.0048 | 1.0046 | 1.0049 |
| 0.25 | 1.0147 | 1.0145 | 1.0141 | 1.0186 | 1.0231 | 1.0076 | 1.0072 | 1.0078 |
| 0.50 | 1.0266 | 1.0265 | 1.0256 | 1.0351 | 1.0450 | 1.0123 | 1.0118 | 1.0127 |
| 0.75 | 1.0386 | 1.0388 | 1.0374 | 1.0523 | 1.0685 | 1.0172 | 1.0165 | 1.0177 |
| 1.00 | 1.0508 | 1.0515 | 1.0496 | 1.0703 | 1.0936 | 1.0222 | 1.0215 | 1.0228 |
| 1.50 | 1.0759 | 1.0780 | 1.0750 | 1.1086 | 1.1491 | 1.0324 | 1.0319 | 1.0333 |

(Continued on next page)

Table 2-5 (continued)

| $\xi = m_B / c_B$ ($dm^3$ of solution per kg of $H_2O$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 2.00 | 1.1019 | 1.1062 | 1.1019 | | 1.2125 | 1.0430 | 1.0429 | 1.0441 |
| 3.00 | 1.1571 | 1.1678 | 1.1605 | | 1.3689 | 1.0654 | 1.0668 | 1.0666 |
| 4.00 | 1.2171 | 1.2374 | 1.2264 | | | 1.0893 | 1.0930 | 1.0904 |
| 5.00 | 1.2826 | 1.3167 | | | | 1.1147 | 1.1218 | 1.1156 |
| 6.00 | 1.3547 | 1.4077 | | | | 1.1418 | | 1.1423 |
| $c$ (M) | KCl | $NH_4Cl$ | $MgCl_2$ | $CaCl_2$ | NaBr | $HNO_3$ | $NaNO_3$ | $LiNO_3$ |
| 0.10 | 1.0057 | 1.0066 | 1.0049 | 1.0044 | 1.0054 | 1.0056 | 1.0058 | 1.0059 |
| 0.25 | 1.0099 | 1.0123 | 1.0080 | 1.0069 | 1.0090 | 1.0097 | 1.0102 | 1.0103 |
| 0.50 | 1.0172 | 1.0219 | 1.0135 | 1.0119 | 1.0154 | 1.0169 | 1.0177 | 1.0178 |
| 0.75 | 1.0248 | 1.0318 | 1.0195 | 1.0176 | 1.0220 | 1.0242 | 1.0256 | 1.0256 |
| 1.00 | 1.0326 | 1.0420 | 1.0258 | 1.0239 | 1.0287 | 1.0319 | 1.0338 | 1.0335 |
| 1.50 | 1.0489 | 1.0632 | 1.0393 | 1.0382 | 1.0428 | 1.0478 | 1.0510 | 1.0497 |
| 2.00 | 1.0662 | 1.0855 | 1.0540 | 1.0546 | 1.0576 | 1.0647 | 1.0692 | 1.0667 |
| 3.00 | 1.1037 | 1.1339 | 1.0867 | 1.0934 | 1.0893 | 1.1012 | 1.1090 | 1.1028 |
| 4.00 | 1.1453 | 1.1877 | 1.1241 | 1.1406 | 1.1240 | 1.1417 | 1.1534 | 1.1420 |
| 5.00 | | 1.2477 | | 1.1974 | 1.1619 | 1.1865 | 1.2030 | 1.1846 |
| 6.00 | | | | | 1.2033 | 1.2361 | 1.2585 | 1.2309 |
| $c$ (M) | $NH_4NO_3$ | $H_2SO_4$ | $Na_2SO_4$ | $(NH_4)_2SO_4$ | $H_3PO_4$ | $Na_2CO_3$ | $K_2CO_3$ | NaSCN |
| 0.10 | 1.0077 | 1.0064 | 1.0044 | 1.0082 | 1.0074 | 1.0027 | 1.0042 | 1.0069 |
| 0.25 | 1.0151 | 1.0116 | 1.0071 | 1.0166 | 1.0143 | 1.0030 | 1.0068 | 1.0130 |
| 0.50 | 1.0276 | 1.0209 | 1.0127 | 1.0319 | 1.0261 | 1.0043 | 1.0121 | 1.0234 |
| 0.75 | 1.0405 | 1.0305 | 1.0194 | 1.0486 | 1.0383 | 1.0065 | 1.0185 | 1.0342 |
| 1.00 | 1.0539 | 1.0406 | 1.0268 | 1.0665 | 1.0509 | 1.0094 | 1.0259 | 1.0453 |
| 1.50 | 1.0818 | 1.0619 | 1.0441 | 1.1062 | 1.0773 | 1.0170 | 1.0430 | 1.0686 |
| 2.00 | 1.1116 | 1.0848 | | 1.1514 | 1.1055 | 1.0268 | 1.0632 | 1.0934 |
| 3.00 | 1.1769 | 1.1355 | | 1.2610 | 1.1675 | | 1.1130 | 1.1474 |
| 4.00 | 1.2512 | 1.1935 | | 1.4037 | 1.2383 | | 1.1764 | 1.2083 |
| 5.00 | 1.3365 | 1.2600 | | | 1.3194 | | 1.2560 | 1.2773 |
| 6.00 | 1.4351 | 1.3365 | | | 1.4131 | | | 1.3557 |

## 2.3 Standard and reference conditions

### 2.3.1 Standard state

A precise definition of the term “standard state” has been given by IUPAC [1982LAF]. The fact that only changes in thermodynamic parameters, but not their absolute values, can be determined experimentally, makes it important to have a well-defined standard state that forms a base line to which the effect of variations can be referred. The IUPAC [1993MIL/CVI] definition of the standard state has been adopted in the NEA TDB Project. The standard state pressure, $p^\circ = 0.1$ MPa (1 bar), has therefore also been adopted, *cf.* Section 2.3.2. The application of the standard state principle to pure substances and mixtures is summarised below. It should be noted that the standard state is always linked to a reference temperature, *cf.* Section 2.3.3.

- The standard state for a gaseous substance, whether pure or in a gaseous mixture, is the pure substance at the standard state pressure and in a (hypothetical) state in which it exhibits ideal gas behaviour.
- The standard state for a pure liquid substance is (ordinarily) the pure liquid at the standard state pressure.
- The standard state for a pure solid substance is (ordinarily) the pure solid at the standard state pressure.
- The standard state for a solute in a liquid or solid solution is referenced to the ideal dilute behaviour of the solute. It is the (hypothetical) state of solute B at the standard molality $m^\circ$, standard pressure $p^\circ$ and exhibiting infinitely dilute solution behaviour.

It should be emphasised that the use of superscript, $^\circ$, *e.g.*, in $\Delta_f H^\circ_m$, implies that the compound in question is in the standard state and that the elements are in their reference states. The reference states of the elements at the reference temperature (*cf.* Section 2.3.3) are listed in Table 2-6.

Table 2-6: Reference states for some elements at the reference temperature of 298.15 K and standard pressure of 0.1 MPa [1982WAG/EVA], [1989COX/WAG], [1991DIN], [2005GAM/BUG], [2005OLI/NOL].

| | | | |
|---|---|---|---|
| $O_2$ | gaseous | Zn | crystalline, hexagonal |
| $H_2$ | gaseous | Cd | crystalline, hexagonal |
| He | gaseous | Hg | liquid |
| Ne | gaseous | Cu | crystalline, cubic |
| Ar | gaseous | Ag | crystalline, cubic |
| Kr | gaseous | Ni | crystalline, fcc |
| Xe | gaseous | Fe | crystalline, cubic, bcc |
| $F_2$ | gaseous | Tc | crystalline, hexagonal |
| $Cl_2$ | gaseous | V | crystalline, cubic |
| $Br_2$ | liquid | Ti | crystalline, hexagonal |
| $I_2$ | crystalline, orthorhombic | Am | crystalline, dhcp |
| S | crystalline, orthorhombic | Pu | crystalline, monoclinic |
| Se | crystalline, trigonal | Np | crystalline, orthorhombic |
| Te | crystalline, hexagonal | U | crystalline, orthorhombic |
| $N_2$ | gaseous | Th | crystalline, cubic |
| P | crystalline, cubic (“white”) | Be | crystalline, hexagonal |
| As | crystalline, rhombohedral (“grey”) | Mg | crystalline, hexagonal |
| Sb | crystalline, rhombohedral | Ca | crystalline, cubic, fcc |
| Bi | crystalline, rhombohedral | Sr | crystalline, cubic, fcc |
| C | crystalline, hexagonal (graphite) | Ba | crystalline, cubic |
| Si | crystalline, cubic | Li | crystalline, cubic |
| Ge | crystalline, cubic | Na | crystalline, cubic |
| Sn | crystalline, tetragonal (“white”) | K | crystalline, cubic |
| Pb | crystalline, cubic | Rb | crystalline, cubic |
| B | crystalline, rhombohedral | Cs | crystalline, cubic |
| Al | crystalline, cubic | | |

### 2.3.2 Standard state pressure

The standard state pressure chosen for all selected data is 0.1 MPa (1 bar) as recommended by IUPAC [1982LAF].

However, the majority of the thermodynamic data published in the scientific literature, and used for the evaluations in this review, refers to the old standard state pressure of 1 "standard atmosphere" (= 0.101325 MPa). The difference between the thermodynamic data for the two standard state pressures is not large and lies in most cases within the uncertainty limits. It is nevertheless essential to make the corrections for the change in the standard state pressure in order to avoid inconsistencies and propagation of errors. In practice the parameters affected by the change between these two standard state pressures are the Gibbs energy and entropy changes of all processes that involve gaseous species. Consequently, changes occur also in the Gibbs energies of formation of species that consist of elements whose reference state is gaseous (H, O, F, Cl, N, and the noble gases). No other thermodynamic quantities are affected significantly. A large part of the following discussion has been taken from the NBS tables of chemical thermodynamic properties [1982WAG/EVA], see also Freeman [1984FRE].

The following expressions define the effect of pressure on the properties of all substances:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1-\alpha T) \tag{2.41}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{2.42}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \tag{2.43}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{2.44}$$

$$\text{where } \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{2.45}$$

For ideal gases, $V = RT/p$ and $\alpha = R/pV = 1/T$. The conversion equations listed below (Eqs. (2.46) to (2.53)) apply to the small pressure change from 1 atm to 1 bar (0.1 MPa). The quantities that refer to the old standard state pressure of 1 atm are assigned the superscript $^{(atm)}$, and those that refer to the new standard state pressure of 1 bar are assigned the superscript $^{(bar)}$.

For all substances the changes in the enthalpy of formation and heat capacity are much smaller than the experimental accuracy and can be disregarded. This is exactly true for ideal gases.

$$\Delta_f H^{(\text{bar})}(T) - \Delta_f H^{(\text{atm})}(T) = 0 \quad (2.46)$$

$$C_p^{(\text{bar})}(T) - C_p^{(\text{atm})}(T) = 0 \quad (2.47)$$

For gaseous substances, the entropy difference is:

$$S^{(\text{bar})}(T) - S^{(\text{atm})}(T) = R \ln\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right) = R \ln 1.01325$$

$$= 0.1094 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad (2.48)$$

This is exactly true for ideal gases, as follows from Eq. (2.43) with $\alpha = R / pV$. The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

$$\Delta_r S^{(\text{bar})} - \Delta_r S^{(\text{atm})} = \delta R \ln\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right)$$

$$= 0.1094\ \delta \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad (2.49)$$

where $\delta$ is the net increase in moles of gas in the process.

Similarly, the change in the Gibbs energy of a process between the two standard state pressures is:

$$\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})} = -\ \delta RT \ln\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right)$$

$$= -\ 0.03263\ \delta \text{ kJ}\cdot\text{mol}^{-1} \text{ at } 298.15 \text{ K}. \quad (2.50)$$

Eq. (2.50) applies also to $\Delta_f G^{(\text{bar})} - \Delta_f G^{(\text{atm})}$, since the Gibbs energy of formation describes the formation process of a compound or complex from the reference states of the elements involved:

$$\Delta_f G^{(\text{bar})} - \Delta_f G^{(\text{atm})} = -\ 0.03263\ \delta \text{ kJ}\cdot\text{mol}^{-1} \text{ at } 298.15 \text{ K}. \quad (2.51)$$

The changes in the equilibrium constants and cell potentials with the change in the standard state pressure follows from the expression for Gibbs energy changes, Eq. (2.50),

$$\log_{10} K^{(\text{bar})} - \log_{10} K^{(\text{atm})} = -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{RT \ln 10}$$

$$= \delta \frac{\ln\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right)}{\ln 10} = \delta \log_{10}\left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}}\right)$$

$$= 0.005717\ \delta \quad (2.52)$$

$$E^{(\mathrm{bar})} - E^{(\mathrm{atm})} = -\frac{\Delta_r G^{(\mathrm{bar})} - \Delta_r G^{(\mathrm{atm})}}{nF}$$

$$= \delta \frac{RT \ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right)}{nF}$$

$$= \delta \frac{0.0003382}{n} \text{ V} \quad \text{at } 298.15 \text{ K} \tag{2.53}$$

It should be noted that the standard potential of the hydrogen electrode is equal to 0.00 V exactly, by definition.

$$\mathrm{H^+ + e^- \rightleftharpoons \tfrac{1}{2} H_2(g)} \qquad E^{\circ} \stackrel{\text{def}}{=} 0.00\text{V} \tag{2.54}$$

This definition will not be changed, although a gaseous substance, $\mathrm{H_2(g)}$, is involved in the process. The change in the potential with pressure for an electrode potential conventionally written as:

$$\mathrm{Ag^+ + e^- \rightleftharpoons Ag(cr)}$$

should thus be calculated from the balanced reaction that includes the hydrogen electrode,

$$\mathrm{Ag^+ + \tfrac{1}{2} H_2\,(g) \rightleftharpoons Ag\,(cr) + H^+}.$$

Here $\delta = -0.5$. Hence, the contribution to $\delta$ from an electron in a half cell reaction is the same as the contribution of a gas molecule with the stoichiometric coefficient of 0.5. This leads to the same value of $\delta$ as the combination with the hydrogen half cell.

Example:

| | | |
|---|---|---|
| $\mathrm{Fe(cr) + 2\,H^+ \rightleftharpoons Fe^{2+} + H_2(g)}$ | $\delta = 1$ | $E^{(\mathrm{bar})} - E^{(\mathrm{atm})} = 0.00017$ V |
| $\mathrm{CO_2(g) \rightleftharpoons CO_2(aq)}$ | $\delta = -1$ | $\log_{10} K^{(\mathrm{bar})} - \log_{10} K^{(\mathrm{atm})} = -0.0057$ |
| $\mathrm{NH_3(g) + \tfrac{5}{4} O_2(g) \rightleftharpoons NO(g) + \tfrac{3}{2} H_2O(g)}$ | $\delta = 0.25$ | $\Delta_r G^{(\mathrm{bar})} - \Delta_r G^{(\mathrm{atm})} = -0.008$ kJ·mol$^{-1}$ |
| $\mathrm{\tfrac{1}{2} Cl_2(g) + 2\,O_2(g) + e^- \rightleftharpoons ClO_4^-}$ | $\delta = -3$ | $\Delta_f G^{(\mathrm{bar})} - \Delta_f G^{(\mathrm{atm})} = 0.098$ kJ·mol$^{-1}$ |

### 2.3.3 Reference temperature

The definitions of standard states given in Section 2.3 make no reference to fixed temperature. Hence, it is theoretically possible to have an infinite number of standard states of a substance as the temperature varies. It is, however, convenient to complete the definition of the standard state in a particular context by choosing a reference temperature. As recommended by IUPAC [1982LAF], the reference temperature chosen in the NEA TDB Project is $T = 298.15$ K or $t = 25.00$ °C. Where necessary for the discussion, values of experimentally measured temperatures are reported after

conversion to the IPTS–68 [1969COM]. The relation between the absolute temperature $T$ (K, kelvin) and the Celsius temperature $t$ (°C) is defined by $t$ / °C = $T$ /K – 273.15.

## 2.4 Fundamental physical constants

To ensure the consistency with other NEA TDB Reviews, the fundamental physical constants are taken from a publication by CODATA [1986COD]. Those relevant to this review are listed in Table 2-7. Updated values of the fundamental constants can be obtained from CODATA, notably through its Internet site. In most cases, recalculation of the NEA TDB database entries with the updated values of the fundamental constants will not introduce significant (with respect to their quoted uncertainties) excursions from the current NEA TDB selections.

Table 2-7: Fundamental physical constants. These values have been taken from CODATA [1986COD]. The digits in parentheses are the one-standard-deviation uncertainty in the last digits of the given value.

| Quantity | Symbol | Value | Units |
|---|---|---|---|
| speed of light in vacuum | $c_0$ | 299 792 458 | $m \cdot s^{-1}$ |
| permeability of vacuum | $\mu_0$ | $4\pi \times 10^{-7}$ = 12.566 370 614… | $10^{-7}\ N \cdot A^{-2}$ |
| permittivity of vacuum | $\epsilon_0$ | $1/\mu_0 c^2$ = 8.854 187 817… | $10^{-12}\ C^2 \cdot J^{-1} \cdot m^{-1}$ |
| Planck constant | $h$ | 6.626 0755(40) | $10^{-34}\ J \cdot s$ |
| elementary charge | $e$ | 1.602 177 33(49) | $10^{-19}$ C |
| Avogadro constant | $N_A$ | 6.022 1367(36) | $10^{23}\ mol^{-1}$ |
| Faraday constant | $F$ | 96 485.309(29) | $C \cdot mol^{-1}$ |
| molar gas constant | $R$ | 8.314 510(70) | $J \cdot K^{-1} \cdot mol^{-1}$ |
| Boltzmann constant, $R/N_A$ | $k_B$ | 1.380 658(12) | $10^{-23}\ J \cdot K^{-1}$ |
| Non-SI units used with SI: | | | |
| electronvolt, (e/C) J | eV | 1.602 177 33(49) | $10^{-19}$ J |
| atomic mass unit, $1\,u = m_u = \frac{1}{12} m(^{12}C)$ | u | 1.660 5402(10) | $10^{-27}$ kg |

## 2.5 Uncertainty estimates

One of the principal objectives of the NEA TDB development effort is to provide an idea of the uncertainties associated with the data selected in the reviews. In general the uncertainties should define the range within which the corresponding data can be reproduced with a probability of 95%. In many cases, a full statistical treatment is limited or impossible due to the availability of only one or a few data points. Appendix C describes in detail the procedures used for the assignment and treatment of uncertainties, as well as the propagation of errors and the standard rules for rounding.

## 2.6 Presentation of the selected data

The selected data are presented in Chapters 3, 4, 5, 6 and 7. Unless otherwise indicated, they refer to standard conditions (*cf.* Section 2.3) and 298.15 K (25 °C) and are provided with an uncertainty which should correspond to the 95% confidence level (see Appendix C).

Chapters 3, 4, 5, 6 and 7 contain tables of selected thermodynamic data for individual compounds and complexes of uranium, neptunium, plutonium, americium and technetium (Tables 3-1, 4-1, 5-1, 6-1 and 7-1, respectively), tables of selected reaction data (Tables 3-2, 4-2, 5-2, 6-2 and 7-2) for reactions concerning uranium, neptunium, plutonium, americium and technetium species, respectively, and tables containing selected thermal functions of the heat capacities of individual species of uranium, neptunium, plutonium, americium and technetium (Tables 3-3, 4-3, 5-3, 6-3 and 7-3, respectively). The selection of these data is discussed in Part III. The fitted heat capacity coefficients for the gaseous species in Tables 3-3, 4-3, 5-3, 6-3 and 7-3 are valid only up to the maximum temperatures given. These temperatures vary in order to retain only small differences (generally $< 0.25\ J \cdot K^{-1} \cdot mol^{-1}$) between the fitted and calculated heat capacities.

Chapter 8 contains tables of thermodynamic data for individual species (Table 8-1) and reaction data (Table 8-2), for auxiliary compounds and complexes that do not contain uranium, neptunium, plutonium, americium or technetium. Most of these values are the CODATA Key Values [1989COX/WAG]. The selection of the remaining auxiliary data is discussed in [1992GRE/FUG], [1999RAR/RAN], [2001LEM/FUG], [2005GAM/BUG], [2005OLI/NOL] and [2008RAN/FUG]. We have also included in Chapter 14 thermodynamic data from the Glushko handbooks ([1965GLU/MED] – [1982GLU/GUR]).

All the selected data presented in Tables 3-1, 3-2, 4-1, 4-2, 5-1, 5-2, 6-1, 6-2, 7-1 and 7-2 are internally consistent. This consistency is maintained by the internal consistency verification and recalculation software developed at the NEA Data Bank in conjunction with the NEA TDB database system. Therefore, when using the selected data for uranium, neptunium, plutonium, americium or technetium species, the auxiliary data in Chapters 8 and 14 must be used together with the data in Chapters 3, 4, 5, 6 and 7 to ensure internal consistency of the data set.

It is important to note that Tables 3-2, 4-2, 5-2, 6-2, 7-2 and 8-2 include only those species for which the primary selected data are reaction data. The formation data derived therefrom and listed in Tables 3-1, 4-1, 5-1, 6-1, 7-1 and 8-1 are obtained using auxiliary data, and their uncertainties are propagated accordingly. In order to maintain the uncertainties originally assigned to the selected data in this review, the user is advised to make direct use of the reaction data presented in Tables 3-2, 4-2, 5-2, 6-2, 7-2 and 8-2, rather than taking the derived values in Tables 3-1, 4-1, 5-1, 6-1, 7-1 and 8-1 to calculate the reaction data. The latter approach would imply a twofold

propagation of the uncertainties and result in reaction data whose uncertainties would be considerably larger than those originally assigned.

The thermodynamic data in the selected set refer to a temperature of 298.15 K (25.00 °C), but they can be recalculated to other temperatures if the corresponding data (enthalpies, entropies, heat capacities) are available [1997PUI/RAR]. For example, the temperature dependence of the standard reaction Gibbs energy as a function of the standard reaction entropy at the reference temperature ( $T_0 = 298.15$ K), and of the heat capacity function is:

$$\Delta_r G_m^o(T) = \Delta_r H_m^o(T_0) + \int_{T_0}^{T} \Delta_r C_{p,m}^o(T)\, dT - T\left( \Delta_r S_m^o(T_0) + \int_{T_0}^{T} \frac{\Delta_r C_{p,m}^o(T)}{T} dT \right),$$

and the temperature dependence of the standard equilibrium constant as a function of the standard reaction enthalpy and heat capacity is:

$$\log_{10} K^o(T) = \log_{10} K^o(T_0) - \frac{\Delta_r H_m^o(T_0)}{R \ln(10)} \left( \frac{1}{T} - \frac{1}{T_0} \right) - \frac{1}{RT \ln(10)} \int_{T_0}^{T} \Delta_r C_{p,m}^o(T)\, dT + \frac{1}{R \ln(10)} \int_{T_0}^{T} \frac{\Delta_r C_{p,m}^o(T)}{T} dT,$$

where $R$ is the gas constant (*cf.* Table 2-7).

In the case of aqueous species, for which enthalpies of reaction are selected or can be calculated from the selected enthalpies of formation, but for which there are no selected heat capacities, it is in most cases possible to recalculate equilibrium constants to temperatures up to 100 to 150 °C, with an additional uncertainty of perhaps about ± 1 to ± 2 in $\log_{10} K$, due to neglect of the heat-capacity contributions to the temperature correction. For isocoulombic/isoelectric reactions the uncertainty may be smaller; for a detailed discussion see [1997PUI/RAR]. However, it is important to observe that "new" aqueous species, *i.e.*, species not present in significant amounts at 298.15 K and therefore not detected, may be significant at higher temperatures, see for example the work by Ciavatta *et al.* [1987CIA/IUL]. Additional high-temperature experiments may therefore be needed in order to ascertain that proper chemical models are used in the modelling of hydrothermal systems. For many species, experimental thermodynamic data are not available to allow a selection of parameters describing the temperature dependence of equilibrium constants and Gibbs energies of formation. The user may find information on various procedures to estimate the temperature dependence of these thermodynamic parameters in [1997PUI/RAR]. The thermodynamic data in the selected set refer to infinite dilution for soluble species. Extrapolation of an equilibrium constant $K$, usually measured at high ionic strength, to $K^o$ at $I = 0$ using activity coefficients $\gamma$, is explained in Appendix B. The corresponding Gibbs energy of dilution is:

$$\Delta_{dil}G_m = \Delta_r G_m^o - \Delta_r G_m \quad (2.55)$$

$$= -RT\,\Delta_r \ln \gamma_{\pm} \quad (2.56)$$

Similarly $\Delta_{dil}S_m$ can be calculated from $\ln \gamma_{\pm}$ and its variations with *T*, while:

$$\Delta_{dil}H_m = RT^2 \frac{\partial}{\partial T}(\Delta_r \ln \gamma_{\pm})_p \quad (2.57)$$

depends only on the variation of $\gamma$ with *T*, which is neglected in this review, when no data on the temperature dependence of $\gamma$s are available. In this case the Gibbs energy of dilution $\Delta_{dil}G_m$ is entirely assigned to the entropy difference. This entropy of reaction is calculated using $\Delta_r G_m^o = \Delta_r H_m^o - T\Delta_r S_m^o$, the value of $\Delta_{dil}G_m$ and with the approximation that $\Delta_{dil}H_m = 0$.

# Part II

# Tables of selected data

# Chapter 3

# Selected Data for Uranium

## 3.1 General considerations

This chapter presents updated chemical thermodynamic data for uranium species, as described in detail in Chapter 9 of this volume. The selected data contain both data previously selected and in some cases revisions of some of them; in addition there is a large number of data that were not included in [1992GRE/FUG] and [2003GUI/FAN]. New species selected in this review are marked with an asterisk, "*"; revised data for species selected in [2003GUI/FAN] are also marked with an asterisk. Table 3-1 contains the selected thermodynamic data of the uranium compounds and complexes, Table 3-2 the selected thermodynamic data of chemical equilibrium reactions by which the uranium compounds and complexes are formed, and Table 3-3 the temperature coefficients of the heat capacity data of Table 3-1 where available.

The species and reactions in Table 3-1, Table 3-2 and Table 3-3 appear in standard order of arrangement (*cf.* Figure 2-1). These selected reaction data are used, together with data for key uranium species (for example $U^{4+}$) and auxiliary data listed in Table 8-1, to derive the corresponding formation quantities in Table 3-1. The uncertainties associated with values for the key uranium species and for some of the auxiliary data are substantial, leading to comparatively large uncertainties in the thermodynamic data. By including a table for reaction data (Table 3-2), the users obtain information of equilibrium constants and their uncertainties that are directly based on the experimental data and their uncertainty.

The selected thermal functions of the heat capacities, listed in Table 3-3, are described with the empirical function:

$$C_{p,m}(T) = a + bT + cT^2 + eT^{-2} + jT^3 \qquad (3.1)$$

The selected values in [1992GRE/FUG] and [2003GUI/FAN] are discussed there and retained in the present review. New and revised thermal functions are discussed in the relevant Appendix A entries. No references are given in these tables since the selected data are generally not directly attributable to a specific published source. A detailed discussion of the selection procedure is presented in [1992GRE/FUG], [2003GUI/FAN] and in Chapter 9 of this volume.

## 3.2 Precautions to be observed in the use of the tables

Geochemical modelling in aquatic systems requires the careful use of the data selected in the NEA TDB reviews. The selected data in the tables must not be adopted without taking into account the chemical background information discussed in the corresponding sections of this book. In particular the following precautions should be observed when using data from the Tables.

- The addition of new thermodynamic data to this internally consistent database should be made with care, it is straight forward to see if the new species has any significant effect on the experimental data, or if it results in changes in the speciation. However, if a significant change occurs, it is necessary to make a scrutiny of the experimental data on which the value is based and possibly also on the selected data.
- Gaps are pointed out in both the previous NEA TDB review and the present update.
- Solubility data for crystalline phases are well defined in the initial state, but not necessarily in the final state after "equilibrium" has been attained. Hence, the solubility calculated from these phases may be misleading, as discussed in [2003GUI/FAN] for the solubility data of $MO_2$(cr), M = U, Np, Pu.
- The selected thermodynamic data in [1992GRE/FUG], [1995SIL/BID] and [2001LEM/FUG] contained thermodynamic data for amorphous phases including Gibbs energy of formation deduced from solubility measurements. Following the criteria outlined in [2003GUI/FAN], the present review has not selected the Gibbs energy of formation of these phases. However, the corresponding $\log_{10}K$ values have been retained. The reasons for this choice are:
    - Thermodynamic data are only meaningful if they refer to well-defined systems; this is not the case for amorphous phases. It is well known that their solubility may change with time, due to re-crystallisation, with a resulting change in water content and surface area/crystal size; the time scale for these changes can vary widely.
    - The solubility of amorphous phases may be of interest for users of the database in chemical modelling even though they are not thermodynamic quantities.

Table 3-1: Selected thermodynamic data for uranium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values in bold typeface are CODATA Key Values and are taken directly from reference [1989COX/WAG] without further evaluation. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk (*). Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| U(cr) | 0.000 | 0.000 | 50.200 ± 0.200 | 27.660 [c] ± 0.050 |
| U(g) | 488.400 [a] ± 8.000 | 533.000 ± 8.000 | 199.790 ± 0.030 | 23.690 [c] ± 0.030 |
| $U^{3+}$ | – 476.473 [b] ± 1.810 | – 489.100 [b] ± 3.712 | – 188.172 [b] ± 13.853 | – 150.000 ± 50.000 |
| $U^{4+}$ | – 529.860 [b] ± 1.765 | – 591.200 ± 3.300 | – 416.895 [a] ± 12.553 | – 220.000 ± 50.000 |
| UO(g) | 5.327 [a] ± 10.018 | 35.000 ± 10.000 | 252.300 ± 2.000 | 39.600 [c] ± 2.000 |
| $UO_2$(cr) | **– 1031.833** [a] **± 1.004** | **– 1085.000 ± 1.000** | **77.030 ± 0.200** | **63.600** [c] **± 0.080** |
| $UO_2$(g) | – 481.064 [a] ± 20.036 | – 477.800 ± 20.000 | 266.300 ± 4.000 | 59.500 [c] ± 2.000 |
| $UO_2^+$ | – 961.021 [b] ± 1.752 | – 1025.127 [a] ± 2.960 | – 25.000 ± 8.000 | |
| $UO_2^{2+}$ | **– 952.551** [a] **± 1.747** | **– 1019.000 ± 1.500** | **– 98.200 ± 3.000** | **42.400** [c] **± 3.000** |
| β-$UO_{2.25}$ [d] | – 1069.083 [a] ± 1.702 | – 1127.400 ± 1.700 | 85.400 ± 0.200 | [c] |
| $UO_{2.25}$(cr) [e] | – 1069.125 [a] ± 1.702 | – 1128.000 ± 1.700 | 83.530 ± 0.170 | 73.340 [c] ± 0.150 |
| α-$UO_{2.3333}$ | | | 82.170 ± 0.500 | 71.420 [c] ± 0.300 |

(Continued on next page)

Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| β-$UO_{2.3333}$ | – 1079.572 [a] ± 2.002 | – 1141.000 ± 2.000 | 83.510 ± 0.200 | 71.840 [c] ± 0.140 |
| $UO_{2.6667}$(cr) | – 1123.157 [a] ± 0.804 | – 1191.600 ± 0.800 | 94.180 ± 0.170 | 79.310 [c] ± 0.160 |
| $UO_{2.86}$·0.5$H_2O$(cr) | | – 1367.000 ± 10.000 | | |
| $UO_{2.86}$·1.5$H_2O$(cr) | | – 1666.000 ± 10.000 | | |
| α-$UO_{2.95}$ | | – 1211.280 [b] ± 1.284 | | |
| α-$UO_3$ | – 1135.330 [a] ± 1.482 | – 1212.410 ± 1.450 | 99.400 ± 1.000 | 81.840 ± 0.300 |
| β-$UO_3$ | – 1142.301 [a] ± 1.307 | – 1220.300 ± 1.300 | 96.320 ± 0.400 | 81.340 [c] ± 0.160 |
| γ-$UO_3$ | **– 1145.739 [a] ± 1.207** | **– 1223.800 ± 1.200** | **96.110 ± 0.400** | **81.670 [c] ± 0.160** |
| δ-$UO_3$ | | – 1213.730 ± 1.440 | | |
| ε-$UO_3$ | | – 1217.200 ± 1.300 | | |
| $UO_3$(g) | – 784.761 [a] ± 15.012 | – 799.200 ± 15.000 | 309.500 ± 2.000 | 64.500 [c] ± 2.000 |
| β-$UH_3$ | – 72.556 [a] ± 0.148 | – 126.980 ± 0.130 | 63.680 ± 0.130 | 49.290 ± 0.080 |
| $UOH^{3+}$ | – 763.918 [b] ± 1.798 | – 830.120 [b] ± 9.540 | – 199.946 [b] ± 32.521 | |
| $U(OH)_2^{2+}$ * | – 993.295* ± 2.102 | | | |
| $U(OH)_3^{+}$ * | – 1211.598* ± 2.886 | | | |
| $U(OH)_4$(aq) | – 1421.309 [b] ± 8.189 | – 1624.607 [a] ± 11.073 | 40.000 ± 25.000 | 205.000 ± 80.000 |
| $UO_2OH^+$ | – 1159.724 [b] ± 2.221 | – 1261.530* ± 2.746 | 16.468* ± 9.467 | |
| $UO_3$·0.393$H_2O$(cr) | | – 1347.800 ± 1.300 | | |

(Continued on next page)

Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_3 \cdot 0.648H_2O$(cr) | | – 1424.600 ± 1.300 | | |
| α-$UO_3 \cdot 0.85H_2O$ | | – 1491.900 ± 1.300 | | |
| α-$UO_3 \cdot 0.9H_2O$ | – 1374.560 [a] ± 2.460 | – 1506.300 ± 1.300 | 126.000 ± 7.000 | 140.000 ± 30.000 |
| δ-$UO_3H_{0.83}$ | | – 1285.140 [b] ± 2.020 | | |
| $UO_2(OH)_2$(aq) | – 1357.479 [b] ± 1.794 | | | |
| β-$UO_2(OH)_2$ | – 1398.683 [a] ± 1.765 | – 1533.800 ± 1.300 | 138.000 ± 4.000 | 141.000 [c] ± 15.000 |
| γ-$UO_2(OH)_2$ | | – 1531.400 ± 1.300 | | |
| $UO_2(OH)_3^-$ | – 1548.384 [b] ± 2.969 | | | |
| $UO_3 \cdot 2H_2O$(cr) | – 1636.506 [a] ± 1.705 | – 1826.100 ± 1.700 | 188.540 ± 0.380 | 172.070 [c] ± 0.340 |
| $UO_2(OH)_4^{2-}$ | – 1716.171 [b] ± 4.260 | | | |
| $UO_4 \cdot 2H_2O$(cr) | | – 1784.000 ± 4.200 | | |
| $UO_4 \cdot 4H_2O$(cr) | | – 2384.700 ± 2.100 | | |
| $(UO_2)_2OH^{3+}$ | – 2126.830 [b] ± 6.693 | | | |
| $(UO_2)_2(OH)_2^{2+}$ | – 2347.303** [b] ± 3.525 | – 2561.860* ± 3.042 | – 3.772* ± 6.416 | |
| $(UO_2)_3(OH)_4^{2+}$ | – 3738.288 [b] ± 5.517 | – 4101.120* ± 4.531 | 90.095* ± 10.808 | |
| $(UO_2)_3(OH)_5^+$ | – 3954.594 [b] ± 5.291 | – 4365.450*[b] ± 4.544 | 162.277* ± 9.505 | |
| $(UO_2)_3(OH)_7^-$ | – 4333.835 [b] ± 6.958 | | | |
| $(UO_2)_4(OH)_7^+$ | – 5345.178 [b] ± 9.028 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| UF(g) | – 76.876 [a]<br>± 20.020 | – 47.000<br>± 20.000 | 251.800<br>± 3.000 | 37.900 [c]<br>± 3.000 |
| $UF^{3+}$ | – 865.153 [b]<br>± 3.474 | – 932.150 [b]<br>± 3.400 | – 269.133 [b]<br>± 16.012 | |
| $UF_2$(g) | – 558.697 [a]<br>± 25.177 | – 540.000<br>± 25.000 | 315.700<br>± 10.000 | 56.200 [c]<br>± 5.000 |
| $UF_2^{2+}$ | – 1187.431 [b]<br>± 4.632 | – 1265.400 [b]<br>± 3.597 | – 139.195 [b]<br>± 18.681 | |
| $UF_3$(cr) | – 1433.545* [a]<br>± 4.759 | – 1501.400<br>± 4.700 | 126.800*<br>± 2.500 | 94.010* [c]<br>± 0.400 |
| $UF_3$(g) | – 1062.947 [a]<br>± 20.221 | – 1065.000<br>± 20.000 | 347.500<br>± 10.000 | 76.200 [c]<br>± 5.000 |
| $UF_3^+$ | – 1499.378 [b]<br>± 5.466 | – 1596.750 [b]<br>± 5.540 | – 37.537 [b]<br>± 24.410 | |
| $UF_4$(aq) | – 1806.302 [b]<br>± 6.388 | – 1941.030 [b]<br>± 8.565 | 3.905 [b]<br>± 21.374 | |
| $UF_4$(cr) | – 1823.538 [a]<br>± 4.201 | – 1914.200<br>± 4.200 | 151.700<br>± 0.200 | 116.000 [c]<br>± 0.100 |
| $UF_4$(g) | – 1576.851 [a]<br>± 6.698 | – 1605.200 [b]<br>± 6.530 | 360.700<br>± 5.000 | 95.100 [c]<br>± 3.000 |
| α-$UF_5$ | – 1968.688 [a]<br>± 6.995 | – 2075.300<br>± 5.900 | 199.600<br>± 12.600 | 132.200 [c]<br>± 4.200 |
| β-$UF_5$ | – 1970.595 [a]<br>± 5.635 | – 2083.200<br>± 4.200 | 179.500<br>± 12.600 | 132.200 [c]<br>± 12.000 |
| $UF_5$(g) | – 1862.083 [a]<br>± 15.294 | – 1913.000<br>± 15.000 | 386.400<br>± 10.000 | 110.600 [c]<br>± 5.000 |
| $UF_5^-$ | – 2095.760 [b]<br>± 5.739 | | | |
| $UF_6$(cr) | – 2069.205 [a]<br>± 1.842 | – 2197.700<br>± 1.800 | 227.600<br>± 1.300 | 166.800 [c]<br>± 0.200 |
| $UF_6$(g) | – 2064.440 [a]<br>± 1.893 | – 2148.600 [b]<br>± 1.868 | 376.300<br>± 1.000 | 129.400 [c]<br>± 0.500 |
| $UF_6^{2-}$ | – 2389.098 [b]<br>± 6.028 | | | |
| $U_2F_9$(cr) | – 3812.000<br>± 17.000 | – 4015.923 [a]<br>± 18.016 | 329.000<br>± 20.000 | 251.000 [c]<br>± 16.700 |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $U_2F_{10}$(g) | | – 3993.200 [b] ± 30.366 | | |
| $U_4F_{17}$(cr) | – 7464.000 ± 30.000 | – 7849.665 [a] ± 32.284 | 631.000 ± 40.000 | 485.300 [c] ± 33.000 |
| $UOF_2$(cr) | – 1434.127 [a] ± 6.424 | – 1504.600 ± 6.300 | 119.200 ± 4.200 | |
| $UOF_4$(cr) | – 1816.264 [a] ± 4.269 | – 1924.600 ± 4.000 | 195.000 ± 5.000 | |
| $UOF_4$(g) | – 1704.814 [a] ± 20.142 | – 1763.000 ± 20.000 | 363.200 ± 8.000 | 108.100 [c] ± 5.000 |
| $UO_2F^+$ | – 1263.527 [b] ± 1.911 | – 1354.890*[b] ± 1.655 | – 15.024*[b] ± 3.423 | |
| $UO_2F_2$(aq) | – 1565.999 [b] ± 2.276 | – 1691.040*[b] ± 1.993 | 38.755*[b] ± 3.778 | |
| $UO_2F_2$(cr) | – 1557.322 [a] ± 1.307 | – 1653.500 ± 1.300 | 135.560 ± 0.420 | 103.220 [c] ± 0.420 |
| $UO_2F_2$(g) | – 1318.081 [a] ± 10.242 | – 1352.500 [b] ± 10.084 | 342.700 ± 6.000 | 86.400 [c] ± 3.000 |
| $UO_2F_3^-$ | – 1859.338 [b] ± 2.774 | – 2026.230*[b] ± 2.478 | 65.119*[b] ± 4.409 | |
| $UO_2F_4^{2-}$ | – 2146.226 [b] ± 3.334 | – 2362.520*[b] ± 3.038 | 66.163*[b] ± 5.115 | |
| $U_2O_3F_6$(cr) | – 3372.730 [a] ± 14.801 | – 3579.200 [b] ± 13.546 | 324.000 ± 20.000 | |
| $U_3O_5F_8$(cr) | – 4890.135 [a] ± 9.771 | – 5192.950 [b] ± 3.929 | 459.000 ± 30.000 | 304.100 ± 4.143 |
| $H_3OUF_6$(cr) | | – 2641.400 [b] ± 3.157 | | |
| UOFOH(cr) | – 1336.930 [a] ± 12.948 | – 1426.700 ± 12.600 | 121.000 ± 10.000 | |
| UOFOH·0.5$H_2O$(cr) | – 1458.117 [a] ± 6.970 | – 1576.100 ± 6.300 | 143.000 ± 10.000 | |
| $UOF_2$·$H_2O$(cr) | – 1674.474 [a] ± 4.143 | – 1802.000 ± 3.300 | 161.100 ± 8.400 | |
| $UF_4$·2.5$H_2O$(cr) | – 2440.282 [a] ± 6.188 | – 2671.475 ± 4.277 | 263.500 ± 15.000 | 263.700 ± 15.000 |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2FOH·H_2O$(cr) | – 1721.700 ± 7.500 | – 1894.500 ± 8.400 | 178.345 [a] ± 37.770 | |
| $UO_2FOH·2H_2O$(cr) | – 1961.032 [b] ± 8.408 | – 2190.010 [b] ± 9.392 | 223.180 [b] ± 38.244 | |
| $UO_2F_2·3H_2O$(cr) | – 2269.658 [a] ± 6.939 | – 2534.390 [b] ± 4.398 | 270.000 ± 18.000 | |
| UCl(g) | 155.945 [a] ± 20.020 | 187.000 ± 20.000 | 265.900 ± 3.000 | 43.200 [c] ± 3.000 |
| $UCl^{3+}$ | – 670.895 [b] ± 1.918 | – 777.280 [b] ± 9.586 | – 391.093 [b] ± 32.788 | |
| $UCl_2$(g) | – 174.624 [a] ± 20.221 | – 155.000 ± 20.000 | 339.100 ± 10.000 | 59.900 [c] ± 5.000 |
| $UCl_3$(cr) | – 797.832*[a] ± 2.088 | – 863.700 ± 2.000 | 163.900* ± 2.000 | 102.520 [c] ± 0.500 |
| $UCl_3$(g) | – 521.652 [a] ± 20.221 | – 523.000 ± 20.000 | 380.300 ± 10.000 | 82.400 [c] ± 5.000 |
| $UCl_4$(cr) | – 929.605 [a] ± 2.512 | – 1018.800 ± 2.500 | 197.200 ± 0.800 | 121.800 [c] ± 0.400 |
| $UCl_4$(g) | – 789.442 [a] ± 4.947 | – 815.400 [b] ± 4.717 | 409.300 ± 5.000 | 103.500 [c] ± 3.000 |
| $UCl_5$(cr) | – 930.115 [a] ± 3.908 | – 1039.000 ± 3.000 | 242.700 ± 8.400 | 150.600 [c] ± 8.400 |
| $UCl_5$(g) | – 849.552 [a] ± 15.074 | – 900.000 [b] ± 15.000 | 438.700 ± 10.000 | 123.600 [c] ± 5.000 |
| $UCl_6$(cr) | – 937.120 [a] ± 3.043 | – 1066.500 ± 3.000 | 285.500 ± 1.700 | 175.700 [c] ± 4.200 |
| $UCl_6$(g) | – 901.588 [a] ± 5.218 | – 985.500 [b] ± 5.000 | 438.000 ± 5.000 | 147.200 [c] ± 3.000 |
| $U_2Cl_{10}$(g) | | – 1965.300 [b] ± 10.208 | | |
| UOCl(cr) | – 785.654 [a] ± 4.890 | – 833.900 ± 4.200 | 102.500 ± 8.400 | 71.000 [c] ± 5.000 |
| $UOCl_2$(cr) | – 998.478 [a] ± 2.701 | – 1069.300 ± 2.700 | 138.320 ± 0.210 | 95.060 [c] ± 0.420 |
| $UOCl_3$(cr) | – 1045.576 [a] ± 8.383 | – 1140.000 ± 8.000 | 170.700 ± 8.400 | 117.200 [c] ± 4.200 |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2Cl$(cr) | – 1095.253 [a] ± 8.383 | – 1171.100 ± 8.000 | 112.500 ± 8.400 | 88.000 [c] ± 5.000 |
| $UO_2Cl^+$ | – 1084.738 [b] ± 1.755 | – 1178.080 [b] ± 2.502 | – 11.513 [b] ± 7.361 | |
| $UO_2Cl_2$(aq) | – 1208.707 [b] ± 2.885 | – 1338.160 [b] ± 6.188 | 44.251 [b] ± 21.744 | |
| $UO_2Cl_2$(cr) | – 1145.838 [a] ± 1.303 | – 1243.600 ± 1.300 | 150.540 ± 0.210 | 107.860 [c] ± 0.170 |
| $UO_2Cl_2$(g) | – 938.984 [a] ± 15.106 | – 970.300 ± 15.000 | 373.400 ± 6.000 | 92.600 [c] ± 3.000 |
| $U_2O_2Cl_5$(cr) | – 2037.306 [a] ± 4.891 | – 2197.400 ± 4.200 | 326.300 ± 8.400 | 219.400 [c] ± 5.000 |
| $(UO_2)_2Cl_3$(cr) | – 2234.755 [a] ± 2.931 | – 2404.500 ± 1.700 | 276.000 ± 8.000 | 203.600 [c] ± 5.000 |
| $UO_2ClO_3^+$ | – 963.308 [b] ± 2.239 | – 1126.900 [b] ± 1.828 | 60.592 [b] ± 4.562 | |
| $U_5O_{12}Cl$(cr) | – 5517.951 [a] ± 12.412 | – 5854.400 ± 8.600 | 465.000 ± 30.000 | |
| $UO_2Cl_2·H_2O$(cr) | – 1405.003 [a] ± 3.269 | – 1559.800 ± 2.100 | 192.500 ± 8.400 | |
| $UO_2ClOH·2H_2O$(cr) | – 1782.219 [a] ± 4.507 | – 2010.400 ± 1.700 | 236.000 ± 14.000 | |
| $UO_2Cl_2·3H_2O$(cr) | – 1894.616 [a] ± 3.028 | – 2164.800 ± 1.700 | 272.000 ± 8.400 | |
| $UCl_3F$(cr) | – 1146.573 [a] ± 5.155 | – 1243.000 ± 5.000 | 162.800 ± 4.200 | 118.800 ± 4.200 |
| $UCl_2F_2$(cr) | – 1375.967 [a] ± 5.592 | – 1466.000 ± 5.000 | 174.100 ± 8.400 | 119.700 ± 4.200 |
| $UClF_3$(cr) | – 1606.360 [a] ± 5.155 | – 1690.000 ± 5.000 | 185.400 ± 4.200 | 120.900 ± 4.200 |
| UBr(g) | 199.623 [a] ± 15.027 | 245.000 ± 15.000 | 278.500 ± 3.000 | 44.500 [c] ± 3.000 |
| $UBr^{3+}$ | – 642.044 [b] ± 2.109 | | | |
| $UBr_2$(g) | – 86.896 [a] ± 15.294 | – 40.000 ± 15.000 | 359.700 ± 10.000 | 61.400 [c] ± 5.000 |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UBr_3$(cr) | – 673.198 [a] ± 4.205 | – 698.700 ± 4.200 | 192.980 ± 0.500 | 105.830 [c] ± 0.500 |
| $UBr_3$(g) | – 408.115 [a] ± 20.494 | – 371.000 ± 20.000 | 403.000 ± 15.000 | 85.200 [c] ± 5.000 |
| $UBr_4$(cr) | – 767.479 [a] ± 3.544 | – 802.100 ± 2.500 | 238.500 ± 8.400 | 128.000 [c] ± 4.200 |
| $UBr_4$(g) | – 634.604 [a] ± 4.951 | – 605.600 [b] ± 4.717 | 451.900 ± 5.000 | 106.900 [c] ± 3.000 |
| $UBr_5$(cr) | – 769.308 [a] ± 9.205 | – 810.400 ± 8.400 | 292.900 ± 12.600 | 160.700 [c] ± 8.000 |
| $UBr_5$(g) | – 668.212 [a] ± 15.295 | – 647.945 [b] ± 15.000 | 498.700 ± 10.000 | 129.000 [c] ± 5.000 |
| $UOBr_2$(cr) | – 929.648 [a] ± 8.401 | – 973.600 ± 8.400 | 157.570 ± 0.290 | 98.000 [c] ± 0.400 |
| $UOBr_3$(cr) | – 901.498 [a] ± 21.334 | – 954.000 ± 21.000 | 205.000 ± 12.600 | 120.900 [c] ± 4.200 |
| $UO_2Br^+$ | – 1057.657 [b] ± 1.759 | | | |
| $UO_2Br_2$(cr) | – 1066.422 [a] ± 1.808 | – 1137.400 ± 1.300 | 169.500 ± 4.200 | 116.000 [c] ± 8.000 |
| $UO_2BrO_3^+$ | – 937.077 [b] ± 1.914 | – 1085.600 [b] ± 1.609 | 75.697 [b] ± 3.748 | |
| $UO_2Br_2 \cdot H_2O$(cr) | – 1328.644 [a] ± 2.515 | – 1455.900 ± 1.400 | 214.000 ± 7.000 | |
| $UO_2BrOH \cdot 2H_2O$(cr) | – 1744.162 [a] ± 4.372 | – 1958.200 ± 1.300 | 248.000 ± 14.000 | |
| $UO_2Br_2 \cdot 3H_2O$(cr) | – 1818.486 [a] ± 5.573 | – 2058.000 ± 1.500 | 304.000 ± 18.000 | |
| $UBr_2Cl$(cr) | – 714.389 [a] ± 9.765 | – 750.600 ± 8.400 | 192.500 ± 16.700 | |
| $UBr_3Cl$(cr) | – 807.114 [a] ± 9.766 | – 852.300 ± 8.400 | 238.500 ± 16.700 | |
| $UBrCl_2$(cr) | – 760.315 [a] ± 9.765 | – 812.100 ± 8.400 | 175.700 ± 16.700 | |
| $UBr_2Cl_2$(cr) | – 850.896 [a] ± 9.765 | – 907.900 ± 8.400 | 234.300 ± 16.700 | |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UBrCl_3$(cr) | – 893.500 [a] ± 9.202 | – 967.300 ± 8.400 | 213.400 ± 12.600 | |
| UI(g) | 288.861 [a] ± 25.045 | 342.000 ± 25.000 | 286.500 ± 5.000 | 44.800 [c] ± 5.000 |
| $UI^{3+}$ | – 588.719 [b] ± 2.462 | | | |
| $UI_2$(g) | 40.341 [a] ± 25.177 | 103.000 ± 25.000 | 376.500 ± 10.000 | 61.900 [c] ± 5.000 |
| $UI_3$(cr) | – 466.122 [a] ± 4.892 | – 466.900 ± 4.200 | 221.800 ± 8.400 | 112.100 [c] ± 6.000 |
| $UI_3$(g) | – 198.654 [a] ± 25.178 | – 137.000 ± 25.000 | 431.200 ± 10.000 | 86.000 [c] ± 5.000 |
| $UI_4$(cr) | – 512.671 [a] ± 3.761 | – 518.300 ± 2.800 | 263.600 ± 8.400 | 126.400 [c] ± 4.200 |
| $UI_4$(g) | – 369.585 [a] ± 6.210 | – 305.000 [b] ± 5.731 | 499.100 ± 8.000 | 108.800 [c] ± 4.000 |
| $UO_2IO_3^+$ | – 1090.305 [b] ± 1.917 | – 1228.900 [b] ± 1.819 | 90.959 [b] ± 4.718 | |
| $UO_2(IO_3)_2$(aq) | – 1225.718 [b] ± 2.493 | | | |
| $UO_2(IO_3)_2$(cr) | – 1250.206 [b] ± 2.410 | – 1461.281 [a] ± 3.609 | 279.000 ± 9.000 | |
| $UClI_3$(cr) | – 615.789 [a] ± 11.350 | – 643.800 ± 10.000 | 242.000 ± 18.000 | |
| $UCl_2I_2$(cr) | – 723.356 [a] ± 11.350 | – 768.800 ± 10.000 | 237.000 ± 18.000 | |
| $UCl_3I$(cr) | – 829.877 [a] ± 8.766 | – 898.300 ± 8.400 | 213.400 ± 8.400 | |
| $UBrI_3$(cr) | | – 589.600 ± 10.000 | | |
| $UBr_2I_2$(cr) | | – 660.400 ± 10.000 | | |
| $UBr_3I$(cr) | | – 727.600 ± 8.400 | | |
| US(cr) | – 320.929 [a] ± 12.600 | – 322.200 ± 12.600 | 77.990 ± 0.210 | 50.540 [c] ± 0.080 |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $US_{1.90}$(cr) | – 509.470 [a] ± 20.900 | – 509.900 ± 20.900 | 109.660 ± 0.210 | 73.970 [c] ± 0.130 |
| $US_2$(cr) | – 519.241 [a] ± 8.001 | – 520.400 ± 8.000 | 110.420 ± 0.210 | 74.640 [c] ± 0.130 |
| $US_3$(cr) | – 537.253 [a] ± 12.600 | – 539.600 ± 12.600 | 138.490 ± 0.210 | 95.600 [c] ± 0.250 |
| $U_2S_3$(cr) | – 879.787 [a] ± 67.002 | – 879.000 ± 67.000 | 199.200 ± 1.700 | 133.700 [c] ± 0.800 |
| $U_2S_5$(cr) | | | 243.000 ± 25.000 | |
| $U_3S_5$(cr) | – 1425.076 [a] ± 100.278 | – 1431.000 ± 100.000 | 291.000 ± 25.000 | |
| $USO_4^{2+}$ | – 1311.423 [b] ± 2.113 | – 1492.540 [b] ± 4.283 | – 245.591 [b] ± 15.906 | |
| $UO_2SO_3$(aq) | – 1477.696 [b] ± 5.563 | | | |
| $UO_2SO_3$(cr) | – 1530.370 [a] ± 12.727 | – 1661.000 ± 12.600 | 157.000 ± 6.000 | |
| $UO_2S_2O_3$(aq) | – 1487.824 [b] ± 11.606 | | | |
| $UO_2SO_4$(aq) | – 1714.535** [b] ± 1.885 | – 1908.840 [b] ± 2.229 | 46.010** [b] ± 6.452 | |
| $UO_2SO_4$(cr) | – 1685.775 [a] ± 2.642 | – 1845.140 ± 0.840 | 163.200 ± 8.400 | 145.000 [c] ± 3.000 |
| $U(SO_3)_2$(cr) | – 1712.826 [a] ± 21.171 | – 1883.000 ± 21.000 | 159.000 ± 9.000 | |
| $U(SO_4)_2$(aq) | – 2077.860 [b] ± 2.262 | – 2377.180 [b] ± 4.401 | – 69.007 [b] ± 16.158 | |
| $U(SO_4)_2$(cr) | – 2084.521 [a] ± 14.070 | – 2309.600 ± 12.600 | 180.000 ± 21.000 | |
| $UO_2(SO_4)_2^{2-}$ | – 2464.190** [b] ± 2.117 | – 2802.580 [b] ± 1.972 | 135.786** [b] ± 5.397 | |
| $UO_2(SO_4)_3^{4-}$ | – 3201.801 [b] ± 3.054 | | | |
| $U(OH)_2SO_4$(cr) | – 1766.223 [b] ± 3.385 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2SO_4 \cdot 2.5H_2O$(cr) | – 2298.475 [b] ± 1.803 | – 2607.000 ± 0.900 | 246.053 [a] ± 6.762 | |
| $UO_2SO_4 \cdot 3H_2O$(cr) | – 2416.561 [b] ± 1.811 | – 2751.500 ± 4.600 | 274.087 [a] ± 16.582 | |
| $UO_2SO_4 \cdot 3.5H_2O$(cr) | – 2535.595 [b] ± 1.806 | – 2901.600 ± 0.800 | 286.520 [a] ± 6.628 | |
| $U(SO_4)_2 \cdot 4H_2O$(cr) | – 3033.310 [a] ± 11.433 | – 3483.200 ± 6.300 | 359.000 ± 32.000 | |
| $U(SO_4)_2 \cdot 8H_2O$(cr) | – 3987.898 [a] ± 16.735 | – 4662.600 ± 6.300 | 538.000 ± 52.000 | |
| USe(cr) | – 276.908 [a] ± 14.600 | – 275.700 ± 14.600 | 96.520 ± 0.210 | 54.810 [c] ± 0.170 |
| α-$USe_2$ | – 427.072 [a] ± 42.000 | – 427.000 ± 42.000 | 134.980 ± 0.250 | 79.160 [c] ± 0.170 |
| β-$USe_2$ | – 427.972 [a] ± 42.179 | – 427.000 ± 42.000 | 138.000 ± 13.000 | |
| $USe_3$(cr) | – 451.997 [a] ± 42.305 | – 452.000 ± 42.000 | 177.000 ± 17.000 | |
| $U_2Se_3$(cr) | – 721.194 [a] ± 75.002 | – 711.000 ± 75.000 | 261.400 ± 1.700 | |
| $U_3Se_4$(cr) | – 988.760 [a] ± 85.752 | – 983.000 ± 85.000 | 339.000 ± 38.000 | |
| $U_3Se_5$(cr) | – 1130.611 [a] ± 113.567 | – 1130.000 ± 113.000 | 364.000 ± 38.000 | |
| $UO_2SeO_3$(cr) | | – 1522.000 ± 2.300 | | |
| $UO_2SeO_4$(cr) | | – 1539.300 ± 3.300 | | |
| $UO_2SeO_4$(aq) * | – 1408.761*[b] ± 2.270 | – 1602.500*[b] ± 4.301 | 57.941*[b] ± 14.681 | |
| $UO_2(SeO_4)_2^{2-}$ * | – 1854.524*[b] ± 3.392 | – 2195.000*[b] ± 8.201 | 148.857*[b] ± 28.910 | |
| $UO_2HSeO_3^+$ * | – 1381.328*[b] ± 2.268 | | | |
| $UO_2(HSeO_3)_2$(aq) * | – 1804.226*[b] ± 2.981 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| UOTe(cr) | | | 111.700 ± 1.300 | 80.600 ± 0.800 |
| $UTeO_5$(cr) | | – 1603.100 ± 2.800 | | |
| $UTe_3O_9$(cr) | | – 2275.800 ± 8.000 | | |
| UN(cr) | – 265.082 [a] ± 3.001 | – 290.000 ± 3.000 | 62.430 ± 0.220 | 47.570 [c] ± 0.400 |
| β-$UN_{1.466}$ | | – 362.200 ± 2.300 | | |
| α-$UN_{1.59}$ | – 338.202 [a] ± 5.201 | – 379.200 ± 5.200 | 65.020 ± 0.300 | |
| α-$UN_{1.606}$ | | – 381.400 ± 5.000 | | |
| α-$UN_{1.674}$ | | – 390.800 ± 5.000 | | |
| α-$UN_{1.73}$ | – 353.753 [a] ± 7.501 | – 398.500 ± 7.500 | 65.860 ± 0.300 | |
| $UO_2N_3^+$ | – 619.077 [b] ± 2.705 | | | |
| $UO_2(N_3)_2$(aq) | – 280.867 [b] ± 4.558 | | | |
| $UO_2(N_3)_3^-$ | 59.285 [b] ± 6.374 | | | |
| $UO_2(N_3)_4^{2-}$ | 412.166 [b] ± 8.302 | | | |
| $UNO_3^{3+}$ | – 649.045 [b] ± 1.960 | | | |
| $UO_2NO_3^+$ | – 1062.260*[b] ± 1.990 | – 1204.950*[b] ± 3.829 | 114.960*[b] ± 12.458 | |
| $U(NO_3)_2^{2+}$ | – 764.576 [b] ± 2.793 | | | |
| $UO_2(NO_3)_2$(cr) | – 1106.094 [a] ± 5.675 | – 1351.000 ± 5.000 | 241.000 ± 9.000 | |
| $UO_2(NO_3)_2 \cdot H_2O$(cr) | – 1362.965 [a] ± 10.524 | – 1664.000 ± 10.000 | 286.000 ± 11.000 | |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2(NO_3)_2 \cdot 2H_2O$(cr) | – 1620.500 ± 2.000 | – 1978.700 ± 1.700 | 327.520 [a] ± 8.806 | 278.000 ± 4.000 |
| $UO_2(NO_3)_2 \cdot 3H_2O$(cr) | – 1864.694 [a] ± 1.965 | – 2280.400 ± 1.700 | 367.900 ± 3.300 | 320.100 ± 1.700 |
| $UO_2(NO_3)_2 \cdot 6H_2O$(cr) | – 2584.213 [a] ± 1.615 | – 3167.500 ± 1.500 | 505.600 ± 2.000 | 468.000 ± 2.500 |
| UNCl(cr) * | – 510.996 *[a] ± 4.000 | – 559.000* ± 4.000 | 96.540* ± 0.100 | 68.080*[c] ± 0.100 |
| UP(cr) | – 265.921[a] ± 11.101 | – 269.800 ± 11.100 | 78.280 ± 0.420 | 50.290 ± 0.500 |
| $UP_2$(cr) | – 294.555 [a] ± 15.031 | – 304.000 ± 15.000 | 100.700 ± 3.200 | 78.800 ± 3.500 |
| $U_3P_4$(cr) | – 826.435 [a] ± 26.014 | – 843.000 ± 26.000 | 259.400 ± 2.600 | 176.900 ± 3.600 |
| $UPO_5$(cr) | – 1924.713 [a] ± 4.990 | – 2064.000 ± 4.000 | 137.000 ± 10.000 | 124.000 [c] ± 12.000 |
| $UO_2PO_4^-$ | – 2040.887*[b] ± 3.611 | | | |
| $UP_2O_7$(cr) | – 2659.272 [a] ± 5.369 | – 2852.000 ± 4.000 | 204.000 ± 12.000 | 184.000 ± 18.000 |
| $(UO_2)_2P_2O_7$(cr) | – 3930.002 [a] ± 6.861 | – 4232.600 ± 2.800 | 296.000 ± 21.000 | 258.000 [c] ± 26.000 |
| $(UO_2)_3(PO_4)_2$(cr) | – 5115.975 [a] ± 5.452 | – 5491.300 ± 3.500 | 410.000 ± 14.000 | 339.000 [c] ± 17.000 |
| $UO_2HPO_4$(aq) | – 2089.862 [b] ± 2.777 | | | |
| $UO_2HPO_4$(cr) * | – 2094.408*[a] ± 5.660 | – 2274.814* ± 4.812 | 167.000* ± 10.000 | 146.000* ± 10.000 |
| $UO_2H_2PO_4^+$ | – 2108.311 [b] ± 2.378 | | | |
| $UO_2H_3PO_4^{2+}$ | – 2106.256 [b] ± 2.504 | | | |
| $UO_2(H_2PO_4)_2$(aq) | – 3254.938 [b] ± 3.659 | | | |
| $UO_2(H_2PO_4)(H_3PO_4)^+$ | – 3260.703 [b] ± 3.659 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2HPO_4 \cdot 4H_2O$(cr) | – 3064.749 [b] ± 2.414 | – 3475.334* [a] ± 3.838 | 328.000* ± 10.000 | 317.000* ± 10.000 |
| $UH_2PO_4^{3+}$ * | – 1705.826* [b] ± 4.641 | | | |
| $U(HPO_4)_2 \cdot 4H_2O$(cr) | – 3844.453 [b] ± 3.717 | – 4334.818 [a] ± 8.598 | 372.000 ± 26.000 | 460.000 ± 50.000 |
| $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr) | – 6138.968 [b] ± 6.355 | – 6739.105 [a] ± 9.136 | 589.000 ± 22.000 | |
| $(UO_2)_3(PO_4)_2 \cdot 6H_2O$(cr) | – 6613.025 [a] ± 13.392 | – 7328.400 ± 10.700 | 669.000 ± 27.000 | |
| $NH_4[(UO_2)(PO_4)] \cdot 3H_2O$(cr) * | – 2917.839* [b] ± 6.181 | | | |
| UAs(cr) | – 237.908 [a] ± 8.024 | – 234.300 ± 8.000 | 97.400 ± 2.000 | 57.900 ± 1.200 |
| $UAs_2$(cr) | – 252.790 [a] ± 13.005 | – 252.000 ± 13.000 | 123.050 ± 0.200 | 79.960 ± 0.100 |
| $U_3As_4$(cr) | – 725.388 [a] ± 18.016 | – 720.000 ± 18.000 | 309.070 ± 0.600 | 187.530 ± 0.200 |
| $UAsO_5$(cr) | | | | 138.000 [c] ± 14.000 |
| $UO_2(AsO_3)_2$(cr) | – 1944.911 [a] ± 12.006 | – 2156.600 ± 8.000 | 231.000 ± 30.000 | 201.000 [c] ± 20.000 |
| $(UO_2)_2As_2O_7$(cr) | – 3130.254 [a] ± 12.006 | – 3426.000 ± 8.000 | 307.000 ± 30.000 | 273.000 [c] ± 27.000 |
| $(UO_2)_3(AsO_4)_2$(cr) | – 4310.789 [a] ± 12.007 | – 4689.400 ± 8.000 | 387.000 ± 30.000 | 364.000 [c] ± 36.000 |
| $(UO_2)_3(AsO_4)_2 \cdot 12H_2O$(cr) * | – 7258.797* [b] ± 11.160 | | | |
| $UO_2HAsO_4$(aq) | – 1707.994 [b] ± 4.717 | | | |
| $UO_2H_2AsO_4^+$ | – 1726.260 [b] ± 4.582 | | | |
| $UO_2(H_2AsO_4)_2$(aq) | – 2486.326 [b] ± 8.283 | | | |
| $UO_2HAsO_4 \cdot 4H_2O$(cr) * | – 2680.755* [b] ± 4.698 | – 3083.293* [a] ± 5.567 | 349.000* ± 10.000 | 326.000* ± 10.000 |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| UAsS(cr) | | | 114.500 ± 3.400 | 80.900 ± 2.400 |
| UAsSe(cr) | | | 131.900 ± 4.000 | 83.500 ± 2.500 |
| UAsTe(cr) | | | 139.900 ± 4.200 | 81.300 ± 2.400 |
| $NH_4[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) * | – 2532.717*[b] ± 7.197 | | | |
| USb(cr) | – 140.969 [a] ± 7.711 | – 138.500 ± 7.500 | 104.000 ± 6.000 | 75.000 ± 7.000 |
| $USb_2$(cr) | – 173.666 [a] ± 10.901 | – 173.600 ± 10.900 | 141.460 ± 0.130 | 80.200 ± 0.100 |
| $U_4Sb_3$(cr) | | | 379.000 ± 20.000 | |
| $U_3Sb_4$(cr) | – 457.004 [a] ± 22.602 | – 451.900 ± 22.600 | 349.800 ± 0.400 | 188.200 ± 0.200 |
| α-$Bi_2UO_6$ * | | | 238.800* ± 7.700 | 185.100* ± 5.600 |
| UC(cr) | – 98.900 ± 3.000 | – 97.900 ± 4.000 | 59.294 [a] ± 16.772 | 50.100 [c] ± 1.000 |
| α-$UC_{1.94}$ | – 87.400 ± 2.100 | – 85.324 [a] ± 2.185 | 68.300 ± 2.000 | 60.800 [c] ± 1.500 |
| $U_2C_3$(cr) | – 189.317 [a] ± 10.002 | – 183.300 ± 10.000 | 137.800 ± 0.300 | 107.400 [c] ± 2.000 |
| $UO_2CO_3$(aq) | – 1537.188 [b] ± 1.799 | – 1689.230 [b] ± 2.512 | 58.870 [b] ± 7.438 | |
| $UO_2CO_3$(cr) | – 1564.701 [b] ± 1.794 | – 1691.302 [a] ± 1.798 | 144.200 ± 0.300 | 120.100 ± 0.100 |
| $UO_2(CO_3)_2^{2-}$ | – 2103.161 [b] ± 1.982 | – 2350.960 [b] ± 4.301 | 181.846 [b] ± 13.999 | |
| $UO_2(CO_3)_3^{4-}$ | – 2660.914 [b] ± 2.116 | – 3083.890 [b] ± 4.430 | 38.446 [b] ± 14.411 | |
| $UO_2(CO_3)_3^{5-}$ | – 2584.392 [b] ± 2.943 | | | |
| $U(CO_3)_4^{4-}$ | – 2841.926 [b] ± 5.958 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $U(CO_3)_5^{6-}$ | – 3363.432 [b] ± 5.772 | – 3987.350 [b] ± 5.334 | – 83.051 [b] ± 25.680 | |
| $(UO_2)_3(CO_3)_6^{6-}$ | – 6333.285 [b] ± 8.096 | – 7171.080 [b] ± 5.316 | 228.926 [b] ± 23.416 | |
| $(UO_2)_2CO_3(OH)_3^-$ | – 3139.526 [b] ± 4.517 | | | |
| $(UO_2)_3O(OH)_2(HCO_3)^+$ | – 4100.695 [b] ± 5.973 | | | |
| $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$ | – 16698.986 [b] ± 22.383 | | | |
| $UO_2CO_3F^-$ | – 1840.459 [b] ± 1.987 | | | |
| $UO_2CO_3F_2^{2-}$ | – 2132.371 [b] ± 2.400 | | | |
| $UO_2CO_3F_3^{3-}$ | – 2418.518 [b] ± 2.813 | | | |
| $(NH_4)_4[UO_2(CO_3)_3](cr)$* | | – 3555.100* ± 4.600 | | |
| $USCN^{3+}$ | – 454.113 [b] ± 4.385 | – 541.800 [b] ± 9.534 | – 306.326 [b] ± 35.198 | |
| $U(SCN)_2^{2+}$ | – 368.776 [b] ± 8.257 | – 456.400 [b] ± 9.534 | – 107.174 [b] ± 42.302 | |
| $UO_2SCN^+$ | – 867.842 [b] ± 4.558 | – 939.380 [b] ± 4.272 | 83.671 [b] ± 19.708 | |
| $UO_2(SCN)_2(aq)$ | – 774.229 [b] ± 8.770 | – 857.300 [b] ± 8.161 | 243.927 [b] ± 39.546 | |
| $UO_2(SCN)_3^-$ | – 686.438 [b] ± 12.458 | – 783.800 [b] ± 12.153 | 394.934 [b] ± 57.938 | |
| $UO_2SiO(OH)_3^+$ | – 2251.021*[b] ± 2.294 | – 2440.070*[b] ± 6.308 | 181.074*[b] ± 20.820 | |
| $(UO_2)_2SiO_4{\cdot}2H_2O(cr)$ * | – 3655.762*[b] ± 3.931 | | | |
| $Pb[(UO_2)(AsO_4)]_2{\cdot}10H_2O(cr)$ * | – 5861.741*[b] ± 10.458 | | | |
| $UO_2(BO_2)_2(cr)$* | – 2391.354*[a] ± 3.458 | – 2541.400* ± 3.400 | 174.200* ± 2.100 | 159.900* ± 1.000 |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Tl_2U_4O_{11}$(cr) | | | | 360.200 [(c)] ± 20.000 |
| $Zn_{0.12}UO_{2.95}$(cr) | | – 1938.070 ± 1.060 | | |
| $Zn[UO_2(SO_4)_2]\cdot 5H_2O$(cr) * | – 3774.458*[(a)] ± 4.778 | – 4332.260* ± 4.736 | 477.100* ± 2.100 | 447.500* ± 1.500 |
| $Zn[(UO_2)(PO_4)]_2\cdot 8H_2O$(cr)* | – 6284.666*[(b)] ± 7.409 | | | |
| $Zn[(UO_2)(PO_4)]_2\cdot 10H_2O$(cr)* | – 6758.946*[(b)] ± 7.413 | | | |
| $Zn[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr) * | – 5503.576*[(b)] ± 10.451 | | | |
| $Cd[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr) * | – 5435.819*[(b)] ± 10.475 | | | |
| $Cu[UO_2(SO_4)_2]\cdot 5H_2O$(cr) * | – 3574.897*[(a)] ± 4.827 | – 4119.110* ± 4.785 | 514.200* ± 2.100 | 483.300* ± 1.500 |
| $Cu[(UO_2)(PO_4)]_2\cdot 8H_2O$(cr) * | – 6089.547*[(b)] ± 5.254 | | | |
| $Cu[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr) * | – 5294.758*[(b)] ± 10.563 | | | |
| $Ni[UO_2(SO_4)_2]\cdot 5H_2O$(cr) * | – 3729.858*[(a)] ± 4.761 | – 4253.057* ± 4.719 | 581.400* ± 2.100 | 535.400* ± 1.500 |
| $Ni[(UO_2)(PO_4)]_2\cdot 8H_2O$(cr) * | – 6183.807*[(b)] ± 7.445 | | | |
| $Ni[(UO_2)(PO_4)]_2\cdot 10H_2O$(cr) * | – 6658.087*[(b)] ± 7.449 | | | |
| $Ni[(UO_2)(AsO_4)]_2\cdot 10H_2O$(cr) * | – 5880.993*[(b)] ± 10.479 | | | |
| $Co[UO_2(SO_4)_2]\cdot 5H_2O$(cr) * | – 3725.645*[(a)] ± 5.072 | – 4243.140* ± 5.033 | 600.700* ± 2.100 | 590.600* ± 1.500 |
| $Co[(UO_2)(PO_4)]_2\cdot 7H_2O$(cr) * | – 5952.821*[(b)] ± 7.413 | | | |
| $Co[(UO_2)(PO_4)]_2\cdot 8H_2O$(cr) * | – 6189.961*[(b)] ± 7.415 | | | |
| $Co[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr) * | – 5418.004*[(b)] ± 10.455 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $FeUO_4$(cr) * | | – 1599.700* ± 3.100 | | |
| $Fe[UO_2(SO_4)_2]\cdot 5H_2O$(cr) * | – 3761.166*[a] ± 4.692 | – 4285.562* ± 4.649 | 574.600* ± 2.100 | 548.200* ± 1.500 |
| $Fe[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr) * | – 5452.800*[b] ± 15.319 | | | |
| $Mn[UO_2(SO_4)_2]\cdot 5H_2O$(cr) * | – 3910.045*[a] ± 5.097 | – 4426.160* ± 5.058 | 607.300* ± 2.100 | 591.900* ± 1.500 |
| $Mn[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr) * | – 5583.338*[b] ± 10.523 | | | |
| $CrUO_4$(cr) * | | – 1753.600* ± 4.800 | | |
| $UO_2MoO_4$(cr) * | – 1835.486*[a] ± 8.004 | – 1985.000* ± 8.000 | 192.800* ± 0.800 | 162.700* ± 0.300 |
| $(UO_2)_2(V_2O_7)$(cr) * | – 3661.898*[a] ± 6.136 | – 3939.200* ± 6.100 | 356.000* ± 2.100 | 296.700* ± 2.100 |
| $H[UO_2VO_4]\cdot 2H_2O$(cr) * | − 2480.089*[a] ± 3.262 | – 2757.600* ± 3.200 | 295.400* ± 2.100 | 324.900* ± 1.500 |
| $U_{0.952}Ti_{2.04806}O_6$(cr) * | | | 175.560* ± 3.500 | 179.460* ± 3.400 |
| $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$ | – 6140.119 [b] ± 9.582 | | | |
| $(UO_2)_2(NpO_2)(CO_3)_6^{6-}$ | – 6176.973 [b] ± 16.977 | | | |
| $Be_{13}U$(cr) | – 165.508 [a] ± 17.530 | – 163.600 ± 17.500 | 180.100 ± 3.300 | 242.300 ± 4.200 |
| α-$Mg_{0.17}UO_{2.95}$ | | – 1291.440 ± 0.990 | | |
| $MgUO_4$(cr) | – 1750.601*[a] ± 1.502 | – 1858.300* ± 1.500 | 131.950 ± 0.170 | 128.100 ± 0.300 |
| $MgU_3O_{10}$(cr) | | | 338.600 ± 1.000 | 305.600 ± 5.000 |
| $Mg[(UO_2)(PO_4)]_2\cdot 8H_2O$(cr) * | – 6589.413*[b] ± 8.423 | | | |
| $Mg[(UO_2)(AsO_4)]_2\cdot 10H_2O$(cr) * | – 6283.174*[b] ± 9.304 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Mg[UO_2(CO_3)_3]^{2-}$ * | – 3141.177*[(b)] ± 2.740 | | | |
| $Mg_2[UO_2(CO_3)_3](aq)$ * | – 3601.689*[(b)] ± 4.825 | | | |
| $Mg_2[UO_2(CO_3)_3](cr)$* | | – 5451.300* ± 5.800 | | |
| $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O(cr)$* | | – 9173.200* ± 4.200 | | |
| $Mg[UO_2BO_3]_2(cr)$ * | – 4094.383*[(a)] ± 4.052 | – 4363.800* ± 4.000 | 267.000* ± 2.100 | 242.200* ± 1.500 |
| $Mg[UO_2BO_3]_2\cdot 4H_2O(cr)$ * | | | 410.200* ± 3.400 | 389.300* ± 1.500 |
| $Mg[UO_2VO_4]_2\cdot 5H_2O(cr)$ * | | | 631.600* ± 4.000 | 627.500* ± 3.000 |
| β-$CaUO_4$ | | | | 124.700 ± 2.700 |
| $CaUO_4(cr)$ | – 1886.798*[(a)] ± 2.404 | – 2002.300 ± 2.300 | 114.700* ± 2.300 | 115.400* ± 3.500 |
| $Ca_3UO_6(cr)$ | | – 3305.400 ± 4.100 | | |
| $CaU_6O_{19}\cdot 11H_2O(cr)$ | – 10305.460 [(b)] ± 13.964 | | | |
| $Ca[(UO_2)(PO_4)]_2\cdot 6H_2O(cr)$ * | – 6217.131*[(b)] ± 7.476 | | | |
| $Ca[(UO_2)(AsO_4)]_2\cdot 6H_2O(cr)$ * | – 5434.899*[(b)] ± 10.498 | | | |
| $Ca[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$ * | – 6383.459*[(b)] ± 10.503 | | | |
| $Ca[UO_2(CO_3)_3]^{2-}$ * | – 3243.174*[(b)] ± 2.613 | – 3634.690*[(b)] ± 6.310 | 54.872*[(b)] ± 20.944 | |
| $Ca_2[UO_2(CO_3)_3](aq)$ * | – 3817.671*[(b)] ± 3.747 | – 4177.690*[(b)] ± 7.471 | 71.424*[(b)] ± 25.136 | |
| $Ca_2[UO_2(CO_3)_3](cr)$ * | | – 5017.400* ± 5.500 | | |
| $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O(cr)$ * | | – 7044.700* ± 3.700 | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O$(cr) * | – 6196.253*[b] ± 4.281 | | | |
| $Ca[UO_2BO_3]_2$(cr) * | – 4226.617*[a] ± 3.560 | – 4491.300* ± 3.500 | 291.800* ± 2.100 | 252.900* ± 1.500 |
| $Ca[UO_2VO_4]_2$(cr) * | | – 4798.700* ± 7.100 | | |
| $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr) * | – 5743.784*[a] ± 7.204 | – 6327.300* ± 7.100 | 639.400* ± 4.000 | 589.600* ± 3.000 |
| $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr) * | – 6455.436*[a] ± 7.030 | – 7203.700* ± 7.000 | 786.600* ± 2.000 | 777.500* ± 3.000 |
| $SrUO_3$(cr) | | – 1672.600 ± 8.600 | | |
| α-$SrUO_4$ | | – 1989.600 ± 2.800 | – * | – * |
| β-$SrUO_4$ | – 1878.381* ± 5.469 | – 1988.400 ± 5.400 | 147.200* ± 2.900 | 119.700* ± 3.600 |
| $Sr_2UO_{4.5}$(cr) | | – 2494.000 ± 2.800 | | |
| $Sr_2UO_5$(cr) | | – 2632.900 ± 1.900 | | |
| $Sr_3UO_6$(cr) | | – 3263.500 ± 3.000 | | |
| $Sr_3U_2O_9$(cr) | | – 4620.000 ± 8.000 | | 301.800[c] ± 3.000 |
| $Sr_2U_3O_{11}$(cr) | | – 5243.700 ± 5.000 | | |
| $SrU_4O_{13}$(cr) | | – 5920.000 ± 20.000 | | |
| $Sr_5U_3O_{14}$(cr) | | – 7248.600 ± 7.500 | | |
| $Sr_3U_{11}O_{36}$(cr) | | – 15903.800 ± 16.500 | | 1064.200[c] ± 10.600 |
| $Sr[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) * | – 6235.609*[b] ± 7.443 | | | |
| $Sr[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) * | – 5920.237*[b] ± 10.477 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Sr[UO_2(CO_3)_3]^{2-}$ * | – 3247.953*[(b)] ± 2.517 | | | |
| $Sr_2[UO_2(CO_3)_3](aq)$ * | – 3833.508*[(b)] ± 3.874 | | | |
| $Sr_2[UO_2(CO_3)_3](cr)$ * | | – 4915.800* ± 6.800 | | |
| $Sr_2[UO_2(CO_3)_3]\cdot 8H_2O(cr)$ * | | – 6508.400* ± 5.500 | | |
| α-$Sr[UO_2BO_3]_2$ * | | – 4512.900* ± 4.300 | | |
| β-$Sr[UO_2BO_3]_2$ * | | – 4503.700* ± 4.500 | | |
| $Sr[UO_2BO_3]_2\cdot 2H_2O(cr)$ * | | | 351.500* ± 2.300 | 316.400* ± 1.500 |
| $Sr_3In_2UO_9(cr)$ * | | | 384.600* ± 11.500 | 321.300* ± 1.900 |
| $Sr[UO_2VO_4]_2(cr)$ * | | – 4858.200* ± 17.800 | | |
| $Sr[UO_2VO_4]_2\cdot 5H_2O(cr)$* | – 5797.913*[(a)] ± 16.744 | – 6372.100* ± 16.700 | 684.800* ± 4.000 | 650.000* ± 3.000 |
| $BaUO_3(cr)$ | | – 1690.000 ± 10.000 | | |
| $BaUO_4(cr)$ | – 1883.805 [(a)] ± 3.393 | – 1993.800 ± 3.300 | 154.000 ± 2.500 | 125.300 ± 2.500 |
| $Ba_3UO_6(cr)$ | – 3042.149*[(a)] ± 8.173 | – 3210.400 ± 8.000 | 288.600* ± 5.000 | 216.300*[(c)] ± 6.500 |
| $BaU_2O_7(cr)$ | – * | – 3237.200 ± 5.000 | – * | |
| $Ba_2U_2O_7(cr)$ | – * | – 3740.000 ± 6.300 | – * | |
| $Ba_{2.875}UO_{5.875}(cr)$ * | – 2959.312*[(a)] ± 8.170 | – 3118.700* ± 8.000 | 297.700* ± 5.000 | 215.100* ± 6.500 |
| $Ba_2U_3O_{11}(cr)$ * | – 4917.754*[(a)] ± 6.721 | – 5210.500* ± 6.000 | 421.900* ± 10.000 | 325.800* ± 9.800 |
| $Ba[(UO_2)(PO_4)]_2\cdot 6H_2O(cr)$ * | – 6234.538*[(b)] ± 7.839 | | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Ba[(UO_2)(AsO_4)]_2 \cdot 7H_2O$(cr) * | – 5674.606*[(b)] ± 10.761 | | | |
| $Ba[UO_2(CO_3)_3]^{2-}$ * | – 3240.033*[(b)] ± 3.744 | | | |
| $Ba_2[UO_2(CO_3)_3]$(cr) * | | – 4645.800* ± 6.900 | | |
| $Ba_2[UO_2(CO_3)_3] \cdot 6H_2O$(cr) * | | – 5882.800* ± 5.600 | | |
| α-$Ba[UO_2BO_3]_2$ * | – 4235.185*[(a)] ± 4.640 | – 4509.000* ± 4.600 | 282.000* ± 1.800 | 229.700* ± 1.000 |
| β-$Ba[UO_2BO_3]_2$ * | | – 4499.100* ± 4.600 | | |
| $Ba[UO_2BO_3]_2 \cdot 2H_2O$(cr) * | – 4740.459*[(a)] ± 8.042 | – 5129.900* ± 8.000 | 360.700* ± 2.600 | 311.800* ± 1.500 |
| $Ba_3In_2UO_9$(cr) * | | | 417.900* ± 12.500 | 329.100* ± 2.000 |
| $Ba[UO_2VO_4]_2$(cr) * | | | 432.100* ± 4.000 | 365.000* ± 3.000 |
| $Ba[UO_2VO_4]_2 \cdot 4H_2O$(cr) * | | | 631.800* ± 2.000 | 564.900* ± 3.000 |
| $Ba_3Sc_2UO_9$(cr) * | | | 383.100* ± 11.500 | 313.500* ± 1.900 |
| $Ba_3Y_2UO_9$(cr) * | | | 416.400* ± 12.500 | 330.600* ± 2.000 |
| $Ba_2Sm_{2/3}UO_6$(cr) * | | | 244.100* ± 7.300 | 186.400* ± 5.600 |
| $Ba_2MgUO_6$(cr) | | – 3245.900 ± 6.500 | | |
| $Ba_2CaUO_6$(cr) | | – 3295.800* ± 5.900 | | |
| $Ba_2SrUO_6$(cr) | – 3090.695*[(a)] ± 5.754 | – 3257.300 ± 5.700 | 287.400* ± 2.000 | 223.700* ± 1.300 |
| $Li_{0.12}UO_{2.95}$(cr) | | – 1254.970 [(b)] ± 1.225 | | |
| γ-$Li_{0.55}UO_3$ | | – 1394.535 [(b)] ± 2.779 | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| δ-$Li_{0.69}UO_3$ | | – 1434.525 [(b)] ± 2.367 | | |
| $LiUO_3$(cr) | | – 1522.300 ± 1.800 | | |
| $Li_2UO_4$(cr) | – 1853.190 [(a)] ± 2.215 | – 1968.200 ± 1.300 | 133.000 ± 6.000 | |
| $Li_4UO_5$(cr) | | – 2639.400 ± 1.700 | | |
| $Li_2U_2O_7$(cr) | | – 3213.600 ± 5.300 | | |
| $Li_{0.19}U_3O_8$(cr) | | – 3632.955 [(b)] ± 3.113 | | |
| $Li_{0.88}U_3O_8$(cr) | | – 3837.090 [(b)] ± 3.748 | | |
| $Li_2U_3O_{10}$(cr) | | – 4437.400 ± 4.100 | | |
| $Li[(UO_2)(PO_4)]·4H_2O$(cr) * | – 3365.074*[(b)] ± 6.177 | | | |
| $Li[(UO_2)(AsO_4)]·4H_2O$(cr) * | – 2958.832*[(b)] ± 7.193 | | | |
| $Li_4[UO_2(CO_3)_3]·1.5H_2O$(cr) * | | – 4550.800* ± 3.300 | | |
| $Li[UO_2(BO_3)]$(cr) * | – 2147.656*[(a)] ± 3.614 | – 2272.700* ± 3.500 | 178.700* ± 3.000 | 176.300* ± 1.000 |
| $Li[UO_2BO_3]·0.5H_2O$(cr) * | | – 2436.200* ± 3.500 | | |
| $Li[UO_2BO_3]·H_2O$(cr)* | | – 2597.000* ± 3.500 | | |
| $Li[UO_2BO_3]·1.5H_2O$(cr) * | – 2528.265*[(b)] ± 2.257 | – 2753.100* ± 3.500 | 193.887*[(a)] ± 13.971 | |
| $Li[UO_2VO_4]$(cr) * | | – 2398.300* ± 3.500 | | |
| $Na_{0.12}UO_{2.95}$(cr) | | – 1247.372 [(b)] ± 1.877 | | |
| α-$Na_{0.14}UO_3$ | | – 1267.234 [(b)] ± 1.804 | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| δ-$Na_{0.54}UO_3$ | | – 1376.954 [b] ± 5.482 | | |
| $NaUO_3$(cr) | – 1412.483*[a] ± 10.216 | – 1494.900 ± 10.000 | 132.800* ± 7.000 | 108.900*[c] ± 7.000 |
| α-$Na_2UO_4$ | – 1779.303 [a] ± 3.506 | – 1897.700 ± 3.500 | 166.000 ± 0.500 | 146.700 [c] ± 0.500 |
| β-$Na_2UO_4$ | | – 1884.600 ± 3.600 | | |
| $Na_3UO_4$(cr) | – 1899.909 [a] ± 8.003 | – 2024.000 ± 8.000 | 198.200 ± 0.400 | 173.000 [c] ± 0.400 |
| $Na_4UO_5$(cr) | – 2301.729*[a] ± 2.884 | – 2457.000 ± 2.200 | 247.500* ± 6.200 | 220.600* ± 6.700 |
| $Na_2U_2O_7$(cr) | – 3011.454 [a] ± 4.015 | – 3203.800 ± 4.000 | 275.900 ± 1.000 | 227.300 [c] ± 1.000 |
| $Na_2U_2O_7 \cdot H_2O$(cr)* | – 3238.292*[b] ± 4.182 | | | |
| $Na_{0.20}U_3O_8$(cr) | | – 3626.450 [b] ± 3.252 | | |
| $Na_6U_7O_{24}$(cr) | | – 10841.700 ± 10.000 | | |
| $Na[(UO_2)(PO_4)] \cdot 3H_2O$(cr) * | – 3090.120*[b] ± 6.176 | | | |
| $Na[(UO_2)(AsO_4)] \cdot 3H_2O$(cr) * | – 2704.427*[b] ± 7.192 | | | |
| $Na_4[UO_2(CO_3)_3]$(cr) | – 3719.960*[a] ± 2.575 | – 4003.100* ± 2.400 | 451.300* ± 3.000 | 420.100* ± 2.400 |
| $Na(UO_2)(SiO_3OH) \cdot H_2O$(cr) * | – 2727.681*[b] ± 3.226 | | | |
| $Na[UO_2(BO_3)]$(cr) * | – 2122.814*[a] ± 3.517 | – 2257.900* ± 3.400 | 167.200* ± 3.000 | 145.800* ± 1.000 |
| $Na[UO_2BO_3] \cdot 0.5H_2O$(cr) * | | – 2428.100* ± 3.500 | | |
| $Na[UO_2BO_3] \cdot H_2O$(cr) * | – 2379.358*[b] ± 2.256 | – 2579.039*[a] ± 2.428 | 183.800* ± 3.000 | 159.000* ± 1.000 |
| $Na[UO_2VO_4]$(cr) * | – 2270.335*[a] ± 4.296 | – 2430.300* ± 4.200 | 209.100* ± 3.000 | 180.200* ± 1.500 |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Na[UO_2VO_4]\cdot H_2O$(cr) * | | – 2734.100* ± 3.300 | | |
| $Na[UO_2VO_4]\cdot 2H_2O$(cr) * | – 2760.469*[a] ± 5.179 | – 3032.900* ± 5.100 | 298.400* ± 3.000 | 267.700* ± 1.500 |
| $NaK_3[UO_2(CO_3)_3]$(cr) * | – 3707.740*[a] ± 3.857 | – 3992.800* ± 3.800 | 485.000* ± 2.100 | 389.000* ± 2.000 |
| $KUO_3$(cr) | | – 1522.900 ± 1.700 | | 137.000[c] ± 10.000 |
| $K_2UO_4$(cr) | – 1798.499[a] ± 3.248 | – 1920.700 ± 2.200 | 180.000 ± 8.000 | |
| $K_2U_2O_7$(cr) | | – 3250.500 ± 4.500 | | 229.000[c] ± 20.000 |
| $K_2U_4O_{13}$(cr) | | | | 425.000[c] ± 50.000 |
| $K_2U_6O_{19}\cdot 11H_2O$(cr) | – 10337.081[b] ± 10.956 | | | |
| $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr) * | – 3117.526*[b] ± 6.176 | | | |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) * | – 2727.838*[b] ± 7.192 | | | |
| $K_4UO_2(CO_3)_3$(cr) * | – 3720.960*[a] ± 4.890 | – 4021.100* ± 4.800 | 447.800* ± 3.000 | 362.600* ± 1.800 |
| $K(UO_2)(SiO_3OH)\cdot H_2O$(cr) * | – 2755.830*[b] ± 6.979 | – 2990.993*[a] ± 7.843 | 259.000* ± 12.000 | |
| $K[UO_2(BO_3)]$(cr) * | – 2156.688*[a] ± 3.517 | – 2289.800* ± 3.400 | 187.200* ± 3.000 | 157.600* ± 1.000 |
| $K[UO_2BO_3]\cdot 0.2H_2O$(cr) * | | – 2355.000* ± 3.400 | | |
| $K[UO_2BO_3]\cdot H_2O$(cr) * | – 2403.168*[b] ± 2.257 | – 2609.800* ± 3.400 | 173.871[a] ± 13.691 | |
| $K[UO_2VO_4]$(cr) * | – 2284.922*[a] ± 6.007 | – 2446.700* ± 6.000 | 216.400* ±0.900 | 177.000* ± 1.000 |
| $K_2[UO_2VO_4]_2\cdot 3H_2O$(cr) * | – 5316.941*[b] ± 5.188 | | | |
| $RbUO_3$(cr) | | – 1520.900 ± 1.800 | | |

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Table 3-1 (continued)

| Compound | $\Delta_f G^o_m$ / kJ·mol$^{-1}$ | $\Delta_f H^o_m$ / kJ·mol$^{-1}$ | $S^o_m$ / J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Rb_2UO_4$(cr) | – 1800.141 [(a)] ± 3.250 | – 1922.700 ± 2.200 | 203.000 ± 8.000 | |
| $Rb_2U_2O_7$(cr) | | – 3232.000 ± 4.300 | | |
| $Rb_2U_4O_{11}$(cr) | | | | 365.600 [(c)] ± 25.000 |
| $Rb_2U_4O_{13}$(cr) | | | | 420.000 [(c)] ± 50.000 |
| $Rb_2U(SO_4)_3$(cr) | | | | 348.000 [(c)] ± 30.000 |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O$(cr) * | – 3120.738*[(b)] ± 6.177 | | | |
| $Rb[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) * | – 2736.757*[(b)] ± 7.193 | | | |
| $Rb[UO_2(BO_3)]$(cr) * | – 2150.773*[(a)] ± 3.421 | – 2288.000* ± 3.300 | 185.500* ± 3.000 | 148.800* ± 1.000 |
| $Rb[UO_2BO_3]\cdot 0.25H_2O$(cr) * | | – 2365.300* ± 3.300 | | |
| $Rb[UO_2BO_3]\cdot H_2O$(cr) * | – 2405.752*[(b)] ± 2.260 | – 2603.500* ± 3.300 | 215.764*[(a)] ± 13.420 | |
| $Rb[UO_2VO_4]$(cr) * | – 2267.680*[(a)] ± 1.924 | – 2430.800* ± 1.900 | 224.000* ± 0.900 | 181.900* ± 0.900 |
| $Cs_2UO_4$(cr) | – 1805.370 [(a)] ± 1.232 | – 1928.000 ± 1.200 | 219.660 ± 0.440 | 152.760 [(c)] ± 0.310 |
| $Cs_2U_2O_7$(cr) | – 3022.881 [(a)] ± 10.005 | – 3220.000 ± 10.000 | 327.750 ± 0.660 | 231.200 [(c)] ± 0.500 |
| $Cs_2U_4O_{12}$(cr) | – 5251.058 [(a)] ± 3.628 | – 5571.800 ± 3.600 | 526.400 ± 1.000 | 384.000 [(c)] ± 1.000 |
| $Cs_4U_5O_{17}$(cr) | | | | 750.000 [(c)] ± 50.000 |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O$(cr) * | – 3010.185*[(b)] ± 7.804 | | | |
| $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O$(cr) * | – 2629.059*[(b)] ± 7.211 | | | |
| $Cs[UO_2(BO_3)]$(cr) * | – 2153.500*[(a)] ± 4.004 | – 2284.600* ± 3.900 | 214.500* ± 3.000 | 179.800* ± 1.000 |

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Table 3-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Cs[UO_2BO_3]\cdot 0.5H_2O$(cr) * | | – 2446.400* ± 3.900 | | |
| $Cs[UO_2BO_3]\cdot H_2O$(cr) * | – 2412.000*[b] ± 2.317 | – 2597.000* ± 3.900 | 266.971*[a] ± 15.222 | |
| $Cs[UO_2VO_4]$(cr) * | – 2271.566*[a] ± 2.820 | – 2436.400* ± 2.800 | 226.700* ± 1.000 | 179.800* ± 0.900 |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_f G_m^o = \Delta_f H_m^o - T\sum_i S_{m,i}^o$ .
(b) Value calculated internally from reaction data (see Table 3-2).
(c) Temperature coefficients of this function are listed in Table 3-3.
(d) Stable phase of $UO_{2.25}$ ($\equiv U_4O_9$) above 348 K. The thermodynamic parameters, however, refer to 298.15 K.
(e) Stable phase of $UO_{2.25}$ ($\equiv U_4O_9$) below 348 K.
(*) New compound and/or value that has changed from [2003GUI/FAN].
(**) Only the uncertainty has changed from [2003GUI/FAN].

Table 3-2: Selected thermodynamic data for reactions involving uranium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I$ = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. New reactions and data that have been changed from [2003GUI/FAN] are denoted with an asterisk (*). Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $U^{3+}$ | $U^{4+} + e^- \rightleftharpoons U^{3+}$ | | | | |
| | | – 9.353 [(b)] | 53.387 | 102.100 | 163.383 [(a)] |
| | | ± 0.070 | ± 0.400 | ± 1.700 | ± 5.857 |
| $U^{4+}$ | $4H^+ + UO_2^{2+} + 2\,e^- \rightleftharpoons 2H_2O(l) + U^{4+}$ | | | | |
| | | 9.038 | – 51.589 | | |
| | | ± 0.041 | ± 0.234 | | |
| $UO_2$(am, hyd) | $U^{4+} + 4OH^- \rightleftharpoons 2H_2O(l) + UO_2$(am, hyd) | | | | |
| | | 54.500 | – 311.088 | | |
| | | ± 1.000 | ± 5.708 | | |
| $UO_2^+$ | $UO_2^{2+} + e^- \rightleftharpoons UO_2^+$ | | | | |
| | | 1.484 [(b)] | – 8.471 | | |
| | | ± 0.022 | ± 0.126 | | |
| α-$UO_{2.95}$ | $0.15UO_{2.6667}$(cr) + 0.85 γ-$UO_3 \rightleftharpoons$ α-$UO_{2.95}$ | | | | |
| | | | | 7.690 | |
| | | | | ± 0.770 | |
| $UOH^{3+}$ | $H_2O(l) + U^{4+} \rightleftharpoons H^+ + UOH^{3+}$ | | | | |
| | | –0.540 | 3.082 | 46.910 [(a)] | 147.000 |
| | | ± 0.060 | ± 0.342 | ± 8.951 | ± 30.000 |
| $UO_2OH^+$ | $H_2O(l) + UO_2^{2+} \rightleftharpoons H^+ + UO_2OH^+$ | | | | |
| | | – 5.250 | 29.967 | 43.300* | 44.718* |
| | | ± 0.240 | ± 1.370 | ± 2.300 | ± 8.979 |
| δ-$UO_3H_{0.83}$ | $0.415H_2$(g) + δ-$UO_3 \rightleftharpoons$ δ-$UO_3H_{0.83}$ | | | | |
| | | | | – 71.410 | |
| | | | | ± 2.480 | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^{o}$ | $\Delta_r G_m^o$ / kJ·mol$^{-1}$ | $\Delta_r H_m^o$ / kJ·mol$^{-1}$ | $\Delta_r S_m^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2(OH)_2(aq)$ | $2H_2O(l) + UO_2^{2+} \rightleftharpoons 2H^+ + UO_2(OH)_2(aq)$ | | | | |
| | | – 12.150 | 69.353 | | |
| | | ± 0.070 | ± 0.400 | | |
| $U(OH)_2^{2+}$ * | $U^{4+} + 2H_2O(l) \rightleftharpoons U(OH)_2^{2+} + 2H^+$ | | | | |
| | | – 1.900* | 10.845* | | |
| | | ± 0.200 | ± 1.142 | | |
| $U(OH)_3^+$ * | $U^{4+} + 3H_2O(l) \rightleftharpoons U(OH)_3^+ + 3H^+$ | | | | |
| | | – 5.200* | 29.682* | | |
| | | ± 0.400 | ± 2.283 | | |
| $U(OH)_4(aq)$ | $U^{4+} + 4H_2O(l) \rightleftharpoons U(OH)_4(aq) + 4H^+$ | | | | |
| | | – 10.000 | 57.081 | | |
| | | ± 1.400 | ± 7.991 | | |
| $UO_2(OH)_3^-$ | $3H_2O(l) + UO_2^{2+} \rightleftharpoons 3H^+ + UO_2(OH)_3^-$ | | | | |
| | | – 20.250 | 115.588 | | |
| | | ± 0.420 | ± 2.397 | | |
| $UO_2(OH)_4^{2-}$ | $4H_2O(l) + UO_2^{2+} \rightleftharpoons 4H^+ + UO_2(OH)_4^{2-}$ | | | | |
| | | – 32.400 | 184.941 | | |
| | | ± 0.680 | ± 3.881 | | |
| $(UO_2)_2OH^{3+}$ | $H_2O(l) + 2UO_2^{2+} \rightleftharpoons (UO_2)_2OH^{3+} + H^+$ | | | | |
| | | – 2.700 | 15.412 | | |
| | | ± 1.000 | ± 5.708 | | |
| $(UO_2)_2(OH)_2^{2+}$ | $2H_2O(l) + 2UO_2^{2+} \rightleftharpoons (UO_2)_2OH_2^{2+} + 2H^+$ | | | | |
| | | – 5.620** | 32.079 ** | 47.800* | 52.728*[(a)] |
| | | ± 0.080 | ± 0.457 | ± 0.500 | ± 2.271 |
| $(UO_2)_3(OH)_4^{2+}$ | $4H_2O(l) + 3UO_2^{2+} \rightleftharpoons (UO_2)_3OH_4^{2+} + 4H^+$ | | | | |
| | | – 11.900 | 67.926 | 99.200* | 104.895*[(a)] |
| | | ± 0.300 | ± 1.712 | ± 0.500 | ± 5.983 |
| $(UO_2)_3(OH)_5^+$ | $5H_2O(l) + 3UO_2^{2+} \rightleftharpoons (UO_2)_3OH_5^+ + 5H^+$ | | | | |
| | | – 15.550 | 88.760 | 120.700* | 107.127*[(a)] |
| | | ± 0.120 | ± 0.685 | ± 0.600 | ± 3.054 |
| $(UO_2)_3(OH)_7^-$ | $7H_2O(l) + 3UO_2^{2+} \rightleftharpoons (UO_2)_3OH_7^- + 7H^+$ | | | | |
| | | – 32.200 | 183.799 | | |
| | | ± 0.800 | ± 4.566 | | |
| $(UO_2)_4(OH)_7^+$ | $7H_2O(l) + 4UO_2^{2+} \rightleftharpoons (UO_2)_4OH_7^+ + 7H^+$ | | | | |
| | | – 21.900 | 125.006 | | |
| | | ± 1.000 | ± 5.708 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_4{\cdot}4H_2O$(cr) * | $UO_2^{2+} + H_2O_2(aq) + 4H_2O(l) \rightleftharpoons UO_4{\cdot}4H_2O(cr) + 2H^+$ | 2.870* ± 0.020 | – 16.382* ± 0.114 | | |
| $UF^{3+}$ | $F^- + U^{4+} \rightleftharpoons UF^{3+}$ | 9.420 ± 0.510 | – 53.770 ± 2.911 | – 5.600 ± 0.500 | 161.562 [(a)] ± 9.907 |
| $UF_2^{2+}$ | $2F^- + U^{4+} \rightleftharpoons UF_2^{2+}$ | 16.560 ± 0.710 | – 94.525 ± 4.053 | – 3.500 ± 0.600 | 305.300 [(a)] ± 13.741 |
| $UF_3^+$ | $3F^- + U^{4+} \rightleftharpoons UF_3^+$ | 21.890 ± 0.830 | – 124.949 ± 4.738 | 0.500 ± 4.000 | 420.758 [(a)] ± 20.796 |
| $UF_4$(aq) | $4F^- + U^{4+} \rightleftharpoons UF_4(aq)$ | 26.340 ± 0.960 | – 150.350 ± 5.480 | – 8.430 [(a)] ± 7.464 | 476.000 ± 17.000 |
| $UF_4$(g) | $UF_4(cr) \rightleftharpoons UF_4(g)$ | | | 309.000 ± 5.000 | |
| $UF_5^-$ | $5F^- + U^{4+} \rightleftharpoons UF_5^-$ | 27.730 ± 0.740 | – 158.284 ± 4.224 | | |
| $UF_6$(g) | $UF_6(cr) \rightleftharpoons UF_6(g)$ | | | 49.100 ± 0.500 | |
| $UF_6^{2-}$ | $6F^- + U^{4+} \rightleftharpoons UF_6^{2-}$ | 29.800 ± 0.700 | – 170.100 ± 3.996 | | |
| $U_2F_{10}$(g) | $2UF_5(cr) \rightleftharpoons U_2F_{10}(g)$ | | | – 167.200 ± 4.700 | |
| $UO_2F^+$ | $F^- + UO_2^{2+} \rightleftharpoons UO_2F^+$ | 5.160 ± 0.060 | – 29.453 ± 0.342 | – 0.540* ± 0.260 | 96.976*[(a)] ± 1.441 |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2F_2(aq)$ | $2F^- + UO_2^{2+} \rightleftharpoons UO_2F_2(aq)$ | | | | |
| | | 8.830 ± 0.080 | – 50.402 ± 0.457 | – 1.340* ±0.180 | 164.554*[a] ± 1.648 |
| $UO_2F_2(g)$ | $UO_2F_2(cr) \rightleftharpoons UO_2F_2(g)$ | | | | |
| | | | | 301.000 ± 10.000 | |
| $UO_2F_3^-$ | $3F^- + UO_2^{2+} \rightleftharpoons UO_2F_3^-$ | | | | |
| | | 10.900 ± 0.100 | – 62.218 ± 0.571 | – 1.180* ± 0.300 | 204.719*[a] ± 2.163 |
| $UO_2F_4^{2-}$ | $4F^- + UO_2^{2+} \rightleftharpoons UO_2F_4^{2-}$ | | | | |
| | | 11.840 ± 0.110 | – 67.583 ± 0.628 | – 2.120* ± 0.470 | 219.563*[a] ± 2.631 |
| $U_2O_3F_6(cr)$ | $3UOF_4(cr) \rightleftharpoons U_2O_3F_6(cr) + UF_6(g)$ | | | | |
| | | | | 46.000 ± 6.000 | |
| $U_3O_5F_8(cr)$ | $0.5UF_6(g) + 2.5UO_2F_2(cr) \rightleftharpoons U_3O_5F_8(cr)$ | | | | |
| | | | | 15.100[d] ± 2.000 | |
| $H_3OUF_6(cr)$ | $6HF(g) + UF_4(cr) + UO_2F_2(cr) \rightleftharpoons 2H_3OUF_6(cr)$ | | | | |
| | | | | – 75.300 ± 1.700 | |
| $UF_4{\cdot}2.5H_2O(cr)$ | $2.5H_2O(l) + UF_4(cr) \rightleftharpoons UF_4 \cdot 2.5H_2O(cr)$ | | | | |
| | | | | – 42.700 ± 0.800 | |
| $UO_2FOH{\cdot}2H_2O(cr)$ | $H_2O(g) + UO_2F \cdot H_2O(cr) \rightleftharpoons UO_2FOH \cdot 2H_2O(cr)$ | | | | |
| | | 1.883[c] ± 0.666 | – 10.750 ± 3.800 | – 53.684[a] ± 4.200 | – 144.000 ± 6.000 |
| $UO_2F_2{\cdot}3H_2O(cr)$ | $3H_2O(l) + UO_2F_2(cr) \rightleftharpoons UO_2F_2 \cdot 3H_2O(cr)$ | | | | |
| | | | | – 23.400 ± 4.200 | |
| $UCl^{3+}$ | $Cl^- + U^{4+} \rightleftharpoons UCl^{3+}$ | | | | |
| | | 1.720 ± 0.130 | – 9.818 ± 0.742 | – 19.000 ± 9.000 | – 30.797[a] ± 30.289 |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UCl_4(g)$ | $UCl_4(cr) \rightleftharpoons UCl_4(g)$ | | | | |
| | | | | 203.400 | |
| | | | | ± 4.000 | |
| $UCl_6(g)$ | $UCl_6(cr) \rightleftharpoons UCl_6(g)$ | | | | |
| | | | | 81.000 | |
| | | | | ± 4.000 | |
| $U_2Cl_{10}(g)$ | $Cl_2(g) + 2UCl_4(g) \rightleftharpoons U_2Cl_{10}(g)$ | | | | |
| | | | | 72.300 | |
| | | | | ± 8.900 | |
| $UO_2Cl^+$ | $Cl^- + UO_2^{2+} \rightleftharpoons UO_2Cl^+$ | | | | |
| | | 0.170 | – 0.970 | 8.000 | 30.087 [a] |
| | | ± 0.020 | ± 0.114 | ± 2.000 | ± 6.719 |
| $UO_2Cl_2(aq)$ | $2Cl^- + UO_2^{2+} \rightleftharpoons UO_2Cl_2(aq)$ | | | | |
| | | – 1.100 | 6.279 | 15.000 | 29.251 [a] |
| | | ± 0.400 | ± 2.283 | ± 6.000 | ± 21.532 |
| $UO_2ClO_3^+$ | $ClO_3^- + UO_2^{2+} \rightleftharpoons UO_2ClO_3^+$ | | | | |
| | | 0.500 | – 2.854 | – 3.900 | – 3.508 [a] |
| | | ± 0.070 | ± 0.400 | ± 0.300 | ± 1.676 |
| $UBr^{3+}$ | $Br^- + U^{4+} \rightleftharpoons UBr^{3+}$ | | | | |
| | | 1.460 | – 8.334 | | |
| | | ± 0.200 | ± 1.142 | | |
| $UBr_4(g)$ | $UBr_4(cr) \rightleftharpoons UBr_4(g)$ | | | | |
| | | | | 196.500 | |
| | | | | ± 4.000 | |
| $UBr_5(g)$ | $0.5Br_2(g) + UBr_4(g) \rightleftharpoons UBr_5(g)$ | | | | |
| | | | | – 57.800 | |
| | | | | ± 2.700 | |
| $UO_2Br^+$ | $Br^- + UO_2^{2+} \rightleftharpoons UO_2Br^+$ | | | | |
| | | 0.220 | – 1.256 | | |
| | | ± 0.020 | ± 0.114 | | |
| $UO_2BrO_3^+$ | $BrO_3^- + UO_2^{2+} \rightleftharpoons UO_2BrO_3^+$ | | | | |
| | | 0.630 | – 3.596 | 0.100 | 12.397 [a] |
| | | ± 0.080 | ± 0.457 | ± 0.300 | ± 1.833 |
| $UI^{3+}$ | $I^- + U^{4+} \rightleftharpoons UI^{3+}$ | | | | |
| | | 1.250 | – 7.135 | | |
| | | ± 0.300 | ± 1.712 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UI_4(g)$ | $UI_4(cr) \rightleftharpoons UI_4(g)$ | | | | |
| | | | | 213.300 | |
| | | | | ± 5.000 | |
| $UO_2IO_3^+$ | $IO_3^- + UO_2^{2+} \rightleftharpoons UO_2IO_3^+$ | | | | |
| | | 2.000 | – 11.416 | 9.800 | 71.159 [(a)] |
| | | ± 0.020 | ± 0.114 | ± 0.900 | ± 3.043 |
| $UO_2(IO_3)_2(aq)$ | $2IO_3^- + UO_2^{2+} \rightleftharpoons UO_2(IO_3)_2(aq)$ | | | | |
| | | 3.590 | – 20.492 | | |
| | | ± 0.150 | ± 0.856 | | |
| $UO_2(IO_3)_2(cr)$ | $2IO_3^- + UO_2^{2+} \rightleftharpoons UO_2(IO_3)_2(cr)$ | | | | |
| | | 7.880 | – 44.979 | | |
| | | ± 0.100 | ± 0.571 | | |
| $UO_2IO_4^+$ * | $UO_2^{2+} + IO_4^- \rightleftharpoons UO_2IO_4^+$ | | | | |
| | | 2.350* | – 13.414* | | |
| | | ± 0.200 | ± 1.142 | | |
| $USO_4^{2+}$ | $SO_4^{2-} + U^{4+} \rightleftharpoons USO_4^{2+}$ | | | | |
| | | 6.580 | – 37.559 | 8.000 | 152.805 [(a)] |
| | | ± 0.190 | ± 1.085 | ± 2.700 | ± 9.759 |
| $UO_2SO_3(aq)$ | $SO_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2SO_3(aq)$ | | | | |
| | | 6.600 | – 37.673 | | |
| | | ± 0.600 | ± 3.425 | | |
| $UO_2S_2O_3(aq)$ | $S_2O_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2S_2O_3(aq)$ | | | | |
| | | 2.800 | – 15.983 | | |
| | | ± 0.300 | ± 1.712 | | |
| $UO_2SO_4(aq)$ | $SO_4^{2-} + UO_2^{2+} \rightleftharpoons UO_2SO_4(aq)$ | | | | |
| | | 3.150** | – 17.980** | 19.500 | 125.709** [(a)] |
| | | ± 0.100 | ± 0.571 | ± 1.600 | ± 5.698 |
| $U(SO_4)_2(aq)$ | $2SO_4^{2-} + U^{4+} \rightleftharpoons U(SO_4)_2(aq)$ | | | | |
| | | 10.510 | – 59.992 | 32.700 | 310.889 [(a)] |
| | | ± 0.200 | ± 1.142 | ± 2.800 | ± 10.142 |
| $UO_2(SO_4)_2^{2-}$ | $2SO_4^{2-} + UO_2^{2+} \rightleftharpoons UO_2(SO_4)_2^{2-}$ | | | | |
| | | 4.140** | – 23.631** | 35.100 | 196.985** [(a)] |
| | | ± 0.150 | ± 0.856 | ± 1.000 | ± 4.415 |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2(SO_4)_3^{4-}$ | $3SO_4^{2-} + UO_2^{2+} \rightleftharpoons UO_2(SO_4)_3^{4-}$ | 3.020 ± 0.380 | – 17.238 ± 2.169 | | |
| $U(OH)_2SO_4$(cr) | $2OH^- + SO_4^{2-} + U^{4+} \rightleftharpoons U(OH)_2SO_4$(cr) | 31.170 ± 0.500 | – 177.920 ± 2.854 | | |
| $UO_2SO_4 \cdot 2.5H_2O$(cr) | $2.5H_2O(l) + SO_4^{2-} + UO_2^{2+} \rightleftharpoons UO_2SO_4 \cdot 2.5H_2O$(cr) | 1.589 [c] ± 0.019 | – 9.070 ± 0.110 | | |
| $UO_2SO_4 \cdot 3H_2O$(cr) | $UO_2SO_4 \cdot 3.5H_2O$(cr) $\rightleftharpoons 0.5H_2O(g) + UO_2SO_4 \cdot 3H_2O$(cr) | – 0.831 ± 0.023 | 4.743 ± 0.131 | | |
| $UO_2SO_4 \cdot 3.5H_2O$(cr) | $3.5H_2O(l) + SO_4^{2-} + UO_2^{2+} \rightleftharpoons UO_2SO_4 \cdot 3.5H_2O$(cr) | 1.585 [c] ± 0.019 | – 9.050 ± 0.110 | | |
| $UO_2SeO_4$(aq) * | $UO_2^{2+} + SeO_4^{2-} \rightleftharpoons UO_2SeO_4$(aq) | 2.930* ± 0.040 | – 16.725* ± 0.228 | 20.000 * ± 2.000 | 123.176*[a] ± 6.751 |
| $UO_2(SeO_4)_2^{2-}$ * | $UO_2^{2+} + 2SeO_4^{2-} \rightleftharpoons UO_2(SeO_4)_2^{2-}$ | 4.030* ± 0.090 | – 23.003 * ± 0.514 | 31.000* ± 4.000 | 181.127*[a] ± 13.526 |
| $UO_2HSeO_3^+$ * | $UO_2^{2+} + HSeO_3^- \rightleftharpoons UO_2HSeO_3^+$ | 3.270* ± 0.150 | – 18.665* ± 0.856 | | |
| $UO_2(HSeO_3)_2$(aq)* | $UO_2^{2+} + 2HSeO_3^- \rightleftharpoons UO_2(HSeO_3)_2$(aq) | 5.510* ± 0.110 | – 31.451* ± 0.628 | | |
| $UO_2N_3^+$ | $N_3^- + UO_2^{2+} \rightleftharpoons UO_2N_3^+$ | 2.580 ± 0.090 | – 14.727 ± 0.514 | | |
| $UO_2(N_3)_2$(aq) | $2N_3^- + UO_2^{2+} \rightleftharpoons UO_2(N_3)_2$(aq) | 4.330 ± 0.230 | – 24.716 ± 1.313 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2(N_3)_3^-$ | $3N_3^- + UO_2^{2+} \rightleftharpoons UO_2(N_3)_3^-$ | | | | |
| | | 5.740 | – 32.764 | | |
| | | ± 0.220 | ± 1.256 | | |
| $UO_2(N_3)_4^{2-}$ | $4N_3^- + UO_2^{2+} \rightleftharpoons UO_2(N_3)_4^{2-}$ | | | | |
| | | 4.920 | – 28.084 | | |
| | | ± 0.240 | ± 1.370 | | |
| $UNO_3^{3+}$ | $NO_3^- + U^{4+} \rightleftharpoons UNO_3^{3+}$ | | | | |
| | | 1.470 | – 8.391 | | |
| | | ± 0.130 | ± 0.742 | | |
| $UO_2NO_3^+$ | $NO_3^- + UO_2^{2+} \rightleftharpoons UO_2NO_3^+$ | | | | |
| | | – 0.190* | 1.085* | 20.900* | 66.460*[(a)] |
| | | ± 0.150 | ± 0.856 | ± 3.500 | ± 12.085 |
| $U(NO_3)_2^{2+}$ | $2NO_3^- + U^{4+} \rightleftharpoons U(NO_3)_2^{2+}$ | | | | |
| | | 2.300 | – 13.128 | | |
| | | ± 0.350 | ± 1.998 | | |
| $UO_2PO_4^-$ | $PO_4^{3-} + UO_2^{2+} \rightleftharpoons UO_2PO_4^-$ | | | | |
| | | 11.010* | – 62.845* | | |
| | | ± 0.480 | ± 2.740 | | |
| $UO_2HPO_4(aq)$ | $HPO_4^{2-} + UO_2^{2+} \rightleftharpoons UO_2HPO_4(aq)$ | | | | |
| | | 7.240 | – 41.326 | | |
| | | ± 0.260 | ± 1.484 | | |
| $UO_2H_2PO_4^+$ | $H_3PO_4(aq) + UO_2^{2+} \rightleftharpoons H^+ + UO_2H_2PO_4^+$ | | | | |
| | | 1.120 | – 6.393 | | |
| | | ± 0.060 | ± 0.342 | | |
| $UO_2H_3PO_4^{2+}$ | $H_3PO_4(aq) + UO_2^{2+} \rightleftharpoons UO_2H_3PO_4^{2+}$ | | | | |
| | | 0.760 | – 4.338 | | |
| | | ± 0.150 | ± 0.856 | | |
| $UO_2(H_2PO_4)_2(aq)$ | $2H_3PO_4(aq) + UO_2^{2+} \rightleftharpoons 2H^+ + UO_2(H_2PO_4)_2(aq)$ | | | | |
| | | 0.640 | – 3.653 | | |
| | | ± 0.110 | ± 0.628 | | |
| $UO_2(H_2PO_4)(H_3PO_4)^+$ | $2H_3PO_4(aq) + UO_2^{2+} \rightleftharpoons H^+ + UO_2(H_2PO_4)(H_3PO_4)^+$ | | | | |
| | | 1.650 | – 9.418 | | |
| | | ± 0.110 | ± 0.628 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^{o}$ | $\Delta_r G_m^o$ / kJ·mol$^{-1}$ | $\Delta_r H_m^o$ / kJ·mol$^{-1}$ | $\Delta_r S_m^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2HPO_4{\cdot}4H_2O$(cr) | $UO_2^{2+} + H^+ + PO_4^{3-} + 4H_2O(l) \rightleftharpoons UO_2HPO_4 \cdot 4H_2O$(cr) | 24.202 ± 0.090 | – 138.146 ± 0.514 | | |
| $UH_2PO_4^{3+}$ * | $U^{4+} + H_2PO_4^- \rightleftharpoons UH_2PO_4^{3+}$ | 6.800* ± 0.700 | – 38.815* ± 3.996 | | |
| $U(HPO_4)_2{\cdot}4H_2O$(cr) | $4H_2O(l) + 2H_3PO_4(aq) + U^{4+} \rightleftharpoons 4H^+ + U(HPO_4)_2 \cdot 4H_2O$(cr) | 11.790 ± 0.150 | – 67.298 ± 0.856 | | |
| $(UO_2)_3(PO_4)_2{\cdot}4H_2O$(cr) | $4H_2O(l) + 2H_3PO_4(aq) + 3UO_2^{2+} \rightleftharpoons (UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr) $+ 6H^+$ | 5.960 ± 0.300 | – 34.020 ± 1.712 | | |
| $NH_4[(UO_2)(PO_4)]{\cdot}3H_2O$(cr) * | $UO_2^{2+} + NH_4^+ + PO_4^{3-} + 3H_2O(l) \rightleftharpoons NH_4[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | 26.100* ± 1.000 | – 148.979* ± 5.708 | | |
| $(UO_2)_3(AsO_4)_2{\cdot}12H_2O$(cr) * | $3UO_2^{2+} + 2AsO_4^{3-} + 12H_2O(l) \rightleftharpoons (UO_2)_3(AsO_4)_2\cdot 12H_2O$(cr) | 45.330* ± 1.000 | – 258.744* ± 5.708 | | |
| $UO_2HAsO_4$(aq) | $AsO_4^{3-} + H^+ + UO_2^{2+} \rightleftharpoons UO_2HAsO_4$(aq) | 18.760 ± 0.310 | – 107.083 ± 1.769 | | |
| $UO_2HAsO_4{\cdot}4H_2O$(cr) * | $UO_2^{2+} + H^+ + AsO_4^{3-} + 4H_2O(l) \rightleftharpoons UO_2HAsO_4{\cdot}4H_2O$(cr) | 23.000* ±0.300 | – 131.284* ± 1.713 | | |
| $UO_2H_2AsO_4^+$ | $AsO_4^{3-} + 2H^+ + UO_2^{2+} \rightleftharpoons UO_2H_2AsO_4^+$ | 21.960 ± 0.240 | – 125.349 ± 1.370 | | |
| $UO_2(H_2AsO_4)_2$(aq) | $2AsO_4^{3-} + 4H^+ + UO_2^{2+} \rightleftharpoons UO_2(H_2AsO_4)_2$(aq) | 41.530 ± 0.200 | – 237.055 ± 1.142 | | |
| $NH_4[(UO_2)(AsO_4)]{\cdot}3H_2O$(cr) * | $UO_2^{2+} + NH_4^+ + AsO_4^{3-} + 3H_2O(l) \rightleftharpoons NH_4[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | 24.700* ± 1.000 | – 140.988* ± 5.708 | | |
| $UO_2CO_3$(aq) | $CO_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2CO_3$(aq) | 9.940 ± 0.030 | – 56.738 ± 0.171 | 5.000 ± 2.000 | 207.070 [(a)] ± 6.733 |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2CO_3$(cr) | $CO_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2CO_3$(cr) | | | | |
| | | 14.760 ± 0.020 | – 84.251 ± 0.114 | | |
| $UO_2(CO_3)_2^{2-}$ | $2CO_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2(CO_3)_2^{2-}$ | | | | |
| | | 16.610 ± 0.090 | – 94.811 ± 0.514 | 18.500 ± 4.000 | 380.046 [a] ± 13.526 |
| $UO_2(CO_3)_3^{4-}$ | $3CO_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2(CO_3)_3^{4-}$ | | | | |
| | | 21.840 ± 0.040 | – 124.664 ± 0.228 | – 39.200 ± 4.100 | 286.646 [a] ± 13.773 |
| $UO_2(CO_3)_3^{5-}$ | $3CO_3^{2-} + UO_2^{+} \rightleftharpoons UO_2(CO_3)_3^{5-}$ | | | | |
| | | 6.950 ± 0.360 | – 39.671 ± 2.055 | | |
| $U(CO_3)_4^{4-}$ | $U(CO_3)_5^{6-} \rightleftharpoons CO_3^{2-} + U(CO_3)_4^{4-}$ | | | | |
| | | 1.120 ± 0.250 | – 6.393 ± 1.427 | | |
| $U(CO_3)_5^{6-}$ | $5CO_3^{2-} + U^{4+} \rightleftharpoons U(CO_3)_5^{6-}$ | | | | |
| | | 34.000 ± 0.900 | – 194.073 ± 5.137 | – 20.000 ± 4.000 | 583.845 [a] ± 21.838 |
| $(UO_2)_3(CO_3)_6^{6-}$ | $6CO_3^{2-} + 3UO_2^{2+} \rightleftharpoons (UO_2)_3(CO_3)_6^{6-}$ | | | | |
| | | 54.000 ± 1.000 | – 308.234 ± 5.708 | – 62.700 ± 2.400 | 823.526 [a] ± 20.768 |
| $(UO_2)_2CO_3(OH)_3^-$ | $CO_2(g) + 4H_2O(l) + 2UO_2^{2+} \rightleftharpoons (UO_2)_2CO_3(OH)_3^- + 5H^+$ | | | | |
| | | – 19.010 ± 0.500 | 108.510 ± 2.854 | | |
| $(UO_2)_3O(OH)_2(HCO_3)^+$ | $CO_2(g) + 4H_2O(l) + 3UO_2^{2+} \rightleftharpoons (UO_2)_3O(OH)_2(HCO_3)^+ + 5H^+$ | | | | |
| | | – 17.500 ± 0.500 | 99.891 ± 2.854 | | |
| $(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$ | $6CO_2(g) + 18H_2O(l) + 11UO_2^{2+} \rightleftharpoons (UO_2)_{11}(CO_3)_6(OH)_{12}^{2-} + 24H^+$ | | | | |
| | | – 72.500 ± 2.000 | 413.833 ± 11.416 | | |
| $UO_2CO_3F^-$ | $CO_3^{2-} + F^- + UO_2^{2+} \rightleftharpoons UO_2CO_3F^-$ | | | | |
| | | 13.750 ± 0.090 | – 78.486 ± 0.514 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2CO_3F_2^{2-}$ | $CO_3^{2-} + 2F^- + UO_2^{2+} \rightleftharpoons UO_2CO_3F_2^{2-}$ | | | | |
| | | 15.570 | – 88.874 | | |
| | | ± 0.140 | ± 0.799 | | |
| $UO_2CO_3F_3^{3-}$ | $CO_3^{2-} + 3F^- + UO_2^{2+} \rightleftharpoons UO_2CO_3F_3^{3-}$ | | | | |
| | | 16.380 | – 93.498 | | |
| | | ± 0.110 | ± 0.628 | | |
| $USCN^{3+}$ | $SCN^- + U^{4+} \rightleftharpoons USCN^{3+}$ | | | | |
| | | 2.970 | – 16.953 | – 27.000 | – 33.698 [(a)] |
| | | ± 0.060 | ± 0.342 | ± 8.000 | ± 26.857 |
| $U(SCN)_2^{2+}$ | $2SCN^- + U^{4+} \rightleftharpoons U(SCN)_2^{2+}$ | | | | |
| | | 4.260 | – 24.316 | – 18.000 | 21.185 [(a)] |
| | | ± 0.180 | ± 1.027 | ± 4.000 | ± 13.852 |
| $UO_2SCN^+$ | $SCN^- + UO_2^{2+} \rightleftharpoons UO_2SCN^+$ | | | | |
| | | 1.400 | – 7.991 | 3.220 | 37.603 [(a)] |
| | | ± 0.230 | ± 1.313 | ± 0.060 | ± 4.408 |
| $UO_2(SCN)_2(aq)$ | $2SCN^- + UO_2^{2+} \rightleftharpoons UO_2(SCN)_2(aq)$ | | | | |
| | | 1.240 | – 7.078 | 8.900 | 53.590 [(a)] |
| | | ± 0.550 | ± 3.139 | ± 0.600 | ± 10.720 |
| $UO_2(SCN)_3^-$ | $3SCN^- + UO_2^{2+} \rightleftharpoons UO_2(SCN)_3^-$ | | | | |
| | | 2.100 | – 11.987 | 6.000 | 60.328 [(a)] |
| | | ± 0.500 | ± 2.854 | ± 1.200 | ± 10.384 |
| $UO_2SiO(OH)_3^+$ | $Si(OH)_4(aq) + UO_2^{2+} \rightleftharpoons H^+ + UO_2SiO(OH)_3^+$ | | | | |
| | | – 1.880* | 10.731* | 40.000* | 98.169* [(a)] |
| | | ± 0.190 | ± 1.084 | ± 6.000 | ± 20.450 |
| $(UO_2)_2SiO_4{\cdot}2H_2O(cr)$ * | $2UO_2^{2+} + Si(OH)_4(aq) + 2H_2O(l) \rightleftharpoons (UO_2)_2SiO_4{\cdot}2H_2O(cr) + 4H^+$ | | | | |
| | | – 5.750* | 32.821* | | |
| | | ± 0.260 | ± 1.484 | | |
| $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$ | $PuO_2(CO_3)_3^{4-} + 2UO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_2(PuO_2)(CO_3)_6^{6-} + 3CO_3^{2-}$ | | | | |
| | | – 8.200 | 46.806 | | |
| | | ± 1.300 | ± 7.420 | | |
| $(UO_2)_2(NpO_2)(CO_3)_6^{6-}$ | $NpO_2(CO_3)_3^{4-} + 2UO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_2(NpO_2)(CO_3)_6^{6-} + 3CO_3^{2-}$ | | | | |
| | | – 8.998 | 51.364 | | |
| | | ± 2.690 | ± 15.355 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Pb[(UO_2)(AsO_4)]_2{\cdot}10H_2O(cr)$* | $2UO_2^{2+} + Pb^{2+} + 2AsO_4^{3-} + 10H_2O(l) \rightleftharpoons Pb[(UO_2)(AsO_4)]_2{\cdot}10H_2O(cr)$ | 46.300* ± 1.000 | – 264.281* ± 5.708 | | |
| $Zn[(UO_2)(PO_4)]_2{\cdot}8H_2O(cr)$ * | $2UO_2^{2+} + Zn^{2+} + 2PO_4^{3-} + 8H_2O(l) \rightleftharpoons Zn[(UO_2)(PO_4)]_2{\cdot}8H_2O(cr)$ | 49.800* ± 1.000 | – 284.259* ± 5.708 | | |
| $Zn[(UO_2)(PO_4)]_2{\cdot}10H_2O(cr)$ * | $2UO_2^{2+} + Zn^{2+} + 2PO_4^{3-} + 10H_2O(l) \rightleftharpoons Zn[(UO_2)(PO_4)]_2{\cdot}10H_2O(cr)$ | 49.800* ± 1.000 | – 284.259* ± 5.708 | | |
| $Zn[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ * | $2UO_2^{2+} + Zn^{2+} + 2AsO_4^{3-} + 8H_2O(l) \rightleftharpoons Zn[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ | 45.100* ± 1.000 | – 257.431* ± 5.708 | | |
| $Cd[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ * | $2UO_2^{2+} + Cd^{2+} + 2AsO_4^{3-} + 8H_2O(l) \rightleftharpoons Cd[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ | 45.400* ± 1.000 | – 259.144* ± 5.708 | | |
| $Cu[(UO_2)(PO_4)]_2{\cdot}8H_2O(cr)$ * | $2UO_2^{2+} + Cu^{2+} + 2PO_4^{3-} + 8H_2O(l) \rightleftharpoons Cu[(UO_2)(PO_4)]_2{\cdot}8H_2O(cr)$ | 52.800* ± 0.300 | – 301.383* ± 1.712 | | |
| $Cu[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ * | $2UO_2^{2+} + Cu^{2+} + 2AsO_4^{3-} + 8H_2O(l) \rightleftharpoons Cu[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ | 45.700* ± 1.000 | – 260.856* ± 5.708 | | |
| $Ni[(UO_2)(PO_4)]_2{\cdot}8H_2O(cr)$ * | $2UO_2^{2+} + Ni^{2+} + 2PO_4^{3-} + 8H_2O(l) \rightleftharpoons Ni[(UO_2)(PO_4)]_2{\cdot}8H_2O(cr)$ | 49.900* ± 1.000 | – 284.830* ± 5.708 | | |
| $Ni[(UO_2)(PO_4)]_2{\cdot}10H_2O(cr)$ * | $2UO_2^{2+} + Ni^{2+} + 2PO_4^{3-} + 10H_2O(l) \rightleftharpoons Ni[(UO_2)(PO_4)]_2{\cdot}10H_2O(cr)$ | 49.900* ± 1.000 | – 284.830* ± 5.708 | | |
| $Ni[(UO_2)(AsO_4)]_2{\cdot}10H_2O(cr)$* | $2UO_2^{2+} + Ni^{2+} + 2AsO_4^{3-} + 10H_2O(l) \rightleftharpoons Ni[(UO_2)(AsO_4)]_2{\cdot}10H_2O(cr)$ | 45.900* ± 1.000 | – 261.998* ± 5.708 | | |
| $Co[(UO_2)(PO_4)]_2{\cdot}7H_2O(cr)$ * | $2UO_2^{2+} + Co^{2+} + 2PO_4^{3-} + 7H_2O(l) \rightleftharpoons Co[(UO_2)(PO_4)]_2{\cdot}7H_2O(cr)$ | 49.600* ± 1.000 | – 283.118* ± 5.708 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^{o}$ | $\Delta_r G_m^o$ / kJ·mol$^{-1}$ | $\Delta_r H_m^o$ / kJ·mol$^{-1}$ | $\Delta_r S_m^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Co[(UO_2)(PO_4)]_2{\cdot}8H_2O$(cr) * | $2UO_2^{2+} + Co^{2+} + 2PO_4^{3-} + 8H_2O(l) \rightleftharpoons Co[(UO_2)(PO_4)]_2{\cdot}8H_2O(cr)$ | 49.600* ± 1.000 | – 283.118* ± 5.708 | | |
| $Co[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) * | $2UO_2^{2+} + Co^{2+} + 2AsO_4^{3-} + 8H_2O(l) \rightleftharpoons Co[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ | 46.500* ± 1.000 | – 265.422* ± 5.708 | | |
| $Fe[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) * | $2UO_2^{2+} + Fe^{2+} + 2AsO_4^{3-} + 8H_2O(l) \rightleftharpoons Fe[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ | 46.100* ± 2.200 | – 263.139* ± 12.558 | | |
| $Mn[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) * | $2UO_2^{2+} + Mn^{2+} + 2AsO_4^{3-} + 8H_2O(l) \rightleftharpoons Mn[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ | 44.400* ± 1.000 | – 253.436* ± 5.708 | | |
| $Mg[(UO_2)(PO_4)]_2{\cdot}8H_2O$(cr) * | $2UO_2^{2+} + Mg^{2+} + 2PO_4^{3-} + 8H_2O(l) \rightleftharpoons Mg[(UO_2)(PO_4)]_2{\cdot}8H_2O(cr)$ | 49.200* ± 1.200 | – 280.834* ± 6.850 | | |
| $Mg[(UO_2)(AsO_4)]_2{\cdot}10H_2O$(cr)* | $2UO_2^{2+} + Mg^{2+} + 2AsO_4^{3-} + 10H_2O(l) \rightleftharpoons Mg[(UO_2)(AsO_4)]_2{\cdot}10H_2O(cr)$ | 44.600* ± 0.500 | – 254.577* ± 2.855 | | |
| $Mg[UO_2(CO_3)_3]^{2-}$ * | $Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Mg[UO_2(CO_3)_3]^{2-}$ | 26.200 * ± 0.200 | – 149.551* ± 1.142 | | |
| $Mg_2[UO_2(CO_3)_3]$(aq) * | $2Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Mg_2[UO_2(CO_3)_3](aq)$ | 27.100* ± 0.600 | – 154.688* ± 3.425 | | |
| $CaU_6O_{19}{\cdot}11H_2O$(cr) | $Ca^{2+} + 6UO_2^{2+} + 18H_2O(l) \rightleftharpoons CaU_6O_{19}{\cdot}11H_2O(cr) + 14H^+$ | – 40.500 ± 1.600 | 231.176 ± 9.133 | | |
| $Ca[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) * | $2UO_2^{2+} + Ca^{2+} + 2PO_4^{3-} + 6H_2O(l) \rightleftharpoons Ca[(UO_2)(PO_4)]_2{\cdot}6H_2O(cr)$ | 50.000* ± 1.000 | – 285.400* ± 5.708 | | |
| $Ca[(UO_2)(AsO_4)]_2{\cdot}6H_2O$(cr) * | $2UO_2^{2+} + Ca^{2+} + 2AsO_4^{3-} + 6H_2O(l) \rightleftharpoons Ca[(UO_2)(AsO_4)]_2{\cdot}6H_2O(cr)$ | 45.100* ± 1.000 | – 257.431* ± 5.708 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Ca[(UO_2)(AsO_4)]_2{\cdot}10H_2O(cr)$* | $2UO_2^{2+} + Ca^{2+} + 2AsO_4^{3-} + 10H_2O(l) \rightleftharpoons Ca[(UO_2)(AsO_4)]_2{\cdot}10H_2O(cr)$ | 45.100* ± 1.000 | – 257.431* ± 5.708 | | |
| $Ca[UO_2(CO_3)_3]^{2-}$ * | $Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Ca[UO_2(CO_3)_3]^{2-}$ | 27.000* ± 0.200 | – 154.117* ± 1.142 | – 47.000* ± 6.000 | 359.272*[(a)] ± 20.485 |
| $Ca_2[UO_2(CO_3)_3](aq)$ * | $2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Ca_2[UO_2(CO_3)_3](aq)$ | 30.800* ± 0.400 | – 175.808* ± 2.283 | – 47.000* ± 7.000 | 432.024*[(a)] ± 24.695 |
| $Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O(cr)$* | $Ca^{2+} + 2UO_2^{2+} + 2Si(OH)_4(aq) + 5H_2O(l) \rightleftharpoons Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O(cr) + 6H^+$ | – 11.520* ± 0.160 | 65.757* ± 0.913 | | |
| $Sr[(UO_2)(PO_4)]_2{\cdot}6H_2O(cr)$ * | $2UO_2^{2+} + Sr^{2+} + 2PO_4^{3-} + 6H_2O(l) \rightleftharpoons Sr[(UO_2)(PO_4)]_2{\cdot}6H_2O(cr)$ | 51.300* ± 1.000 | – 292.821* ± 5.708 | | |
| $Sr[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ * | $2UO_2^{2+} + Sr^{2+} + 2AsO_4^{3-} + 8H_2O(l) \rightleftharpoons Sr[(UO_2)(AsO_4)]_2{\cdot}8H_2O(cr)$ | 45.100* ± 1.000 | – 257.431* ± 5.708 | | |
| $Sr[UO_2(CO_3)_3]^{2-}$ * | $Sr^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Sr[UO_2(CO_3)_3]^{2-}$ | 25.900* ± 0.200 | – 147.838* ± 1.142 | | |
| $Sr_2[UO_2(CO_3)_3](aq)$ * | $2Sr^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Sr_2[UO_2(CO_3)_3](aq)$ | 29.700* ± 0.500 | – 169.529* ± 2.854 | | |
| $Ba[(UO_2)(PO_4)]_2{\cdot}6H_2O(cr)$ * | $2UO_2^{2+} + Ba^{2+} + 2PO_4^{3-} + 6H_2O(l) \rightleftharpoons Ba[(UO_2)(PO_4)]_2{\cdot}6H_2O(cr)$ | 52.200* ± 1.000 | – 297.958* ± 5.708 | | |
| $Ba[(UO_2)(AsO_4)]_2{\cdot}7H_2O(cr)$ * | $2UO_2^{2+} + Ba^{2+} + 2AsO_4^{3-} + 7H_2O(l) \rightleftharpoons Ba[(UO_2)(AsO_4)]_2{\cdot}7H_2O(cr)$ | 44.700* ± 1.000 | – 255.148* ± 5.708 | | |
| $Ba[UO_2(CO_3)_3]^{2-}$ * | $Ba^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Ba[UO_2(CO_3)_3]^{2-}$ | 25.600* ± 0.300 | – 146.126* ± 1.712 | | |

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Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Li_{0.12}UO_{2.95}$(cr) | $0.12LiUO_3(cr) + 0.15UO_{2.6667}(cr) + 0.73\,\gamma\text{-}UO_3 \rightleftharpoons Li_{0.12}UO_{2.95}(cr)$ | | | – 0.180<br>± 0.820 | |
| $\gamma\text{-}Li_{0.55}UO_3$ | $0.55LiUO_3(cr) + 0.45\,\gamma\text{-}UO_3 \rightleftharpoons \gamma\text{-}Li_{0.55}UO_3$ | | | – 6.560<br>± 2.540 | |
| $\delta\text{-}Li_{0.69}UO_3$ | $0.69LiUO_3(cr) + 0.31\,\gamma\text{-}UO_3 \rightleftharpoons \delta\text{-}Li_{0.69}UO_3$ | | | – 4.760<br>± 1.980 | |
| $Li_{0.19}U_3O_8$(cr) | $0.19LiUO_3(cr) + 3UO_{2.6667}(cr) \rightleftharpoons Li_{0.19}U_3O_8(cr) + 0.19\,\gamma\text{-}UO_3$ | | | – 1.440<br>± 1.940 | |
| $Li_{0.88}U_3O_8$(cr) | $0.88LiUO_3(cr) + 3UO_{2.6667}(cr) \rightleftharpoons Li_{0.88}U_3O_8(cr) + 0.88\,\gamma\text{-}UO_3$ | | | 0.390<br>± 2.160 | |
| $Li[(UO_2)(PO_4)]\cdot 4H_2O$(cr) * | $UO_2^{2+} + Li^+ + PO_4^{3-} + 4H_2O(l) \rightleftharpoons Li[(UO_2)(PO_4)]\cdot 4H_2O(cr)$ | 25.500*<br>± 1.000 | – 145.554*<br>± 5.708 | | |
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O$(cr) * | $UO_2^{2+} + Li^+ + AsO_4^{3-} + 4H_2O(l) \rightleftharpoons Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr)$ | 20.400*<br>± 1.000 | – 116.443*<br>± 5.708 | | |
| $Li[UO_2BO_3]\cdot 1.5H_2O$(cr) * | $Li^+ + 0.5(UO_2)_2(OH)_2^{2+} + H_3BO_3(aq) + 0.5H_2O(l) \rightleftharpoons Li[UO_2BO_3]\cdot 1.5H_2O(cr) + 2H$ | – 4.580*<br>± 0.200 | 26.142*<br>± 1.142 | | |
| $Na_{0.12}UO_{2.95}$(cr) | $0.12NaUO_3(cr) + 0.15UO_{2.6667}(cr) + 0.73\,\gamma\text{-}UO_3 \rightleftharpoons Na_{0.12}UO_{2.95}(cr)$ | | | 4.130<br>± 1.140 | |
| $\alpha\text{-}Na_{0.14}UO_3$ | $0.14NaUO_3(cr) + 0.86\,\gamma\text{-}UO_3 \rightleftharpoons \alpha\text{-}Na_{0.14}UO_3$ | | | – 5.480<br>± 0.480 | |
| $\delta\text{-}Na_{0.54}UO_3$ | $0.54NaUO_3(cr) + 0.46\,\gamma\text{-}UO_3 \rightleftharpoons \delta\text{-}Na_{0.54}UO_3$ | | | – 6.760<br>± 0.770 | |

(Continued on next page)

Table 3-2 (continued)

| Species | Reaction<br>$\log_{10}K^\circ$ | $\Delta_r G_m^\circ$<br>/ kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$<br>/ kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$<br>/ J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Na_{0.2}U_3O_8$(cr) | $0.2NaUO_3(cr) + 3UO_{2.6667}(cr) \rightleftharpoons Na_{0.2}U_3O_8(cr) + 0.2\,\gamma\text{-}UO_3$ | | 2.570<br>± 0.870 | |
| $Na_2U_2O_7{\cdot}H_2O$(cr) * | $Na^+ + UO_2^{2+} + 2H_2O(l) \rightleftharpoons 0.5Na_2U_2O_7 \cdot H_2O(cr) + 3H^+$<br>– 12.200*<br>± 0.200 | 69.638*<br>± 1.142 | | |
| $Na[(UO_2)(PO_4)]{\cdot}3H_2O$(cr) * | $UO_2^{2+} + Na^+ + PO_4^{3-} + 3H_2O(l) \rightleftharpoons Na[(UO_2)(PO_4)] \cdot 3H_2O(cr)$<br>24.300*<br>± 1.000 | – 138.705*<br>± 5.708 | | |
| $Na[(UO_2)(AsO_4)]{\cdot}3H_2O$(cr) * | $UO_2^{2+} + Na^+ + AsO_4^{3-} + 3H_2O(l) \rightleftharpoons Na[(UO_2)(AsO_4)] \cdot 3H_2O(cr)$<br>22.800*<br>± 1.000 | – 130.143*<br>± 5.708 | | |
| $Na(UO_2)(SiO_3OH){\cdot}H_2O$(cr) * | $Na^+ + UO_2^{2+} + Si(OH)_4(aq) + H_2O(l) \rightleftharpoons Na(UO_2)(SiO_3OH) \cdot H_2O(cr) + 3H^+$<br>– 5.810*<br>± 0.440 | 33.164*<br>± 2.512 | | |
| $Na[UO_2BO_3]{\cdot}H_2O$(cr)* | $Na^+ + 0.5(UO_2)_2(OH)_2^{2+} + H_3BO_3(aq) \rightleftharpoons Na[UO_2BO_3] \cdot H_2O(cr) + 2H^+$<br>– 4.470*<br>± 0.200 | 25.515*<br>± 1.142 | | |
| $K_2U_6O_{19}{\cdot}11H_2O$(cr) | $18H_2O(l) + 2K^+ + 6UO_2^{2+} \rightleftharpoons 14H^+ + K_2U_6O_{19} \cdot 11H_2O(cr)$<br>– 37.100<br>± 0.540 | 211.768<br>± 3.082 | | |
| $K[(UO_2)(PO_4)]{\cdot}3H_2O$(cr) * | $UO_2^{2+} + K^+ + PO_4^{3-} + 3H_2O(l) \rightleftharpoons K[(UO_2)(PO_4)] \cdot 3H_2O(cr)$<br>25.500*<br>± 1.000 | – 145.554*<br>± 5.708 | | |
| $K[(UO_2)(AsO_4)]{\cdot}3H_2O$(cr) * | $UO_2^{2+} + K^+ + AsO_4^{3-} + 3H_2O(l) \rightleftharpoons K[(UO_2)(AsO_4)] \cdot 3H_2O(cr)$<br>23.300*<br>± 1.000 | – 132.997*<br>± 5.708 | | |
| $K(UO_2)(SiO_3OH){\cdot}H_2O$(cr) * | $UO_2^{2+} + K^+ + Si(OH)_4(aq) + H_2O(l) \rightleftharpoons K[(UO_2)(SiO_3OH)] \cdot H_2O(cr) + 3H^+$<br>– 4.480*<br>± 1.170 | 25.572*<br>± 6.678 | | |
| $K[UO_2BO_3]{\cdot}H_2O$(cr)* | $K^+ + 0.5(UO_2)_2(OH)_2^{2+} + H_3BO_3(aq) \rightleftharpoons K[UO_2BO_3] \cdot H_2O(cr) + 2H^+$<br>– 3.900*<br>± 0.200 | 22.261*<br>± 1.142 | | |
| $K_2[UO_2VO_4]_2{\cdot}3H_2O$(cr) * | $2K^+ + 2UO_2^{2+} + 2VO_2^+ + 7H_2O(l) \rightleftharpoons K_2[UO_2VO_4]_2 \cdot 3H_2O(cr) + 8H^+$<br>1.100*<br>± 0.400 | – 6.279*<br>± 2.283 | | |

(Continued on next page)

Table 3-2 (continued)

| Species | Reaction | $\log_{10}K^{o}$ | $\Delta_r G_m^o$ / kJ·mol$^{-1}$ | $\Delta_r H_m^o$ / kJ·mol$^{-1}$ | $\Delta_r S_m^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O(cr)$ * | $UO_2^{2+} + Rb^+ + PO_4^{3-} + 3H_2O(l) \rightleftharpoons Rb[(UO_2)(PO_4)]\cdot 3H_2O(cr)$ | 25.800* ± 1.000 | – 147.267* ± 5.708 | | |
| $Rb[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ * | $UO_2^{2+} + Rb^+ + AsO_4^{3-} + 3H_2O(l) \rightleftharpoons Rb[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | 24.600* ± 1.000 | – 140.417* ± 5.708 | | |
| $Rb[UO_2BO_3]\cdot H_2O(cr)$* | $Rb^+ + 0.5(UO_2)_2(OH)_2^{2+} + H_3BO_3(aq) \rightleftharpoons Rb[UO_2BO_3]\cdot H_2O(cr) + 2H^+$ | – 3.710* ± 0.200 | 21.177* ± 1.142 | | |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O(cr)$ * | $UO_2^{2+} + Cs^+ + PO_4^{3-} + 2.5H_2O(l) \rightleftharpoons Cs[(UO_2)(PO_4)]\cdot 2.5H_2O(cr)$ | 25.900* ± 1.300 | – 147.837* ± 7.420 | | |
| $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr)$* | $UO_2^{2+} + Cs^+ + AsO_4^{3-} + 2.5H_2O(l) \rightleftharpoons Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr)$ | 25.200* ± 1.000 | – 143.842* ± 5.708 | | |
| $Cs[UO_2BO_3]\cdot H_2O(cr)$ * | $Cs^+ + 0.5(UO_2)_2(OH)_2^{2+} + H_3BO_3(aq) \rightleftharpoons Cs[UO_2BO_3]\cdot H_2O(cr) + 2H^+$ | – 3.920* ± 0.200 | 22.376* ± 1.142 | | |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_r G_m^o = \Delta_r H_m^o - T\Delta_r S_m^o$.
(b) Value calculated from a selected standard potential.
(c) Value of $\log_{10}K^{o}$ calculated internally from $\Delta_r G_m^o$.
(d) For the reaction $0.5UF_6(g) + 2.5UO_2F_2(cr) \rightleftharpoons U_3O_5F_8(cr)$ a heat capacity of $\Delta_r C_{p,m}^o$ (298.15 K) = – (18.7 ± 4.0) J·K$^{-1}$·mol$^{-1}$ is selected.
(*) New compound and/or value that has changed from [2003GUI/FAN]
(**) Only the uncertainty has changed from [2003GUI/FAN]

Table 3-3: Selected temperature coefficients for heat capacities marked with [c] in Table 3-1, according to the form $C_{p,\mathrm{m}}(T) = a + bT + cT^2 + eT^{-2} + jT^3$. The functions are valid between the temperatures $T_{min}$ and $T_{max}$ (in K). The notation E ± *nn* indicates the power of 10. $C_{p,\mathrm{m}}$ units are $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

| Compound | *a* | *b* | *c* | *e* | *j* | $T_{min}$ | $T_{max}$ |
|---|---|---|---|---|---|---|---|
| U(cr) | 2.69200E+01 | – 2.50200E–03 | 2.65560E–05 | – 7.69860E+04 | 0 | 298 | 941 |
| U(g) | 3.25160E+01 | – 2.25394E–02 | 1.46050E–05 | – 3.02280E+05 | 0 | 298 | 900 |
| UO(g) | 3.00540E+01 | 5.28803E–02 | – 4.22663E–05 | – 2.21060E+05 | 0 | 298 | 500 |
| $UO_2$(cr) | 6.67437E+01* | 4.31393E–02* | – 3.5640E–05* | – 1.16863E+06* | 1.1655E–08* | 298* | 3000* |
| $UO_2$(g) | 5.78390E+01 | 9.01050E–03 | – 9.36370E–07 | – 7.83110E+04 | 0 | 298 | 1000 |
| $UO_2^{2+}$ | (a) | | | | | 283 | 328 |
| β-$UO_{2.25}$ | 7.90890E+01 | 1.36500E–02 | 0 | – 1.03800E+06 | 0 | 348 | 600 |
| $UO_{2.25}$(cr) | 1.48760E+03 | – 6.97370E+00 | 9.73600E–03 | – 1.78600E+07 | 0 | 250 | 348 |
| α-$UO_{2.3333}$ | 6.41490E+01 | 4.91400E–02 | 0 | – 6.72000E+05 | 0 | 237 | 347 |
| β-$UO_{2.3333}$ | 6.43380E+01 | 4.97900E–02 | 0 | – 6.55000E+05 | 0 | 232 | 346 |
| $UO_{2.6667}$(cr) | 9.30890E+01* | 9.16000E–03* | 0 | – 1.43720E+06* | 0 | 298* | 2000* |
| β-$UO_3$ | 8.61700E+01 | 2.49840E–02 | 0 | – 1.09150E+06 | 0 | 298 | 678 |
| γ-$UO_3$ | 8.81030E+01 | 1.66400E–02 | 0 | – 1.01280E+06 | 0 | 298 | 850 |
| $UO_3$(g) | 6.44290E+01 | 3.17330E–02 | – 1.51980E–05 | – 7.14580E+05 | 0 | 298 | 1000 |
| β-$UO_2(OH)_2$ | 4.18000E+01 | 2.00000E–01 | 0 | 3.53000E+06 | 0 | 298 | 473 |
| $UO_3 \cdot 2H_2O$(cr) | 8.42380E+01 | 2.94590E–01 | 0 | 0 | 0 | 298 | 400 |
| UF(g) | 3.68030E+01 | 3.76720E–02 | – 3.33230E–05 | – 6.33380E+05 | 0 | 298 | 500 |
| $UF_2$(g) | 4.30910E+01 | 4.23483E–02 | – 1.97810E–05 | 1.96710E+05 | 0 | 298 | 900 |
| $UF_3$(cr) | 1.07392E+02* | 8.878000E–04* | 0 | – 1.21310E+06* | 0 | 298 | 1768 |
| $UF_3$(g) | 8.13270E+01 | – 4.30000E–06 | 2.42700E–06 | – 4.76300E+05 | 0 | 298 | 1800 |
| $UF_4$(cr) | 1.38865E+02 | – 3.20680E–02 | 2.79880E–05 | – 1.40200E+06 | 0 | 298 | 1309 |
| $UF_4$(g) | 1.03826E+02 | 9.54900E–03 | – 1.45100E–06 | – 1.02132E+06 | 0 | 298 | 3000 |
| α-$UF_5$ | 1.25159E+02 | 3.02080E–02 | 0 | – 1.92500E+05 | 0 | 298 | 1000 |
| β-$UF_5$ | 1.25159E+02 | 3.02080E–02 | 0 | – 1.92500E+05 | 0 | 298 | 1000 |
| $UF_5$(g) | 1.16738E+02 | 3.13041E–02 | – 1.25380E–05 | – 1.27300E+06 | 0 | 298 | 1100 |
| $UF_6$(cr) | 5.23180E+01 | 3.83798E–01 | 0 | 0 | 0 | 298 | 337 |
| $UF_6$(g) | 1.37373E+02 | 3.96050E–02 | – 2.17880E–05 | – 1.58687E+06 | 0 | 298 | 700 |
| $U_2F_9$(cr) | 2.35978E+02 | 5.99149E–02 | 0 | – 2.17568E+05 | 0 | 298 | 600 |
| $U_4F_{17}$(cr) | 4.53546E+02 | 1.18491E–01 | 0 | – 2.67776E+05 | 0 | 298 | 600 |
| $UOF_4$(g) | 1.16407E+02 | 2.85419E–02 | – 1.38740E–05 | – 1.38364E+06 | 0 | 298 | 900 |
| $UO_2F_2$(cr) | 1.06238E+02 | 2.83260E–02 | 0 | – 1.02080E+06 | 0 | 298 | 2000 |
| $UO_2F_2$(g) | 8.85810E+01 | 3.46640E–02 | – 1.76390E–05 | – 9.74480E+05 | 0 | 298 | 800 |
| UCl(g) | 6.30000E+01 | – 4.14373E–02 | 2.89720E–05 | – 8.93400E+05 | 0 | 298 | 700 |
| $UCl_2$(g) | 5.78070E+01 | 3.46400E–04 | 2.38800E–06 | 1.58480E+05 | 0 | 298 | 1100 |
| $UCl_3$(cr) | 1.06967E+02 | – 2.08595E–02 | 3.63890E–05 | – 1.29994E+05 | 0 | 298 | 1115 |
| $UCl_3$(g) | 8.40180E+01 | – 3.47320E–03 | 3.61300E–06 | – 7.98900E+04 | 0 | 298 | 1700 |
| $UCl_4$(cr) | 1.16320E+02 | 3.10837E–02 | 0 | – 3.40402E+05 | 0 | 298 | 863 |
| $UCl_4$(g) | 1.10634E+02 | 3.23750E–03 | – 3.12000E–07 | – 7.15600E+05 | 0 | 298 | 3000 |
| $UCl_5$(cr) | 1.40164E+02 | 3.55640E–02 | 0 | 0 | 0 | 298 | 600 |
| $UCl_5$(g) | 1.28655E+02 | 1.06600E–02 | – 2.66100E–06 | – 7.10000E+05 | 0 | 298 | 1900 |
| $UCl_6$(cr) | 1.73427E+02 | 3.50619E–02 | 0 | – 7.40568E+05 | 0 | 298 | 452 |
| $UCl_6$(g) | 1.57768E+02 | 9.73000E–05 | – 1.10000E–08 | – 9.46160E+05 | 0 | 298 | 3000 |
| UOCl(cr) | 7.58140E+01 | 1.43510E–02 | 0 | – 8.28430E+05 | 0 | 298 | 900 |
| $UOCl_2$(cr) | 9.88120E+01 | 2.22100E–02 | 0 | – 9.22160E+05 | 0 | 298 | 700 |
| $UOCl_3$(cr) | 1.05270E+02 | 3.99150E–02 | 0 | – 2.09200E+04 | 0 | 298 | 900 |
| $UO_2Cl$(cr) | 9.01230E+01 | 2.22590E–02 | 0 | – 7.74040E+05 | 0 | 298 | 1000 |

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Table 3-3 (continued)

| Compound | *a* | *b* | *c* | *e* | *j* | $T_{min}$ | $T_{max}$ |
|---|---|---|---|---|---|---|---|
| $UO_2Cl_2$(cr) | 1.15000E+02 | 1.82230E–02 | 0 | – 1.14180E+06 | 0 | 298 | 650 |
| $UO_2Cl_2$(g) | 9.59130E+01 | 1.96284E–02 | – 8.92180E–06 | – 7.46590E+05 | 0 | 298 | 1000 |
| $U_2O_2Cl_5$(cr) | 2.34300E+02 | 3.55640E–02 | 0 | – 2.26770E+06 | 0 | 298 | 700 |
| $(UO_2)_2Cl_3$(cr) | 2.25940E+02 | 3.55640E–02 | 0 | – 2.92880E+06 | 0 | 298 | 900 |
| UBr(g) | 6.34750E+01 | – 4.16971E–02 | 2.94940E–05 | – 8.16640E+05 | 0 | 298 | 700 |
| $UBr_2$(g) | 5.81290E+01 | – 1.74200E–04 | 2.62000E–06 | 2.70820E+05 | 0 | 298 | 1100 |
| $UBr_3$(cr) | 9.79710E+01 | 2.63600E–02 | 0 | 0 | 0 | 298 | 600 |
| $UBr_3$(g) | 8.44060E+01 | – 3.95240E–03 | 3.76800E–06 | 1.41230E+05 | 0 | 298 | 1700 |
| $UBr_4$(cr) | 1.19244E+02 | 2.97064E–02 | 0 | 0 | 0 | 298 | 792 |
| $UBr_4$(g) | 1.10817E+02 | 3.13740E–03 | – 3.02000E–07 | – 4.30880E+05 | 0 | 298 | 3100 |
| $UBr_5$(cr) | 1.50624E+02 | 3.34720E–02 | 0 | 0 | 0 | 298 | 400 |
| $UBr_5$(g) | 1.27620E+02 | 1.32749E–02 | – 4.04900E–06 | – 2.01280E+05 | 0 | 298 | 1400 |
| $UOBr_2$(cr) | 1.10580E+02 | 1.36820E–02 | 0 | – 1.47900E+06 | 0 | 298 | 900 |
| $UOBr_3$(cr) | 1.30540E+02 | 2.05020E–02 | 0 | – 1.38070E+06 | 0 | 298 | 1100 |
| $UO_2Br_2$(cr) | 1.04270E+02 | 3.79380E–02 | 0 | 0 | 0 | 298 | 500 |
| UI(g) | 6.35060E+01 | – 4.15266E–02 | 2.95180E–05 | – 7.94920E+05 | 0 | 298 | 700 |
| $UI_2$(g) | 5.81850E+01 | – 2.65300E–04 | 2.66100E–06 | 3.17020E+05 | 0 | 298 | 1100 |
| $UI_3$(cr) | 1.05018E+02 | 2.42672E–02 | 0 | 0 | 0 | 298 | 800 |
| $UI_3$(g) | 8.44400E+01 | – 3.99330E–03 | 3.78200E–06 | 2.11250E+05 | 0 | 298 | 1700 |
| $UI_4$(cr) | 1.45603E+02 | 9.95792E–03 | 0 | – 1.97486E+06 | 0 | 298 | 720 |
| $UI_4$(g) | 1.10978E+02 | 2.95700E–03 | – 2.55000E–07 | – 2.70780E+05 | 0 | 298 | 3000 |
| US(cr) | 5.28560E+01 | 6.51570E–03 | 0 | – 3.78290E+05 | 0 | 298 | 2000 |
| $US_{1.90}$(cr) | 7.80570E+01 | 6.63580E–03 | 0 | – 5.38900E+05 | 0 | 298 | 1900 |
| $US_2$(cr) | 7.56630E+01 | 8.93700E–03 | 0 | – 3.27780E+05 | 0 | 298 | 1800 |
| $US_3$(cr) | 1.00670E+02 | 1.12130E–02 | 0 | – 7.44750E+05 | 0 | 298 | 1100 |
| $U_2S_3$(cr) | 1.29450E+02 | 1.46860E–02 | 0 | 0 | 0 | 298 | 2000 |
| $UO_2SO_4$(cr) | 1.12470E+02 | 1.08780E–01 | 0 | 0 | 0 | 298 | 820 |
| USe(cr) | 5.41470E+01 | 7.96240E–03 | 0 | – 1.52180E+05 | 0 | 298 | 800 |
| α-$USe_2$ | 7.96930E+01 | 8.64870E–03 | 0 | – 2.64830E+05 | 0 | 298 | 800 |
| UN(cr) | 5.05400E+01 | 1.06600E–02 | 0 | – 5.23800E+05 | 0 | 298 | 1000 |
| UNCl(cr) | 8.02380E+01 | 1.87200E–03 | 0 | 1.10558E+06 | 0 | 298 | 1000 |
| $UPO_5$(cr) | 1.10430E+02 | 8.52280E–02 | 0 | – 1.03790E+06 | 0 | 298 | 600 |
| $(UO_2)_2P_2O_7$(cr) | 2.50670E+02 | 1.54300E–01 | 0 | – 3.40030E+06 | 0 | 298 | 600 |
| $(UO_2)_3(PO_4)_2$(cr) | 3.26370E+02 | 1.96440E–01 | 0 | – 4.08400E+06 | 0 | 298 | 600 |
| $UAsO_5$(cr) | 1.30700E+02 | 6.42580E–02 | 0 | – 1.05420E+06 | 0 | 298 | 800 |
| $UO_2(AsO_3)_2$(cr) | 2.08460E+02 | 8.89100E–02 | 0 | – 3.03460E+06 | 0 | 298 | 750 |
| $(UO_2)_2As_2O_7$(cr) | 3.07410E+02 | 1.05820E–01 | 0 | – 5.85130E+06 | 0 | 298 | 850 |
| $(UO_2)_3(AsO_4)_2$(cr) | 3.31150E+02 | 2.11360E–01 | 0 | – 2.68180E+06 | 0 | 298 | 850 |
| α-$Bi_2UO_6$ * | 2.30912E+02* | 1.8120E–02* | 0* | – 4.5526E+06* | 0 | 298* | 1089* |
| UC(cr) | 5.55710E+01 | 9.35940E–03 | 0 | – 7.32310E+05 | 0 | 298 | 600 |
| α-$UC_{1.94}$ | 6.57750E+01 | 2.03740E–02 | 0 | – 9.86520E+05 | 0 | 298 | 600 |
| $U_2C_3$(cr) | 1.14820E+02 | 3.10060E–02 | 0 | – 1.48450E+06 | 0 | 298 | 600 |
| $Tl_2U_4O_{11}$(cr) | 3.68200E+02 | 2.48860E–02 | 0 | – 1.37500E+06 | 0 | 298 | 673 |
| $Sr_3U_2O_9$(cr) | 3.19180E+02 | 1.16020E–01 | 0 | – 4.62010E+06 | 0 | 298 | 1000 |
| $Sr_3U_{11}O_{36}$(cr) | 9.62720E+02 | 3.55260E–01 | 0 | – 3.95400E+05 | 0 | 298 | 1000 |
| $BaUO_4$(cr)* | 1.4643E+02* | 1.6270E–02* | 0* | – 2.30987E+06* | 0 | 484* | 1566* |
| $BaU_2O_7$(cr)* | 2.0895E+02* | 5.3020E–02* | 0* | – 1.58738E+06* | 0 | 299* | 1000* |
| $Ba_2U_3O_{11}$(cr)* | 4.0127E+02* | 2.38900E–02* | 0* | – 7.34208E+06* | 0 | 323* | 1000* |
| $Ba_{2.875}UO_{5.875}$(cr)* | 2.8876E+02* | 5.1100E–03* | 0* | – 6.68314E+06* | 0 | 306* | 1011* |
| $Ba_3UO_6$(cr)* | 3.0994E+02* | 3.0700E–03* | 0* | – 8.40557E+06* | 0 | 302* | 1012* |

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Table 3-3 (continued)

| Compound | *a* | *b* | *c* | *e* | *j* | $T_{min}$ | $T_{max}$ |
|---|---|---|---|---|---|---|---|
| $NaUO_3$(cr) | 1.15490E+02 | 1.91670E–02 | 0 | – 1.09660E+06 | 0 | 415 | 931 |
| α-$Na_2UO_4$ | 1.62540E+02 | 2.58860E–02 | 0 | – 2.09660E+06 | 0 | 618 | 1165 |
| $Na_3UO_4$(cr) | 1.88900E+02 | 2.51790E–02 | 0 | – 2.08010E+06 | 0 | 523 | 1212 |
| $Na_2U_2O_7$(cr) | 2.62830E+02 | 1.46530E–02 | 0 | – 3.54900E+06 | 0 | 390 | 540 |
| $KUO_3$(cr) | 1.33258E+02 | 1.25580E–02 | 0 | 0 | 0 | 298 | 714 |
| $K_2U_2O_7$(cr) | 1.49084E+02 | 2.69500E–01 | 0 | 0 | 0 | 391 | 683 |
| $K_2U_4O_{13}$(cr) | 4.71068E+02 | – 4.68900E–02 | 0 | – 2.87540E+06 | 0 | 411 | 888 |
| $Rb_2U_4O_{11}$(cr) | 3.30400E+02 | 1.41340E–01 | 0 | – 6.19800E+05 | 0 | 396 | 735 |
| $Rb_2U_4O_{13}$(cr) | 4.12560E+02 | 2.50000E–02 | 0 | 0 | 0 | 325 | 805 |
| $Rb_2U(SO_4)_3$(cr) | 3.86672E+02 | 6.88300E–02 | 0 | – 5.25917E+06 | 0 | 298 | 628 |
| $Cs_2UO_4$(cr) | 1.64880E+02 | 1.70230E–02 | 0 | – 1.52850E+06 | 0 | 298 | 1061 |
| $Cs_2U_2O_7$(cr) | 3.55325E+02 | 8.15759E–02 | 0 | – 1.31956E+07 | 0 | 298 | 852 |
| $Cs_2U_4O_{12}$(cr) | 4.23726E+02 | 7.19405E–02 | 0 | – 5.43750E+06 | 0 | 361 | 719 |
| $Cs_4U_5O_{17}$(cr) | 6.99211E+02 | 1.71990E–01 | 0 | 0 | 0 | 368 | 906 |

(a) Thermal function is $C^{o}_{p,m}(UO_2^{2+},T) = (350.5 - 0.8722T - \frac{5308}{T-190})$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for 283 K ≤ $T$ ≤ 328 K

(*) New compound and/or value that has changed from [2003GUI/FAN].

# Chapter 4

# Selected Data for Neptunium

## 4.1 General considerations

This chapter presents updated chemical thermodynamic data for neptunium species, as described in detail in Chapter 10 of this volume. The selected data contain both data previously selected and in some cases revisions of some of them; in addition there is a large number of data that were not included in [1992GRE/FUG] and [2003GUI/FAN]. New species selected in this review are marked with an asterisk, "*"; revised data for species selected in [2003GUI/FAN] are also marked with an asterisk. Table 4-1 contains the selected thermodynamic data of the neptunium compounds and complexes, Table 4-2 the selected thermodynamic data of chemical equilibrium reactions by which the neptunium compounds and complexes are formed, and Table 4-3 the temperature coefficients of the heat capacity data of Table 4-1 where available.

The species and reactions in Table 4-1, Table 4-2 and Table 4-3 appear in standard order of arrangement (*cf.* Figure 2-1). These selected reaction data are used, together with data for key neptunium species (for example $Np^{4+}$) and auxiliary data listed in Table 8-1, to derive the corresponding formation quantities in Table 4-1. The uncertainties associated with values for the key neptunium species and for some of the auxiliary data are substantial, leading to comparatively large uncertainties in the thermodynamic data. By including a table for reaction data (Table 4-2), the users obtain information of equilibrium constants and their uncertainties that are directly based on the experimental data and their uncertainty.

The selected thermal functions of the heat capacities, listed in Table 4-3, are described with the empirical function:

$$C_{p,\mathrm{m}}(T) = a + bT + cT^2 + dT^{-1} + eT^{-2} + jT^3 \qquad (4.1)$$

The selected values in [1992GRE/FUG] and [2003GUI/FAN] are discussed there and retained in the present review. New and revised thermal functions are discussed in the relevant Appendix A entries. No references are given in these tables since the selected data are generally not directly attributable to a specific published source. A detailed discussion of the selection procedure is presented in [1992GRE/FUG], [2003GUI/FAN] and in Chapter 10 of this volume.

## 4.2 Precautions to be observed in the use of the tables

Geochemical modelling in aquatic systems requires the careful use of the data selected in the NEA TDB reviews. The selected data in the tables must not be adopted without taking into account the chemical background information discussed in the corresponding sections of this book. In particular the following precautions should be observed when using data from the Tables.

- The addition of new thermodynamic data to this internally consistent database should be made with care, it is straight forward to see if the new species has any significant effect on the experimental data, or if it results in changes in the speciation. However, if a significant change occurs, it is necessary to make a scrutiny of the experimental data on which the value is based and possibly also on the selected data.
- Gaps are pointed out in both the previous NEA TDB review and the present update.
- Solubility data for crystalline phases are well defined in the initial state, but not necessarily in the final state after "equilibrium" has been attained. Hence, the solubility calculated from these phases may be misleading, as discussed in [2003GUI/FAN] for the solubility data of $MO_2$(cr), M = U, Np, Pu.
- The selected thermodynamic data in [1992GRE/FUG], [1995SIL/BID] and [2001LEM/FUG] contained thermodynamic data for amorphous phases including Gibbs energy of formation deduced from solubility measurements. Following the criteria outlined in [2003GUI/FAN], the present review has not selected the Gibbs energy of formation of these phases. However, the corresponding $\log_{10}K$ values have been retained. The reasons for this choice are:
    - Thermodynamic data are only meaningful if they refer to well-defined systems; this is not the case for amorphous phases. It is well known that their solubility may change with time, due to re-crystallisation, with a resulting change in water content and surface area/crystal size; the time scale for these changes can vary widely.
    - The solubility of amorphous phases may be of interest for users of the database in chemical modelling even though they are not thermodynamic quantities.

Table 4-1: Selected thermodynamic data for neptunium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I$ = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95 % confidence interval. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Compound | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| Np(cr) | 0.000 | 0.000 | 50.460 ± 0.800 | 29.620 [c] ± 0.800 |
| β–Np | | | | [c] |
| γ–Np | | | | [c] |
| Np(g) | 421.195 [a] ± 3.009 | 465.100 [b] ± 3.000 | 197.719 ± 0.005 | 20.824 [c] ± 0.020 |
| $Np^{3+}$ | – 512.866 [b] ± 5.669 | – 527.184 ± 2.092 | – 193.584 ± 20.253 | |
| $Np^{4+}$ | – 491.774 [a] ± 5.586 | – 556.022 ± 4.185 | – 426.390 [b] ± 12.386 | |
| $NpO_2$(cr) | – 1021.731 [a] ± 2.514 | – 1074.000 ± 2.500 | 80.300 ± 0.400 | 66.200 [c] ± 0.500 |
| $NpO_2$(g)* | | – 467.700* ± 3.100 | | |
| $NpO_2^+$ | – 907.765 [a] ± 5.628 | – 978.181 ± 4.629 | – 45.904 ± 10.706 | – 4.000 ± 25.000 |
| $NpO_2^{2+}$ | – 795.939 ± 5.615 | – 860.733 ± 4.662 | – 92.387 [b] ± 10.464 | |
| $Np_2O_5$(cr) | | – 2162.700 ± 9.500 | | 128.600 [c] ± 5.000 |
| $NpOH^{2+}$ | – 711.191 [b] ± 5.922 | | | |

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Table 4-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $NpOH^{3+}$ | – 732.053 [b] ± 5.702 | | | |
| $Np(OH)_2^{2+}$ | – 968.052 [b] ± 5.844 | | | |
| $NpO_2OH(aq)$ | – 1080.405 [b] ± 6.902 | – 1199.226 [a] ± 19.176 | 25.000 ± 60.000 | |
| $NpO_2OH^+$ | – 1003.968 [b] ± 6.062 | | | |
| $NpO_2(OH)_2(cr)$ | – 1239.000 ± 6.400 | – 1377.000 ± 5.000 | 128.590 [a] ± 27.252 | 120.000 ± 20.000 |
| $NpO_2(OH)_2^-$ | – 1247.336 [b] ± 6.311 | – 1431.230 [a] ± 30.476 | 40.000 ± 100.000 | |
| $Np(OH)_4(aq)$ | – 1392.927 [b] ± 8.409 | | | |
| $NpO_2(OH)_3^-$ * | – 1386.348* [b] ± 8.424 | | | |
| $NpO_2(OH)_4^{2-}$ * | – 1561.842* [b] ± 8.425 | | | |
| $NpO_2(OH)_2 \cdot H_2O(cr)$* | – 1476.136* [b] ± 6.063 | | | |
| $(NpO_2)_2(OH)_2^{2+}$ | – 2030.369 [b] ± 11.294 | | | |
| $(NpO_2)_3(OH)_5^+$ | – 3475.795 [b] ± 16.893 | | | |
| NpF(g) | – 109.560 [a] ± 25.046 | – 80.000 ± 25.000 | 251.000 ± 5.000 | 33.800 [c] ± 3.000 |
| $NpF^{3+}$ | – 824.441 [b] ± 5.686 | – 889.872 [b] ± 4.684 | – 263.621 [b] ± 14.361 | |
| $NpF_2(g)$ | – 590.131 [a] ± 30.149 | – 575.000 ± 30.000 | 304.000 ± 10.000 | 55.900 [c] ± 5.000 |
| $NpF_2^{2+}$ | – 1144.436 [b] ± 6.005 | | | |
| $NpF_3(cr)$ | – 1460.501 [a] ± 8.325 | – 1529.000 ± 8.300 | 124.900 ± 2.000 | 94.200 [c] ± 3.000 |
| $NpF_3(g)$ | – 1107.801 [a] ± 25.178 | – 1115.000 ± 25.000 | 330.500 ± 10.000 | 72.200 [c] ± 5.000 |
| $NpF_4(cr)$ | – 1783.797 [a] ± 16.046 | – 1874.000 ± 16.000 | 153.500 ± 4.000 | 116.100 [c] ± 4.000 |
| $NpF_4(g)$ | – 1535.287 [a] ± 22.202 | – 1561.000 [b] ± 22.000 | 369.800 ± 10.000 | 95.300 [c] ± 5.000 |

(Continued on next page)

Table 4-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $NpF_5$(cr) | – 1834.430 [a] ± 25.398 | – 1941.000 ± 25.000 | 200.000 ± 15.000 | 132.800 [c] ± 8.000 |
| $NpF_6$(cr) | – 1841.872 [a] ± 20.002 | – 1970.000 ± 20.000 | 229.090 ± 0.500 | 167.440 [c] ± 0.400 |
| $NpF_6$(g) | – 1837.525 [a] ± 20.002 | – 1921.660 [b] ± 20.000 | 376.643 ± 0.500 | 129.072 [c] ± 1.000 |
| $NpF_6$(l) | | | | [c] |
| $NpO_2F$(aq) | – 1197.279* [b] ± 5.923 | | | |
| $NpO_2F^+$ | – 1103.548 [b] ± 5.672 | | | |
| $NpO_2F_2$(aq) | – 1402.366 [b] ± 5.801 | | | |
| $NpO_2F_2$(cr) | | | | [c] |
| $NpO_2F_2^-$ * | – 1481.656* [b] ± 6.229 | | | |
| $NpCl^{3+}$ | – 631.553 [b] ± 5.844 | | | |
| $NpCl_3$(cr) | – 829.811 [a] ± 3.237 | – 896.800 ± 3.000 | 160.400 ± 4.000 | 101.850 [c] ± 4.000 |
| $NpCl_3$(g) | – 582.357 [a] ± 10.822 | – 589.000 [b] ± 10.400 | 362.800 ± 10.000 | 78.500 [c] ± 5.000 |
| $NpCl_4$(cr) | – 895.562 [a] ± 2.998 | – 984.000 ± 1.800 | 200.000 ± 8.000 | 122.000 [c] ± 6.000 |
| $NpCl_4$(g) | – 765.050 [a] ± 5.487 | – 787.000 [b] ± 4.600 | 423.000 ± 10.000 | 105.000 [c] ± 5.000 |
| $NpCl_4$(l) | | | | [c] |
| $NpOCl_2$(cr) | – 960.645 [a] ± 8.141 | – 1030.000 ± 8.000 | 143.500 ± 5.000 | 95.000 [c] ± 4.000 |
| $NpO_2Cl^+$ | – 929.440 [b] ± 5.699 | | | |
| $NpO_2ClO_4$(aq) | | | | – 32.000 [c] ± 25.000 |
| $NpBr_3$(cr) | – 705.521 [a] ± 3.765 | – 730.200 ± 2.900 | 196.000 ± 8.000 | 103.800 [c] ± 6.000 |
| $NpBr_4$(cr) | – 737.843 [a] ± 3.495 | – 771.200 ± 1.800 | 243.000 ± 10.000 | 128.000 [c] ± 4.000 |

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Table 4-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $NpOBr_2$(cr) | – 906.933 [a] ± 11.067 | – 950.000 ± 11.000 | 160.800 ± 4.00 | 98.200 [c] ± 4.000 |
| $NpI^{3+}$ | – 552.059 [b] ± 6.036 | | | |
| $NpI_3$(cr) | – 512.498 [a] ± 3.715 | – 512.400 ± 2.200 | 225.000 ± 10.000 | 110.000 [c] ± 8.000 |
| $NpO_2IO_3$(aq) | – 1036.957 [b] ± 5.934 | | | |
| $NpO_2IO_3^+$ | – 929.126 [b] ± 5.922 | | | |
| $NpSO_4^{2+}$ | – 1274.887 [b] ± 5.809 | – 1435.522 [b] ± 9.796 | – 176.635 [b] ± 32.277 | |
| $NpO_2SO_4$(aq) | – 1558.666 [b] ± 5.641 | – 1753.373 [b] ± 4.706 | 44.920 [b] ± 10.667 | |
| $NpO_2SO_4^-$ | – 1659.189* [b] ± 5.758 | – 1865.521* [b] ± 8.402 | 71.271* [b] ± 26.090 | |
| $Np(SO_4)_2$(aq) | – 2042.873 [b] ± 6.360 | – 2319.322 [b] ± 5.871 | 7.964 [b] ± 18.924 | |
| $NpO_2(SO_4)_2^{2-}$ | – 2310.775 [b] ± 5.705 | – 2653.413 [b] ± 4.880 | 121.798 [b] ± 11.402 | |
| NpN(cr) | – 280.443 [a] ± 10.013 | – 305.000 ± 10.000 | 63.900 ± 1.500 | 48.700 [c] ± 0.900 |
| $NpNO_3^{3+}$ | – 613.413 [b] ± 5.667 | | | |
| $NpO_2(NO_3)_2 \cdot 6H_2O$(cr) | – 2428.069 [a] ± 5.565 | – 3008.241 ± 5.022 | 516.306 ± 8.000 | |
| $NpO_2HPO_4$(aq) | – 1927.314 [b] ± 7.067 | | | |
| $NpO_2HPO_4^-$ | – 2020.589 [b] ± 5.870 | – 2288.181* [b] ± 12.028 | – 59.820* [b] ± 38.493 | |
| $NpO_2H_2PO_4$(aq)* | – 2052.908* [b] ± 5.953 | | | |
| $NpO_2H_2PO_4^+$ | – 1952.042 [b] ± 6.491 | | | |
| $NpO_2(HPO_4)_2^{2-}$ | – 3042.135 [b] ± 8.598 | | | |
| NpSb(cr) | | | 101.400 ± 6.100 | 48.900 ± 2.900 |
| $NpC_{0.91}$(cr) | – 76.024 [a] ± 10.028 | – 71.100 ± 10.000 | 72.200 ± 2.400 | 50.000 [c] ± 1.000 |

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Table 4-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Np_2C_3$(cr) | – 192.427 [a] ± 19.436 | – 187.400 ± 19.200 | 135.000 ± 10.000 | 110.000 ± 8.000 |
| $NpO_2CO_3$(aq) | – 1380.120* [b] ± 5.657 | | | |
| $NpO_2CO_3$(cr) | – 1408.489* [b] ± 5.780 | | | |
| $NpO_2CO_3^-$ | – 1463.988 [b] ± 5.652 | | | |
| $NpO_2(CO_3)_2^{3-}$ | – 2000.861 [b] ± 5.685 | | | |
| $Np(CO_3)_3^{3-}$ | – 2185.949 [b] ± 15.451 | | | |
| $NpO_2(CO_3)_3^{4-}$ | – 2493.229* [b] ± 6.406 | – 2928.323 [b] ± 6.254 | – 1.938* [b] ± 19.981 | |
| $NpO_2(CO_3)_3^{5-}$ | – 2522.859 [b] ± 5.733 | – 3017.120 [b] ± 6.893 | – 135.050 [b] ± 20.467 | |
| $Np(CO_3)_4^{4-}$ | – 2812.775 [b] ± 8.240 | | | |
| $Np(CO_3)_5^{6-}$ | – 3334.567 [b] ± 8.425 | | | |
| $(NpO_2)_3(CO_3)_6^{6-}$ | – 5848.772* [b] ± 20.951 | | | |
| $NpO_2(CO_3)_2OH^{4-}$ | – 2170.417 [b] ± 8.785 | | | |
| $(NpO_2)_2CO_3(OH)_3^-$ | – 2820.953* [b] ± 15.702 | | | |
| $(NH_4)_4NpO_2(CO_3)_3$(cr) | – 2853.306* [b] ± 6.720 | | | |
| $Np(SCN)^{3+}$ | – 416.198 [b] ± 7.081 | – 486.622 [b] ± 6.520 | – 248.165 [b] ± 25.449 | |
| $Np(SCN)_2^{2+}$ | – 329.777 [b] ± 10.166 | – 412.222 [b] ± 12.748 | – 89.545 [b] ± 50.953 | |
| $Np(SCN)_3^+$ | – 241.072 [b] ± 13.541 | – 339.822 [b] ± 15.573 | 54.707 [b] ± 66.304 | |
| $Ca[NpO_2(OH)_2]^+$ * | – 1817.265* [b] ± 5.838 | | | |
| $Ca_3[NpO_2(OH)_5]^{2+}$ * | – 3439.082* [b] ± 6.676 | | | |
| $Ca_{0.5}NpO_2(OH)_2 \cdot 1.3H_2O$(cr)* | – 1896.521* [b] ± 5.668 | | | |

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Table 4-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Sr_3NpO_6$(cr) | | – 3125.800 ± 5.900 | | |
| $Ba_3NpO_6$(cr) | | – 3085.600 ± 9.600 | | |
| $Ba_2MgNpO_6$(cr) | | – 3096.900 ± 8.200 | | |
| $Ba_2CaNpO_6$(cr) | | – 3159.300 ± 7.900 | | |
| $Ba_2SrNpO_6$(cr) | | – 3122.500 ± 7.800 | | |
| $Li_2NpO_4$(cr) | | – 1828.200 ± 5.800 | | |
| α–$Na_2NpO_4$ | – 1648.993* [a] ± 5.848 | – 1763.800 ± 5.700 | 178.300* ± 4.300 | 151.900* ± 4.600 |
| β–$Na_2NpO_4$ | | – 1748.500 ± 6.100 | | |
| β–$Na_4NpO_5$ | – 2160.052* [a] ± 6.002 | – 2315.400 ± 5.700 | 247.500* ± 6.200 | 219.000* ± 6.600 |
| $Na_2Np_2O_7$(cr) | | – 2894.000 ± 11.000 | | |
| $Na_3NpF_8$(cr) | – 3521.239 [a] ± 21.305 | – 3714.000 [b] ± 21.000 | 369.000 [b] ± 12.000 | 272.250 [c] ± 12.000 |
| $Na_3NpO_2(CO_3)_2$(cr) | – 2830.592 [b] ± 6.365 | | | |
| $NaNpO_2CO_3·3.5H_2O$(cr) | –2590.397 [b] ± 5.808 | | | |
| $K_2NpO_4$(cr) | | – 1784.300 ± 6.400 | | |
| $K_2Np_2O_7$(cr) | | – 2932.000 ± 11.000 | | |
| $KNpO_2CO_3$(cr) | – 1793.235 [b] ± 5.746 | | | |
| $K_3NpO_2(CO_3)_2$(cr) | – 2899.340 [b] ± 5.765 | | | |
| $K_4NpO_2(CO_3)_3$(cr) | – 3663.416* [b] ± 8.140 | | | |
| $Rb_2Np_2O_7$(cr) | | – 2914.000 ± 12.000 | | |
| $Cs_2NpO_4$(cr) | | – 1788.100 ± 5.700 | | |

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Table 4-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Cs_2NpCl_6$(cr) | – 1833.039 [(a)]<br>± 4.871 | – 1976.200<br>± 1.900 | 410.000<br>± 15.000 | |
| $Cs_2NpO_2Cl_4$(cr) | | – 2056.100<br>± 5.400 | | |
| $Cs_3NpO_2Cl_4$(cr) | | – 2449.100<br>± 4.800 | | |
| $Cs_2NpBr_6$(cr) | – 1620.121 [(a)]<br>± 3.616 | – 1682.300<br>± 2.000 | 469.000<br>± 10.000 | |
| $Cs_2NaNpCl_6$(cr) | | – 2217.200<br>± 3.100 | | |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_f G_m^o = \Delta_f H_m^o - T\sum_i S_{m,i}^o$
(b) Value calculated internally from reaction data (see Table 4-2).
(c) Temperature coefficients of this function are listed in Table 4-3.
(*) New compound and/or value that has changed from [2003GUI/FAN].

Table 4-2: Selected thermodynamic data for reactions involving neptunium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I$ = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| Np(g) | $Np(cr) \rightleftharpoons Np(g)$ | | | | |
| | | | | 465.100 ± 3.000 | |
| $Np^{3+}$ | $0.5H_2(g) + Np^{4+} \rightleftharpoons H^+ + Np^{3+}$ | | | | |
| | | 3.695 [(c)] ± 0.169 | − 21.092 ± 0.965 | | |
| $Np^{4+}$ | $3H^+ + 0.5H_2(g) + NpO_2^+ \rightleftharpoons 2H_2O(l) + Np^{4+}$ | | | | |
| | | | | | − 305.930 ± 6.228 |
| $NpO_2$(am, hyd) | $Np^{4+} + 4OH^- \rightleftharpoons 2H_2O(l) + NpO_2(am, hyd)$ | | | | |
| | | 56.700 ± 0.500 | − 323.646 ± 2.854 | | |
| $NpO_2^+$ | $0.5H_2(g) + NpO_2^{2+} \rightleftharpoons H^+ + NpO_2^+$ | | | | |
| | | | | | − 18.857 ± 2.264 |
| $NpO_2^{2+}$ | $NpO_2(NO_3)_2 \cdot 6H_2O(s) \rightleftharpoons 6H_2O(l) + 2NO_3^- + NpO_2^{2+}$ | | | | |
| | | | | | 104.410 ± 6.695 |
| $NpOH^{2+}$ | $H_2O(l) + Np^{3+} \rightleftharpoons H^+ + NpOH^{2+}$ | | | | |
| | | − 6.800 ± 0.300 | 38.815 ± 1.712 | | |
| $NpOH^{3+}$ | $H_2O(l) + Np^{4+} \rightleftharpoons H^+ + NpOH^{3+}$ | | | | |
| | | 0.550 ± 0.200 | − 3.139 ± 1.142 | | |
| $Np(OH)_2^{2+}$ | $2H_2O(l) + Np^{4+} \rightleftharpoons 2H^+ + Np(OH)_2^{2+}$ | | | | |
| | | 0.350 ± 0.300 | − 1.998 ± 1.712 | | |

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Table 4-2 (continued)

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $NpO_2OH(am)$ | $H_2O(l) + NpO_2^+ \rightleftharpoons H^+ + NpO_2OH(am)$ | | | | |
| | | – 5.300 | 30.253 | | |
| | | ± 0.200 | ± 1.142 | | |
| $NpO_2OH(aq)$ | $H_2O(l) + NpO_2^+ \rightleftharpoons H^+ + NpO_2OH(aq)$ | | | | |
| | | – 11.300 | 64.501 | | |
| | | ± 0.700 | ± 3.996 | | |
| $NpO_2OH^+$ | $H_2O(l) + NpO_2^{2+} \rightleftharpoons H^+ + NpO_2OH^+$ | | | | |
| | | – 5.100 | 29.111 | | |
| | | ± 0.400 | ± 2.283 | | |
| $NpO_2(OH)_2^-$ | $2H_2O(l) + NpO_2^+ \rightleftharpoons 2H^+ + NpO_2(OH)_2^-$ | | | | |
| | | – 23.600 | 134.710 | | |
| | | ± 0.500 | ± 2.854 | | |
| $Np(OH)_4(aq)$ | $4H_2O(l) + Np^{4+} \rightleftharpoons 4H^+ + Np(OH)_4(aq)$ | | | | |
| | | – 8.300 | 47.377 | | |
| | | ± 1.100 | ± 6.279 | | |
| $NpO_2(OH)_3^-$ * | $3H_2O(l) + NpO_2^{2+} \rightleftharpoons 3H^+ + NpO_2(OH)_3^-$ | | | | |
| | | – 21.200* | 121.011* | | |
| | | ± 1.100 | ± 6.279 | | |
| $NpO_2(OH)_4^{2-}$ * | $4H_2O(l) + NpO_2^{2+} \rightleftharpoons 4H^+ + NpO_2(OH)_4^{2-}$ | | | | |
| | | – 32.000* | 182.657* | | |
| | | ± 1.100 | ± 6.279 | | |
| $NpO_2(OH)_2{\cdot}H_2O(cr)$* | $3H_2O(l) + NpO_2^{2+} \rightleftharpoons 2H^+ + NpO_2(OH)_2{\cdot}H_2O(cr)$ | | | | |
| | | – 5.470* | 31.223* | | |
| | | ± 0.400 | ± 2.283 | | |
| $(NpO_2)_2(OH)_2^{2+}$ | $2H_2O(l) + 2NpO_2^{2+} \rightleftharpoons (NpO_2)_2(OH)_2^{2+} + 2H^+$ | | | | |
| | | – 6.270 | 35.789 | | |
| | | ± 0.210 | ± 1.199 | | |
| $(NpO_2)_3(OH)_5^+$ | $5H_2O(l) + 3NpO_2^{2+} \rightleftharpoons (NpO_2)_3(OH)_5^+ + 5H^+$ | | | | |
| | | – 17.120 | 97.722 | | |
| | | ± 0.220 | ± 1.256 | | |
| $NpF^{3+}$ | $F^- + Np^{4+} \rightleftharpoons NpF^{3+}$ | | | | |
| | | 8.960 | – 51.144 | 1.500 | 176.570 [(a)] |
| | | ± 0.140 | ± 0.799 | ± 2.000 | ± 7.224 |

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Table 4-2 (continued)

| Species | Reaction | | | |
|---|---|---|---|---|
| | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
| $NpF_2^{2+}$ | $2F^- + Np^{4+} \rightleftharpoons NpF_2^{2+}$ | | | |
| | 15.700 ± 0.300 | – 89.616 ± 1.712 | | |
| $NpF_4(g)$ | $NpF_4(cr) \rightleftharpoons NpF_4(g)$ | | | |
| | | | 313.000 ± 15.000 | |
| $NpF_6(g)$ | $NpF_6(cr) \rightleftharpoons NpF_6(g)$ | | | |
| | | | 48.340 ± 0.070 | |
| $NpO_2F(aq)$ | $F^- + NpO_2^+ \rightleftharpoons NpO_2F(aq)$ | | | |
| | 1.400* ± 0.300 | – 7.991* ± 1.712 | | |
| $NpO_2F^+$ | $F^- + NpO_2^{2+} \rightleftharpoons NpO_2F^+$ | | | |
| | 4.570 ± 0.070 | – 26.086 ± 0.400 | | |
| $NpO_2F_2(aq)$ | $2F^- + NpO_2^{2+} \rightleftharpoons NpO_2F_2(aq)$ | | | |
| | 7.600 ± 0.080 | – 43.381 ± 0.457 | | |
| $NpO_2F_2^-$ * | $2F^- + NpO_2^+ \rightleftharpoons NpO_2F_2^-$ | | | |
| | 1.900* ± 0.400 | – 10.845* ± 2.283 | | |
| $NpCl^{3+}$ | $Cl^- + Np^{4+} \rightleftharpoons NpCl^{3+}$ | | | |
| | 1.500 ± 0.300 | – 8.562 ± 1.712 | | |
| $NpCl_3(g)$ | $NpCl_3(cr) \rightleftharpoons NpCl_3(g)$ | | | |
| | | | 307.800 ± 10.000 | |
| $NpCl_4(g)$ | $NpCl_4(cr) \rightleftharpoons NpCl_4(g)$ | | | |
| | | | 197.000 ± 3.000 | |
| $NpO_2Cl^+$ | $Cl^- + NpO_2^{2+} \rightleftharpoons NpO_2Cl^+$ | | | |
| | 0.400 ± 0.170 | – 2.283 ± 0.970 | | |

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Table 4-2 (continued)

| Species | Reaction | | | |
|---|---|---|---|---|
| | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
| $NpI^{3+}$ | $I^- + Np^{4+} \rightleftharpoons NpI^{3+}$ | | | |
| | 1.500 ± 0.400 | – 8.562 ± 2.283 | | |
| $NpO_2IO_3(aq)$ | $IO_3^- + NpO_2^+ \rightleftharpoons NpO_2IO_3(aq)$ | | | |
| | 0.500 ± 0.300 | – 2.854 ± 1.712 | | |
| $NpO_2IO_3^+$ | $IO_3^- + NpO_2^{2+} \rightleftharpoons NpO_2IO_3^+$ | | | |
| | 1.200 ± 0.300 | – 6.850 ± 1.712 | | |
| $NpSO_4^{2+}$ | $HSO_4^- + Np^{4+} \rightleftharpoons H^+ + NpSO_4^{2+}$ | | | |
| | 4.870 ± 0.150 | – 27.798 ± 0.856 | 7.400 ± 8.800 | 118.055 [(a)] ± 29.655 |
| $NpO_2SO_4(aq)$ | $NpO_2^{2+} + SO_4^{2-} \rightleftharpoons NpO_2SO_4(aq)$ | | | |
| | 3.280 ± 0.060 | – 18.722 ± 0.342 | 16.700 ± 0.500 | 118.807 [(a)] ± 2.033 |
| $NpO_2SO_4^-$ | $NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^-$ | | | |
| | 1.300* ± 0.200 | – 7.420* ± 1.142 | 22.000* ± 7.000 | 98.675*[(a)] ± 23.789 |
| $Np(SO_4)_2(aq)$ | $2HSO_4^- + Np^{4+} \rightleftharpoons 2H^+ + Np(SO_4)_2(aq)$ | | | |
| | 7.090 ± 0.250 | – 40.470 ± 1.427 | 10.500 ± 3.600 | 170.954 [(a)] ± 12.988 |
| $NpO_2(SO_4)_2^{2-}$ | $NpO_2^{2+} + 2SO_4^{2-} \rightleftharpoons NpO_2(SO_4)_2^{2-}$ | | | |
| | 4.700 ± 0.100 | – 26.828 ± 0.571 | 26.000 ± 1.200 | 177.185 [(a)] ± 4.457 |
| $NpNO_3^{3+}$ | $NO_3^- + Np^{4+} \rightleftharpoons NpNO_3^{3+}$ | | | |
| | 1.900 ± 0.150 | – 10.845 ± 0.856 | | |
| $NpO_2HPO_4(aq)$ | $HPO_4^{2-} + NpO_2^{2+} \rightleftharpoons NpO_2HPO_4(aq)$ | | | |
| | 6.200 ± 0.700 | – 35.390 ± 3.996 | | |
| $NpO_2HPO_4^-$ | $HPO_4^{2-} + NpO_2^+ \rightleftharpoons NpO_2HPO_4^-$ | | | |
| | 2.950 ± 0.100 | – 16.839 ± 0.571 | – 11.000* ± 11.000 | 19.584*[(a)] ± 36.944 |

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Table 4-2 (continued)

| Species | Reaction | | | |
|---|---|---|---|---|
| | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
| $NpO_2H_2PO_4(aq)$ * | $H_2PO_4^- + NpO_2^+ \rightleftharpoons NpO_2H_2PO_4(aq)$ | | | |
| | 1.400* ± 0.200 | – 7.991* ± 1.142 | | |
| $NpO_2H_2PO_4^+$ | $H_2PO_4^- + NpO_2^{2+} \rightleftharpoons NpO_2H_2PO_4^+$ | | | |
| | 3.320 ± 0.500 | – 18.951 ± 2.854 | | |
| $NpO_2(HPO_4)_2^{2-}$ | $2HPO_4^{2-} + NpO_2^{2+} \rightleftharpoons NpO_2(HPO_4)_2^{2-}$ | | | |
| | 9.500 ± 1.000 | – 54.226 ± 5.708 | | |
| $NpO_2CO_3(aq)$ | $CO_3^{2-} + NpO_2^{2+} \rightleftharpoons NpO_2CO_3(aq)$ | | | |
| | 9.860* ± 0.100 | – 56.281* ± 0.571 | | |
| $NpO_2CO_3(cr)$ | $CO_3^{2-} + NpO_2^{2+} \rightleftharpoons NpO_2CO_3(cr)$ | | | |
| | 14.830* ± 0.230 | – 84.650* ± 1.313 | | |
| $NpO_2CO_3^-$ | $CO_3^{2-} + NpO_2^+ \rightleftharpoons NpO_2CO_3^-$ | | | |
| | 4.962 ± 0.061 | – 28.323 ± 0.348 | | |
| $NpO_2(CO_3)_2^{3-}$ | $CO_3^{2-} + NpO_2CO_3^- \rightleftharpoons NpO_2(CO_3)_2^{3-}$ | | | |
| | 1.572 ± 0.083 | – 8.973 ± 0.474 | | |
| $Np(CO_3)_3^{3-}$ | $Np(CO_3)_5^{6-} + e^- \rightleftharpoons 2CO_3^{2-} + Np(CO_3)_3^{3-}$ | | | |
| | – 16.261 ± 2.265 | 92.818 ± 12.929 | | |
| $NpO_2(CO_3)_3^{4-}$ | $3CO_3^{2-} + NpO_2^{2+} \rightleftharpoons NpO_2(CO_3)_3^{4-}$ | | | |
| | 19.900* ± 0.500 | – 113.590* ± 2.854 | – 41.900 ± 4.100 | 240.449*[a] ± 16.755 |
| $NpO_2(CO_3)_3^{5-}$ | $CO_3^{2-} + NpO_2(CO_3)_2^{3-} \rightleftharpoons NpO_2(CO_3)_3^{5-}$ | | | |
| | – 1.034 ± 0.110 | 5.902 ± 0.628 | | |
| $NpO_2(CO_3)_3^{5-}$ | $NpO_2(CO_3)_3^{4-} + e^- \rightleftharpoons NpO_2(CO_3)_3^{5-}$ | | | |
| | | | – 88.800 ± 2.900 | |

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Table 4-2 (continued)

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Np(CO_3)_4^{4-}$ | $4CO_3^{2-} + 2H_2O(l) + NpO_2(am,hyd) \rightleftharpoons Np(CO_3)_4^{4-} + 4OH^-$ | | | | |
| | | – 17.790 ± 0.220 | 101.550 ± 1.256 | | |
| $Np(CO_3)_5^{6-}$ | $CO_3^{2-} + Np(CO_3)_4^{4-} \rightleftharpoons Np(CO_3)_5^{6-}$ | | | | |
| | | – 1.070 ± 0.300 | 6.108 ± 1.712 | | |
| $(NpO_2)_3(CO_3)_6^{6-}$ | $3NpO_2(CO_3)_3^{4-} \rightleftharpoons (NpO_2)_3(CO_3)_6^{6-} + 3CO_3^{2-}$ | | | | |
| | | – 8.272 [c] ± 1.447 | 47.215 ± 8.260 | | |
| $NpO_2(CO_3)_2OH^{4-}$ | $NpO_2(CO_3)_3^{5-} + OH^- \rightleftharpoons CO_3^{2-} + NpO_2(CO_3)_2OH^{4-}$ | | | | |
| | | 3.195 [c] ± 1.164 | – 18.238 ± 6.644 | | |
| $(NpO_2)_2CO_3(OH)_3^-$ | $7H^+ + 2NpO_2(CO_3)_3^{4-} \rightleftharpoons (NpO_2)_2CO_3(OH)_3^- + 5CO_2(g) + 2H_2O(l)$ | | | | |
| | | 49.166 [c] ± 1.586 | – 280.640 ± 9.053 | | |
| $(NH_4)_4NpO_2(CO_3)_3(cr)$ | $4NH_4^+ + NpO_2(CO_3)_3^{4-} \rightleftharpoons (NH_4)_4NpO_2(CO_3)_3(cr)$ | | | | |
| | | 7.443 [c] ± 0.297 | – 42.485 ± 1.698 | | |
| $Np(SCN)^{3+}$ | $Np^{4+} + SCN^- \rightleftharpoons Np(SCN)^{3+}$ | | | | |
| | | 3.000 ± 0.300 | – 17.124 ± 1.712 | – 7.000 ± 3.000 | 33.956 [a] ± 11.586 |
| $Np(SCN)_2^{2+}$ | $Np^{4+} + 2SCN^- \rightleftharpoons Np(SCN)_2^{2+}$ | | | | |
| | | 4.100 ± 0.500 | – 23.403 ± 2.854 | – 9.000 ± 9.000 | 48.308 [a] ± 31.668 |
| $Np(SCN)_3^+$ | $Np^{4+} + 3SCN^- \rightleftharpoons Np(SCN)_3^+$ | | | | |
| | | 4.800 ± 0.500 | – 27.399 ± 2.854 | – 13.000 ± 9.000 | 48.293 [a] ± 31.668 |
| $Ca[NpO_2(OH)_2]^+$ * | $2H_2O(l) + NpO_2^+ + Ca^{2+} \rightleftharpoons 2H^+ + Ca[NpO_2(OH)_2]^+$ | | | | |
| | | – 20.600* ± 0.200 | 117.586* ± 1.142 | | |
| $Ca_3[NpO_2(OH)_5]^{2+}$ * | $5H_2O(l) + NpO_2^+ + 3Ca^{2+} \rightleftharpoons 5H^+ + Ca_3[NpO_2(OH)_5]^{2+}$ | | | | |
| | | – 54.800* ± 0.300 | 312.801* ± 1.712 | | |

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Table 4-2 (continued)

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Ca_{0.5}NpO_2(OH)_2 \cdot 1.3H_2O(cr)$ * | $NpO_2^+ + 0.5Ca^{2+} + 3.3H_2O(l) \rightleftharpoons 2H^+ + Ca_{0.5}NpO_2(OH)_2 \cdot 1.3H_2O(cr)$ | | | | |
| | | – 12.300* ± 0.070 | 70.209* ± 0.400 | | |
| $Na_3NpF_8(cr)$ | $3NaF(cr) + NpF_6(g) \rightleftharpoons 0.5F_2(g) + Na_3NpF_8(cr)$ | | | | |
| | | 7.876 [(c)] ± 1.350 | – 44.954 [(a)] ± 7.705 | – 62.678 ± 6.900 | – 59.447 ± 11.500 |
| $Na_3NpO_2(CO_3)_2(cr)$ | $2CO_3^{2-} + 3Na^+ + NpO_2^+ \rightleftharpoons Na_3NpO_2(CO_3)_2(cr)$ | | | | |
| | | 14.220 ± 0.500 | – 81.168 ± 2.854 | | |
| $NaNpO_2CO_3 \cdot 3.5H_2O(cr)$ | $CO_3^{2-} + 3.5H_2O(l) + Na^+ + NpO_2^+ \rightleftharpoons NaNpO_2CO_3 \cdot 3.5H_2O(cr)$ | | | | |
| | | 11.000 ± 0.240 | – 62.788 ± 1.370 | | |
| $0.5Na_2Np_2O_7 \cdot xH_2O(cr)$ * | $Na^+ + NpO_2^{2+} + (1.5 + 0.5x)H_2O(l) \rightleftharpoons 3H^+ + 0.5Na_2Np_2O_7 \cdot xH_2O(cr)$ | | | | |
| | | – 12.600* ± 1.100 | 71.921* ± 6.279 | | |
| $KNpO_2CO_3(cr)$ | $CO_3^{2-} + K^+ + NpO_2^+ \rightleftharpoons KNpO_2CO_3(cr)$ | | | | |
| | | 13.150 ± 0.190 | – 75.061 ± 1.085 | | |
| $K_3NpO_2(CO_3)_2(cr)$ | $2CO_3^{2-} + 3K^+ + NpO_2^+ \rightleftharpoons K_3NpO_2(CO_3)_2(cr)$ | | | | |
| | | 15.460 ± 0.160 | – 88.246 ± 0.913 | | |
| $K_4NpO_2(CO_3)_3(cr)$ | $4K^+ + NpO_2(CO_3)_3^{4-} \rightleftharpoons K_4NpO_2(CO_3)_3(cr)$ | | | | |
| | | 7.033[(c)] ± 0.876 | – 40.147 ± 5.001 | | |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_r G_m^\circ = \Delta_r H_m^\circ - T\,\Delta_r S_m^\circ$

(b) Value calculated from a selected standard potential.

(c) Value of $\log_{10} K^\circ$ calculated internally from $\Delta_r G_m^\circ$.

(*) New compound and/or value that has changed from [2003GUI/FAN].

Table 4-3: Selected temperature coefficients for heat capacities marked with [c] in Table 4-1, according to the form $C_{p,\mathrm{m}}(T) = a + bT + cT^2 + dT^{-1} + eT^{-2} + jT^3$ . The functions are valid between the temperatures $T_{min}$ and $T_{max}$ (in K). The notation E ± *nn* indicates the power of 10. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. $C_{p,\mathrm{m}}$ units are J·K$^{-1}$·mol$^{-1}$.

| Compound | *a* | *b* | *c* | *d*/*j* (†) | *e* | $T_{min}$ | $T_{max}$ |
|---|---|---|---|---|---|---|---|
| Np(cr) | –4.05430E+00 | 8.25540E–02 | 0 | 0 | 8.05710E+05 | 298 | 553 |
| β–Np | 3.93300E+01 | 0 | 0 | 0 | 0 | 553 | 849 |
| γ–Np | 3.64010E+01 | 0 | 0 | 0 | 0 | 849 | 912 |
| Np(g) | 1.77820E+01 | 3.35250E–03 | 6.68070E–06 | 0 | 1.28800E+05 | 298 | 800 |
| | 1.41320E+01 | 1.55670E–02 | –1.59546E–06 | 0 | –3.98870E+05 | 800 | 2000 |
| $NpO_2$(cr) | 6.47712E+01* | 4.38574 E–02* | –3.50695E–05 * | 1.31917E–08[j]* | –7.89320E+05 * | 298* | 3072* |
| $Np_2O_5$(cr) | 9.92000E+01 | 9.86000E–02 | 0 | 0 | 0 | 298 | 750 |
| NpF(g) | 3.59880E+01 | 2.30310E–03 | –7.30170E–07 | 0 | –2.50010E+05 | 298 | 1400 |
| $NpF_2$(g) | 6.74740E+01 | 5.56480E–03 | –5.95160E–06 | 0 | –1.12930E+06 | 298 | 600 |
| $NpF_3$(cr) | 1.05200E+02 | 8.12000E–04 | 0 | 0 | –1.00000E+06 | 298 | 1735 |
| $NpF_3$(g) | 8.16540E+01 | 1.20840E–03 | –2.42780E–07 | 0 | –8.67160E+05 | 298 | 3000 |
| $NpF_4$(cr) | 1.22640E+02 | 9.68400E–03 | 0 | 0 | –8.36470E+05 | 298 | 1305 |
| $NpF_4$(g) | 1.05840E+02 | 8.61400E–04 | 1.57430E–06 | 0 | –9.75640E+05 | 298 | 1500 |
| $NpF_5$(cr) | 1.26000E+02 | 3.00000E–02 | 0 | 0 | –1.90000E+05 | 298 | 600 |
| $NpF_6$(cr) | 6.23330E+01 | 3.52550E–01 | 0 | 0 | 0 | 298 | 328 |
| $NpF_6$(g) | 1.43240E+02 | 2.44160E–02 | –1.13120E–05 | 0 | –1.81740E+06 | 298 | 1000 |
| $NpF_6$(l) | 1.50340E+02 | 1.10080E–01 | 0 | 0 | 0 | 328 | 350 |
| $NpO_2F_2$(cr) | 1.06240E+02 | 2.83260E–02 | 0 | 0 | –1.02080E+06 | 298 | 1000 |
| $NpCl_3$(cr) | 8.96000E+01 | 2.75000E–02 | 0 | 0 | 3.60000E+05 | 298 | 1075 |
| $NpCl_3$(g) | 7.19890E+01 | 2.47410E–02 | –8.48420E–06 | 0 | –1.15000E+04 | 298 | 1000 |
| $NpCl_4$(cr) | 1.12500E+02 | 3.60000E–02 | 0 | 0 | –1.10000E+05 | 298 | 811 |
| $NpCl_4$(g) | 1.08770E+02 | –2.86580E–03 | 3.15880E–06 | 0 | –2.80770E+05 | 298 | 1800 |
| $NpCl_4$(l) | 1.08000E+02 | 6.00000E–02 | 0 | 0 | 0 | 811 | 1000 |
| $NpOCl_2$(cr) | 9.88000E+01 | 2.20000E–02 | 0 | 0 | –9.20000E+05 | 298 | 1000 |
| $NpO_2ClO_4$(aq)[a] | 3.56770E+03 | –4.95930E+0 | 0 | –6.32340E+05 | 0 | 291 | 398 |
| $NpBr_3$(cr) | 1.01230E+02 | 2.06800E–02 | 0 | 0 | –3.20000E+05 | 298 | 975 |
| $NpBr_4$(cr) | 1.19000E+02 | 3.00000E–02 | 0 | 0 | 0 | 298 | 800 |
| $NpOBr_2$(cr) | 1.11000E+02 | 1.37000E–02 | 0 | 0 | –1.50000E+06 | 298 | 800 |
| $NpI_3$(cr) | 1.04000E+02 | 2.00000E–02 | 0 | 0 | 0 | 298 | 975 |
| NpN(cr) | 4.76700E+01 | 1.31740E–02 | 0 | 0 | –2.57620E+05 | 298 | 2000 |
| $NpC_{0.91}$(cr) | 6.12500E+01 | –3.52750E–02 | 3.62830E–05 | 0 | –3.48420E+05 | 298 | 1000 |
| $Na_3NpF_8$(cr) | 2.70000E+02 | 5.66000E–02 | 0 | 0 | –1.30000E+06 | 298 | 800 |

(a) Partial molar heat capacity of solute.

(*) New compound and/or value that has changed from [2003GUI/FAN].

(†) Term is $dT^{-1}$ if unmarked, or $jT^3$ if marked "*j*".

# Chapter 5

# Selected Data for Plutonium

## 5.1 General considerations

This chapter presents updated chemical thermodynamic data for plutonium species, as described in detail in Chapter 11 of this volume. The selected data contain both data previously selected and in some cases revisions of some of them; in addition there is a large number of data that were not included in [1992GRE/FUG] and [2003GUI/FAN]. New species selected in this review are marked with an asterisk, "*"; revised data for species selected in [2003GUI/FAN] are also marked with an asterisk. Table 5-1 contains the selected thermodynamic data of the plutonium compounds and complexes, Table 5-2 the selected thermodynamic data of chemical equilibrium reactions by which the plutonium compounds and complexes are formed, and Table 5-3 the temperature coefficients of the heat capacity data of Table 5-1 where available.

The species and reactions in Table 5-1, Table 5-2 and Table 5-3 appear in standard order of arrangement (*cf.* Figure 2-1). These selected reaction data are used, together with data for key plutonium species (for example $Pu^{4+}$) and auxiliary data listed in Table 8-1, to derive the corresponding formation quantities in Table 5-1. The uncertainties associated with values for the key plutonium species and for some of the auxiliary data are substantial, leading to comparatively large uncertainties in the thermodynamic data. By including a table for reaction data (Table 5-2), the users obtain information of equilibrium constants and their uncertainties that are directly based on the experimental data and their uncertainty.

The selected thermal functions of the heat capacities, listed in Table 5-3, are described with the empirical function:

$$C_{p,m}(T) = a + bT + cT^2 + eT^{-2} + jT^3 \quad (5.1)$$

The selected values in [1992GRE/FUG] and [2003GUI/FAN] are discussed there and retained in the present review. New and revised thermal functions are discussed in the relevant Appendix A entries. No references are given in these tables since the selected data are generally not directly attributable to a specific published source. A detailed discussion of the selection procedure is presented in [1992GRE/FUG], [2003GUI/FAN] and in Chapter 11 of this volume.

## 5.2 Precautions to be observed in the use of the tables

Geochemical modelling in aquatic systems requires the careful use of the data selected in the NEA TDB reviews. The selected data in the tables must not be adopted without taking into account the chemical background information discussed in the corresponding sections of this book. In particular the following precautions should be observed when using data from the Tables.

- The addition of new thermodynamic data to this internally consistent database should be made with care, it is straight forward to see if the new species has any significant effect on the experimental data, or if it results in changes in the speciation. However, if a significant change occurs, it is necessary to make a scrutiny of the experimental data on which the value is based and possibly also on the selected data.
- Gaps are pointed out in both the previous NEA TDB review and the present update.
- Solubility data for crystalline phases are well defined in the initial state, but not necessarily in the final state after "equilibrium" has been attained. Hence, the solubility calculated from these phases may be misleading, as discussed in [2003GUI/FAN] for the solubility data of $MO_2$(cr), M = U, Np, Pu.
- The selected thermodynamic data in [1992GRE/FUG], [1995SIL/BID] and [2001LEM/FUG] contained thermodynamic data for amorphous phases including Gibbs energy of formation deduced from solubility measurements. Following the criteria outlined in [2003GUI/FAN], the present review has not selected the Gibbs energy of formation of these phases. However, the corresponding $\log_{10}K$ values have been retained. The reasons for this choice are:
    - Thermodynamic data are only meaningful if they refer to well-defined systems; this is not the case for amorphous phases. It is well known that their solubility may change with time, due to re-crystallisation, with a resulting change in water content and surface area/crystal size; the time scale for these changes can vary widely.
    - The solubility of amorphous phases may be of interest for users of the database in chemical modelling even though they are not thermodynamic quantities.

Table 5-1: Selected thermodynamic data for plutonium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I$ = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| Pu(cr) | 0.000 | 0.000 | 54.460 ± 0.800 | 31.490 [(c)] ± 0.400 |
| β–Pu | | | | [(c)] |
| δ–Pu | | | | [(c)] |
| δ'–Pu | | | | [(c)] |
| γ–Pu | | | | [(c)] |
| ε–Pu | | | | [(c)] |
| Pu(g) | 312.415 [(a)] ± 3.009 | 349.000 [(b)] ± 3.000 | 177.167 ± 0.005 | 20.854 [(c)] ± 0.010 |
| $Pu^{3+}$ | – 578.984 ± 2.688 | – 591.790 ± 1.964 | – 184.510 [(b)] ± 6.154 | |
| $Pu^{4+}$ | – 477.988 ± 2.705 | – 539.895 ± 3.103 | – 414.535 ± 10.192 | |
| $PuO_{1.61}$(bcc) | – 834.771 [(a)] ± 10.113 | – 875.500 ± 10.000 | 83.000 ± 5.000 | 60.200*[(c)] ± 5.000 |
| $PuO_2$(cr) | – 998.113 [(a)] ± 1.031 | – 1055.800 ± 1.000 | 66.130** ± 0.300 | 66.250**[(c)] ± 0.300 |
| $PuO_2^+$ | – 852.646 [(b)] ± 2.868 | – 910.127 [(a)] ± 8.920 | 1.480 [(b)] ± 30.013 | |
| $PuO_2^{2+}$ | – 762.353 ± 2.821 | – 822.036 ± 6.577 | – 71.246 ± 22.120 | |

(Continued on next page)

Table 5-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Pu_2O_3$(cr) | – 1580.375 [(a)] ± 10.013 | – 1656.000 ± 10.000 | 163.000 ± 0.600 | 117.000[(c)] ± 0.500 |
| $PuOH^{2+}$ | – 780.848*[(b)] ± 3.921 | | | |
| $PuOH^{3+}$ | – 718.553 [(b)] ± 2.936 | | | |
| $Pu(OH)_2^{2+}$ | – 955.693 [(b)] ± 3.203 | | | |
| $Pu(OH)_3^+$ | – 1176.280 [(b)] ± 3.542 | | | |
| $PuO_2OH$(aq) | ≥ – 1034.247 [(b)] | | | |
| $PuO_2OH^+$ | – 968.099 [(b)] ± 4.013 | – 1079.866 [(b)] ± 16.378 | – 12.680 [(b)] ± 55.786 | |
| $PuO_2(OH)_2$(aq) | – 1161.287 [(b)] ± 9.015 | | | |
| $Pu(OH)_4$(aq) | – 1378.031 [(b)] ± 3.936 | | | |
| $PuO_2(OH)_3^-$ * | – 1336.780* [(b)] ± 9.559 | | | |
| $(PuO_2)_2(OH)_2^{2+}$ | – 1956.176 [(b)] ± 8.026 | | | |
| PuF(g) | – 140.967 [(a)] ± 10.113 | – 112.600 ± 10.000 | 251.000 ± 5.000 | 33.500 [(c)] ± 3.000 |
| $PuF^{3+}$ | – 809.970 [(b)] ± 2.850 | – 866.145 [(b)] ± 3.859 | – 228.573 [(b)] ± 12.753 | |
| $PuF_2$(g) | – 626.151 [(a)] ± 6.704 | – 614.300 ± 6.000 | 297.000 ± 10.000 | 51.500 [(c)] ± 5.000 |
| $PuF_2^{2+}$ | – 1130.651 [(b)] ± 3.246 | – 1199.595 [(b)] ± 6.026 | – 104.666 [(b)] ± 20.058 | |
| $PuF_3$(cr) | – 1517.369 [(a)] ± 3.709 | – 1586.700 ± 3.700 | 126.110 ± 0.360 | 92.640 [(c)] ± 0.280 |
| $PuF_3$(g) | – 1161.081 [(a)] ± 4.758 | – 1167.800 [(b)] ± 3.700 | 336.110 ± 10.000 | 72.240 [(c)] ± 5.000 |
| $PuF_4$(cr) | – 1756.741 [(a)] ± 20.002 | – 1850.000 ± 20.000 | 147.250 ± 0.370 | 116.190 ± 0.290 |

(Continued on next page)

Table 5-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $PuF_4$(g) | – 1517.874 [a] ± 22.202 | – 1548.000 [b] ± 22.000 | 359.000 ± 10.000 | 92.400 [c] ± 5.000 |
| $PuF_6$(cr) | – 1729.856 [a] ±20.174 | – 1861.350 [b] ±20.170 | 221.800 ± 1.100 | 168.100 [c] ± 2.000 |
| $PuF_6$(g) | – 1725.064 [a] ± 20.104 | – 1812.700 [b] ± 20.100 | 368.900 ± 1.000 | 129.320 [c] ± 1.000 |
| PuOF(cr) | – 1091.571 [a] ± 20.222 | – 1140.000 ± 20.000 | 96.000 ± 10.000 | 69.400 [c] ± 10.000 |
| $PuO_2F^+$ | – 1069.905 [b] ± 3.121 | | | |
| $PuO_2F_2$(aq) | – 1366.783 [b] ± 4.059 | | | |
| $PuCl^{3+}$ | – 619.480 [b] ± 3.204 | | | |
| $PuCl_3$(cr) | – 891.806 [a] ± 2.024 | – 959.600 ± 1.800 | 161.700 ± 3.000 | 101.200 [c] ± 4.000 |
| $PuCl_3$(g) | – 641.299 [a] ± 3.598 | – 647.400 [b] ± 1.868 | 368.620 ± 10.000 | 78.470 [c] ± 5.000 |
| $PuCl_4$(cr) | – 879.368 [a] ± 5.826 | – 968.700 ± 5.000 | 201.000 ± 10.000 | 121.400 ± 4.000 |
| $PuCl_4$(g) | – 764.683 [a] ± 10.438 | – 792.000 [b] ± 10.000 | 409.000 ± 10.000 | 103.400 [c] ± 5.000 |
| PuOCl(cr) | – 882.409 [a] ± 1.936 | – 931.000 ± 1.700 | 105.600 [b] ± 3.000 | 71.600 [c] ± 4.000 |
| $PuO_2Cl^+$ | – 894.883 [b] ± 2.829 | | | |
| $PuO_2Cl_2$(aq) | – 1018.224 [b] ± 3.308 | | | |
| $PuCl_3 \cdot 6H_2O$(cr) | – 2365.347 [a] ± 2.586 | – 2773.400 ± 2.100 | 420.000 ± 5.000 | |
| $PuBr^{3+}$ | – 590.971 [b] ± 3.206 | | | |
| $PuBr_3$(cr) | – 767.324 [a] ± 2.697 | – 792.600 ± 2.000 | 198.000 ± 6.000 | 101.800 [c] ± 6.000 |
| $PuBr_3$(g) | – 529.808 [a] ± 15.655 | – 488.000 [b] ± 15.000 | 423.000 [b] ± 15.000 | 81.600 [c] ± 10.000 |

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Table 5-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| PuOBr(cr) | – 838.354 [a] ± 8.541 | – 870.000 [b] ± 8.000 | 127.000 [b] ± 10.000 | 73.000 [c] ± 8.000 |
| $PuI^{2+}$ | – 636.987 [b] ± 3.529 | | | |
| $PuI_3$(cr) | – 579.000 [a] ± 4.551 | – 579.200 ± 2.800 | 228.000 ± 12.000 | 110.000 [c] ± 8.000 |
| $PuI_3$(g) | – 366.517 [a] ± 15.655 | – 305.000 ± 15.000 | 435.000 ± 15.000 | 82.000 [c] ± 5.000 |
| PuOI(cr) | – 776.626 [a] ± 20.495 | – 802.000 ± 20.000 | 130.000 ± 15.000 | 75.600 [c] ± 10.000 |
| $PuSO_4^+$ | – 1345.315 [b] ± 4.599 | – 1483.890 [b] ± 2.976 | – 33.301 [b] ± 15.108 | |
| $PuSO_4^{2+}$ | – 1261.329 [b] ± 3.270 | | | |
| $PuO_2SO_4$(aq) | – 1525.650 [b] ± 3.072 | – 1715.276 [b] ± 6.616 | 65.963 [b] ± 22.543 | |
| $PuO_2SO_4^-$ * | – 1603.842*[b] ± 2.978 | | | |
| $Pu(SO_4)_2$(aq) | – 2029.601 [b] ± 4.225 | | | |
| $Pu(SO_4)_2^-$ | – 2099.545 [b] ± 5.766 | – 2398.590 [b] ± 16.244 | 1.520 [b] ± 56.262 | |
| $PuO_2(SO_4)_2^{2-}$ | – 2275.477 [b] ± 3.156 | – 2597.716 [b] ± 11.176 | 194.214 [b] ± 37.627 | |
| PuSe(cr) | | | 92.100 ± 1.800 | 59.700 ± 1.200 |
| PuTe(cr) | | | 107.900 ± 4.300 | 73.100 ± 2.900 |
| PuN(cr) | – 273.719 [a] ± 2.551 | – 299.200 ± 2.500 | 64.800 ± 1.500 | 49.600 [c] ± 1.000 |
| $PuNO_3^{3+}$ | – 599.913 [b] ± 2.868 | | | |
| $PuO_2(NO_3)_2 \cdot 6H_2O$(cr) | – 2393.300 ± 3.200 | | | |
| PuP(cr) | – 313.757 [a] ± 21.078 | – 318.000 ± 21.000 | 81.320 ± 6.000 | 50.200 ± 4.000 |

(Continued on next page)

Table 5-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $PuPO_4$(cr) | | | 137.000* ± 2.700 | 114.500*[(c)] ± 2.500 |
| $PuH_2PO_4^{2+}$ * | – 1728.694*[(b)] ± 4.627 | | | |
| $PuH_3PO_4^{4+}$ | – 1641.055 [(b)] ± 3.569 | | | |
| PuAs(cr) | – 241.413 [(a)] ± 20.111 | – 240.000 ± 20.000 | 94.300 ± 7.000 | 51.600 ± 4.000 |
| PuSb(cr) | – 152.063 [(a)] ± 20.126 | – 150.000 ± 20.000 | 106.900 ± 7.500 | 52.800 ± 3.500 |
| PuBi(cr) | – 119.624 [(a)] ± 20.223 | – 117.000 ± 20.000 | 120.000 ± 10.000 | |
| $PuBi_2$(cr) | – 124.527 [(a)] ± 22.395 | – 126.000 ± 22.000 | 163.000 ± 14.000 | |
| $PuC_{0.84}$(cr) | – 49.827 [(a)] ± 8.028 | – 45.200 ± 8.000 | 74.800 ± 2.100 | 47.100 [(c)] ± 1.000 |
| $Pu_3C_2$(cr) | – 123.477 [(a)] ± 30.046 | – 113.000 ± 30.000 | 210.000 ± 5.000 | 136.800 [(c)] ± 2.500 |
| $Pu_2C_3$(cr) | – 156.514 [(a)] ± 16.729 | – 149.400 ± 16.700 | 150.000 ± 2.900 | 114.000 [(c)] ± 0.400 |
| $PuO_2CO_3$(aq) | – 1344.479 [(b)] ± 4.032 | | | |
| $PuO_2CO_3$(cr) | – 1374.846*[(b)] ± 2.929 | | | |
| $PuO_2CO_3^-$ | – 1409.257*[(b)] ± 2.974 | | | |
| $PuO_2(CO_3)_2^{2-}$ | – 1902.061 [(b)] ± 4.088 | – 2199.496 [(b)] ± 7.714 | 19.625 [(b)] ± 27.657 | |
| $PuO_2(CO_3)_2^{3-}$ * | – 1944.635*[(b)] ± 3.184 | | | |
| $PuO_2(CO_3)_3^{4-}$ | – 2448.797 [(b)] ± 4.180 | – 2886.326 [(b)] ± 6.915 | – 6.103 [(b)] ± 25.198 | |
| $PuO_2(CO_3)_3^{5-}$ | – 2468.368*[(b)] ± 3.387 | | | |
| $Pu(CO_3)_4^{4-}$ | – 2800.785 [(b)] ± 7.013 | | | |

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Table 5-1 (continued)

| Compound | $\Delta_f G_m^o$ / kJ·mol$^{-1}$ | $\Delta_f H_m^o$ / kJ·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Pu(CO_3)_5^{6-}$ | – 3320.979 (b) ± 7.261 | | | |
| $PuSCN^{2+}$ | – 493.704 (b) ± 5.333 | – 515.390 (b) ± 5.988 | – 15.355 (a) ± 26.906 | |
| $(UO_2)_2PuO_2(CO_3)_6^{6-}$ * | – 6140.119*(b) ± 9.582 | | | |
| $Sr_3PuO_6$(cr) | | – 3042.100 ± 7.900 | | |
| $BaPuO_3$(cr) | | – 1654.200 ± 8.300 | | |
| $Ba_3PuO_6$(cr) | | – 2997.000 ± 10.000 | | |
| $Ba_2MgPuO_6$(cr) | | – 2995.800 ± 8.800 | | |
| $Ba_2CaPuO_6$(cr) | | – 3067.500 ± 8.900 | | |
| $Ba_2SrPuO_6$(cr) | | – 3023.300 ± 9.000 | | |
| $Cs_2PuCl_6$(cr) | – 1838.243 (a) ± 6.717 | – 1982.000 ± 5.000 | 412.000 ± 15.000 | |
| $Cs_3PuCl_6$(cr) | – 2208.045 (b) ± 9.491 | – 2364.415 (b) ± 9.040 | 454.925 (b) ± 10.959 | 258.600 (c) ± 10.000 |
| $CsPu_2Cl_7$(cr) | – 2235.119 (b) ± 5.284 | – 2399.380 (b) ± 5.734 | 424.000 (b) ± 7.281 | 254.900 (c) ± 10.000 |
| $Cs_2PuBr_6$(cr) | – 1634.326 (a) ± 6.150 | – 1697.400 ± 4.200 | 470.000 ± 15.000 | |
| $Cs_2NaPuCl_6$(cr) | – 2143.496 (a) ± 5.184 | – 2294.200 ± 2.600 | 440.000 ± 15.000 | |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_f G_m^o = \Delta_f H_m^o - T\sum_i S_{m,i}^o$ .
(b) Value calculated internally from reaction data (see Table 5-2).
(c) Temperature coefficients of this function are listed in Table 5-3.
(*) New compound and/or value that has changed from [2003GUI/FAN].
(**) Only the uncertainty has changed from [2003GUI/FAN].

Table 5-2: Selected thermodynamic data for reactions involving plutonium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Species | Reaction | | | |
|---|---|---|---|---|
| | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
| Pu(g) | $Pu(cr) \rightleftharpoons Pu(g)$ | | | |
| | | | 349.000<br>± 3.000 | |
| $Pu^{3+}$ | $PuCl_3 \cdot 6H_2O(cr) \rightleftharpoons 3Cl^- + 6H_2O(l) + Pu^{3+}$ | | | |
| | | | | – 15.010<br>± 3.533 |
| $Pu^{4+}$ | $H^+ + Pu^{3+} \rightleftharpoons 0.5H_2(g) + Pu^{4+}$ | | | |
| | | | | – 164.680<br>± 8.124 |
| $PuO_2$(am, hyd) | $4OH^- + Pu^{4+} \rightleftharpoons 2H_2O(l) + PuO_2$(am, hyd) | | | |
| | 58.330<br>± 0.520 | – 332.950<br>± 2.968 | | |
| $PuO_2^+$ | $0.5H_2(g) + PuO_2^{2+} \rightleftharpoons H^+ + PuO_2^+$ | | | |
| | 15.819 [c]<br>± 0.090 | – 90.293<br>± 0.515 | – 88.091<br>± 6.026 | 7.386 [a]<br>± 20.285 |
| $PuOH^{2+}$ | $H_2O(l) + Pu^{3+} \rightleftharpoons H^+ + PuOH^{2+}$ | | | |
| | – 6.180*<br>± 0.500 | 35.276*<br>± 2.854 | | |
| $PuOH^{3+}$ | $H_2O(l) + Pu^{4+} \rightleftharpoons H^+ + PuOH^{3+}$ | | | |
| | 0.600<br>± 0.200 | – 3.425<br>± 1.142 | | |
| $Pu(OH)_2^{2+}$ | $2H_2O(l) + Pu^{4+} \rightleftharpoons 2H^+ + Pu(OH)_2^{2+}$ | | | |
| | 0.600<br>± 0.300 | – 3.425<br>± 1.712 | | |

(Continued on next page)

Table 5-2 (continued)

| Species | Reaction | | | |
|---|---|---|---|---|
| | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
| $Pu(OH)_3(am)$ | $3H_2O(l) + Pu^{3+} \rightleftharpoons 3H^+ + Pu(OH)_3(am)$ | | | |
| | – 14.580* | 83.223* | | |
| | ± 0.750 | ± 4.281 | | |
| $Pu(OH)_3^+$ | $3H_2O(l) + Pu^{4+} \rightleftharpoons 3H^+ + Pu(OH)_3^+$ | | | |
| | – 2.300 | 13.128 | | |
| | ± 0.400 | ± 2.283 | | |
| $PuO_2OH(am)$ | $H_2O(l) + PuO_2^+ \rightleftharpoons H^+ + PuO_2OH(am)$ | | | |
| | – 5.000 | 28.540 | | |
| | ± 0.500 | ± 2.854 | | |
| $PuO_2OH(aq)$ | $H_2O(l) + PuO_2^+ \rightleftharpoons H^+ + PuO_2OH(aq)$ | | | |
| | ≤ – 9.730 | ≥ 55.539 | | |
| $PuO_2OH^+$ | $H_2O(l) + PuO_2^{2+} \rightleftharpoons H^+ + PuO_2OH^+$ | | | |
| | – 5.500 | 31.394 | 28.000 | – 11.384 [a] |
| | ± 0.500 | ± 2.854 | ± 15.000 | ± 51.213 |
| $PuO_2(OH)_2(aq)$ | $2H_2O(l) + PuO_2^{2+} \rightleftharpoons 2H^+ + PuO_2(OH)_2(aq)$ | | | |
| | – 13.200 | 75.346 | | |
| | ± 1.500 | ± 8.562 | | |
| $PuO_2(OH)_2(am, hyd)$* | $PuO_2^{2+} + 2OH^- \rightleftharpoons PuO_2(OH)_2(am, hyd)$ | | | |
| | 22.830* | – 130.315* | | |
| | ± 0.650 | ± 3.710 | | |
| $Pu(OH)_4(aq)$ | $4H_2O(l) + Pu^{4+} \rightleftharpoons 4H^+ + Pu(OH)_4(aq)$ | | | |
| | – 8.500 | 48.518 | | |
| | ± 0.500 | ± 2.854 | | |
| $PuO_2(OH)_3^-$ * | $3H_2O(l) + PuO_2^{2+} \rightleftharpoons 3H^+ + PuO_2(OH)_3^-$ | | | |
| | – 24.000* | 136.993* | | |
| | ± 1.600 | ± 9.133 | | |
| $(PuO_2)_2(OH)_2^{2+}$ | $2H_2O(l) + 2PuO_2^{2+} \rightleftharpoons (PuO_2)_2(OH)_2^{2+} + 2H^+$ | | | |
| | – 7.500 | 42.810 | | |
| | ± 1.000 | ± 5.708 | | |
| $PuF^{3+}$ | $F^- + Pu^{4+} \rightleftharpoons PuF^{3+}$ | | | |
| | 8.840 | – 50.459 | 9.100 | 199.762 [a] |
| | ± 0.100 | ± 0.571 | ± 2.200 | ± 7.623 |
| $PuF_2^{2+}$ | $2F^- + Pu^{4+} \rightleftharpoons PuF_2^{2+}$ | | | |
| | 15.700 | – 89.616 | 11.000 | 337.469 [a] |
| | ± 0.200 | ± 1.142 | ± 5.000 | ± 17.202 |

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Table 5-2 (continued)

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $PuF_3(g)$ | $PuF_3(cr) \rightleftharpoons PuF_3(g)$ | | | | |
| | | | | 418.900 ± 0.500 | |
| $PuF_4(g)$ | $PuF_4(cr) \rightleftharpoons PuF_4(g)$ | | | | |
| | | | | 301.800 ± 3.600 | |
| $PuF_6(cr)$ | $PuF_6(g) \rightleftharpoons PuF_6(cr)$ | | | | |
| | | | | – 48.650 ± 1.000 | |
| $PuF_6(g)$ | $F_2(g) + PuF_4(cr) \rightleftharpoons PuF_6(g)$ | | | | |
| | | | | 37.300 ± 2.400 | |
| $PuO_2F^+$ | $F^- + PuO_2^{2+} \rightleftharpoons PuO_2F^+$ | | | | |
| | | 4.560 ± 0.200 | – 26.029 ± 1.142 | | |
| $PuO_2F_2(aq)$ | $2F^- + PuO_2^{2+} \rightleftharpoons PuO_2F_2(aq)$ | | | | |
| | | 7.250 ± 0.450 | – 41.383 ± 2.569 | | |
| $PuCl^{3+}$ | $Cl^- + Pu^{4+} \rightleftharpoons PuCl_3(g)$ | | | | |
| | | 1.800 ± 0.300 | – 10.274 ± 1.712 | | |
| $PuCl_3(g)$ | $PuCl_3(cr) \rightleftharpoons PuCl_3(g)$ | | | | |
| | | | | 312.200 ± 0.500 | |
| $PuCl_4(g)$ | $0.5Cl_2(g) + PuCl_3(cr) \rightleftharpoons PuCl_4(g)$ | | | | |
| | | | | 167.600 ± 1.000 | |
| $PuOCl(cr)$ | $H_2O(g) + PuCl_3(cr) \rightleftharpoons 2HCl(g) + PuOCl(cr)$ | | | | |
| | | | | | 128.710 ± 0.490 |
| $PuO_2Cl^+$ | $Cl^- + PuO_2^{2+} \rightleftharpoons PuO_2Cl^+$ | | | | |
| | | 0.230 ± 0.030 | – 1.313 ± 0.171 | | |
| $PuO_2Cl_2(aq)$ | $2Cl^- + PuO_2^{2+} \rightleftharpoons PuO_2Cl_2(aq)$ | | | | |
| | | – 1.150 ± 0.300 | 6.564 ± 1.712 | | |

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Table 5-2 (continued)

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $PuBr^{3+}$ | $Br^- + Pu^{4+} \rightleftharpoons PuBr^{3+}$ | | | | |
| | | 1.600 ± 0.300 | – 9.133 ± 1.712 | | |
| $PuBr_3(g)$ | $PuBr_3(cr) \rightleftharpoons PuBr_3(g)$ | | | | |
| | | – 41.565 [c] ± 2.728 | 237.257 [a] ± 15.570 | 304.400 ± 15.000 | 225.200 ± 14.000 |
| PuOBr(cr) | $H_2O(g) + PuBr_3(cr) \rightleftharpoons 2HBr(g) + PuOBr(cr)$ | | | | |
| | | – 8.893 [c] ± 0.914 | 50.764 [a] ± 5.218 | 91.700 ± 5.000 | 137.300 ± 5.000 |
| $PuI^{2+}$ | $I^- + Pu^{3+} \rightleftharpoons PuI^{2+}$ | | | | |
| | | 1.100 ± 0.400 | – 6.279 ± 2.283 | | |
| $PuSO_4^+$ | $HSO_4^- + Pu^{3+} \rightleftharpoons H^+ + PuSO_4^+$ | | | | |
| | | 1.930 ± 0.610 | – 11.017 ± 3.482 | – 5.200 ± 2.000 | 19.509 [a] ± 13.468 |
| $PuSO_4^{2+}$ | $HSO_4^- + Pu^{4+} \rightleftharpoons H^+ + PuSO_4^{2+}$ | | | | |
| | | 4.910 ± 0.220 | – 28.026 ± 1.256 | | |
| $PuO_2SO_4(aq)$ | $PuO_2^{2+} + SO_4^{2-} \rightleftharpoons PuO_2SO_4(aq)$ | | | | |
| | | 3.380 ± 0.200 | – 19.293 ± 1.142 | 16.100 ± 0.600 | 118.709 [a] ± 4.326 |
| $Pu(SO_4)_2(aq)$ | $2HSO_4^- + Pu^{4+} \rightleftharpoons 2H^+ + Pu(SO_4)_2(aq)$ | | | | |
| | | 7.180 ± 0.320 | – 40.984 ± 1.827 | | |
| $Pu(SO_4)_2^-$ | $2HSO_4^- + Pu^{3+} \rightleftharpoons 2H^+ + Pu(SO_4)_2^-$ | | | | |
| | | 1.740 ± 0.760 | – 9.932 ± 4.338 | – 33.000 ± 16.000 | – 77.370 [a] ± 55.602 |
| $PuO_2SO_4^-$ * | $PuO_2^+ + SO_4^{2-} \rightleftharpoons PuO_2SO_4^-$ | | | | |
| | | 1.260* ± 0.120 | – 7.192* ± 0.685 | | |
| $PuO_2(SO_4)_2^{2-}$ | $PuO_2^{2+} + 2SO_4^{2-} \rightleftharpoons PuO_2(SO_4)_2^{2-}$ | | | | |
| | | 4.400 ± 0.200 | – 25.115 ± 1.142 | 43.000 ± 9.000 | 228.460 [a] ± 30.428 |
| $PuNO_3^{3+}$ | $NO_3^- + Pu^{4+} \rightleftharpoons PuNO_3^{3+}$ | | | | |
| | | 1.950 ± 0.150 | – 11.131 ± 0.856 | | |

(Continued on next page)

Table 5-2 (continued)

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $PuPO_4$(am, hyd)* | $PO_4^{3-} + Pu^{3+} \rightleftharpoons PuPO_4$(am, hyd) | | | | |
| | | 24.440* ± 0.550 | – 139.505* ± 3.139 | | |
| $PuH_2PO_4^{2+}$ * | $Pu^{3+} + H_2PO_4^- \rightleftharpoons PuH_2PO_4^{2+}$ | | | | |
| | | 2.200* ± 0.060 | – 12.558* ± 3.425 | | |
| $PuH_3PO_4^{4+}$ | $H_3PO_4$(aq) + $Pu^{4+} \rightleftharpoons PuH_3PO_4^{4+}$ | | | | |
| | | 2.400 ± 0.300 | – 13.699 ± 1.712 | | |
| $Pu(HPO_4)_2$(am, hyd) | $2HPO_4^{2-} + Pu^{4+} \rightleftharpoons Pu(HPO_4)_2$(am, hyd) | | | | |
| | | 30.450 ± 0.510 | – 173.810 ± 2.911 | | |
| $(PuO_2)_3(PO_4)_2 \cdot 4H_2O$(am) * | $3PuO_2^{2+} + 2PO_4^{3-} + 4H_2O(l) \rightleftharpoons (PuO_2)_3(PO_4)_2 \cdot 4H_2O$(am) | | | | |
| | | 48.970* ± 0.690 | – 279.523* ± 3.939 | | |
| $PuO_2CO_3$(aq) | $CO_3^{2-} + PuO_2^{2+} \rightleftharpoons PuO_2CO_3$(aq) | | | | |
| | | 9.500 ± 0.500 | – 54.226 ± 2.854 | | |
| $PuO_2CO_3$(cr) | $CO_3^{2-} + PuO_2^{2+} \rightleftharpoons PuO_2CO_3$(cr) | | | | |
| | | 14.820* ± 0.120 | – 84.593* ± 0.685 | | |
| $PuO_2CO_3^-$ | $CO_3^{2-} + PuO_2^+ \rightleftharpoons PuO_2CO_3^-$ | | | | |
| | | 5.030* ± 0.120 | – 28.711* ± 0.685 | | |
| $PuO_2(CO_3)_2^{2-}$ | $2CO_3^{2-} + PuO_2^{2+} \rightleftharpoons PuO_2(CO_3)_2^{2-}$ | | | | |
| | | 14.700 ± 0.500 | – 83.908 ± 2.854 | – 27.000 ± 4.000 | 190.871 [(a)] ± 16.481 |
| $PuO_2(CO_3)_2^{3-}$ * | $2CO_3^{2-} + PuO_2^+ \rightleftharpoons PuO_2(CO_3)_2^{3-}$ | | | | |
| | | 6.340* ± 0.200 | – 36.189* ± 1.142 | | |
| $PuO_2(CO_3)_3^{4-}$ | $3CO_3^{2-} + PuO_2^{2+} \rightleftharpoons PuO_2(CO_3)_3^{4-}$ | | | | |
| | | 18.000 ± 0.500 | – 102.745 ± 2.854 | – 38.600 ± 2.000 | 215.143 [(a)] ± 11.689 |
| $PuO_2(CO_3)_3^{5-}$ | $3CO_3^{2-} + PuO_2^+ \rightleftharpoons PuO_2(CO_3)_3^{5-}$ | | | | |
| | | 5.610* ± 0.240 | – 32.022* ± 1.370 | | |

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Table 5-2 (continued)

| Species | Reaction | | | |
|---|---|---|---|---|
| | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ / kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ / J·K$^{-1}$·mol$^{-1}$ |
| $Pu(CO_3)_4^{4-}$ | $4CO_3^{2-} + Pu^{4+} \rightleftharpoons Pu(CO_3)_4^{4-}$ | | | |
| | 37.000 ± 1.100 | – 211.198 ± 6.279 | | |
| $Pu(CO_3)_5^{6-}$ | $5CO_3^{2-} + Pu^{4+} \rightleftharpoons Pu(CO_3)_5^{6-}$ | | | |
| | 35.650 ± 1.130 | – 203.492 ± 6.450 | | |
| $(PuO_2)_3(CO_3)_6^{6-}$ [(d)] * | $6CO_3^{2-} + 3PuO_2^{2+} \rightleftharpoons (PuO_2)_3(CO_3)_6^{6-}$ | | | |
| | 51.000* ± 2.500 | – 291.110* ± 14.270 | | |
| $PuSCN^{2+}$ | $Pu^{3+} + SCN^- \rightleftharpoons PuSCN^{2+}$ | | | |
| | 1.300 ± 0.400 | – 7.420 ± 2.283 | 0.000 ± 4.000 | 24.888 [(a)] ± 15.448 |
| $(UO_2)_2PuO_2(CO_3)_6^{6-}$ * | $PuO_2(CO_3)_3^{4-} + 2UO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_2PuO_2(CO_3)_6^{6-} + 3CO_3^{2-}$ | | | |
| | – 8.200* ± 1.300 | 46.806* ± 7.420 | | |
| $Cs_3PuCl_6(cr)$ | $CsCl(cr) + 0.2CsPu_2Cl_7(cr) \rightleftharpoons 0.4Cs_3PuCl_6(cr)$ | | | |
| | 3.922 [(c)] ± 0.638 | – 22.387 [(a)] ± 3.640 | – 23.580 ± 3.426 | – 4.000 ± 4.130 |
| $CsPu_2Cl_7(cr)$ | $CsCl(cr) + 2PuCl_3(cr) \rightleftharpoons CsPu_2Cl_7(cr)$ | | | |
| | 6.605 [(c)] ± 0.594 | – 37.700 [(a)] ± 3.390 | – 37.870 ± 3.160 | – 0.570 ± 4.120 |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_r G_m^\circ = \Delta_r H_m^\circ - T\,\Delta_r S_m^\circ$.
(b) Value calculated from a selected standard potential.
(c) Value of $\log_{10} K^\circ$ calculated internally from $\Delta_r G_m^\circ$.
(d) As discussed in [2001LEM/FUG], the value for $(PuO_2)_3(CO_3)_6^{6-}$ is valid only for $I$ = 3 M $NaClO_4$
(*) New compound and/or value that has changed from [2003GUI/FAN].

Table 5-3: Selected temperature coefficients for heat capacities marked with [c] in Table 5-1, according to the form $C_{p,\mathrm{m}}(T) = a + bT + cT^2 + eT^{-2} + jT^3$. The functions are valid between the temperatures $T_{min}$ and $T_{max}$ (in K). The notation E ± *nn* indicates the power of 10. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. $C^{\circ}_{p,\mathrm{m}}$ units are $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

| Compound | *a* | *b* | *c* | *e* | *j* | $T_{min}$ | $T_{max}$ |
|---|---|---|---|---|---|---|---|
| Pu(cr) | 1.81260E+01 | 4.48200E–02 | 0 | 0 | 0 | 298 | 398 |
| β–Pu | 2.74160E+01 | 1.30600E–02 | 0 | 0 | 0 | 398 | 488 |
| δ–Pu | 2.84780E+01 | 1.08070E–02 | 0 | 0 | 0 | 593 | 736 |
| δ'–Pu | 3.55600E+01 | 0 | 0 | 0 | 0 | 736 | 756 |
| γ–Pu | 2.20230E+01 | 2.29590E–02 | 0 | 0 | 0 | 488 | 593 |
| ε–Pu | 3.37200E+01 | 0 | 0 | 0 | 0 | 756 | 913 |
| Pu(g) | 2.05200E+01 | –9.39140E–03 | 2.57550E–05 | 7.51200E+04 | 0 | 298 | 500 |
| | 4.59200E+00 | 3.31521E–02 | –5.64466E–06 | 7.01590E+05 | 0 | 500 | 1100 |
| | –9.58800E+00 | 4.60885E–02 | –8.63248E–06 | 5.01446E+05 | 0 | 1100 | 2000 |
| $PuO_{1.61}$(bcc) | 5.87251E+00* | 4.06849E–02* | –2.84361E–05* | –7.41537E+05* | 7.98358E–09* | 298 | 1422 |
| $PuO_2$(cr) | 3.52952E+01* | 1.52250E–01* | –1.29255E–04* | –3.47593E+05* | 3.62890E–08* | 298 | 3017* |
| $Pu_2O_3$(cr) | 1.30667E+02* | 1.84357E–02* | 0* | –1.70530E+06* | 0* | 298* | 2300* |
| PuF(g) | 3.66410E+01 | 9.20600E–04 | –1.44430E–07 | –3.02540E+05 | 0 | 298 | 3000 |
| $PuF_2$(g) | 5.73100E+01 | 7.27000E–04 | –1.47210E–07 | –5.38960E+05 | 0 | 298 | 3000 |
| $PuF_3$(cr) | 1.04080E+02 | 7.07000E–04 | 0 | –1.03550E+06 | 0 | 298 | 1700 |
| $PuF_3$(g) | 7.92670E+01 | 5.60920E–03 | –2.20240E–06 | –7.55940E+05 | 0 | 298 | 1300 |
| $PuF_4$(g) | 1.05110E+02 | 2.84120E–03 | –6.88730E–07 | –1.19680E+06 | 0 | 298 | 2400 |
| $PuF_6$(cr) | 7.23480E+01 | 3.21300E–01 | 0 | 0 | 0 | 298 | 325 |
| $PuF_6$(g) | 1.43990E+02 | 2.32110E–02 | –1.07640E–05 | –1.83430E+06 | 0 | 298 | 1000 |
| PuOF(cr) | 7.20000E+01 | 1.60000E–02 | –3.30000E–06 | –6.20000E+05 | 0 | 298 | 1500 |
| $PuCl_3$(cr) | 9.13500E+01 | 2.40000E–02 | 0 | 2.40000E+05 | 0 | 298 | 1041 |
| $PuCl_3$(g) | 7.71030E+01 | 1.29970E–02 | –4.31250E–06 | –1.88730E+05 | 0 | 298 | 1100 |
| $PuCl_4$(g) | 1.10430E+02 | 4.08180E–03 | –9.76160E–07 | –7.23430E+05 | 0 | 298 | 3000 |
| PuOCl(cr) | 7.30300E+01 | 1.71000E–02 | 0 | –5.83000E+05 | 0 | 298 | 1100 |
| $PuBr_3$(cr) | 1.04500E+02 | 1.50000E–02 | 0 | –6.38000E+05 | 0 | 298 | 935 |
| $PuBr_3$(g) | 8.31350E+01 | 3.90000E–06 | 0 | –1.38320E+05 | 0 | 298 | 1500 |
| PuOBr(cr) | 7.37000E+01 | 1.70000E–02 | 0 | –5.15000E+05 | 0 | 298 | 1100 |
| $PuI_3$(cr) | 1.04000E+02 | 2.00000E–02 | 0 | 0 | 0 | 298 | 930 |
| $PuI_3$(g) | 8.31500E+01 | 1.40000E–06 | 0 | –1.00000E+05 | 0 | 298 | 1500 |
| PuOI(cr) | 6.70000E+01 | 3.57000E–02 | –1.20000E–05 | –9.00000E+04 | 0 | 298 | 1000 |
| PuN(cr)* | 4.50020E+01* | 1.54200E–02* | 0* | 0* | 0* | 298* | 1562* |
| $PuPO_4$(cr)* | 1.26600E+02* | 3.29990E-02* | 0 | –1.95030 E+06* | 0* | 298* | 1400* |
| $PuC_{0.84}$(cr) | 7.15910E+01 | –5.95040E–02 | 4.94350E–05 | –9.93200E+05 | 0 | 298 | 1875 |
| $Pu_3C_2$(cr) | 1.20670E+02 | 4.68600E–02 | 0 | 1.94560E+05 | 0 | 298 | 850 |
| $Pu_2C_3$(cr) | 1.56000E+02 | –7.98730E–02 | 7.04170E–05 | –2.17570E+06 | 0 | 298 | 2285 |
| $Cs_3PuCl_6$(cr) | 2.56600E+02 | 3.46000E–02 | 0 | –7.40000E+05 | 0 | 298 | 900 |
| $CsPu_2Cl_7$(cr) | 2.37800E+02 | 5.15000E–02 | 0 | 1.55000E+05 | 0 | 298 | 900 |

(*) New compound and/or value that has changed from [2003GUI/FAN].

# Chapter 6

# Selected Data for Americium

## 6.1 General considerations

This chapter presents updated chemical thermodynamic data for americium species, as described in detail in Chapter 12 of this volume. The selected data contain both data previously selected and in some cases revisions of some of them; in addition there is a large number of data that were not included in [1992GRE/FUG] and [2003GUI/FAN]. New species selected in this review are marked with an asterisk, "*"; revised data for species selected in [2003GUI/FAN] are also marked with an asterisk. Table 6-1 contains the selected thermodynamic data of the americium compounds and complexes, Table 6-2 the selected thermodynamic data of chemical equilibrium reactions by which the americium compounds and complexes are formed, and Table 6-3 the temperature coefficients of the heat capacity data of Table 6-1 where available.

The species and reactions in Table 6-1, Table 6-2 and Table 6-3 appear in standard order of arrangement (*cf.* Figure 2-1). These selected reaction data are used, together with data for key americium species (for example $Am^{3+}$) and auxiliary data listed in Table 8-1, to derive the corresponding formation quantities in Table 6-1. The uncertainties associated with values for the key americium species and for some of the auxiliary data are substantial, leading to comparatively large uncertainties in the thermodynamic data. By including a table for reaction data (Table 6-2), the users obtain information of equilibrium constants and their uncertainties that are directly based on the experimental data and their uncertainty.

The selected thermal functions of the heat capacities, listed in Table 6-3, are described with the empirical function:

$$C_{p,m}(T) = a + bT + cT^2 + eT^{-2} + jT^3 + lT^4 \qquad (6.1)$$

The selected values in [1992GRE/FUG] and [2003GUI/FAN] are discussed there and retained in the present review. New and revised thermal functions are discussed in the relevant Appendix A entries. No references are given in these tables since the selected data are generally not directly attributable to a specific published source. A detailed discussion of the selection procedure is presented in [1992GRE/FUG], [2003GUI/FAN] and in Chapter 12 of this volume.

## 6.2 Precautions to be observed in the use of the tables

Geochemical modelling in aquatic systems requires the careful use of the data selected in the NEA TDB reviews. The selected data in the tables must not be adopted without taking into account the chemical background information discussed in the corresponding sections of this book. In particular the following precautions should be observed when using data from the Tables.

- The addition of new thermodynamic data to this internally consistent database should be made with care, it is straight forward to see if the new species has any significant effect on the experimental data, or if it results in changes in the speciation. However, if a significant change occurs, it is necessary to make a scrutiny of the experimental data on which the value is based and possibly also on the selected data.
- Gaps are pointed out in both the previous NEA TDB review and the present update.
- Solubility data for crystalline phases are well defined in the initial state, but not necessarily in the final state after "equilibrium" has been attained. Hence, the solubility calculated from these phases may be misleading, as discussed in [2003GUI/FAN] for the solubility data of $MO_2$(cr), M = U, Np, Pu.
- The selected thermodynamic data in [1992GRE/FUG], [1995SIL/BID] and [2001LEM/FUG] contained thermodynamic data for amorphous phases including Gibbs energy of formation deduced from solubility measurements. Following the criteria outlined in [2003GUI/FAN], the present review has not selected the Gibbs energy of formation of these phases. However, the corresponding $\log_{10}K$ values have been retained. The reasons for this choice are:
    - Thermodynamic data are only meaningful if they refer to well-defined systems; this is not the case for amorphous phases. It is well known that their solubility may change with time, due to re-crystallisation, with a resulting change in water content and surface area/crystal size; the time scale for these changes can vary widely.
    - The solubility of amorphous phases may be of interest for users of the database in chemical modelling even though they are not thermodynamic quantities.

Table 6-1: Selected thermodynamic data for americium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I$ = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| Am(cr) | 0.000 | 0.000 | 55.400<br>± 2.000 | 25.500 [(c)]<br>± 1.500 |
| β–Am | | | | [(c)] |
| γ–Am | | | | [(c)] |
| Am(l) | | | | [(c)] |
| Am(g) | 244.000* [(a)]<br>± 3.000 | 285.500*<br>± 3.000 | 194.657*<br>± 0.050 | 20.786 [(c)]<br>± 0.010 |
| $Am^{2+}$ | – 376.780 [(b)]<br>± 15.236 | – 354.633 [(a)]<br>± 15.890 | – 1.000<br>± 15.000 | |
| $Am^{3+}$ | – 598.698 [(a)]<br>± 4.755 | – 616.700<br>± 1.500 | – 201.000<br>± 15.000 | |
| $Am^{4+}$ | – 346.358 [(a)]<br>± 8.692 | – 406.000<br>± 6.000 | – 406.000<br>± 21.000 | |
| $AmO_2$(cr) | – 877.000* [(a)]<br>± 4.300 | – 932.200<br>± 3.000 | 75.500*<br>± 3.000 | 64.300* [(c)]<br>± 3.000 |
| $AmO_2^+$ | – 739.796 [(a)]<br>± 6.208 | – 804.260 [(b)]<br>± 5.413 | – 21.000<br>± 10.000 | |
| $AmO_2^{2+}$ | – 585.801 [(a)]<br>± 5.715 | – 650.760 [(b)]<br>± 4.839 | – 88.000<br>± 10.000 | |
| $Am_2O_3$(cr) | – 1605.600* [(a)]<br>± 8.300 | – 1690.400<br>± 8.000 | 134.200*<br>± 5.000 | 116.500* [(c)]<br>± 5.000 |
| $AmH_2$(cr) | – 134.661 [(a)]<br>± 15.055 | – 175.800<br>± 15.000 | 48.100<br>± 3.800 | 38.200 [(c)]<br>± 2.500 |

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Table 6-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $AmOH^{2+}$ | – 794.740 [b] ± 5.546 | | | |
| $Am(OH)_2^+$ | – 986.787 [b] ± 6.211 | | | |
| $Am(OH)_3$(aq) | – 1160.568 [b] ± 5.547 | | | |
| $Am(OH)_3$(cr) | – 1221.073 [b] ± 5.861 | – 1353.198 [a] ± 6.356 | 116.000 ± 8.000 | |
| $AmF^{2+}$ | – 899.628 [b] ± 5.320 | – 939.950* [b] ± 2.741 | – 109.125* [b] ± 18.404 | |
| $AmF_2^+$ | – 1194.851 [b] ± 5.082 | – 1242.300* [b] ± 14.604 | 33.708* [b] ± 51.063 | |
| $AmF_3$(cr) | – 1519.765 [a] ± 14.126 | – 1594.000 ± 14.000 | 110.600 ± 6.000 | |
| $AmF_3$(g) | – 1147.798 [a] ± 16.771 | – 1156.500 [b] ± 16.589 | 330.400 ± 8.000 | 72.200 ± 5.000 |
| $AmF_4$(cr) | – 1632.503* [a] ± 17.177 | – 1724.000 ± 17.000 | 154.100 ± 8.000 | |
| $AmCl^{2+}$ | – 731.285** [b] ± 5.160 | | | |
| $AmCl_2^+$ | – 856.508* [b] ± 5.163 | – 895.960* [b] ± 4.748 | 80.827* [b] ± 22.313 | |
| $AmCl_3$(cr) | – 905.105 [a] ± 2.290 | – 977.800 ± 1.300 | 146.200 ± 6.000 | 103.000 ± 10.000 |
| AmOCl(cr) | – 897.052 [a] ± 6.726 | – 949.800 [b] ± 6.000 | 92.600 [b] ± 10.000 | 70.400 [c] ± 10.000 |
| $AmBr_3$(cr) | – 773.674 [a] ± 6.728 | – 804.000 ± 6.000 | 182.000 ± 10.000 | |
| AmOBr(cr) | – 848.485 [a] ± 9.794 | – 887.000 [b] ± 9.000 | 104.900 [b] ± 12.800 | |
| $AmI_3$(cr) | – 609.451 [a] ± 10.068 | – 615.000 ± 9.000 | 211.000 ± 15.000 | |
| AmS(cr) | | | 92.000 ± 12.000 | |
| $AmSO_4^+$ | – 1362.680* [b] ± 5.071 | – 1486.040* [b] ± 4.291 | 18.667* [b] ± 20.931 | |

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Table 6-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Am(SO_4)_2^-$ | – 2115.246* [b] ± 7.476 | – 2365.380* [b] ± 7.203 | 166.505* [b] ± 33.814 | |
| AmSe(cr) | | | 109.000 ± 12.000 | |
| AmTe(cr) | | | 121.000 ± 12.000 | |
| $AmN_3^{2+}$ | – 260.030 [b] ± 5.190 | | | |
| $AmNO_3^{2+}$ | – 716.798* [b] ± 4.782 | – 821.750* [b] ± 1.847 | – 23.758* [b] ± 15.406 | |
| $Am(NO_3)_2^+$ * | – 825.309* [b] ± 4.868 | – 1019.600* [b] ± 2.780 | 145.471* [b] ± 16.868 | |
| $AmH_2PO_4^{2+}$ | – 1749.892* [b] ± 5.061 | | | |
| $Am_2C_3$(cr) | – 156.063 [a] ± 42.438 | – 151.000 ± 42.000 | 145.000 ± 20.000 | |
| $AmCO_3^+$ | – 1172.262 [b] ± 5.289 | | | |
| $AmO_2CO_3^-$ | – 1296.807 [b] ± 6.844 | | | |
| $Am(CO_3)_2^-$ | – 1728.131 [b] ± 5.911 | | | |
| $AmO_2(CO_3)_2^{3-}$ | – 1833.840 [b] ± 7.746 | | | |
| $Am(CO_3)_3^{3-}$ | – 2268.019** [b] ± 5.668 | | | |
| $AmO_2(CO_3)_3^{5-}$ | – 2352.607 [b] ± 8.514 | | | |
| $Am(CO_3)_5^{6-}$ | – 3209.086 [b] ± 9.141 | | | |
| $AmHCO_3^{2+}$ | – 1203.238 [b] ± 5.060 | | | |
| $AmCO_3OH{\cdot}0.5\ H_2O$(cr) | – 1530.248 [b] ± 5.560 | – 1682.900 ± 2.600 | 141.413 [a] ± 20.683 | |
| $AmSiO(OH)_3^{2+}$ | – 1898.340* [b] ± 4.998 | – 2029.853* [b] ± 4.481 | 108.758* [b] ± 20.727 | |

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Table 6-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $AmSCN^{2+}$ | – 513.418 [(b)] ± 6.445 | | | |
| $SrAmO_3$(cr) | | – 1539.000 ± 4.100 | | |
| $BaAmO_3$(cr) | | – 1544.600 ± 3.400 | | |
| $NaAmO_2CO_3$(s) | – 1591.867 [(b)] ± 6.627 | | | |
| $NaAm(CO_3)_2 \cdot 5H_2O$(cr) | – 3222.021 [(b)] ± 5.605 | | | |
| $Cs_2NaAmCl_6$(cr) | – 2159.151 [(a)] ± 4.864 | – 2315.800 ± 1.800 | 421.000 ± 15.000 | 260.000 ± 15.000 |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_f G_m^o = \Delta_f H_m^o - T\sum_i S_{m,i}^o$ .
(b) Value calculated internally from reaction data (see Table 6-2).
(c) Temperature coefficients of this function are listed in Table 6-3.
(*) New compound and/or value that has changed from [2003GUI/FAN].
(**) Only the uncertainty has changed from [2003GUI/FAN].

Table 6-2: Selected thermodynamic data for reactions involving americium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| Am(g) | $Am(cr) \rightleftharpoons Am(g)$ | | | | |
| | | | | 283.800 ± 1.500 | |
| $Am^{2+}$ | $Am^{3+} + e^- \rightleftharpoons Am^{2+}$ | | | | |
| | | – 38.878 [(b)] ± 2.536 | 221.920 ± 14.476 | | |
| $AmO_2^+$ | $Am^{3+} + 2H_2O(l) \rightleftharpoons AmO_2^+ + 4H^+ + 2e^-$ | | | | |
| | | | | 384.100 ± 5.200 | |
| $AmO_2^{2+}$ | $Am^{3+} + 2H_2O(l) \rightleftharpoons AmO_2^{2+} + 4H^+ + 3e^-$ | | | | |
| | | | | 537.600 ± 4.600 | |
| $AmOH^{2+}$ | $Am^{3+} + H_2O(l) \rightleftharpoons AmOH^{2+} + H^+$ | | | | |
| | | – 7.200 ± 0.500 | 41.098 ± 2.854 | | |
| $Am(OH)_2^+$ | $Am^{3+} + 2H_2O(l) \rightleftharpoons Am(OH)_2^+ + 2H^+$ | | | | |
| | | – 15.100 ± 0.700 | 86.191 ± 3.996 | | |
| $AmO_2OH(am)$ | $AmO_2^+ + H_2O(l) \rightleftharpoons AmO_2OH(am) + H^+$ | | | | |
| | | – 5.300 ± 0.500 | 30.253 ± 2.854 | | |
| $Am(OH)_3(cr)$ | $Am^{3+} + 3H_2O(l) \rightleftharpoons Am(OH)_3(cr) + 3H^+$ | | | | |
| | | – 15.600 ± 0.600 | 89.045 ± 3.425 | | |

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Table 6-2 (continued)

| Species | Reaction | $\log_{10} K^{o}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Am(OH)_3(am)$ | $Am^{3+} + 3H_2O(l) \rightleftharpoons Am(OH)_3(am) + 3H^+$ | | | | |
| | | – 16.900 ± 0.800 | 96.466 ± 4.566 | | |
| $Am(OH)_3(aq)$ | $Am^{3+} + 3H_2O(l) \rightleftharpoons Am(OH)_3(aq) + 3H^+$ | | | | |
| | | – 26.200 ± 0.500 | 149.551 ± 2.854 | | |
| $AmF^{2+}$ | $Am^{3+} + F^- \rightleftharpoons AmF^{2+}$ | | | | |
| | | 3.400 ± 0.400 | – 19.407 ± 2.283 | 12.100* ± 2.200 | 105.675* [a] ± 10.634 |
| $AmF_2^+$ | $Am^{3+} + 2F^- \rightleftharpoons AmF_2^+$ | | | | |
| | | 5.800 ± 0.200 | – 33.107 ± 1.142 | 45.100* ± 14.500 | 262.308* [a] ± 48.784 |
| $AmF_3(g)$ | $AmF_3(cr) \rightleftharpoons AmF_3(g)$ | | | | |
| | | | | 437.500 ± 8.900 | |
| $AmCl^{2+}$ | $Am^{3+} + Cl^- \rightleftharpoons AmCl^{2+}$ | | | | |
| | | 0.240** ± 0.350 | – 1.370** ± 2.000 | | |
| $AmCl_2^+$ | $Am^{3+} + 2Cl^- \rightleftharpoons AmCl_2^+$ | | | | |
| | | – 0.810* ± 0.350 | 4.624* ± 1.998 | 54.900* ± 4.500 | 168.627* [a] ± 16.514 |
| AmOCl(cr) | $AmCl_3(cr) + H_2O(g) \rightleftharpoons AmOCl(cr) + 2HCl(g)$ | | | | |
| | | – 8.066 [c] ± 1.115 | 46.042 [a] ± 6.364 | 85.213 ± 5.900 | 131.380 ± 8.000 |
| AmOBr(cr) | $AmBr_3(cr) + H_2O(g) \rightleftharpoons AmOBr(cr) + 2HBr(g)$ | | | | |
| | | – 8.246 [c] ± 2.661 | 47.070 [a] ± 15.188 | 86.256 ± 15.000 | 131.430 ± 8.000 |
| $AmSO_4^+$ | $Am^{3+} + SO_4^{2-} \rightleftharpoons AmSO_4^+$ | | | | |
| | | 3.500* ± 0.300 | – 19.978* ± 1.712 | 40.000* ± 4.000 | 201.167* [a] ± 14.593 |
| $Am(SO_4)_2^-$ | $Am^{3+} + 2SO_4^{2-} \rightleftharpoons Am(SO_4)_2^-$ | | | | |
| | | 5.000* ± 1.000 | – 28.540* ± 5.708 | 70.000* ± 7.000 | 330.505* [a] ± 30.294 |
| $AmN_3^{2+}$ | $Am^{3+} + N_3^- \rightleftharpoons AmN_3^{2+}$ | | | | |
| | | 1.670 ± 0.100 | – 9.532 ± 0.571 | | |

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Table 6-2 (continued)

| Species | Reaction | $\log_{10} K^{o}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $AmNO_2^{2+}$ | $Am^{3+} + NO_2^- \rightleftharpoons AmNO_2^{2+}$ | | | | |
| | | 2.100 ± 0.200 | – 11.987 ± 1.142 | | |
| $AmNO_3^{2+}$ | $Am^{3+} + NO_3^- \rightleftharpoons AmNO_3^{2+}$ | | | | |
| | | 1.280* ± 0.050 | – 7.306* ± 0.285 | 1.800* ± 1.000 | 30.542* [(a)] ± 3.489 |
| $Am(NO_3)_2^+$ * | $Am^{3+} + 2NO_3^- \rightleftharpoons Am(NO_3)_2^+$ | | | | |
| | | 0.880* ± 0.110 | – 5.023* ± 0.628 | 10.800* ± 2.200 | 53.071* [(a)] ± 7.674 |
| $AmPO_4$(am, hyd) | $Am^{3+} + PO_4^{3-} \rightleftharpoons AmPO_4(am, hyd)$ | | | | |
| | | 24.790 ± 0.600 | – 141.500 ± 3.425 | | |
| $AmH_2PO_4^{2+}$ | $Am^{3+} + H_2PO_4^- \rightleftharpoons AmH_2PO_4^{2+}$ | | | | |
| | | 2.460* ± 0.130 | – 14.042* ± 0.742 | | |
| $AmCO_3^+$ | $Am^{3+} + CO_3^{2-} \rightleftharpoons AmCO_3^+$ | | | | |
| | | 8.000 ± 0.400 | – 45.664 ± 2.283 | | |
| $AmO_2CO_3^-$ | $AmO_2^+ + CO_3^{2-} \rightleftharpoons AmO_2CO_3^-$ | | | | |
| | | 5.100 ± 0.500 | – 29.111 ± 2.854 | | |
| $Am(CO_3)_2^-$ | $Am^{3+} + 2CO_3^{2-} \rightleftharpoons Am(CO_3)_2^-$ | | | | |
| | | 12.900 ± 0.600 | – 73.634 ± 3.425 | | |
| $AmO_2(CO_3)_2^{3-}$ | $AmO_2^+ + 2CO_3^{2-} \rightleftharpoons AmO_2(CO_3)_2^{3-}$ | | | | |
| | | 6.700 ± 0.800 | – 38.244 ± 4.566 | | |
| $Am(CO_3)_3^{3-}$ | $Am^{3+} + 3CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-}$ | | | | |
| | | 15.000** ± 0.500 | – 85.621** ± 2.854 | | |
| $Am_2(CO_3)_3$(am) | $2Am^{3+} + 3CO_3^{2-} \rightleftharpoons Am_2(CO_3)_3(am)$ | | | | |
| | | 33.400 ± 2.200 | – 190.649 ± 12.558 | | |

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Table 6-2 (continued)

| Species | Reaction | $\log_{10} K^{o}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $AmO_2(CO_3)_3^{5-}$ | $AmO_2^+ + 3CO_3^{2-} \rightleftharpoons AmO_2(CO_3)_3^{5-}$ | | | | |
| | | 5.100 | –29.111 | | |
| | | ± 1.000 | ± 5.708 | | |
| $Am(CO_3)_5^{6-}$ | $Am(CO_3)_3^{3-} + 2CO_3^{2-} \rightleftharpoons Am(CO_3)_5^{6-} + e^-$ | | | | |
| | | – 20.100 (c) | 114.730 | | |
| | | ± 0.900 | ± 5.137 | | |
| $AmHCO_3^{2+}$ | $Am^{3+} + HCO_3^- \rightleftharpoons AmHCO_3^{2+}$ | | | | |
| | | 3.100 | – 17.695 | | |
| | | ± 0.300 | ± 1.712 | | |
| $AmCO_3OH{\cdot}0.5H_2O$(cr) | $Am^{3+} + CO_3^{2-} + 0.5H_2O(l) + OH^- \rightleftharpoons AmCO_3OH.\ 0.5H_2O$(cr) | | | | |
| | | 22.400 | – 127.860 | | |
| | | ± 0.500 | ± 2.854 | | |
| $AmCO_3OH$(am, hyd) | $Am^{3+} + CO_3^{2-} + OH^- \rightleftharpoons AmCO_3OH$(am, hyd) | | | | |
| | | 20.200 | – 115.302 | | |
| | | ± 1.000 | ± 5.708 | | |
| $AmSiO(OH)_3^{2+}$ | $Am^{3+} + SiO(OH)_3^- \rightleftharpoons AmSiO(OH)_3^{2+}$ | | | | |
| | | 8.130* | – 46.406* | 18.600* | 218.031*(a) |
| | | ± 0.200 | ± 1.142 | ± 4.000 | ± 13.952 |
| $AmSCN^{2+}$ | $Am^{3+} + SCN^- \rightleftharpoons AmSCN^{2+}$ | | | | |
| | | 1.300 | – 7.420 | | |
| | | ± 0.300 | ± 1.712 | | |
| $NaAmO_2CO_3$(cr) | $AmO_2^+ + CO_3^{2-} + Na^+ \rightleftharpoons NaAmO_2CO_3$(cr) | | | | |
| | | 10.900 | – 62.218 | | |
| | | ± 0.400 | ± 2.283 | | |
| $NaAm(CO_3)_2{\cdot}5H_2O$(cr) | $Am^{3+} + 2CO_3^{2-} + 5H_2O(l) + Na^+ \rightleftharpoons NaAm(CO_3)_2 \cdot 5H_2O$(cr) | | | | |
| | | 21.000 | – 119.869 | | |
| | | ± 0.500 | ± 2.854 | | |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_r G_m^o = \Delta_r H_m^o - T\Delta_r S_m^o$.
(b) Value calculated from a selected standard potential.
(c) Value of $\log_{10} K^{o}$ calculated internally from $\Delta_r G_m^o$.
(*) New compound and/or value that has changed from [2003GUI/FAN].
(**) Only the uncertainty has changed from [2003GUI/FAN].

Table 6-3: Selected temperature coefficients for heat capacities marked with [c] in Table 6-1, according to the form $C_{p,\mathrm{m}}(T) = a + bT + cT^2 + eT^{-2} + jT^3 + lT^4$. The functions are valid between the temperatures $T_{min}$ and $T_{max}$ (in K). The notation E ± *nn* indicates the power of 10. $C_{p,\mathrm{m}}$ units are $J \cdot K^{-1} \cdot mol^{-1}$.

| Compound | *a* | *b* | *c* | *e* | *j* | *l* | $T_{min}$ | $T_{max}$ |
|---|---|---|---|---|---|---|---|---|
| Am(cr) | 3.0399E+01* | – 2.9053E–02* | 5.2026E–05* | 0 | – 1.8961E–08 | 0 | 298 | 1042 |
| β–Am | 8.4570E+00* | 3.3167E–02* | – 7.5870E–06* | 0 | 0 | 0 | 1042 | 1350 |
| γ–Am | 4.3000E+01* | 0 | 0 | 0 | 0 | 0 | 1350 | 1449 |
| Am(l) | 5.2000E+01* | 0 | 0 | 0 | 0 | 0 | 1449 | 3000 |
| Am(g) | 2.0786E+01 | 0 | 0 | 0 | 0 | 0 | 298 | 900* |
| Am(g) | 1.9986E+01* | 4.3365E–01* | 1.6974E–06* | 2.1403E+05* | – 1.5984E–09* | 4.4407E–13* | 900* | 2400* |
| Am(g) | 2.6881E+02* | – 1.7944E–01* | 4.5918E–05* | – 1.7767E+08* | – 3.5637E–09* | 0 | 2400* | 4000* |
| $AmO_2$(cr) | 7.89718E+01* | 3.8365E–03* | 0 | – 1.40591E+06* | 0 | 0 | 298 | 1200 |
| $Am_2O_3$(cr) | 1.260084E+02* | 8.0097E–03* | 0 | – 1.05752E+06* | 0 | 0 | 298 | 2350 |
| $AmH_2$(cr) | 2.48000E+01 | 4.50000E–02 | 0 | 0 | 0 | 0 | 298 | 1200 |
| $AmF_3$(g) | 8.16540E+01 | 1.20840E–03 | – 2.42780E–07 | – 8.67160E+05 | 0 | 0 | 298 | 3000 |
| AmOCl(cr) | 6.12840E+01 | 4.58930E–02 | –1.73070E–05 | – 2.69380E+05 | 0 | 0 | 298 | 1100 |
| AmN(cr)* | 4.24400E+01* | 1.56300E–02* | 0 | 0 | 0 | 0 | 354* | 1071* |

(*) New compound and/or value that has changed from [2003GUI/FAN].

# Chapter 7

# Selected Data for Technetium

## 7.1 General considerations

This chapter presents updated chemical thermodynamic data for technetium species, as described in detail in Chapter 13 of this volume. The selected data contain both data previously selected and in some cases revisions of some of them; in addition there is a large number of data that were not included in [1992GRE/FUG] and [2003GUI/FAN]. New species selected in this review are marked with an asterisk, "*"; revised data for species selected in [2003GUI/FAN] are also marked with an asterisk. Table 7-1 contains the selected thermodynamic data of the technetium compounds and complexes, Table 7-2 the selected thermodynamic data of chemical equilibrium reactions by which the technetium compounds and complexes are formed, and Table 7-3 the temperature coefficients of the heat capacity data of Table 7-1 where available.

The species and reactions in Table 7-1, Table 7-2 and Table 7-3 appear in standard order of arrangement (*cf.* Figure 2-1). These selected reaction data are used, together with data for key technetium species (for example $Tc(OH)_2(aq)$) and auxiliary data listed in Table 8-1, to derive the corresponding formation quantities in Table 7-1. The uncertainties associated with values for the key technetium species and for some of the auxiliary data are substantial, leading to comparatively large uncertainties in the thermodynamic data. By including a table for reaction data (Table 7-2), the users obtain information of equilibrium constants and their uncertainties that are directly based on the experimental data and their uncertainty.

The selected thermal functions of the heat capacities, listed in Table 7-3, are described with the empirical function:

$$C_{p,m}(T) = a + bT + cT^2 + eT^{-2} \qquad (7.1)$$

The selected values in [1992GRE/FUG] and [2003GUI/FAN] are discussed there and retained in the present review. New and revised thermal functions are discussed in the relevant Appendix A entries. No references are given in these tables since the selected data are generally not directly attributable to a specific published source. A detailed discussion of the selection procedure is presented in [1992GRE/FUG], [2003GUI/FAN] and in Chapter 13 of this volume.

## 7.2 Precautions to be observed in the use of the tables

Geochemical modelling in aquatic systems requires the careful use of the data selected in the NEA TDB reviews. The selected data in the tables must not be adopted without taking into account the chemical background information discussed in the corresponding sections of this book. In particular the following precautions should be observed when using data from the Tables.

- The addition of new thermodynamic data to this internally consistent database should be made with care, it is straight forward to see if the new species has any significant effect on the experimental data, or if it results in changes in the speciation. However, if a significant change occurs, it is necessary to make a scrutiny of the experimental data on which the value is based and possibly also on the selected data.
- Gaps are pointed out in both the previous NEA TDB review and the present update.
- Solubility data for crystalline phases are well defined in the initial state, but not necessarily in the final state after "equilibrium" has been attained. Hence, the solubility calculated from these phases may be misleading, as discussed in [2003GUI/FAN] for the solubility data of $MO_2$(cr), M = U, Np, Pu.
- The selected thermodynamic data in [1992GRE/FUG], [1995SIL/BID] and [2001LEM/FUG] contained thermodynamic data for amorphous phases including Gibbs energy of formation deduced from solubility measurements. Following the criteria outlined in [2003GUI/FAN], the present review has not selected the Gibbs energy of formation of these phases. However, the corresponding $\log_{10}K$ values have been retained. The reasons for this choice are:
    - Thermodynamic data are only meaningful if they refer to well-defined systems; this is not the case for amorphous phases. It is well known that their solubility may change with time, due to re-crystallisation, with a resulting change in water content and surface area/crystal size; the time scale for these changes can vary widely.
    - The solubility of amorphous phases may be of interest for users of the database in chemical modelling even though they are not thermodynamic quantities.

Table 7-1: Selected thermodynamic data for technetium compounds and complexes. Selected thermodynamic functions for some Tc species are also given in Appendix B. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapter V. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. It should be noted that insufficient auxiliary data are available in a number of cases to derive formation data from the reactions listed in Table 7-2. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Compound | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| Tc(cr) | 0.000 | 0.000 | 32.506 ± 0.700 | 24.879 [(c)] ± 1.000 |
| Tc(g) | 630.711 [(a)] ± 25.001 | 675.000 [(b)] ± 25.000 | 181.052 ± 0.010 | 20.795 [(c)] ± 0.010 |
| TcO(g) | 357.494 [(a)] ± 57.001 | 390.000 ± 57.000 | 244.109 ± 0.600 | 31.256 [(c)] ± 0.750 |
| $TcO_2$(cr) | – 401.850 [(a)] ± 11.762 | – 457.800 ± 11.700 | 50.000 ± 4.000 | |
| $TcO_2$(am, hyd, fresh) * | – 379.055 *[(b)] ± 8.372 | | | |
| $TcO_2$(am, hyd, aged) * | – 385.105*[(b)] ± 11.127 | | | |
| $TcO_4^-$ | – 637.406 [(a)] ± 7.616 | – 729.400 ± 7.600 | 199.600 ± 1.500 | – 15.000 ± 8.000 |
| $TcO_4^{2-}$ | – 575.759 [(b)] ± 8.133 | | | |
| $Tc_2O_7$(cr) | – 950.280 [(a)] ± 15.562 | – 1126.500 ± 14.900 | 192.000 ± 15.000 | 160.400 [(c)] ± 15.000 |
| $Tc_2O_7$(g) | – 904.820 [(a)] ± 16.462 | – 1008.100 [(b)] ± 16.063 | 436.641 ± 12.000 | 146.736 ± 5.000 |
| $TcO(OH)_2$(aq) | – 572.471*[(b)] ± 10.890 | | | |

(Continued on next page)

Table 7-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $TcO(OH)_3^-$ | – 747.279*[b] ± 10.933 | | | |
| $Tc_2O_2(OH)_2^{2+}$ * | – 744.809*[b] ± 21.905 | | | |
| $Tc_2O_7 \cdot H_2O$(s) | – 1194.300 ± 15.500 | – 1414.146 [b] ± 14.905 | 278.933 [a] ± 72.138 | |
| $TcF_6$(cr, cubic) | | | 253.520 ± 0.510 | 157.840 ± 0.320 |
| $TcF_6$(g) | | | 359.136 ± 4.500 | 120.703 ± 2.629 |
| $TcO_3F$(g) | | | 306.879 ± 0.677 | 77.261 [c] ± 0.308 |
| $TcCl_5^-$ * | – 542.994*[b] ± 11.988 | | | |
| $TcCl_6^{2-}$ * | – 662.338*[b] ± 14.069 | | | |
| $TcO_3Cl$(g) | | | 317.636 ± 0.797 | 80.365 [c] ± 0.308 |
| $Tc_2OCl_{10}^{4-}$ * | – 1343.276 *[b] ± 22.817 | | | |
| $(NH_4)_2TcCl_6$(cr) * | – 866.730 *[b] ± 15.193 | | | |
| TcS(g) | 491.925 [a] ± 65.001 | 549.000 ± 65.000 | 255.990 ± 1.000 | 34.474 ± 1.000 |
| $NH_4TcO_4$(cr) | – 721.998 [b] ± 7.632 | | | |
| TcC(g) | 765.602 [a] ± 40.250 | 826.500 ± 40.000 | 242.500 ± 15.000 | |
| $TcCO_3(OH)_2$(aq) | – 973.123*[b] ± 11.025 | | | |
| $TcCO_3(OH)_3^-$ | – 1162.886*[b] ± 11.417 | | | |
| $TlTcO_4$(cr) | – 700.173 [b] ± 7.653 | | | |
| $AgTcO_4$(cr) | – 578.975 [b] ± 7.654 | | | |

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Table 7-1 (continued)

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $NaTcO_4 \cdot 4H_2O$(s) | – 1843.411 (b) ± 7.622 | | | |
| $K_2TcCl_6$(cr) * | – 1282.212* (b) ± 15.185 | | | |
| $KTcO_4$(cr) | – 932.921 (a) ± 7.604 | – 1035.100 ± 7.600 | 164.780 ± 0.330 | 123.300 ± 0.250 |
| $Rb_2TcCl_6$(cr) * | – 1293.829* (b) ± 15.186 | | | |
| $Cs_2TcCl_6$(cr) * | – 1310.493*(b) ± 15.220 | | | |
| $CsTcO_4$(cr) | – 949.700 (b) ± 7.700 | | | |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_f G_m^o = \Delta_f H_m^o - T\sum_i S_{m,i}^o$ .
(b) Value calculated internally from reaction data.
(c) Temperature coefficients of this function are listed in Table 7-3.
(*) New compound and/or value that has changed from [2003GUI/FAN].

Table 7-2: Selected thermodynamic data for reactions involving technetium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I$ = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. New compounds and data that have been changed from [2003GUI/FAN] are denoted with an asterisk. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapter 13. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| Tc(g) | $Tc(cr) \rightleftharpoons Tc(g)$ | | | | |
| | | | | 675.000 ± 25.000 | |
| $TcO_2$(am, hyd,fresh) * | $TcO_4^- + 3e^- + 4H^+ \rightleftharpoons TcO_2(am, hyd, fresh) + 2H_2O(l)$ | | | | |
| | | 37.831*[b] ± 0.609 | – 215.940* ± 3.476 | | |
| $TcO_2$(am, hyd, aged) * | $TcO(OH)_2(aq) \rightleftharpoons TcO_2(am, hyd, aged) + H_2O(l)$ | | | | |
| | | 8.720* ± 0.400 | – 49.774* ± 2.283 | | |
| $TcO_4^{2-}$ | $TcO_4^- + e^- \rightleftharpoons TcO_4^{2-}$ | | | | |
| | | – 10.800 [b] ± 0.500 | 61.647 ± 2.854 | | |
| $Tc_2O_7$(g) | $Tc_2O_7(cr) \rightleftharpoons Tc_2O_7(g)$ | | | | |
| | | | | 118.400 ± 6.000 | |
| $Tc_2O_2(OH)_2^{2+}$ * | $2TcO(OH)_2(aq) + 2H^+ \rightleftharpoons Tc_2O_2(OH)_2^{2+} + 2H_2O(l)$ | | | | |
| | | 12.990* ± 0.410 | – 74.147* ± 2.340 | | |
| $TcO(OH)_3^-$ | $H_2O(l) + TcO(OH)_2(aq) \rightleftharpoons H^+ + TcO(OH)_3^-$ | | | | |
| | | – 10.920* ± 0.170 | 62.332* ± 0.97 | | |

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Table 7-2 (continued)

| Species | Reaction | $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ | $\Delta_r H_m^\circ$ | $\Delta_r S_m^\circ$ |
|---|---|---|---|---|---|
| $Tc_2O_7{\cdot}H_2O$(s) | $H_2O(g) + Tc_2O_7(cr) \rightleftharpoons Tc_2O_7{\cdot}H_2O(s)$ | | | | |
| | | | | – 45.820<br>± 0.400 | |
| $TcF_6$(g) | $TcF_6(cr, cubic) \rightleftharpoons TcF_6(g)$ | | | | |
| | | – 0.535 [c]<br>± 0.327 | 3.055 [a]<br>± 1.867 | 3.540<br>± 1.300 | 105.600<br>± 4.500 |
| $TcCl_5^-$ * | $Tc_2OCl_{10}^{4-} + 2H^+ \rightleftharpoons 2TcCl_5^- + H_2O(l)$ | | | | |
| | | – 3.530*<br>± 1.290 | 20.149*<br>± 7.363 | | |
| $TcCl_6^{2-}$ * | $TcCl_5^- + Cl^- \rightleftharpoons TcCl_6^{2-}$ | | | | |
| | | – 2.080*<br>± 1.290 | 11.873*<br>± 7.363 | | |
| $Tc_2OCl_{10}^{4-}$ * | $Tc_2O_2(OH)_2^{2+} + 10Cl^- + 4H^+ \rightleftharpoons Tc_2OCl_{10}^{4-} + 3H_2O(l)$ | | | | |
| | | – 0.400*<br>± 1.100 | 2.283*<br>± 6.279 | | |
| $TcO_2Cl_4^{3-}$ | $H_2O(l) + TcOCl_5^{2-} \rightleftharpoons Cl^- + 2H^+ + TcO_2Cl_4^{3-}$ | | | | |
| | | – 2.950<br>± 0.150 | 16.839<br>± 0.856 | | |
| $(NH_4)_2TcCl_6$(cr) | $2NH_4^+ + TcCl_6^{2-} \rightleftharpoons (NH_4)_2TcCl_6(cr)$ | | | | |
| | | 7.988<br>± 1.000 | – 45.596<br>± 5.708 | | |
| $NH_4TcO_4$(cr) | $NH_4^+ + TcO_4^- \rightleftharpoons NH_4TcO_4(cr)$ | | | | |
| | | 0.910<br>± 0.070 | – 5.194<br>± 0.400 | | |
| $(NH_4)_2TcBr_6$(cr) | $2NH_4^+ + TcBr_6^{2-} \rightleftharpoons (NH_4)_2TcBr_6(cr)$ | | | | |
| | | 6.680<br>± 1.000 | – 38.130<br>± 5.708 | | |
| $TcCO_3(OH)_2$(aq) | $CO_2(g) + TcO(OH)_2(aq) \rightleftharpoons TcCO_3(OH)_2(aq)$ | | | | |
| | | 1.100<br>± 0.300 | – 6.279<br>± 1.712 | | |

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Table 7-2 (continued)

| Species | Reaction | $\log_{10} K^{o}$ | $\Delta_r G_m^o$ | $\Delta_r H_m^o$ | $\Delta_r S_m^o$ |
|---|---|---|---|---|---|
| $TcCO_3(OH)_3^-$ | $CO_2(g) + H_2O(l) + TcO(OH)_2(aq) \rightleftharpoons H^+ + TcCO_3(OH)_3^-$ | | | | |
| | | – 7.200 | 41.098 | | |
| | | ± 0.600 | ± 3.425 | | |
| $TlTcO_4(cr)$ | $TcO_4^- + Tl^+ \rightleftharpoons TlTcO_4(cr)$ | | | | |
| | | 5.320 | – 30.367 | | |
| | | ± 0.120 | ± 0.685 | | |
| $AgTcO_4(cr)$ | $Ag^+ + TcO_4^- \rightleftharpoons AgTcO_4(cr)$ | | | | |
| | | 3.270 | – 18.665 | | |
| | | ± 0.130 | ± 0.742 | | |
| $NaTcO_4 \cdot 4H_2O(s)$ | $4H_2O(l) + Na^+ + TcO_4^- \rightleftharpoons NaTcO_4 \cdot 4H_2O(s)$ | | | | |
| | | – 0.790 | 4.509 | | |
| | | ± 0.040 | ± 0.228 | | |
| $KTcO_4(cr)$ | $K^+ + TcO_4^- \rightleftharpoons KTcO_4(cr)$ | | | | |
| | | 2.288 | – 13.060 | – 53.620 | – 136.039 [a] |
| | | ± 0.026 | ± 0.148 | ± 0.420 | ± 1.494 |
| $K_2TcCl_6(cr)$ | $2K^+ + TcCl_6^{2-} \rightleftharpoons K_2TcCl_6(cr)$ | | | | |
| | | 9.610 | – 54.854 | | |
| | | ± 1.000 | ± 5.708 | | |
| $K_2TcBr_6(cr)$ | $2K^+ + TcBr_6^{2-} \rightleftharpoons K_2TcBr_6(cr)$ | | | | |
| | | 6.920 | – 39.500 | | |
| | | ± 1.000 | ± 5.708 | | |
| $Rb_2TcCl_6(cr)$ | $2Rb^+ + TcCl_6^{2-} \rightleftharpoons Rb_2TcCl_6(cr)$ | | | | |
| | | 11.120 | – 63.473 | | |
| | | ± 1.000 | ± 5.708 | | |
| $Rb_2TcBr_6(cr)$ | $2Rb^+ + TcBr_6^{2-} \rightleftharpoons Rb_2TcBr_6(cr)$ | | | | |
| | | 9.470 | – 54.055 | | |
| | | ± 1.000 | ± 5.708 | | |
| $CsTcO_4(cr)$ | $Cs^+ + TcO_4^- \rightleftharpoons CsTcO_4(cr)$ | | | | |
| | | 3.617 | – 20.646 | | |
| | | ± 0.047 | ± 0.268 | | |
| $Cs_2TcCl_6(cr)$ | $2Cs^+ + TcCl_6^{2-} \rightleftharpoons Cs_2TcCl_6(cr)$ | | | | |
| | | 11.430 | – 65.243 | | |
| | | ± 1.000 | ± 5.708 | | |
| $Cs_2TcBr_6(cr)$ | $2Cs^+ + TcBr_6^{2-} \rightleftharpoons Cs_2TcBr_6(cr)$ | | | | |
| | | 11.240 | – 64.158 | | |
| | | ± 1.000 | ± 5.708 | | |

(a) Value calculated internally with the Gibbs–Helmholtz equation, $\Delta_r G_m^o = \Delta_r H_m^o - T\Delta_r S_m^o$.

(b) Value calculated from a selected standard potential.

(c) Value of $\log_{10} K^{o}$ calculated internally from $\Delta_r G_m^o$.

Table 7-3: Selected temperature coefficients for heat capacities marked with [c] in Table 7-1, according to the form $C_{p,\mathrm{m}}(T) = a + bT + cT^{-2} + eT^{-2}$. The functions are valid between the temperatures $T_{min}$ and $T_{max}$ (in K). The notation E ± *nn* indicates the power of 10. $C_{p,\mathrm{m}}$ units are $J \cdot K^{-1} \cdot mol^{-1}$.

| Compound | *a* | *b* | *c* | *e* | $T_{min}$ | $T_{max}$ |
|---|---|---|---|---|---|---|
| Tc(cr) | 2.50940E+01 | 4.31450E–03 | –2.75460E–07 | –1.31300E+05 | 298 | 2430 |
| Tc(g) | 2.49130E+01 | –1.91830E–02 | 2.51280E–05 | –5.61800E+04 | 298 | 600 |
| $Tc_2O_7$(cr) | 1.55000E+02 | 8.60000E–02 | 0 | –1.80000E+06 | 298 | 392 |
| $TcF_6$(cr, cubic) | 7.20810E+01 | 2.87666E–01 | 0 | 0 | 268 | 311 |
| $TcO_3F$(g) | 7.61200E+01 | 5.34274E–02 | –2.53393E–05 | –1.11446E+06 | 298 | 1000 |
| $TcO_3Cl$(g) | 8.03360E+01 | 4.63950E–02 | –2.20086E–05 | –1.05321E+06 | 298 | 1000 |

# Chapter 8

# Selected auxiliary data

This chapter presents the chemical thermodynamic data for auxiliary compounds and complexes which are used within the NEA TDB Project. Most of these auxiliary species are used in the evaluation of the recommended uranium, neptunium, plutonium, americium and technetium data in Table 3-1, Table 3-2, Table 4-1, Table 4-2, Table 5-1, Table 5-2, Table 6-1, Table 6-2, Table 7-1 and Table 7-2. It is therefore essential to always use these auxiliary data in conjunction with the selected data of Chapters 3-7. The use of other auxiliary data can lead to inconsistencies and erroneous results.

The values in the tables of this chapter for auxiliary compounds and complexes are either CODATA Key Values, taken from [1989COX/WAG], or were evaluated within the NEA TDB Project, as described in the corresponding chapters of the uranium review [1992GRE/FUG], the technetium review [1999RAR/RAN], the neptunium and plutonium review [2001LEM/FUG], the Update review [2003GUI/FAN], the nickel review [2005GAM/BUG], the selenium review [2005OLI/NOL], the tin review [2012GAM/GAJ], the forthcoming Ancillary Data review and in Chapter 14 of this review. Table 8-1 contains the selected thermodynamic data of the auxiliary species and Table 8-2 the selected thermodynamic data of chemical reactions involving auxiliary species. The reason for listing both reaction data and entropies, enthalpies and Gibbs energies of formation is, as described in Chapters 3-7, that uncertainties in reaction data are often smaller than the derived $S_m^o$, $\Delta_f H_m^o$ and $\Delta_f G_m^o$, due to uncertainty accumulation during the calculations. All data in Table 8-1 and Table 8-2 refer to a temperature of 298.15 K, the standard state pressure of 0.1 MPa and, for aqueous species and reactions, to the infinite dilution standard state ($I = 0$).

The uncertainties listed below each reaction value in Table 8-2 are total uncertainties, and correspond mainly to the statistically defined 95% confidence interval. The uncertainties listed below each value in Table 8-1 have the following significance:

- for CODATA values from [1989COX/WAG], the ± terms have the meaning: "it is probable, but not at all certain, that the true values of the thermodynamic quantities differ from the recommended values given in this report by no more than twice the ± terms attached to the recommended values".
- for values from [1992GRE/FUG], [1999RAR/RAN], [2003GUI/FAN], [2005GAM/BUG], [2005OLI/NOL], [2012GAM/GAJ] and the forthcoming Ancillary Data review, the ± terms are derived from total uncertainties in the corresponding equilibrium constant of reaction (*cf.* Table 8-2), and from the ± terms listed for the necessary CODATA key values.

CODATA [1989COX/WAG] values are available for $CO_2(g)$, $HCO_3^-$, $CO_3^{2-}$, $H_2PO_4^-$ and $HPO_4^{2-}$. From the values given for $\Delta_f H_m^o$ and $S_m^o$ the values of $\Delta_f G_m^o$ and, consequently, all the relevant equilibrium constants and enthalpy changes can be calculated. The propagation of errors during this procedure, however, leads to uncertainties in the resulting equilibrium constants that are significantly higher than those obtained from experimental determination of the constants. Therefore, reaction data for $CO_2(g)$, $HCO_3^-$, $CO_3^{2-}$, which were absent form the corresponding Table 8-2 in [1992GRE/FUG], are included in this volume to provide the user of selected data with the data needed to obtain the lowest possible uncertainties on reaction properties.

Note that the values in Table 8-1 and Table 8-2 may contain more digits than those listed in either [1989COX/WAG] or in the chapters devoted to data selection in [1992GRE/FUG], [2001LEM/FUG], [2003GUI/FAN], [2005GAM/BUG], [2005OLI/NOL], [2012GAM/GAJ] and the forthcoming Ancillary Data review, because the data in the present chapter are retrieved directly from the computerised database and rounded to three digits after the decimal point throughout.

Table 8-1: Selected thermodynamic data for auxiliary compounds and complexes adopted in the NEA TDB Project, including the CODATA Key Values [1989COX/WAG]. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a standard state of infinite dilution ($I$ = 0). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95 % confidence interval. Values in bold typeface are CODATA Key Values and are taken directly from [1989COX/WAG] without further evaluation. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in the chapters devoted to data selection in [1992GRE/FUG], [2001LEM/FUG], [2003GUI/FAN], [2005GAM/BUG], [2005OLI/NOL], [2012GAM/GAJ] and the forthcoming Ancillary Data review. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The reference listed for each entry in this table indicates the NEA TDB Review where the corresponding data have been adopted as NEA TDB Auxiliary data. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| O(g)<br>[1992GRE/FUG] | **231.743** [(a)]<br>± **0.100** | **249.180**<br>± **0.100** | **161.059**<br>± **0.003** | **21.912**<br>± **0.001** |
| $O_2$(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **205.152**<br>± **0.005** | **29.378**<br>± **0.003** |
| H(g)<br>[1992GRE/FUG] | **203.276** [(a)]<br>± **0.006** | **217.998**<br>± **0.006** | **114.717**<br>± **0.002** | **20.786**<br>± **0.001** |
| $H^+$<br>[1992GRE/FUG] | **0.000** | **0.000** | **0.000** | **0.000** |
| $H_2$(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **130.680**<br>± **0.003** | **28.836**<br>± **0.002** |
| $OH^-$<br>[1992GRE/FUG] | **– 157.220** [(a)]<br>± **0.072** | **– 230.015**<br>± **0.040** | **– 10.900**<br>± **0.200** | |
| $H_2O$(g)<br>[1992GRE/FUG] | **– 228.582** [(a)]<br>± **0.040** | **– 241.826**<br>± **0.040** | **188.835**<br>± **0.010** | **33.609**<br>± **0.030** |
| $H_2O$(l)<br>[1992GRE/FUG] | **– 237.140** [(a)]<br>± **0.041** | **– 285.830**<br>± **0.040** | **69.950**<br>± **0.030** | **75.351**<br>± **0.080** |
| $H_2O_2$(aq)<br>[1992GRE/FUG] | | – 191.170<br>± 0.100 | | |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| He(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **126.153**<br>**± 0.002** | **20.786**<br>**± 0.001** |
| Ne(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **146.328**<br>**± 0.003** | **20.786**<br>**± 0.001** |
| Ar(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **154.846**<br>**± 0.003** | **20.786**<br>**± 0.001** |
| Kr(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **164.085**<br>**± 0.003** | **20.786**<br>**± 0.001** |
| Xe(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **169.685**<br>**± 0.003** | **20.786**<br>**± 0.001** |
| F(g)<br>[1992GRE/FUG] | **62.280** [(a)]<br>**± 0.300** | **79.380**<br>**± 0.300** | **158.751**<br>**± 0.004** | **22.746**<br>**± 0.002** |
| $F^-$<br>[1992GRE/FUG] | **– 281.523** [(a)]<br>**± 0.692** | **– 335.350**<br>**± 0.650** | **– 13.800**<br>**± 0.800** | |
| $F_2$(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **202.791**<br>**± 0.005** | **31.304**<br>**± 0.002** |
| HF(aq)<br>[1992GRE/FUG] | – 299.675<br>± 0.702 | – 323.150<br>± 0.716 | 88.000 [(a)]<br>± 3.362 | |
| HF(g)<br>[1992GRE/FUG] | **– 275.400** [(a)]<br>**± 0.700** | **– 273.300**<br>**± 0.700** | **173.779**<br>**± 0.003** | **29.137**<br>**± 0.002** |
| $HF_2^-$<br>[1992GRE/FUG] | – 583.709<br>± 1.200 | – 655.500<br>± 2.221 | 92.683 [(a)]<br>± 8.469 | |
| Cl(g)<br>[1992GRE/FUG] | **105.305** [(a)]<br>**± 0.008** | **121.301**<br>**± 0.008** | **165.190**<br>**± 0.004** | **21.838**<br>**± 0.001** |
| $Cl^-$<br>[1992GRE/FUG] | **– 131.217** [(a)]<br>**± 0.117** | **– 167.080**<br>**± 0.100** | **56.600**<br>**± 0.200** | |
| $Cl_2$(g)<br>[1992GRE/FUG] | **0.000** | **0.000** | **223.081**<br>**± 0.010** | **33.949**<br>**± 0.002** |
| $ClO_3^-$<br>[1992GRE/FUG] | – 7.903 [(a)]<br>± 1.342 | – 104.000<br>± 1.000 | 162.300<br>± 3.000 | |
| $ClO_4^-$<br>[1992GRE/FUG] | **– 7.890** [(a)]<br>**± 0.600** | **– 128.100**<br>**± 0.400** | **184.000**<br>**± 1.500** | |
| HCl(g)<br>[1992GRE/FUG] | **– 95.298** [(a)]<br>**± 0.100** | **– 92.310**<br>**± 0.100** | **186.902**<br>**± 0.005** | **29.136**<br>**± 0.002** |
| Br(g)<br>[1992GRE/FUG] | **82.379** [(a)]<br>**± 0.128** | **111.870**<br>**± 0.120** | **175.018**<br>**± 0.004** | **20.786**<br>**± 0.001** |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Br^-$ | **– 103.850** [(a)] | **– 121.410** | **82.550** | |
| [1992GRE/FUG] | **± 0.167** | **± 0.150** | **± 0.200** | |
| $Br_2$(g) | **3.105** [(a)] | **30.910** | **245.468** | **36.057** |
| [1992GRE/FUG] | **± 0.142** | **± 0.110** | **± 0.005** | **± 0.002** |
| $Br_2$(l) | **0.000** | **0.000** | **152.210** | |
| [1992GRE/FUG] | | | **± 0.300** | |
| $BrO_3^-$ | 19.070 [(a)] | – 66.700 | 161.500 | |
| [1992GRE/FUG] | ± 0.634 | ± 0.500 | ± 1.300 | |
| HBr(g) | **– 53.361** [(a)] | **– 36.290** | **198.700** | **29.141** |
| [1992GRE/FUG] | **± 0.166** | **± 0.160** | **± 0.004** | **± 0.003** |
| I(g) | **70.172** [(a)] | **106.760** | **180.787** | **20.786** |
| [1992GRE/FUG] | **± 0.060** | **± 0.040** | **± 0.004** | **± 0.001** |
| $I^-$ | **– 51.724** [(a)] | **– 56.780** | **106.450** | |
| [1992GRE/FUG] | **± 0.112** | **± 0.050** | **± 0.300** | |
| $I_2$(cr) | **0.000** | **0.000** | **116.140** | |
| [1992GRE/FUG] | | | **± 0.300** | |
| $I_2$(g) | **19.323** [(a)] | **62.420** | **260.687** | **36.888** |
| [1992GRE/FUG] | **± 0.120** | **± 0.080** | **± 0.005** | **± 0.002** |
| $IO_3^-$ | – 126.338 [(a)] | – 219.700 | 118.000 | |
| [1992GRE/FUG] | ± 0.779 | ± 0.500 | ± 2.000 | |
| HI(g) | **1.700** [(a)] | **26.500** | **206.590** | **29.157** |
| [1992GRE/FUG] | **± 0.110** | **± 0.100** | **± 0.004** | **± 0.003** |
| $HIO_3$(aq) | – 130.836 | | | |
| [1992GRE/FUG] | ± 0.797 | | | |
| S(cr)(orthorhombic) | **0.000** | **0.000** | **32.054** | **22.750** |
| [1992GRE/FUG] | | | **± 0.050** | **± 0.050** |
| S(g) | **236.689** [(a)] | **277.170** | **167.829** | **23.674** |
| [1992GRE/FUG] | **± 0.151** | **± 0.150** | **± 0.006** | **± 0.001** |
| $S^{2-}$ | 120.695 | | | |
| [1992GRE/FUG] | ± 11.610 | | | |
| $S_2$(g) | **79.686** [(a)] | **128.600** | **228.167** | **32.505** |
| [1992GRE/FUG] | **± 0.301** | **± 0.300** | **± 0.010** | **± 0.010** |
| $SO_2$(g) | **– 300.095** [(a)] | **– 296.810** | **248.223** | **39.842** |
| [1992GRE/FUG] | **± 0.201** | **± 0.200** | **± 0.050** | **± 0.020** |
| $SO_3^{2-}$ | – 487.472 | | | |
| [1992GRE/FUG] | ± 4.020 | | | |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $SO_4^{2-}$ [1992GRE/FUG] | **– 744.004** [(a)] **± 0.418** | **– 909.340 ± 0.400** | **18.500 ± 0.400** | |
| $HS^-$ [1992GRE/FUG] | **12.243** [(a)] **± 2.115** | **– 16.300 ± 1.500** | **67.000 ± 5.000** | |
| $H_2S$(aq) [1992GRE/FUG] | **– 27.648** [(a)] **± 2.115** | **– 38.600 ± 1.500** | **126.000 ± 5.000** | |
| $H_2S$(g) [1992GRE/FUG] | **– 33.443** [(a)] **± 0.500** | **– 20.600 ± 0.500** | **205.810 ± 0.050** | **34.248 ± 0.010** |
| $HSO_3^-$ [1992GRE/FUG] | – 528.684 ± 4.046 | | | |
| $H_2SO_3$(aq) [1992GRE/FUG] | – 539.187 ± 4.072 | | | |
| $HSO_4^-$ [1992GRE/FUG] | **– 755.315** [(a)] **± 1.342** | **– 886.900 ± 1.000** | **131.700 ± 3.000** | |
| Se(cr) (trigonal) [2005OLI/NOL] | 0.000 | 0.000 | 42.090 ± 0.330 | 25.090 [(c)] ± 0.300 |
| Se(monoclinic) [2005OLI/NOL] | 1.281 [(a)] ± 0.184 | 2.140 ± 0.100 | 44.970 ± 0.400 | 25.090 [(c)] ± 0.800 |
| Se(l) [2005OLI/NOL] | | | | [(c)] |
| Se(g) [2005OLI/NOL] | 195.927 [(a)] ± 1.524 | 236.070 [(b)] ± 1.521 | 176.729 ± 0.006 | 20.819 [(c)] ± 0.001 |
| $Se^{2-}$ [2005OLI/NOL] | 128.600 [(b)] ± 3.000 | | | |
| $Se_2$(g) [2005OLI/NOL] | 92.442 [(a)] ± 3.009 | 141.100 ± 3.000 | 247.380 ± 0.400 | 41.710 [(c)] ± 0.200 |
| $Se_2^{2-}$ [2005OLI/NOL] | 112.670 [(b)] ± 6.294 | | | |
| $Se_3$(g) [2005OLI/NOL] | 123.549 [(a)] ± 10.439 | 178.000 ± 10.000 | 308.900 ± 10.000 | |
| $Se_3^{2-}$ [2005OLI/NOL] | 100.590 [(b)] ± 9.198 | | | |
| $Se_4$(g) [2005OLI/NOL] | 111.647 [(a)] ± 13.406 | 163.000 ± 12.000 | 340.600 ± 20.000 | |
| $Se_4^{2-}$ [2005OLI/NOL] | 97.580 [(b)] ± 12.149 | | | |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Se_5$(g) [2005OLI/NOL] | 88.393 [(a)] ± 5.256 | 144.400 ± 4.300 | 398.300 ± 10.000 | |
| $Se_6$(g) [2005OLI/NOL] | 83.638[(a)] ± 4.866 | 136.100 ± 3.800 | 428.500 ± 10.000 | |
| $Se_7$(g) [2005OLI/NOL] | 92.845[(a)] ± 4.891 | 150.200 ± 4.500 | 487.000 ± 6.000 | |
| $Se_8$(g) [2005OLI/NOL] | 100.307[(a)] ± 3.580 | 156.800 ± 3.000 | 526.200 ± 6.000 | |
| SeO(g) [2005OLI/NOL] | 30.855 [(a)] ± 6.218 | 57.400 ± 6.210 | 233.700 ± 1.000 | 32.520 [(c)] ± 0.250 |
| $SeO_2$(cr) [2005OLI/NOL] | –171.797 [(a)] ± 0.620 | –225.390 ± 0.600 | 67.490 ± 0.400 | 58.230 [(c)] ± 0.180 |
| $SeO_2$(g) [2005OLI/NOL] | –115.166 [(a)] ± 2.600 | –110.590 [(b)] ± 2.571 | 262.590 ± 1.250 | 43.360 [(c)] ± 0.150 |
| $SeO_3$(cr) [2005OLI/NOL] | –86.154 [(a)] ± 2.222 | –163.100 ± 2.200 | 91.740 ± 1.000 | 77.240 [(c)] ± 0.790 |
| $SeO_3^{2-}$ [2005OLI/NOL] | –362.392 [(b)] ± 1.756 | –507.160 ± 1.130 | –5.055 [(a)] ± 7.011 | |
| $SeO_4^{2-}$ [2005OLI/NOL] | –439.485 [(b)] ± 1.431 | –603.500 [(b)] ± 3.500 | 32.965 [(b)] ± 12.687 | |
| $Se_2O_5$(cr) [2005OLI/NOL] | | –414.590 [(b)] ± 2.577 | | |
| $HSe^-$ [2005OLI/NOL] | 43.471 [(b)] ± 2.024 | | | |
| $H_2Se$(g) [2005OLI/NOL] | 15.217 [(a)] ± 2.003 | 29.000 ± 2.000 | 219.000 ± 0.100 | 34.700 [(c)] ± 0.100 |
| $H_2Se$(aq) [2005OLI/NOL] | 21.495 [(b)] ± 2.003 | 14.300 [(b)] ± 2.022 | 148.637 [(b)] ± 1.029 | |
| $HSeO_3^-$ [2005OLI/NOL] | –410.112 [(b)] ± 1.166 | –512.330 ± 1.010 | 137.656 [(a)] ± 5.184 | |
| $HSeO_4^-$ [2005OLI/NOL] | –449.474 [(b)] ± 1.312 | –582.700 ± 4.700 | 136.232 [(a)] ± 16.370 | |
| $H_2SeO_3$(cr) [2005OLI/NOL] | | –524.720 [(b)] ± 0.650 | | |
| $H_2SeO_3$(aq) [2005OLI/NOL] | –425.181 [(b)] ± 0.849 | –505.320 ± 0.650 | 211.710 [(a)] ± 3.601 | |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $H_2SeO_4$(cr) [2005OLI/NOL] | | –530.500 ± 1.880 | | |
| Te(cr) [1992GRE/FUG] | 0.000 | 0.000 | 49.221 ± 0.050 | 25.550 ± 0.100 |
| $TeO_2$(cr) [2003GUI/FAN] | – 265.996 [(a)] ± 2.500 | – 321.000 ± 2.500 | 69.890 ± 0.150 | 60.670 ± 0.150 |
| N(g) [1992GRE/FUG] | **455.537 [(a)] ± 0.400** | **472.680 ± 0.400** | **153.301 ± 0.003** | **20.786 ± 0.001** |
| $N_2$(g) [1992GRE/FUG] | **0.000** | **0.000** | **191.609 ± 0.004** | **29.124 ± 0.001** |
| $NO_3^-$ [1992GRE/FUG] | **– 110.794 [(a)] ± 0.417** | **– 206.850 ± 0.400** | **146.700 ± 0.400** | |
| $NH_3$(aq) [1992GRE/FUG] | – 26.673 ± 0.305 | – 81.170 ± 0.326 | 109.040 ± 0.913 | |
| $NH_3$(g) [1992GRE/FUG] | **– 16.407 [(a)] ± 0.350** | **– 45.940 ± 0.350** | **192.770 ± 0.050** | **35.630 ± 0.005** |
| $NH_4^+$ [1992GRE/FUG] | **– 79.398 [(a)] ± 0.278** | **– 133.260 ± 0.250** | **111.170 ± 0.400** | |
| P(am)(red) [1992GRE/FUG] | | – 7.500 ± 2.000 | | |
| P(cr)(white, cubic) [1992GRE/FUG] | **0.000** | **0.000** | **41.090 ± 0.250** | **23.824 ± 0.200** |
| P(g) [1992GRE/FUG] | **280.093 [(a)] ± 1.003** | **316.500 ± 1.000** | **163.199 ± 0.003** | **20.786 ± 0.001** |
| $P_2$(g) [1992GRE/FUG] | **103.469 [(a)] ± 2.006** | **144.000 ± 2.000** | **218.123 ± 0.004** | **32.032 ± 0.002** |
| $P_4$(g) [1992GRE/FUG] | **24.419 [(a)] ± 0.448** | **58.900 ± 0.300** | **280.010 ± 0.500** | **67.081 ± 1.500** |
| $PO_4^{3-}$ [1992GRE/FUG] | – 1025.491 ± 1.576 | – 1284.400 ± 4.085 | – 220.970 ± 12.846 | |
| $P_2O_7^{4-}$ [1992GRE/FUG] | – 1935.503 ± 4.563 | | | |
| $HPO_4^{2-}$ [1992GRE/FUG] | **– 1095.985 [(a)] ± 1.567** | **– 1299.000 ± 1.500** | **– 33.500 ± 1.500** | |
| $H_2PO_4^-$ [1992GRE/FUG] | **– 1137.152 [(a)] ± 1.567** | **– 1302.600 ± 1.500** | **92.500 ± 1.500** | |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $H_3PO_4$(aq)<br>[1992GRE/FUG] | – 1149.367<br>± 1.576 | – 1294.120<br>± 1.616 | 161.912<br>± 2.575 | |
| $HP_2O_7^{3-}$<br>[1992GRE/FUG] | – 1989.158<br>± 4.482 | | | |
| $H_2P_2O_7^{2-}$<br>[1992GRE/FUG] | – 2027.117<br>± 4.445 | | | |
| $H_3P_2O_7^{-}$<br>[1992GRE/FUG] | – 2039.960<br>± 4.362 | | | |
| $H_4P_2O_7$(aq)<br>[1992GRE/FUG] | – 2045.668<br>± 3.299 | – 2280.210<br>± 3.383 | 274.919<br>± 6.954 | |
| As(cr)<br>[1992GRE/FUG] | 0.000 | 0.000 | 35.100<br>± 0.600 | 24.640<br>± 0.500 |
| $AsO_4^{3-}$<br>[1992GRE/FUG] | – 648.360 [(a)]<br>± 4.008 | – 888.140<br>± 4.000 | – 162.800<br>± 0.600 | |
| $As_2O_5$(cr)<br>[1992GRE/FUG] | – 782.449 [(a)]<br>± 8.016 | – 924.870<br>± 8.000 | 105.400<br>± 1.200 | 116.520<br>± 0.800 |
| $As_4O_6$(cubic)<br>[1992GRE/FUG] | – 1152.445 [(a)]<br>± 16.032 | – 1313.940<br>± 16.000 | 214.200<br>± 2.400 | 191.290<br>± 0.800 |
| $As_4O_6$(monoclinic)<br>[1992GRE/FUG] | – 1154.009 [(a)]<br>± 16.041 | – 1309.600<br>± 16.000 | 234.000<br>± 3.000 | |
| $As_4O_6$(g)<br>[2005GAM/BUG] | – 1092.716 [(a)]<br>± 16.116 | – 1196.250<br>± 16.000 | 408.600<br>± 6.000 | |
| $HAsO_2$(aq)<br>[1992GRE/FUG] | – 402.925 [(a)]<br>± 4.008 | – 456.500<br>± 4.000 | 125.900<br>± 0.600 | |
| $H_2AsO_3^{-}$<br>[1992GRE/FUG] | – 587.078 [(a)]<br>± 4.008 | – 714.790<br>± 4.000 | 110.500<br>± 0.600 | |
| $H_3AsO_3$(aq)<br>[1992GRE/FUG] | – 639.681 [(a)]<br>± 4.015 | – 742.200<br>± 4.000 | 195.000<br>± 1.000 | |
| $HAsO_4^{2-}$<br>[1992GRE/FUG] | – 714.592 [(a)]<br>± 4.008 | – 906.340<br>± 4.000 | – 1.700<br>± 0.600 | |
| $H_2AsO_4^{-}$<br>[1992GRE/FUG] | – 753.203 [(a)]<br>± 4.015 | – 909.560<br>± 4.000 | 117.000<br>± 1.000 | |
| $H_3AsO_4$(aq)<br>[1992GRE/FUG] | – 766.119 [(a)]<br>± 4.015 | – 902.500<br>± 4.000 | 184.000<br>± 1.000 | |
| $(As_2O_5)_3 \cdot 5\ H_2O$(cr)<br>[1992GRE/FUG] | | – 4248.400<br>± 24.000 | | |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| C(cr) | **0.000** | **0.000** | **5.740** | **8.517** |
| [1992GRE/FUG] | | | **± 0.100** | **± 0.080** |
| C(g) | **671.254** [(a)] | **716.680** | **158.100** | **20.839** |
| [1992GRE/FUG] | **± 0.451** | **± 0.450** | **± 0.003** | **± 0.001** |
| CO(g) | **– 137.168** [(a)] | **– 110.530** | **197.660** | **29.141** |
| [1992GRE/FUG] | **± 0.173** | **± 0.170** | **± 0.004** | **± 0.002** |
| $CO_2$(aq) | **– 385.970** [(a)] | **– 413.260** | **119.360** | |
| [1992GRE/FUG] | **± 0.270** | **± 0.200** | **± 0.600** | |
| $CO_2$(g) | **– 394.373** [(a)] | **– 393.510** | **213.785** | **37.135** |
| [1992GRE/FUG] | **± 0.133** | **± 0.130** | **± 0.010** | **± 0.002** |
| $CO_3^{2-}$ | **– 527.900** [(a)] | **– 675.230** | **– 50.000** | |
| [1992GRE/FUG] | **± 0.390** | **± 0.250** | **± 1.000** | |
| $HCO_3^-$ | **– 586.845** [(a)] | **– 689.930** | **98.400** | |
| [1992GRE/FUG] | **± 0.251** | **± 0.200** | **± 0.500** | |
| $CN^-$ | 166.939 [(b)] | 147.350 [(b)] | 101.182 [(b)] | |
| [2005OLI/NOL] | ± 2.519 | ± 3.541 | ± 8.475 | |
| HCN(aq) | 114.368 [(b)] | 103.750 [(b)] | 131.271 [(b)] | |
| [2005OLI/NOL] | ± 2.517 | ± 3.536 | ± 8.440 | |
| HCN(g) | 119.517 [(a)] | 129.900 | 201.710 | |
| [2005OLI/NOL] | ± 2.500 | ± 2.500 | ± 0.100 | |
| $SCN^-$ | 92.700 | 76.400 | 144.268 [(a)] | |
| [1992GRE/FUG] | ± 4.000 | ± 4.000 | ± 18.974 | |
| Si(cr) | **0.000** | **0.000** | **18.810** | **19.789** |
| [1992GRE/FUG] | | | **± 0.080** | **± 0.030** |
| Si(g) | **405.525** [(a)] | **450.000** | **167.981** | **22.251** |
| [1992GRE/FUG] | **± 8.000** | **± 8.000** | **± 0.004** | **± 0.001** |
| $SiO_2$(α– quartz) | **– 856.287** [(a)] | **– 910.700** | **41.460** | **44.602** |
| [1992GRE/FUG] | **± 1.002** | **± 1.000** | **± 0.200** | **± 0.300** |
| $SiO_2(OH)_2^{2-}$ | – 1177.088 [(b)] | – 1386.070 [(b)] | – 10.453 [(b)] | |
| [Ancillary Data–to be published] | ± 1.140 | ± 15.051 | ± 50.402 | |
| $SiO(OH)_3^-$ | – 1253.236 [(b)] | – 1431.753 [(b)] | 91.727 [(b)] | |
| [Ancillary Data–to be published] | ± 1.034 | ± 1.352 | ± 3.153 | |
| $Si(OH)_4$(aq) | – 1309.201 [(b)] | – 1461.070 [(b)] | 181.105 [(b)] | 195.000 |
| [Ancillary Data–to be published] | ± 1.017 | ± 1.239 | ± 2.501 | ± 3.000 |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Si_2O_3(OH)_4^{2-}$ [Ancillary Data–to be published] | – 2272.500 ± 3.000 | | | |
| $Si_2O_2(OH)_5^{-}$ [Ancillary Data–to be published] | – 2335.400 ± 3.000 | | | |
| $Si_3O_6(OH)_3^{3-}$ [Ancillary Data–to be published] | – 3053.100 ± 4.000 | | | |
| $Si_3O_5(OH)_5^{3-}$ [Ancillary Data–to be published] | – 3296.100 ± 4.000 | | | |
| $Si_4O_8(OH)_4^{4-}$ [Ancillary Data–to be published] | – 4080.700 ± 6.000 | | | |
| $Si_4O_7(OH)_5^{3-}$ [Ancillary Data–to be published] | – 4142.200 ± 5.000 | | | |
| $SiF_4$(g) [1992GRE/FUG] | **– 1572.773** [(a)] **± 0.814** | **– 1615.000 ± 0.800** | **282.760 ± 0.500** | **73.622 ± 0.500** |
| Ge(cr) [1992GRE/FUG] | **0.000** | **0.000** | **31.090 ± 0.150** | **23.222 ± 0.100** |
| Ge(g) [1992GRE/FUG] | **331.209** [(a)] **± 3.000** | **372.000 ± 3.000** | **167.904 ± 0.005** | **30.733 ± 0.001** |
| $GeO_2$(tetragonal) [1992GRE/FUG] | **– 521.404** [(a)] **± 1.002** | **– 580.000 ± 1.000** | **39.710 ± 0.150** | **50.166 ± 0.300** |
| $GeF_4$(g) [1992GRE/FUG] | **– 1150.018** [(a)] **± 0.584** | **– 1190.200 ± 0.500** | **301.900 ± 1.000** | **81.602 ± 1.000** |
| Sn(cr) [2012GAM/GAJ] | **0.000** | **0.000** | **51.180 ± 0.080** | **27.110 ± 0.080** |
| Sn(g) [1992GRE/FUG] | **266.223** [(a)] **± 1.500** | **301.200 ± 1.500** | **168.492 ± 0.004** | **21.259 ± 0.001** |
| $Sn^{2+}$ [2012GAM/GAJ] | **– 27.390** [(a)] **± 0.300** | **– 9.617 ± 1.236** | **– 19.889 ± 4.266** | |
| $Sn^{4+}$ [2012GAM/GAJ] | **46.711** [(b)] **± 3.871** | | | |
| SnO(tetragonal) [2012GAM/GAJ] | **– 255.446** [(a)] **± 0.763** | **– 284.240 ± 0.760** | **57.180 ± 0.220** | **47.760 ± 0.080** |
| $SnO_2$(cassiterite, tetragonal) [2012GAM/GAJ] | **– 516.640** [(a)] **± 0.206** | **– 577.630 ± 0.200** | **51.770 ± 0.140** | **55.260 ± 0.090** |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| Pb(cr) | **0.000** | **0.000** | **64.800** | **26.650** |
| [1992GRE/FUG] | | | **± 0.300** | **± 0.100** |
| Pb(g) | **162.232** [(a)] | **195.200** | **175.375** | **20.786** |
| [1992GRE/FUG] | **± 0.805** | **± 0.800** | **± 0.005** | **± 0.001** |
| $Pb^{2+}$ | **– 24.238** [(a)] | **0.920** | **18.500** | |
| [1992GRE/FUG] | **± 0.399** | **± 0.250** | **± 1.000** | |
| $PbSO_4$(cr) | **– 813.036** [(a)] | **– 919.970** | **148.500** | |
| [1992GRE/FUG] | **± 0.447** | **± 0.400** | **± 0.600** | |
| B(cr) | **0.000** | **0.000** | **5.900** | **11.087** |
| [1992GRE/FUG] | | | **± 0.080** | **± 0.100** |
| B(g) | **521.012** [(a)] | **565.000** | **153.436** | **20.796** |
| [1992GRE/FUG] | **± 5.000** | **± 5.000** | **± 0.015** | **± 0.005** |
| $B_2O_3$(cr) | **– 1194.324** [(a)] | **– 1273.500** | **53.970** | **62.761** |
| [1992GRE/FUG] | **± 1.404** | **± 1.400** | **± 0.300** | **± 0.300** |
| $B(OH)_3$(aq) | **– 969.268** [(a)] | **– 1072.800** | **162.400** | |
| [1992GRE/FUG] | **± 0.820** | **± 0.800** | **± 0.600** | |
| $B(OH)_3$(cr) | **– 969.667** [(a)] | **– 1094.800** | **89.950** | **86.060** |
| [1992GRE/FUG] | **± 0.820** | **± 0.800** | **± 0.600** | **± 0.400** |
| $BF_3$(g) | **– 1119.403** [(a)] | **– 1136.000** | **254.420** | **50.463** |
| [1992GRE/FUG] | **± 0.803** | **± 0.800** | **± 0.200** | **± 0.100** |
| Al(cr) | **0.000** | **0.000** | **28.300** | **24.200** |
| [1992GRE/FUG] | | | **± 0.100** | **± 0.070** |
| Al(g) | **289.376** [(a)] | **330.000** | **164.554** | **21.391** |
| [1992GRE/FUG] | **± 4.000** | **± 4.000** | **± 0.004** | **± 0.001** |
| $Al^{3+}$ | **– 491.507** [(a)] | **– 538.400** | **– 325.000** | |
| [1992GRE/FUG] | **± 3.338** | **± 1.500** | **± 10.000** | |
| $Al_2O_3$(corundum) | **– 1582.257** [(a)] | **– 1675.700** | **50.920** | **79.033** |
| [1992GRE/FUG] | **± 1.302** | **± 1.300** | **± 0.100** | **± 0.200** |
| $AlF_3$(cr) | **– 1431.096** [(a)] | **– 1510.400** | **66.500** | **75.122** |
| [1992GRE/FUG] | **± 1.309** | **± 1.300** | **± 0.500** | **± 0.400** |
| $Tl^+$ | – 32.400 | | | |
| [1999RAR/RAN] | ± 0.300 | | | |
| Zn(cr) | **0.000** | **0.000** | **41.630** | **25.390** |
| [1992GRE/FUG] | | | **± 0.150** | **± 0.040** |
| Zn(g) | **94.813** [(a)] | **130.400** | **160.990** | **20.786** |
| [1992GRE/FUG] | **± 0.402** | **± 0.400** | **± 0.004** | **± 0.001** |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Zn^{2+}$ [1992GRE/FUG] | **– 147.203** [(a)] **± 0.254** | **– 153.390 ± 0.200** | **– 109.800 ± 0.500** | |
| ZnO(cr) [1992GRE/FUG] | **– 320.479** [(a)] **± 0.299** | **– 350.460 ± 0.270** | **43.650 ± 0.400** | |
| Cd(cr) [1992GRE/FUG] | **0.000** | **0.000** | **51.800 ± 0.150** | **26.020 ± 0.040** |
| Cd(g) [1992GRE/FUG] | **77.230** [(a)] **± 0.205** | **111.800 ± 0.200** | **167.749 ± 0.004** | **20.786 ± 0.001** |
| $Cd^{2+}$ [1992GRE/FUG] | **– 77.733** [(a)] **± 0.750** | **– 75.920 ± 0.600** | **– 72.800 ± 1.500** | |
| CdO(cr) [1992GRE/FUG] | **– 228.661** [(a)] **± 0.602** | **– 258.350 ± 0.400** | **54.800 ± 1.500** | |
| $CdSO_4$ ⅜ $H_2O$(cr) [1992GRE/FUG] | **– 1464.959** [(a)] **± 0.810** | **– 1729.300 ± 0.800** | **229.650 ± 0.400** | |
| Hg(g) [1992GRE/FUG] | **31.842** [(a)] **± 0.054** | **61.380 ± 0.040** | **174.971 ± 0.005** | **20.786 ± 0.001** |
| Hg(l) [1992GRE/FUG] | **0.000** | **0.000** | **75.900 ± 0.120** | |
| $Hg^{2+}$ [1992GRE/FUG] | **164.667** [(a)] **± 0.313** | **170.210 ± 0.200** | **– 36.190 ± 0.800** | |
| $Hg_2^{2+}$ [1992GRE/FUG] | **153.567** [(a)] **± 0.559** | **166.870 ± 0.500** | **65.740 ± 0.800** | |
| HgO(montroydite, red) [1992GRE/FUG] | **– 58.523** [(a)] **± 0.154** | **– 90.790 ± 0.120** | **70.250 ± 0.300** | |
| $Hg_2Cl_2$(cr) [1992GRE/FUG] | **– 210.725** [(a)] **± 0.471** | **– 265.370 ± 0.400** | **191.600 ± 0.800** | |
| $Hg_2SO_4$(cr) [1992GRE/FUG] | **– 625.780** [(a)] **± 0.411** | **– 743.090 ± 0.400** | **200.700 ± 0.200** | |
| Cu(cr) [1992GRE/FUG] | **0.000** | **0.000** | **33.150 ± 0.080** | **24.440 ± 0.050** |
| Cu(g) [1992GRE/FUG] | **297.672** [(a)] **± 1.200** | **337.400 ± 1.200** | **166.398 ± 0.004** | **20.786 ± 0.001** |
| $Cu^{2+}$ [1992GRE/FUG] | **65.040** [(a)] **± 1.557** | **64.900 ± 1.000** | **– 98.000 ± 4.000** | |
| $CuSO_4$(cr) [1992GRE/FUG] | **– 662.185** [(a)] **± 1.206** | **– 771.400 ± 1.200** | **109.200 ± 0.400** | |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| Ag(cr)<br>[1992GRE/FUG] | **0.000**<br> | **0.000**<br> | **42.550**<br>**± 0.200** | **25.350**<br>**± 0.100** |
| Ag(g)<br>[1992GRE/FUG] | **246.007** [(a)]<br>**± 0.802** | **284.900**<br>**± 0.800** | **172.997**<br>**± 0.004** | **20.786**<br>**± 0.001** |
| $Ag^+$<br>[1992GRE/FUG] | **77.096** [(a)]<br>**± 0.156** | **105.790**<br>**± 0.080** | **73.450**<br>**± 0.400** | |
| AgCl(cr)<br>[1992GRE/FUG] | **– 109.765** [(a)]<br>**± 0.098** | **– 127.010**<br>**± 0.050** | **96.250**<br>**± 0.200** | |
| Ni(cr)<br>[2005GAM/BUG] | 0.000<br>± 0.000 | 0.000<br>± 0.000 | 29.870<br>± 0.200 | 26.070<br>± 0.100 |
| $Ni^{2+}$<br>[2005GAM/BUG] | – 45.773<br>± 0.771 | – 55.012 [(a)]<br>± 0.878 | – 131.800<br>± 1.400 | – 46.100<br>± 7.500 |
| $NiF_2$(cr)<br>[2005GAM/BUG] | –609.852 [(a)]<br>± 8.001 | –657.300<br>± 8.000 | 73.520<br>± 0.400 | 63.210<br>± 2.000 |
| Ti(cr)<br>[1992GRE/FUG] | **0.000**<br> | **0.000**<br> | **30.720**<br>**± 0.100** | **25.060**<br>**± 0.080** |
| Ti(g)<br>[1992GRE/FUG] | **428.403** [(a)]<br>**± 3.000** | **473.000**<br>**± 3.000** | **180.298**<br>**± 0.010** | **24.430**<br>**± 0.030** |
| $TiO_2$(rutile)<br>[1992GRE/FUG] | **– 888.767** [(a)]<br>**± 0.806** | **– 944.000**<br>**± 0.800** | **50.620**<br>**± 0.300** | **55.080**<br>**± 0.300** |
| $TiCl_4$(g)<br>[1992GRE/FUG] | **– 726.324** [(a)]<br>**± 3.229** | **– 763.200**<br>**± 3.000** | **353.200**<br>**± 4.000** | **95.408**<br>**± 1.000** |
| U(cr)<br>[1992GRE/FUG] | **0.000**<br> | **0.000**<br> | **50.200**<br>**± 0.200** | 27.660<br>± 0.050 |
| $UO_2^{2+}$<br>[1992GRE/FUG] | **–952.551** [(a)]<br>**± 1.747** | **–1019.000**<br>**± 1.500** | **–98.200**<br>**± 3.000** | 42.400<br>± 3.000 |
| Be(cr)<br>[1992GRE/FUG] | **0.000**<br> | **0.000**<br> | **9.500**<br>**± 0.080** | **16.443**<br>**± 0.060** |
| Be(g)<br>[1992GRE/FUG] | **286.202** [(a)]<br>**± 5.000** | **324.000**<br>**± 5.000** | **136.275**<br>**± 0.003** | **20.786**<br>**± 0.001** |
| BeO(bromellite)<br>[1992GRE/FUG] | **– 580.090** [(a)]<br>**± 2.500** | **– 609.400**<br>**± 2.500** | **13.770**<br>**± 0.040** | **25.565**<br>**± 0.100** |
| Mg(cr)<br>[1992GRE/FUG] | **0.000**<br> | **0.000**<br> | **32.670**<br>**± 0.100** | **24.869**<br>**± 0.020** |
| Mg(g)<br>[1992GRE/FUG] | **112.521** [(a)]<br>**± 0.801** | **147.100**<br>**± 0.800** | **148.648**<br>**± 0.003** | **20.786**<br>**± 0.001** |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Mg^{2+}$ | **– 455.375** [(a)] | **– 467.000** | **– 137.000** | |
| [1992GRE/FUG] | **± 1.335** | **± 0.600** | **± 4.000** | |
| MgO(cr) | **– 569.312** [(a)] | **– 601.600** | **26.950** | **37.237** |
| [1992GRE/FUG] | **± 0.305** | **± 0.300** | **± 0.150** | **± 0.200** |
| $MgF_2$(cr) | **– 1071.051** [(a)] | **– 1124.200** | **57.200** | **61.512** |
| [1992GRE/FUG] | **± 1.210** | **± 1.200** | **± 0.500** | **± 0.300** |
| Ca(cr) | **0.000** | **0.000** | **41.590** | **25.929** |
| [1992GRE/FUG] | | | **± 0.400** | **± 0.300** |
| Ca(g) | **144.021** [(a)] | **177.800** | **154.887** | **20.786** |
| [1992GRE/FUG] | **± 0.809** | **± 0.800** | **± 0.004** | **± 0.001** |
| $Ca^{2+}$ | **– 552.806** [(a)] | **– 543.000** | **– 56.200** | |
| [1992GRE/FUG] | **± 1.050** | **± 1.000** | **± 1.000** | |
| CaO(cr) | **– 603.296** [(a)] | **– 634.920** | **38.100** | **42.049** |
| [1992GRE/FUG] | **± 0.916** | **± 0.900** | **± 0.400** | **± 0.400** |
| Sr(cr) | 0.000 | 0.000 | 55.700 | |
| [1992GRE/FUG] | | | ± 0.210 | |
| $Sr^{2+}$ | – 563.864 [(a)] | – 550.900 | – 31.500 | |
| [1992GRE/FUG] | ± 0.781 | ± 0.500 | ± 2.000 | |
| SrO(cr) | – 559.400 [(a)] | – 590.600 | 53.630 | 45.150 |
| This review | ± 0.903 | ± 0.900 | ± 0.100 | ± 0.100 |
| $SrCl_2$(cr) | – 784.974 [(a)] | – 833.850 | 114.850 | |
| [1992GRE/FUG] | ± 0.714 | ± 0.700 | ± 0.420 | |
| $Sr(NO_3)_2$(cr) | – 783.146 [(a)] | – 982.360 | 194.600 | |
| [1992GRE/FUG] | ± 1.018 | ± 0.800 | ± 2.100 | |
| Ba(cr) | 0.000 | 0.000 | 62.420 | |
| [1992GRE/FUG] | | | ± 0.840 | |
| $Ba^{2+}$ | – 557.656 [(a)] | – 534.800 | 8.400 | |
| [1992GRE/FUG] | ± 2.582 | ± 2.500 | ± 2.000 | |
| BaO(cr) | – 519.780 [(a)] | – 548.100 | 70.010 | 47.060 |
| This review | ± 2.513 | ± 2.500 | ± 0.100 | ± 0.100 |
| $BaCl_2$(cr) | – 806.953 [(a)] | – 855.200 | 123.680 | |
| [1992GRE/FUG] | ± 2.514 | ± 2.500 | ± 0.250 | |
| Li(cr) | **0.000** | **0.000** | **29.120** | **24.860** |
| [1992GRE/FUG] | | | **± 0.200** | **± 0.200** |
| Li(g) | **126.604** [(a)] | **159.300** | **138.782** | **20.786** |
| [1992GRE/FUG] | **± 1.002** | **± 1.000** | **± 0.010** | **± 0.001** |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Li^+$ [1992GRE/FUG] | **– 292.918 [(a)] ± 0.109** | **– 278.470 ± 0.080** | **12.240 ± 0.150** | |
| Na(cr) [1992GRE/FUG] | **0.000** | **0.000** | **51.300 ± 0.200** | **28.230 ± 0.200** |
| Na(g) [1992GRE/FUG] | **76.964 [(a)] ± 0.703** | **107.500 ± 0.700** | **153.718 ± 0.003** | **20.786 ± 0.001** |
| $Na^+$ [1992GRE/FUG] | **– 261.953 [(a)] ± 0.096** | **– 240.340 ± 0.060** | **58.450 ± 0.150** | |
| NaF(cr) [2001LEM/FUG] | – 546.327 [(a)] ± 0.704 | – 576.600 ± 0.700 | 51.160 ± 0.150 | |
| NaCl(cr) [2001LEM/FUG] | – 384.221 ± 0.147 | – 411.260 ± 0.120 | 72.150 ± 0.200 | 50.500 |
| $NaNO_3$(cr) [2003GUI/FAN] | | – 467.580 ± 0.410 | | |
| K(cr) [1992GRE/FUG] | **0.000** | **0.000** | **64.680 ± 0.200** | **29.600 ± 0.100** |
| K(g) [1992GRE/FUG] | **60.479 [(a)] ± 0.802** | **89.000 ± 0.800** | **160.341 ± 0.003** | **20.786 ± 0.001** |
| $K^+$ [1992GRE/FUG] | **– 282.510 [(a)] ± 0.116** | **– 252.140 ± 0.080** | **101.200 ± 0.200** | |
| KCl(cr) [2005GAM/BUG] | | – 436.461 ± 0.129 | | |
| KBr(cr) [2005GAM/BUG] | | – 393.330 ± 0.188 | | |
| KI(cr) [2005GAM/BUG] | | – 329.150 ± 0.137 | | |
| Rb(cr) [1992GRE/FUG] | **0.000** | **0.000** | **76.780 ± 0.300** | **31.060 ± 0.100** |
| Rb(g) [1992GRE/FUG] | **53.078 [(a)] ± 0.805** | **80.900 ± 0.800** | **170.094 ± 0.003** | **20.786 ± 0.001** |
| $Rb^+$ [1992GRE/FUG] | **– 284.009 [(a)] ± 0.153** | **– 251.120 ± 0.100** | **121.750 ± 0.250** | |
| Cs(cr) [1992GRE/FUG] | **0.000** | **0.000** | **85.230 ± 0.400** | **32.210 ± 0.200** |
| Cs(g) [1992GRE/FUG] | **49.556 [(a)] ± 1.007** | **76.500 ± 1.000** | **175.601 ± 0.003** | **20.786 ± 0.001** |

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Table 8-1 (continued)

| Compound and review where adopted | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Cs^+$ | **– 291.456** [(a)] | **– 258.000** | **132.100** | |
| [1992GRE/FUG] | **± 0.535** | **± 0.500** | **± 0.500** | |
| CsCl(cr) | – 413.807 [(a)] | – 442.310 | 101.170 | 52.470 |
| [2001LEM/FUG] | ± 0.208 | ± 0.160 | ± 0.200 | |
| CsBr(cr) | – 391.171 | – 405.600 | 112.940 | 52.930 |
| [2001LEM/FUG] | ± 0.305 | ± 0.250 | ± 0.400 | |

(a) Value calculated internally using $\Delta_f G_m^o = \Delta_f H_m^o - T\sum S_{m,i}^o$ .
(b) Value calculated internally from reaction data (see Table 8-2).
(c) Temperature coefficients of this function are listed in Table III-3 of [2005OLI/NOL].

Table 8-2: Selected thermodynamic data for reactions involving auxiliary compounds and complexes used in the evaluation of thermodynamic data for the NEA TDB Project data. All ionic species listed in this table are aqueous species. The selection of these data is described in Chapter VI of [1992GRE/FUG] and [2005OLI/NOL]. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a standard state of infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95 % confidence interval. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The reference listed for each entry in this table indicates the NEA TDB Review where the corresponding data have been adopted as NEA TDB Auxiliary data. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency [2019MAR/SAN].

| Species and review where adopted | Reaction $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| HF(aq) | $F^- + H^+ \rightleftharpoons HF(aq)$ | | | |
| [1992GRE/FUG] | 3.180 ± 0.020 | – 18.152 ± 0.114 | 12.200 ± 0.300 | 101.800 [(a)] ± 1.077 |
| $HF_2^-$ | $F^- + HF(aq) \rightleftharpoons HF_2^-$ | | | |
| [1992GRE/FUG] | 0.440 ± 0.120 | – 2.511 ± 0.685 | 3.000 ± 2.000 | 18.486 [(a)] ± 7.090 |
| $HIO_3(aq)$ | $H^+ + IO_3^- \rightleftharpoons HIO_3(aq)$ | | | |
| [1992GRE/FUG] | 0.788 ± 0.029 | – 4.498 ± 0.166 | | |
| $S^{2-}$ | $HS^- \rightleftharpoons H^+ + S^{2-}$ | | | |
| [1992GRE/FUG] | – 19.000 ± 2.000 | 108.450 ± 11.416 | | |
| $SO_3^{2-}$ | $H_2O(l) + SO_4^{2-} + 2\,e^- \rightleftharpoons 2OH^- + SO_3^{2-}$ | | | |
| [1992GRE/FUG] | – 31.400 [(b)] ± 0.700 | 179.230 ± 3.996 | | |
| $H_2S(aq)$ | $H_2S(aq) \rightleftharpoons H^+ + HS^-$ | | | |
| [1992GRE/FUG] | – 6.990 ± 0.170 | 39.899 ± 0.970 | | |
| $HSO_3^-$ | $H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$ | | | |
| [1992GRE/FUG] | 7.220 ± 0.080 | – 41.212 ± 0.457 | 66.000 ± 30.000 | 359.590 [(a)] ± 100.630 |
| $H_2SO_3(aq)$ | $H^+ + HSO_3^- \rightleftharpoons H_2SO_3(aq)$ | | | |
| [1992GRE/FUG] | 1.840 ± 0.080 | – 10.503 ± 0.457 | 16.000 ± 5.000 | 88.891 [(a)] ± 16.840 |

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Table 8-2 (continued)

| Species and review where adopted | Reaction $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $HSO_4^-$ | $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$ | | | |
| [1992GRE/FUG] | 1.980 ± 0.050 | – 11.302 ± 0.285 | | |
| Se(g) | ½ $Se_2$(g) $\rightleftharpoons$ Se(g) | | | |
| [2005OLI/NOL] | | | –165.520 ± 0.250 | |
| $Se^{2-}$ | Se(cr) + 2 $e^-$ $\rightleftharpoons$ $Se^{2-}$ | | | |
| [2005OLI/NOL] | –22.530 ± 0.526 | 128.600 ± 3.000 | | |
| $Se_2^{2-}$ | $2Se^{2-} \rightleftharpoons Se_2^{2-} + 2\ e^-$ | | | |
| [2005OLI/NOL] | 25.320 ± 0.333 | –144.530 ± 1.900 | | |
| $Se_3^{2-}$ | $3Se^{2-} \rightleftharpoons Se_3^{2-} + 4\ e^-$ | | | |
| [2005OLI/NOL] | 49.966 ± 0.333 | –285.210 ± 1.900 | | |
| $Se_4^{2-}$ | $4Se^{2-} \rightleftharpoons Se_4^{2-} + 6\ e^-$ | | | |
| [2005OLI/NOL] | 73.023 ± 0.333 | –416.820 ± 1.900 | | |
| $SeO_2$(g) | $SeO_2$(cr) $\rightleftharpoons$ $SeO_2$(g) | | | |
| [2005OLI/NOL] | | | 114.800 ± 2.500 | |
| $SeO_3^{2-}$ | $HSeO_3^- \rightleftharpoons H^+ + SeO_3^{2-}$ | | | |
| [2005OLI/NOL] | –8.360 ± 0.230 | 47.719 ± 1.313 | | |
| $SeO_4^{2-}$ | $HSeO_4^- \rightleftharpoons H^+ + SeO_4^{2-}$ | | | |
| [2005OLI/NOL] | –1.750 ± 0.100 | 9.989 ± 0.571 | –20.800 ± 3.200 | –103.267 [(a)] ± 10.902 |
| $Se_2O_5$(cr) | $SeO_2$(cr) + $SeO_3$(cr) $\rightleftharpoons$ $Se_2O_5$(cr) | | | |
| [2005OLI/NOL] | | | –26.100 ± 1.200 | |
| $HSe^-$ | $H_2Se$(aq) $\rightleftharpoons$ $H^+ + HSe^-$ | | | |
| [2005OLI/NOL] | –3.850 ± 0.050 | 21.976 ± 0.285 | | |

(Continued on next page)

Table 8-2 (continued)

| Species and review where adopted | Reaction $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $H_2Se(aq)$ | $H_2Se(g) \rightleftharpoons H_2Se(aq)$ | | | |
| [2005OLI/NOL] | –1.100 ± 0.010 | 6.279 ± 0.057 | –14.700 ± 0.300 | –70.363 [a] ± 1.024 |
| $HSeO_3^-$ | $H_2SeO_3(aq) \rightleftharpoons H^+ + HSeO_3^-$ | | | |
| [2005OLI/NOL] | –2.640 ± 0.140 | 15.069 ± 0.799 | | |
| $HSeO_4^-$ | $H_2O(l) + H_2SeO_3(aq) \rightleftharpoons 3H^+ + HSeO_4^- + 2\,e^-$ | | | |
| [2005OLI/NOL] | –37.289 [c] ± 0.175 | 212.847 ± 1.000 | | |
| $H_2SeO_3(cr)$ | $H_2O(l) + SeO_2(cr) \rightleftharpoons H_2SeO_3(cr)$ | | | |
| [2005OLI/NOL] | | | –13.500 ± 0.180 | |
| $H_2SeO_3(aq)$ | $3H_2O(l) + Se(cr) \rightleftharpoons 2H_2(g) + H_2SeO_3(aq)$ | | | |
| [2005OLI/NOL] | –50.147 ± 0.147 | 286.240 ± 0.840 | | |
| $N_3(aq)$ | $H^+ + N_3^- \rightleftharpoons HN_3(aq)$ | | | |
| [1992GRE/FUG] | 4.700 ± 0.080 | – 26.828 ± 0.457 | – 15.000 ± 10.000 | 39.671 [a] ± 33.575 |
| $NH_3(aq)$ | $NH_4^+ \rightleftharpoons H^+ + NH_3(aq)$ | | | |
| [1992GRE/FUG] | – 9.237 ± 0.022 | 52.725 ± 0.126 | 52.090 ± 0.210 | – 2.130 [a] ± 0.821 |
| $PO_4^{3-}$ | $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ | | | |
| [1992GRE/FUG] | – 12.350 ± 0.030 | 70.494 ± 0.171 | 14.600 ± 3.800 | – 187.470 [a] ± 12.758 |
| $P_2O_7^{4-}$ | $HP_2O_7^{3-} \rightleftharpoons H^+ + P_2O_7^{4-}$ | | | |
| [1992GRE/FUG] | – 9.400 ± 0.150 | 53.656 ± 0.856 | | |
| $H_2PO_4^-$ | $H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$ | | | |
| [1992GRE/FUG] | 7.212 ± 0.013 | – 41.166 ± 0.074 | – 3.600 ± 1.000 | 126.000 [a] ± 3.363 |
| $H_3PO_4(aq)$ | $H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4(aq)$ | | | |
| [1992GRE/FUG] | 2.140 ± 0.030 | – 12.215 ± 0.171 | 8.480 ± 0.600 | 69.412 [a] ± 2.093 |

(Continued on next page)

Table 8-2 (continued)

| Species and review where adopted | Reaction $\log_{10} K^\circ$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $HP_2O_7^{3-}$ | $H_2P_2O_7^{2-} \rightleftharpoons H^+ + HP_2O_7^{3-}$ | | | |
| [1992GRE/FUG] | – 6.650 ± 0.100 | 37.958 ± 0.571 | | |
| $H_2P_2O_7^{2-}$ | $H_3P_2O_7^- \rightleftharpoons H^+ + H_2P_2O_7^{2-}$ | | | |
| [1992GRE/FUG] | – 2.250 ± 0.150 | 12.843 ± 0.856 | | |
| $H_3P_2O_7^-$ | $H_4P_2O_7(aq) \rightleftharpoons H^+ + H_3P_2O_7^-$ | | | |
| [1992GRE/FUG] | – 1.000 ± 0.500 | 5.708 ± 2.854 | | |
| $H_4P_2O_7(aq)$ | $2H_3PO_4(aq) \rightleftharpoons H_2O(l) + H_4P_2O_7(aq)$ | | | |
| [1992GRE/FUG] | – 2.790 ± 0.170 | 15.925 ± 0.970 | 22.200 ± 1.000 | 21.045 [(a)] ± 4.673 |
| $CO_2(aq)$ | $H^+ + HCO_3^- \rightleftharpoons CO_2(aq) + H_2O(l)$ | | | |
| [1992GRE/FUG] | 6.354 ± 0.020 | – 36.269 ± 0.114 | | |
| $CO_2(g)$ | $CO_2(aq) \rightleftharpoons CO_2(g)$ | | | |
| [1992GRE/FUG] | 1.472 ± 0.020 | – 8.402 ± 0.114 | | |
| $HCO_3^-$ | $CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$ | | | |
| [1992GRE/FUG] | 10.329 ± 0.020 | – 58.958 ± 0.114 | | |
| $CN^-$ | $HCN(aq) \rightleftharpoons CN^- + H^+$ | | | |
| [2005OLI/NOL] | – 9.210 ± 0.020 | 52.571 ± 0.114 | 43.600 ± 0.200 | – 30.089 [(a)] ± 0.772 |
| HCN(aq) | $HCN(g) \rightleftharpoons HCN(aq)$ | | | |
| [2005OLI/NOL] | 0.902 ± 0.050 | – 5.149 ± 0.285 | – 26.150 ± 2.500 | – 70.439 [(a)] ± 8.440 |
| $SiO_2(OH)_2^{2-}$ | $Si(OH)_4(aq) \rightleftharpoons 2H^+ + SiO_2(OH)_2^{2-}$ | | | |
| [Ancillary Data–to be published] | – 23.145 ± 0.090 | 132.113 ± 0.514 | 75.000 ± 15.000 | – 191.558 [(a)] ± 50.340 |
| $SiO(OH)_3^-$ | $Si(OH)_4(aq) \rightleftharpoons H^+ + SiO(OH)_3^-$ | | | |
| [Ancillary Data–to be published] | – 9.804 ± 0.033 | 55.965 ± 0.188 | 29.317 ± 0.541 | – 89.378 [(a)] ± 1.921 |

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Table 8-2 (continued)

| Species and review where adopted | Reaction $\log_{10} K^{\circ}$ | $\Delta_r G_m^{\circ}$ /kJ·mol$^{-1}$ | $\Delta_r H_m^{\circ}$ /kJ·mol$^{-1}$ | $\Delta_r S_m^{\circ}$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Si(OH)_4$(aq) | $2H_2O(l) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons Si(OH)_4(aq)$ | | | |
| [Ancillary Data–to be published] | – 3.743<br>± 0.027 | 21.366<br>± 0.154 | 21.290<br>± 0.727 | – 0.255 [(a)]<br>± 2.492 |

(a) Value calculated internally using $\Delta_r G_m^{\circ} = \Delta_r H_m^{\circ} - T\,\Delta_r S_m^{\circ}$ .
(b) Value calculated from a selected standard potential.
(c) Value of $\log_{10} K^{\circ}$ calculated internally from $\Delta_r G_m^{\circ}$ .

# Part 3

# Discussion of new data selection

# Chapter 9

# Discussion of new data selection for Uranium

Since the latest review, [2003GUI/FAN], a number of review articles on the chemistry and thermodynamics of uranium have appeared in *The Chemistry of the Actinide and Transactinide Elements* [2006MOR/EDE] that contain information of uranium structure chemistry, magnetic and optical properties and some thermodynamic data of compounds; in addition there are some phase diagrams that may be used as a complement to the information in the present book.

The present review covers the literature up to 2015 (with some publications up to 2017), but also contains a number of publications from Russian literature that were not identified in [1992GRE/FUG] and [2003GUI/FAN]. The present review notes that there are a number of publications that do not contain new thermodynamic data, which might, nevertheless, be of interest for the users of the current update. These publications have been listed in groups below; some of them may have a review comment in Appendix A, but most not, although their titles will give an idea about the content.

- Reviews and papers describing modelling of chemical systems and the use of existing databases, experiments in ground- and surface water systems:

  [2002FAN/NEC], [2002KUL/FUJ], [2002MOR/FUJ], [2003RIT/PHE], [2004GAS/BUK], [2004GIA/MIL], [2004IWA/ART], [2004KEU/LEE], [2004KIR/KIM], [2004SPA/DEV], [2004SUT/BUR], [2005AMM/WIS], [2005DEN/GAR], [2005MOR/SAS], [2005MUR/SAT], [2006MEI/LIS], [2006BAT/KAL], [2006GAS], [2006KUB/BUR2], [2006KUB/UNR], [2006MEI/LIS], [2006MOR/SAS], [2006PER/KUL], [2006SAV], [2006SCH/HAW], [2006SCH/MAN], [2007DED/UTS], [2007DUF/CLA], [2007LUC/BOR], [2007MEL/CHE], [2007RED/WOO], [2007SCH/HAW2], [2007WEL/GUN], [2008KEE/NOE], [2008MAT/WEL], [2008OLL], [2008PER/MAS], [2008TRO/KUL], [2009KIM/BAI], [2009KIM/KIM],

[2009SCH/FRE], [2010KIN/EDW], [2010WAN/ALE], [2011CAN/DEU], [2011DU/BOO], [2011NAI/MER], [2011RAI/YUI], [2011SCH/HAW], [2012KIM/LEE], [2012KNY/KUZ], [2012MAL/WAL], [2013CRE/SZE], [2013FAN/YOO], [2013LUC/BOR], [2013WAN/NI], [2013YAN/WAN], [2014BAN/BRE], [2014MEH/MAI].

- Papers describing structures of solid compounds:

  [2003BRU/BUR], [2003BEA/SCO], [2004AMA/ARN], [2004CHA/HUL], [2004LOC/BUR], [2004WOO/ALM], [2005CRA/MAY], [2005DOU/CLA], [2005VOL/MAY], [2006BRA/BEI], [2006DAC/CLA], [2006KUB/BUR2], [2007FOR], [2007KUB/FOR], [2007MUR], [2007SCH/HAW], [2008DED/UTS], [2008GOR/SKA], [2008KRI], [2008SOD/SKA], [2008ZEH/BAT], [2009ARM], [2009KNY/ERS], [2009POI/DED], [2011DES/BAL], [2011FOR/HOR], [2011KOC/ESE], [2011WAN/VIL], [2012MER/POL], [2013LEL/OGU], [2013LYU/AND], [2013PLA/KAM], [2013SZE/COS], [2013WAN/ZHA], [2014BAL/DES], [2014SMI/RAI].

- Papers dealing with properties of solid phases:

  [2002BAI/CHA], [2002FAN/NEC], [2002GUE/BAI], [2002KUL/FUJ], [2002KUR], [2002MAN/RON], [2002MOR], [2003CHA/GUE], [2003HEL/NAV], [2003LAB/DUG], [2003LAB/DUG2], [2003MAN/RON], [2003SRI/SAN], [2004BAN/DAS], [2004GIA/HER], [2004HAL/SAL], [2004MAN/SHE], [2004MOL/FOR], [2004SUL/JEN], [2005ALE], [2005ARI/YAM], [2005CON/BEG], [2005DON/STE], [2005KUR/ADA], [2005MAN/PFL], [2005MAN/RON], [2005RUE/DES], [2005SOB], [2005TAY], [2005YAM/KUR], [2006BAI/CHA], [2006BAI/CHA2], [2006MAN/YET], [2006SCH/HAW], [2006SCH/MAN], [2006YAK/RON], [2007MAN/RON], [2007OST/ZEL], [2007WEC/KIM], [2008GOR/FEI], [2008HIE/GOT], [2008MAN/LYN], [2008PER/MOI], [2008REY/GIM], [2008VEN/MAN], [2009AND/LEZ], [2009BER/RAD], [2009BUL/GED], [2009MCN/SCH], [2009MUL/FOE], [2009WEL/THO], [2010LI/TIA], [2010LU/WAN], [2010TAY/LOO], [2010VEN/JEN], [2011BER/DUP], [2011LU/WAN], [2011RAG/ADA], [2011SWE/HEN], [2011TOK/TAN], [2012BEE/DEO], [2012TOK/KIM], [2012YUN/LEG], [2013BAR/DEV], [2013BEI/BEN], [2013REY/KEN], [2013SHR/CHA], [2014TIF/GIL].

- Other papers:

  [2004MAS/MIK], [2004NEU/SOD], [2004SPA/DEV], [2013PRI/SAM], [2014MOL/ROS].

## 9.1 Elemental uranium

Since [2003GUI/FAN] the only new study concerning elemental uranium is the review by [2010KON/BEN], which does not review any new papers since the last Thermochemical Database (TDB) publication. The only correction made is to the melting point of γ-U that is corrected for the International Temperature Scale (ITS-90). The heat capacity data are fitted to a polynomial with negligible differences in its coefficients from the values in [1992GRE/FUG] and the values reported there are retained. The following transition temperatures are selected:

$$\alpha\text{-U} \rightarrow \beta\text{-U } \mathbf{(941 \pm 1)}\text{ K}$$

$$\beta\text{-U} \rightarrow \gamma\text{-U } \mathbf{(1049 \pm 2)}\text{ K}$$

$$\gamma\text{-U} \rightarrow \text{U(l) } \mathbf{(1407 \pm 2)}\text{ K}$$

## 9.2 Simple uranium aqua ions

No new experimental studies of thermodynamic data referring to this section have appeared since the publication by Guillaumont *et al.* [2003GUI/FAN] and the values selected there are retained in the present review. There are, however, a significant number of studies based on quantum chemical methods, QC, that are of interest because they provide detailed microscopic information on structures and IR/Raman frequencies that can be compared with experimental data; the thermodynamic data on reaction energies, however, are not yet accurate enough to match the experimental ones. There is an extensive literature discussing specific quantum chemical methods and models and the following section is intended to illustrate this, but we have not had the ambition to make a complete and critical literature review.

Quantum chemical studies have been made on the structure and constitution of actinide aqua-ions that allow comparison with experimental X-ray absorption spectroscopy data, EXAFS/XAS, in [2009BRE/BAN], [2009IKE/HEN], [2011DU/BOO], [2011CHA/DIA], High Energy X-ray Scattering, HEXS, in [2004NEU/SOD], and Raman data, in [2005CAO/BAL]. A useful review of the constitution and relative energies of $UO_2(OH_2)_n^{2+}$, $PuO_2(OH_2)_n^{2+}$, and $NpO_2(OH_2)_n^{2+}$ aqua complexes is given by Cao and Balasubramaian [2005CAO/BAL]. Davide and Vokhmin [2003DAV/VOK] have used a semi-empirical method to calculate ion entropies and Gibbs energies of solvation of $An^{4+}$ and $An^{3+}$ aqua-ions, which have been used to estimate the standard redox potential for the $U^{4+}/U^{3+}$ couple. Redox potentials of the $AnO_2^{2+}/AnO_2^{+}$ couple have been discussed in [1999VAL/MAR], [2000HAY/MAR], [2005SHA/SCH] and [2006TSU/WAH]. The mechanism of electron transfers in U(VI)-U(V) complexes has been discussed by Privalov *et al.* [2004PRI/MAC]. Other quantum chemical studies deal with the mechanism of water-exchange reactions in actinide aqua-ions ([2000FAR/GRE], [2001VAL/WAH], [2004VAL/PRI], [2008WAH/DAN]).

The constitution of $AnO_2^{2+}(aq)$ and $AnO_2^{+}(aq)$ ions, the enthalpy and Gibbs energy of solvation and the redox potential of $AnO_2^{2+}/AnO_2^{+}$ couples based on different quantum chemical methods are also discussed in [2004MOS/KRU], [2005MOS/MAT], [2005CAO/BAL], [2005GIB/HAI], [2012RAI/TIW], [2006SHA/SCH], [2007OST/ZEL], [2013POM/TIW]. As a review of the different chemical models and quantum chemical methods has been outside the scope of the present review, we have only made Appendix A comments on a few of these papers. The theory based structures are in general in good agreement with experimental data from EXAFS and other structure chemical methods, but this is rarely the case for thermodynamic data, an exception is reactions in gas-phase as discussed in Sections 9.3 and 9.4. The quantum chemical studies discussed provide information on the development of the field and indications of their possibilities for estimates of thermodynamic data. The following points might be of interest: Quantum chemical studies in general begin with a determination of structure(s) in gas phase and their electronic energy and vibration energy levels; when reactions in solutions are studied, these are followed by a calculation of "absolute" electronic energies and reaction energies in the solvent. This requires a model, in most studies, *e.g.* in water, the solvent is described as a dielectric continuum, characterised by a macroscopic dielectric permittivity. Other models are based on molecular dynamics where the solvent is described by an explicit number of water molecules and where the solvent-solute interactions are described using potential functions and solute-solute interactions based on quantum chemistry *e.g.* [2013POM/TIW]. The conclusion from [2013POM/TIW] is that all $AnO_2^{+}$ and $AnO_2^{2+}$ aqua-ions, An = U, Np, Pu, Am, have five water ligands coordinated in a plane perpendicular to the linear $AnO_2$-group. Other methods, like Car-Parrinello molecular dynamics and quantum mechanical charge field dynamics (QMCF-MD) have also been used and may give rise to different results, *e.g.* in the (QMCF-MD) study by Frick *et al.* [2009FRI/PRI], [2010FRI/HOF], the constitution of $UO_2^{+}(aq)$ is given as $UO_2(OH_2)_4^{+}$ while in the Car-Parrinello study by Atta-Fynn *et al.* [2012ATT/JOH] it is reported as $UO_2(OH_2)_5^{+}$; both studies report the same constitution of the U(IV) aqua-ion, $U(OH_2)_9^{4+}$.

### 9.2.1 $UO_2^{2+}$

There are no new thermodynamic data for the uranyl(VI) aqua-ion and those selected in [2003GUI/FAN] are retained. The constitution of $UO_2^{2+}(aq)$ in highly acidic non-complexing media has been discussed in both experimental studies and by using quantum chemical methods and the information is contradictory, but this review considers $UO_2(OH_2)_5^{2+}$ to be the most likely stable species, as it is supported by EXAFS data that provide the number of coordinated water ligands and the distances between U(VI) coordinated yl- and water oxygen that agree well with quantum chemistry calculations. However the experimental uncertainty in the coordination number is at best 10 %.

A different experimental method to study the hydration in $UO_2^{2+}(aq)$ has been described by Neuefind *et al.* [2004NEU/SOD] that determined the integrated electron density in $UO_2^{2+}(aq)$ and based on this, suggested that there is an equilibrium in solution between $UO_2(H_2O)_5^{2+}$ and $UO_2(H_2O)_4^{2+}$. Farkas *et al.* [2000FAR/BAN] studied the exchange Reaction (9.1) experimentally and determined its activation energy, $\Delta H^{\neq}(9.1) = (26.1 \pm 1.4)$ kJ·mol$^{-1}$. The same reaction was later studied by Vallet *et al.* [2001VAL/WAH], using quantum chemistry in which they compared dissociative and associative reaction mechanisms with the intermediates $UO_2(H_2O)_4^{2+}$ and $UO_2(H_2O)_6^{2+}$ respectively; they noted that the activation energy for the associative mechanism, $\Delta E_m^{\neq}$ = 18.7 kJ·mol$^{-1}$, was in much better agreement with the experiment than the one for the dissociative mechanism, $\Delta H_m^{\neq} = 74$ kJ·mol$^{-1}$, which suggests that $UO_2(H_2O)_4^{2+}$, if formed at all, is a minor species. Note that Reaction (9.1) is an isotope exchange reaction.

$$UO_2(OH_2)_n^{2+} + H_2O^* \rightleftharpoons UO_2(^*OH_2)_n^{2+} + H_2O \qquad (9.1)$$

Cao *et al.*, [2005CAO/BAL] have made a comprehensive study of the structure and relative energies of uranyl aqua-ions and conclude, in agreement with most other studies, that the U(VI) aqua-ion has the constitution $UO_2(H_2O)_5^{2+}$; based on all evidence presented, this review agrees.

Shamov and Schreckenbach [2005SHA/SCH] and Tsushima *et al.* [2006TSU/WAH] have estimated the redox potential of the $AnO_2^{2+}(aq)/AnO_2^{+}(aq)$ couples and report the following data in Table 9-1, where the experimental values are from [2003GUI/FAN] and the calculated data using two different estimates of the solvation energy.

Table 9-1: Estimated redox potentials for the $AnO_2^{2+}(aq)/AnO_2^{+}(aq)$, An = U, Np, Pu, Am obtained from [2005SHA/SCH] and [2006TSU/WAH] using quantum chemical methods. The experimental values are selected from NEA reviews.

| Redox couple data from [2005SHA/SCH] | Redox potential *vs.* NHE in V, exp. data | Calculated redox potential in V, model 1 | Calculated redox potential in V, model 2 |
|---|---|---|---|
| $UO_2^{2+}(aq)/UO_2^{+}(aq)$ | 0.088 | – 0.10 | – 0.51 |
| $NpO_2^{2+}(aq)/NpO_2^{+}(aq)$ | 1.16 | 1.72 | 0.87 |
| $PuO_2^{2+}(aq)/PuO_2^{+}(aq)$ | 0.94 | 0.91 | 0.43 |
| Data from [2006TSU/WAH] | | CASPT2 | CCSD(T) |
| | 0.088 | 0.003 | 0.082 |
| $NpO_2^{2+}(aq)/NpO_2^{+}(aq)$ | 1.16 | 1.525 | – |
| $PuO_2^{2+}(aq)/PuO_2^{+}(aq)$ | 0.94 | 0.730 | – |
| $AmO_2^{2+}(aq)/AmO_2^{+}(aq)$ | 1.59 | 1.984 | – |

CASPT2 and CCSD(T) denote coupled-cluster calculations, where the latter is considered as the "gold-standard" in quantum chemical calculations. The calculated redox potentials are given for information only.

### 9.2.2 $U^{4+}$ and $U^{3+}$

There are no new experimental thermodynamic data published since the review of Guillaumont *et al.*, [2003GUI/FAN], and the data selected there are retained by the present review. However, a number of theory based studies of interest for the present review have appeared. David and Vokhmin [2003DAV/VOK] have used a semi-empirical model to calculate Gibbs energies of formation and ion entropies for $An^{3+}$ and $An^{4+}$ ions, information that was used to calculate the NHE-redox potentials of the $U^{4+}/U^{3+}$ couple. The ion entropies are in fair agreement with those based on the data that were selected in [1992GRE/FUG] and [2003GUI/FAN], this is also true for the Gibbs energies of formation, as shown by the difference between the calculated and experimental redox potential for the $U^{4+}/U^{3+}$ couple, $E^{o}_{NHE}$(calc) = – 0.473 V, *vs.* $E^{o}_{NHE}$(exp) = – (0.553 ± 0.004) V.

The reduction of U(VI) by Fe(II) has been studied by Du and co-workers, [2011DU/BOO], confirming the current thermodynamic data for uranium and iron.

The constitution of $U^{4+}$(aq) has been studied in strongly acid solutions in a number of EXAFS experiments, [2009BRE/BAN], [2009IKE/HEN] and [2011DU/BOO], in which bond distances and coordination number of $[U(OH_2)_n]^{4+}$ are reported; the latter varies between nine and ten in the different studies. However, the uncertainty in the coordination number derived from EXAFS is at least 10 %, so the difference might be more apparent than real, which means that all studies are consistent with a coordination number (9 ± 1). The same constitution was obtained in the QM/MD studies of Frick *et al.* [2009FRI/PRI], [2010FRI/HOF] and Atta-Fynn *et al.* [2012ATT/JOH]. The present review notes that these coordination numbers are consistent with known coordination geometries, bi- and tri-capped trigonal prisms for 8- and 9-coordination and bi-capped square anti-prism for 10-coordination.

The water exchange between $U^{4+}$(aq) and water using $^{17}O$ enriched water, Reaction (9.2), was studied by Farkas *et al.* [2000FAR/GRE] that determined the activation enthalpy, $\Delta H^{\neq}_{m} = (36 \pm 4)$ kJ·mol$^{-1}$ and suggested a dissociative exchange mechanism, but the evidence for this is not considered conclusive by the present review.

$$U(OH_2)_n^{4+} + H_2O^* \rightleftharpoons U(^*OH_2)_n^{4+} + H_2O \qquad (9.2)$$

# 9.3 Uranium oxygen and hydrogen compounds and complexes

## 9.3.1 Gaseous uranium oxides and hydroxides

### 9.3.1.1 $UO_2^+(g)$ and $UO_2^{2+}(g)$

No thermodynamic data for these ions were reported in [1992GRE/FUG] and [2003GUI/FAN]. Gibson *et al.* [2005GIB/HAI] have published an experimental study of gas phase reactions involving $An^{2+}(g)$-ions, An = Th, U, Np, Pu, Am, that are oxidised to $AnO_2^{2+}(g)$, An = U, Np, Pu. Gibson *et al.* [2005GIB/HAI] and Marcus [1975MAR] report the enthalpy of formation of $UO_2^{2+}(g)$, $\Delta_f H_m^o(UO_2^{2+}, g, 298.15\,K)$ = (1524 ± 63) kJ·mol$^{-1}$ and $\Delta_f H_m^o(UO_2^{2+}, g, 298.15\,K)$ = 1210 kJ·mol$^{-1}$, respectively. As thermodynamic data for gaseous ions are not included in the NEA reviews, no value of $\Delta_f H_m^o(UO_2^{2+}, g, 298.15\,K)$ is included among the selected thermodynamic values. For the same reason, the energies of hydration of $UO_2^+(g)$ and $UO_2^{2+}(g)$, studied using quantum chemistry ([2004MOS/KRU], [2005MOS/MAT], [2005GIB/HAI]), have not been included.

### 9.3.1.2 Gaseous uranium hydroxides

#### 9.3.1.2.1 $UO_2(OH)_2(g)$

The gas phase molecule $UO_2(OH)_2(g)$ is of key importance to assess the volatility of uranium oxides in the presence of steam, as may occur during severe nuclear accidents. Based on experimental data using the transpiration method, Dhadwarkar *et al.* [1974DHA/TRI] concluded that Reaction (9.3) takes place in vapor phase above $U_3O_{(8-z)}(cr)$ at $P(H_2O$ = 0.030 atm; the experimental conditions), and that $UO_2(OH)_2(g)$ is formed via the gas-phase Reaction (9.5).

$$1/3U_3O_{(8-z)}(cr) + 1/6(1+z)O_2(g) \rightleftharpoons UO_3(g) \quad (9.3)$$

$$1/3U_3O_{(8-z)}(cr) + 1/6(1+z)O_2(g) + H_2O(g) \rightleftharpoons UO_2(OH)_2(g) \quad (9.4)$$

$$UO_3(g) + H_2O(g) \rightleftharpoons UO_2(OH)_2(g) \quad (9.5)$$

The thermodynamic data for $UO_2(OH)_2(g)$ was discussed in detail by Guillaumont *et al.* [2003GUI/FAN] based on experimental data from Dhadwarkar *et al.* [1974DHA/TRI] and a later study by Krikorian *et al.* [2002EBB/KRI]. Guillaumont *et al.* noted significant differences in the enthalpy of formation of $UO_2(OH)_2(g)$ based on different analyses of the experimental data and they suggested that these might be related to a potential problem with the thermal functions, which were based on estimated molecular parameters. In a recent study, Konings *et al.* [2017KON/KOV] have re-analysed the experimental data from Dhadwarkar *et al.* using an improved quantum chemical method to calculate the structure of $UO_2(OH)_2(g)$, its vibration energy levels and moment of inertia and from these the corresponding thermal functions; Konings *et al.*

note that the calculated vibration energy levels are in good agreement, within 4 %, with experimental data from Wang *et al.* [2006WAN/AND]. Based on the new thermal functions, Konings *et al*. report

$$S^{o}_{m}\,(298.15\ \mathrm{K}) = (352.3 \pm 3.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

and

$$C^{o}_{p,m}(T)/\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}} = 120.915 + 29.073\times10^{-3}(T/\mathrm{K}) - 11.495\times10^{-6}(T/\mathrm{K})^{2} + 2.6512\times10^{-9}(T/\mathrm{K})^{3} - 0.2780\times10^{-12}(T/\mathrm{K})^{4} - 1.9609\times10^{6}\,(T/\mathrm{K})^{-2}$$

fitted between 298.15 and 1500 K.

From these data they obtain for the change in Gibbs energy for Reaction (9.5)

$$\Delta_{r}G^{o}_{m}(T)/\mathrm{kJ{\cdot}mol^{-1}} = -(186.1\pm15.6) + (93.0\pm10.5)\times10^{-3}(T) \qquad (9.6)$$

Combining this energy of reaction with the Gibbs energy functions of $H_2O(g)$ and $UO_3(g)$ they obtain the enthalpy of formation, $\Delta_{f}H^{o}_{m}(UO_2(OH)_2, g, 298.15\ \mathrm{K})$ = – (1284 ± 11) kJ·mol$^{-1}$, which is close to the one based on a third-law analysis of the experimental data from Dhadwarkar *et al.* by Gorokhov and Sidorova, [1998GOR/SID],

$$\Delta_{f}H^{o}_{m}\,(UO_2(OH)_2,\ g,\ 298.15\ \mathrm{K}) = -\,(1291.8 \pm 10.4)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

Guillaumont *et al.* [2003GUI/FAN] conclude that "the unexplained large difference between the results of the similar studies by [1974DHA/TRI] and [1993KRI/EBB], plus the appreciably different thermal functions proposed and…the substantial differences in the second- and third law analyses…mean that no reliable data for this species can be selected…"; the present review agrees and notes that the discrepant results are not due to uncertainties in the thermal functions and that new experimental data are needed to obtain reliable values of the enthalpy and Gibbs energy of formation.

Privalov *et al.* [2003PRI/SCH] and Shamov and Schreckenbach [2007SHA/SCH] have used quantum chemical methods to study gas-phase reactions involving uranium oxides and hydroxides and their reactions with gaseous uranium fluorides, where the latter are discussed in Section 9.4.1. Privalov *et al.* calculated the enthalpy of reaction, $\Delta_{r}H^{o}_{m}$ (9.7) = – 166 kJ·mol$^{-1}$, and Shamov and Schreckenbach [2007SHA/SCH], $\Delta_{r}H^{o}_{m}$ (9.8) = 567.7 kJ·mol$^{-1}$, the latter is consistent with the value reported in [2003GUI/FAN], (571 ± 25) kJ·mol$^{-1}$.

$$UO_3(g) + H_2O(g) \rightleftharpoons UO_2(OH)_2(g) \qquad (9.7)$$

$$UO_3(g) \rightleftharpoons UO_2(g) + O(g) \qquad (9.8)$$

The enthalpy of formation of $UO_2(OH)_2(g)$ was discussed in [2003GUI/FAN], but as the experimental data were not in agreement, no value was selected. Using the enthalpy of reaction, $\Delta_{r}H^{o}_{m}$ (9.7) = – 166 kJ·mol$^{-1}$ and the selected enthalpies of formation of $UO_3(g)$ and $H_2O(g)$ from the NEA, this review obtains

$\Delta_f H_m^o(UO_2(OH_2), g) = -1207$ kJ·mol$^{-1}$, with an uncertainty of at least 25 kJ·mol$^{-1}$, which falls within the range of the experimental values discussed by Guillaumont *et al.* ([2003GUI/FAN], Table 9.2, p. 163), but not with the experimental data from Dhadwarkar *et al.* [1974DHA/TRI] and by Gorokhov and Sidorova, [1998GOR/SID]. No value is selected by the present review. This result confirms that quantum chemical calculation of thermodynamic quantities for gas-phase reactions are often in fair agreement, 5-10 %, with experimental data.

## 9.3.2 Aqueous uranium hydroxide complexes

As pointed out in previous reviews, [1992GRE/FUG] and [2003GUI/FAN], both the analysis of experimental data on hydroxide complexes and the choice of selected thermodynamic data are complicated by the presence of several complexes in comparable amounts in the test solutions from which the stoichiometry and equilibrium constants have to be determined. This is usually made by fitting different chemical models to an experimental quantity, such as the free hydrogen ion concentration, $-\log_{10}[H^+]$, by a least-squares program that provides equilibrium constants and their estimated uncertainty for the complexes in the model used; in addition these codes usually provide an overall measure of the fit between model and experiment. A problem is that the uniqueness of the model is rarely established and that only one model is reported, however additional data based on known coordination chemistry and structure data can give important additional information on possible stoichiometries, for example the complexes $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(O)(OH)_3^+ \equiv (UO_2)_3(OH)_5^+$ have been identified both in solid compounds and solution using X-ray diffraction. The complexes $(UO_2)_3(OH)_n^{6-n}$, $n$ = 4, 5, 6, 7 and 8, can all be considered based on three uranyl-units linked by hydroxide bridges to form a triangular unit. On the other hand the complex $(UO_2)_4(OH)_7^+$ is not consistent with any known structure.

### 9.3.2.1 U(VI) hydroxide complexes

Since the publication of the previous review [2003GUI/FAN], a number of new studies on aqueous uranium hydroxide complexes have been published. Some of these do not contain experimentally determined thermodynamic data but are commented in Appendix A. Equilibrium constants of the hydrolysis reactions of U(VI) were reported under a wide range of experimental conditions, including different ionic media (NaCl, $NaNO_3$, $NaClO_4$, KCl, LiCl, $LiClO_4$, TMA($NO_3$)—*i.e.* tetramethyl ammoniumnitrate, TEA($ClO_4$)—*i.e.* tetraethyl ammoniumperchlorate, $CaCl_2$, and $MgCl_2$), ionic strength (0.1-5.0 M), and temperature (1-100 °C) [2002DES/GIA], [2003SAW/SHA], [2004CRE/DES], [2004GIA/MIL], [2004ZAN/DIB], [2005CRE/MIL], [2008AMO/GAM], [2009TEK/ACA], [2012ZAN/DIB], [2014ZAN/DIB], [2016DRO/BAU], and [2017ALT/YAL].

The experimental equilibrium constants of U(VI) hydrolysis that have been published since the previous review [2003GUI/FAN] are summarised in Table 9-2.

These data were critically evaluated in the present review and compared with the selected values in [1992GRE/FUG] and [2003GUI/FAN].

[2002DES/GIA] and [2004GIA/MIL] have studied hydrolysis using chloride or nitrate as the ionic media, systems where weak complexes are formed with the ionic media anions. In these, there is always an issue if they should be described by equilibrium constants, or using an ion-interaction model like SIT. We have used the conditional hydrolysis constants in [2002DES/GIA] to conduct a SIT analysis of the data in [2002DES/GIA] for the (1,1), (2,2) and (n,3) hydrolysis reactions that are shown in Figure 9-1, Figure 9-2, and Figure 9-3, respectively. The resulting values of $\log_{10}{}^{*}\beta^{o}_{n,m}$ from this analysis are identical, within their estimated uncertainties in both the chloride and nitrate systems and nearly identical with the selected values in previous NEA TDB reviews ([1992GRE/FUG], [2003GUI/FAN]). However, the ion interaction parameters derived from the $\Delta\varepsilon$-values of [2002DES/GIA] and [2004GIA/MIL] differ from those previously selected that were all based on experimental data in mixed $Cl^-/ClO_4^-$ and $NO_3^-/ClO_4^-$ media. As discussed in the Appendix A review, these differences in the ionic media make it difficult to make corrections for chloride and nitrate complexes in the pure chloride and nitrate media. Nevertheless, the SIT type plots from [2002DES/GIA] provide a good estimate of the equilibrium constants at zero ionic strength. The values of $\Delta\varepsilon$ derived from [2002DES/GIA] (as well as [2004GIA/MIL]) are empirical parameters that cannot be used to obtain individual ion interaction parameters.

Table 9-2: New experimental equilibrium constants for the aqueous equilibria: $m\mathrm{UO_2^{2+}} + n\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{UO_2})_m(\mathrm{OH})_n^{2m-n} + n\mathrm{H^+}$, $\beta^{*}_{n,m} = [(\mathrm{UO_2})_m(\mathrm{OH})_n^{2m-n}][\mathrm{H^+}]^n/[\mathrm{UO_2^{2+}}]^m$. These constants are discussed in the following sections.

| *n:m* | *t* /°C | Method | *I* /medium | $\log_{10}{}^{*}\beta_{n,m}$ | Reference |
|---|---|---|---|---|---|
| 1:1 | 25 | pot | 0.10 M NaCl | – (5.45 ± 0.03) | [2002DES/GIA] |
| | | | 0.25 M NaCl | – (5.57 ± 0.03) | |
| | | | 0.50 M NaCl | – (5.72 ± 0.02) | |
| | | | 0.75 M NaCl | – (5.84 ± 0.03) | |
| | | | 1.00 M NaCl | – (5.96 ± 0.03) | |
| | | | 2.00 M NaCl | – (6.43 ± 0.05) | |
| | | | 3.00 M NaCl | – (6.92 ± 0.05) | |
| | | | 4.50 M NaCl | – (7.73 ± 0.05) | |
| | | | 0.10 M $NaNO_3$ | – (5.38 ± 0.03) | |
| | | | 0.25 M $NaNO_3$ | – (5.42 ± 0.03) | |
| | | | 0.50 M $NaNO_3$ | – (5.41 ± 0.03) | |
| | | | 0.75 M $NaNO_3$ | – (5.37 ± 0.05) | |
| | | | 1.00 M $NaNO_3$ | – (5.33 ± 0.07) | |

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Table 9-2 (continued)

| *n:m* | *t* /°C | Method | *I* /medium | $\log_{10}{}^{*}\beta_{n,m}$ | Reference |
|---|---|---|---|---|---|
| | 25 | | $I = 0$ | – (5.19 ± 0.05) | [2002DES/GIA] |
| | 25 | cal | 1.00 M $NaClO_4$ | – (5.2 ± 0.2) | [2004CRE/DES] |
| | 10 | pot | 0.10 M $TEA(ClO_4)$[(a)] | – (6.1 ± 0.3) | [2004ZAN/DIB] |
| | 25 | | | – (5.58 ± 0.24) | |
| | 40 | | | – (5.11 ± 0.11) | |
| | 55 | | | – (5.07 ± 0.24) | |
| | 70 | | | – (4.51 ± 0.11) | |
| | 85 | | | – (4.24 ± 0.15) | |
| | 25 | pot | 0.16 M $NaNO_3$ | – (5.79 ± 0.12) | [2005CRE/MIL] |
| | 25 | pot | 0.10 M KCl | – (5.54 ± 0.35) | [2009TEK/ACA] |
| | 37 | | | – (5.33 ± 0.03) | |
| | 45 | | | < 0 | |
| | 25 | pot | 0.10 M $TMA(NO_3)$[(b)] | – (5.20 ± 0.10) | [2012ZAN/DIB] [2014ZAN/DIB] |
| | 1 | fluo | 1.0 M $NaClO_4$ | – (4.6 ± 0.3) | [2016DRO/BAU] |
| | 25 | | $I = 0$ | – (3.9 ± 0.5) | [2016DRO/BAU] |
| | 25 | | $I = 0$ | – (5.2 ± 0.3) | Recal. by this review |
| | 25 | | $I = 0$ | – (5.25 ± 0.24) | [2003GUI/FAN] |
| 2:1 | 1 | fluo | 1.0 M $NaClO_4$ | – (12.2 ± 0.5) | [2016DRO/BAU] |
| | 25 | | $I = 0$ | – (10.9 ± 0.5) | [2016DRO/BAU] |
| | 25 | | $I = 0$ | – (13.5 ± 0.7) | Recal. by this review |
| | 25 | | $I = 0$ | – (12.15 ± 0.07) | [2003GUI/FAN] |
| 3:1 | 25 | pot | 0.10 M $TMA(NO_3)$[(b)] | – (18.75 ± 0.22) | [2012ZAN/DIB] |
| | | | | – (18.81 ± 0.17) | [2014ZAN/DIB] |
| | 1 | fluo | 1.0 M $NaClO_4$ | – (22.3 ± 0.6) | [2016DRO/BAU] |
| | 25 | | $I = 0$ | – (20.7 ± 0.7) | [2016DRO/BAU] |
| | 25 | | $I = 0$ | – (21.1 ± 0.9) | Recal. by this review |
| | 25 | sol | $I = 0$ | – (20.7 ± 0.4) | [2017ALT/YAL] |
| | 25 | | $I = 0$ | – (20.25 ± 0.42) | [2003GUI/FAN] |
| 4:1 | 25 | pot | 0.10 M $TMA(NO_3)$[(b)] | – (31.25 ± 0.50) | [2014ZAN/DIB] |
| | 25 | sol | $I = 0$ | – (31.9 ± 0.2) | [2017ALT/YAL] |
| | 25 | | $I = 0$ | – (32.40 ± 0.68) | [2003GUI/FAN] |
| 1:2 | 25 | pot | 0.16 M $NaNO_3$ | – (3.83 ± 0.05) | [2005CRE/MIL] |
| 2:2 | 25 | pot | 0.10 M NaCl | – (5.98 ± 0.03) | [2002DES/GIA] |
| | | | 0.25 M NaCl | – (6.06 ± 0.02) | |
| | | | 0.50 M NaCl | – (6.14 ± 0.02) | |
| | | | 0.75 M NaCl | – (6.19 ± 0.02) | |
| | | | 1.00 M NaCl | – (6.24 ± 0.02) | |
| | | | 2.00 M NaCl | – (6.41 ± 0.03) | |
| | | | 3.00 M NaCl | – (6.60 ± 0.03) | |
| | | | 4.50 M NaCl | – (6.98 ± 0.04) | |
| | | | 0.10 M $NaNO_3$ | – (5.98 ± 0.02) | |
| | | | 0.25 M $NaNO_3$ | – (6.04 ± 0.02) | |
| | | | 0.50 M $NaNO_3$ | – (6.09 ± 0.03) | |
| | | | 0.75 M $NaNO_3$ | – (6.12 ± 0.04) | |

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Table 9-2 (continued)

| *n:m* | *t* /°C | Method | *I* /medium | $\log_{10}{}^{*}\beta_{n,m}$ | Reference |
|---|---|---|---|---|---|
| | | | 1.00 M $NaNO_3$ | – (6.13 ± 0.05) | |
| | 25 | | $I = 0$ | – (5.76 ± 0.04) | [2002DES/GIA] |
| | 25 | cal | 1.00 M $NaClO_4$ | – (5.95 ± 0.05) | [2004CRE/DES] |
| | 25 | pot | 1.00 M $NaClO_4$ | – (6.15 ± 0.05) | [2003SAW/SHA] |
| | 25 | pot | 0.15 M LiCl | – (6.18 ± 0.02) | [2004GIA/MIL] |
| | | | 1.0 M LiCl | – (6.32 ± 0.02) | |
| | | | 2.0 M LiCl | – (6.55 ± 0.02) | |
| | | | 3.0 M LiCl | – (6.77 ± 0.01) | |
| | 25 | pot | 0.05 M $CaCl_2$ | – (6.02 ± 0.05) | [2004GIA/MIL] |
| | | | 0.10 M $CaCl_2$ | – (6.10 ± 0.05) | |
| | | | 0.20 M $CaCl_2$ | – (6.19 ± 0.05) | |
| | 25 | pot | 0.05 M $MgCl_2$ | – (6.05 ± 0.05) | [2004GIA/MIL] |
| | | | 0.10 M $MgCl_2$ | – (6.14 ± 0.05) | |
| | | | 0.20 M $MgCl_2$ | – (6.27 ± 0.05) | |
| | 10 | pot | 0.10 M TEA($ClO_4$)[(a)] | – (6.30 ± 0.02) | [2004ZAN/DIB] |
| | 25 | | | – (5.83 ± 0.02) | |
| | 40 | | | – (5.43 ± 0.01) | |
| | 55 | | | – (5.06 ± 0.03) | |
| | 70 | | | – (4.73 ± 0.03) | |
| | 85 | | | – (4.49 ± 0.03) | |
| | 25 | pot | 0.16 M $NaNO_3$ | – (5.932 ± 0.002) | [2005CRE/MIL] |
| | 75 | coul-pot | 3.6 m $LiClO_4$ | – (5.36 ± 0.02) | [2008AMO/GAM] |
| | 100 | | | – (4.90 ± 0.02) | |
| | 25 | pot | 0.1 M KCl | – (5.60 ± 0.24) | [2009TEK/ACA] |
| | 37 | | | – (5.42 ± 0.28) | |
| | 45 | | | – (4.97 ± 0.42) | |
| | 25 | pot | 0.10 M TMA($NO_3$)[(b)] | – (5.95 ± 0.03) | [2012ZAN/DIB] |
| | | | | – (5.94 ± 0.03) | [2014ZAN/DIB] |
| | 25 | | $I = 0$ | – (5.62 ± 0.04) | [2003GUI/FAN] |
| 3:2 | 75 | coul-pot | 3.6 m $LiClO_4$ | – (8.70 ± 0.03) | [2008AMO/GAM] |
| | 100 | | | – (8.37 ± 0.05) | |
| 3:3 | 75 | coul-pot | 3.6 m $LiClO_4$ | – (7.42 ± 0.02) | [2008AMO/GAM] |
| | 100 | | | – (6.68 ± 0.08) | |
| 4:3 | 25 | pot | 0.10 M NaCl | – (12.22 ± 0.05) | [2002DES/GIA] |
| | | | 0.25 M NaCl | – (12.33 ± 0.04) | |
| | | | 0.50 M NaCl | – (12.38 ± 0.04) | |
| | | | 0.75 M NaCl | – (12.40 ± 0.03) | |
| | | | 1.00 M NaCl | – (12.41 ± 0.04) | |
| | | | 2.00 M NaCl | – (12.44 ± 0.05) | |
| | | | 3.00 M NaCl | – (12.57 ± 0.05) | |
| | | | 4.50 M NaCl | – (13.01 ± 0.07) | |
| | | | 0.10 M $NaNO_3$ | – (12.29 ± 0.05) | |
| | | | 0.25 M $NaNO_3$ | – (12.50 ± 0.04) | |
| | | | 0.50 M $NaNO_3$ | – (12.73 ± 0.04) | |
| | | | 0.75 M $NaNO_3$ | – (12.90 ± 0.04) | |
| | | | 1.00 M $NaNO_3$ | – (13.06 ± 0.06) | |
| | 25 | | $I = 0$ | – (11.82 ± 0.08) | [2002DES/GIA] |
| | 25 | pot | 0.15 M LiCl | – (12.44 ± 0.01) | [2004GIA/MIL] |
| | | | 1.0 M LiCl | – (12.53 ± 0.03) | |

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Table 9-2 (continued)

| *n*:*m* | *t* /°C | Method | *I* /medium | $\log_{10}{}^{*}\beta_{n,m}$ | Reference |
|---|---|---|---|---|---|
| | | | 2.0 M LiCl | – (12.66 ± 0.02) | |
| | | | 3.0 M LiCl | – (12.88 ± 0.02) | |
| | 25 | pot | 0.05 M $CaCl_2$ | – (12.23 ± 0.07) | [2004GIA/MIL] |
| | | | 0.10 M $CaCl_2$ | – (12.24 ± 0.07) | |
| | | | 0.20 M $CaCl_2$ | – (12.21 ± 0.07) | |
| | 25 | pot | 0.05 M $MgCl_2$ | – (12.24 ± 0.07) | [2004GIA/MIL] |
| | | | 0.10 M $MgCl_2$ | – (12.28 ± 0.07) | |
| | | | 0.20 M $MgCl_2$ | – (12.24 ± 0.07) | |
| | 25 | pot | 0.16 M $NaNO_3$ | – (12.79 ± 0.01) | [2005CRE/MIL] |
| | 25 | pot | 0.10 M KCl | – (11.21 ± 0.31) | [2009TEK/ACA] |
| | 37 | | | – (11.36 ± 0.03) | |
| | 45 | | | – (11.81 ± 0.40) | |
| | 25 | pot | 0.10 M TMA$(NO_3)$[(b)] | – (12.25 ± 0.08) | [2012ZAN/DIB] [2014ZAN/DIB] |
| | 25 | | $I = 0$ | – (11.90 ± 0.30) | [2003GUI/FAN] |
| 5:3 | 25 | pot | 0.10 M NaCl | – (16.55 ± 0.04) | [2002DES/GIA] |
| | | | 0.25 M NaCl | – (16.76 ± 0.03) | |
| | | | 0.50 M NaCl | – (16.93 ± 0.03) | |
| | | | 0.75 M NaCl | – (17.04 ± 0.03) | |
| | | | 1.00 M NaCl | – (17.13 ± 0.03) | |
| | | | 2.00 M NaCl | – (17.44 ± 0.05) | |
| | | | 3.00 M NaCl | – (17.81 ± 0.05) | |
| | | | 4.50 M NaCl | – (18.57 ± 0.04) | |
| | | | 0.10 M $NaNO_3$ | – (16.52 ± 0.03) | |
| | | | 0.25 M $NaNO_3$ | – (16.70 ± 0.03) | |
| | | | 0.50 M $NaNO_3$ | – (16.80 ± 0.03) | |
| | | | 0.75 M $NaNO_3$ | – (16.83 ± 0.04) | |
| | | | 1.00 M $NaNO_3$ | – (16.83 ± 0.06) | |
| | | | $I = 0$ | – (15.89 ± 0.06) | [2002DES/GIA] |
| | 25 | cal | 1.00 M $NaClO_4$ | – (16.2 ± 0.1) | [2004CRE/DES] |
| | 25 | pot | 0.15 M LiCl | – (17.09 ± 0.03) | [2004GIA/MIL] |
| | | | 1.0 M LiCl | – (17.45 ± 0.03) | |
| | | | 2.0 M LiCl | – (18.07 ± 0.01) | |
| | | | 3.0 M LiCl | – (18.72 ± 0.05) | |
| | 25 | pot | 0.05 M $CaCl_2$ | – (16.64 ± 0.04) | [2004GIA/MIL] |
| | | | 0.10 M $CaCl_2$ | – (16.68 ± 0.04) | |
| | | | 0.20 M $CaCl_2$ | – (17.00 ± 0.04) | |
| | 25 | pot | 0.05 M $MgCl_2$ | – (16.67 ± 0.04) | [2004GIA/MIL] |
| | | | 0.10 M $MgCl_2$ | – (16.85 ± 0.04) | |
| | | | 0.20 M $MgCl_2$ | – (17.08 ± 0.04) | |
| | 10 | pot | 0.10 M TEA$(ClO_4)$[(a)] | – (17.52 ± 0.01) | [2004ZAN/DIB] |
| | 25 | | | – (16.37 ± 0.02) | |
| | 40 | | | – (15.35 ± 0.01) | |
| | 55 | | | – (14.45 ± 0.02) | |
| | 70 | | | – (13.61 ± 0.02) | |
| | 85 | | | – (12.94 ± 0.02) | |
| | 25 | pot | 0.16 M $NaNO_3$ | – (16.457 ± 0.007) | [2005CRE/MIL] |
| | 25 | pot | 0.1 M KCl | – (16.07 ± 0.16) | [2009TEK/ACA] |
| | 37 | | | – (15.66 ± 0.45) | |

(Continued on next page)

Table 9-2 (continued)

| *n:m* | *t* /°C | Method | *I* /medium | $\log_{10}{}^{*}\beta_{n,m}$ | Reference |
|---|---|---|---|---|---|
| | 45 | | | – (15.04 ± 0.85) | |
| | 25 | pot | 0.10 M $TMA(NO_3)$[(b)] | – (16.43 ± 0.02) | [2012ZAN/DIB] [2014ZAN/DIB] |
| | 25 | | $I = 0$ | – (15.55 ± 0.12) | [2003GUI/FAN] |
| 6:3 | 25 | pot | 0.10 M $TMA(NO_3)$[(b)] | – (22.68 ± 0.23) | [2012ZAN/DIB] |
| | | | | – (22.69 ± 0.23) | [2014ZAN/DIB] |
| 7:3 | 25 | pot | 0.10 M NaCl | – (29.68 ± 0.09) | [2002DES/GIA] |
| | | | 0.25 M NaCl | – (29.77 ± 0.08) | |
| | | | 0.50 M NaCl | – (29.79 ± 0.07) | |
| | | | 0.75 M NaCl | – (29.79 ± 0.07) | |
| | | | 1.00 M NaCl | – (29.80 ± 0.07) | |
| | | | 2.00 M NaCl | – (29.93 ± 0.10) | |
| | | | 3.00 M NaCl | – (30.35 ± 0.10) | |
| | | | 4.50 M NaCl | – (31.58 ± 0.16) | |
| | | | 0.10 M $NaNO_3$ | – (29.57 ± 0.10) | |
| | | | 0.25 M $NaNO_3$ | – (29.62 ± 0.07) | |
| | | | 0.50 M $NaNO_3$ | – (29.58 ± 0.10) | |
| | | | 0.75 M $NaNO_3$ | – (29.48 ± 0.09) | |
| | | | 1.00 M $NaNO_3$ | – (29.39 ± 0.12) | |
| | 25 | | $I = 0$ | – (29.26 ± 0.10) | [2002DES/GIA] |
| | 25 | pot | 0.15 M LiCl | – (29.93 ± 0.04) | [2004GIA/MIL] |
| | | | 1.0 M LiCl | – (29.99 ± 0.09) | |
| | | | 2.0 M LiCl | – (30.16 ± 0.05) | |
| | | | 3.0 M LiCl | – (30.28 ± 0.02) | |
| | 25 | pot | 0.05 M $CaCl_2$ | – (29.75 ± 0.10) | [2004GIA/MIL] |
| | | | 0.10 M $CaCl_2$ | – (29.86 ± 0.10) | |
| | | | 0.20 M $CaCl_2$ | – (29.97 ± 0.10) | |
| | 25 | pot | 0.05 M $MgCl_2$ | – (29.99 ± 0.10) | [2004GIA/MIL] |
| | | | 0.10 M $MgCl_2$ | – (30.33 ± 0.10) | |
| | | | 0.20 M $MgCl_2$ | – (30.85 ± 0.10) | |
| | 25 | pot | 0.16 M $NaNO_3$ | – (28.58 ± 0.05) | [2005CRE/MIL] |
| | 25 | pot | 0.10 M $TMA(NO_3)$[(b)] | – (28.95 ± 0.12) | [2012ZAN/DIB] |
| | | | | – (28.97 ± 0.07) | [2014ZAN/DIB] |
| | 25 | | $I = 0$ | – (32.20 ± 0.80) | [2003GUI/FAN] |
| 8:3 | 25 | pot | 0.10 M $TMA(NO_3)$[(b)] | – (38.91 ± 0.17) | [2012ZAN/DIB] |
| | | | | – (38.84 ± 0.14) | [2014ZAN/DIB] |
| 6:4 | 25 | pot | 1.00 M $NaClO_4$ | – (18.43 ± 0.09) | [2003SAW/SHA] |
| 7:4 | 25 | pot | 1.00 M $NaClO_4$ | – (23.36 ± 0.07) | [2003SAW/SHA] |
| | 25 | | $I = 0$ | – (21.9 ± 1.0) | [2003GUI/FAN] |

(a) $TEA(ClO_4)$—tetraethylammonium perchlorate.
(b) $TMA(NO_3)$—tetramethylammonium nitrate.

In four studies, [2004CRE/DES], [2004ZAN/DIB], [2009TEK/ACA], and [2014ZAN/DIB], the enthalpies of hydrolysis of U(VI) were determined either by titration calorimetry ([2004CRE/DES], [2004ZAN/DIB], and [2014ZAN/DIB]), or by the Van't Hoff method based on the temperature dependency of equilibrium constants ([2004ZAN/DIB] and [2009TEK/ACA]). The paper by Zanonato *et al.* [2004ZAN/DIB]

is the only study in which the enthalpy of hydrolysis was determined at different temperatures (10-85 °C) and in which the heat capacity of hydrolysis, $\Delta_r C_{p,m}$ was reported.

The enthalpies of hydrolysis of U(VI) that have been published since the previous review [2003GUI/FAN] are summarised in Table 9-3. The experimental values of the enthalpy of hydrolysis were critically evaluated and corrected to the values at $I = 0$ in the present review, *cf.* Table 9-9.

Table 9-3: New experimental data of enthalpy of hydrolysis for the aqueous equilibria: $mUO_2^{2+} + nH_2O(l) \rightleftharpoons (UO_2)_m(OH)_n^{2m-n} + nH^+$.

| *n*:*m* | *t* /°C | Method | *I* /medium | $\Delta H_{n,m}$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| 1:1 | 25 | cal | 0.10 M NaCl | (42.7 ± 2.3) | [2004CRE/DES] |
| | | | 0.50 M NaCl | (40.2 ± 0.5) | |
| | | | 1.00 M NaCl | (35.0 ± 5.0) | |
| | | | 1.00 M $NaClO_4$ | (37 ± 7) | |
| | | | $I = 0$ | (40.7 ± 2.9) | [2004CRE/DES] |
| | 10-85 | pot | 0.10 M TEA($ClO_4$)[(a)] | (46.5 ± 3.7) | [2004ZAN/DIB] |
| | 85 | cal | 0.10 M TEA($ClO_4$)[(a)] | (58 ± 7) | [2004ZAN/DIB] |
| 3:1 | 25 | cal | 0.10 M TMA($NO_3$)[(b)] | (93.7 ± 1.8) | [2014ZAN/DIB] |
| 4:1 | 25 | cal | 0.10 M TMA($NO_3$)[(b)] | (167.6 ± 1.7) | [2014ZAN/DIB] |
| 2:2 | 25 | cal | 0.10 M NaCl | (47.2 ± 0.5) | [2004CRE/DES] |
| | | | 0.50 M NaCl | (43.9 ± 1.9) | |
| | | | 1.00 M NaCl | (43.8 ± 1.5) | |
| | | | 1.00 M $NaClO_4$ | (44.2 ± 1.0) | |
| | | | $I = 0$ | (47.8 ± 1.3) | [2004CRE/DES] |
| | 10 | cal | 0.10 M TEA($ClO_4$) [(a)] | (51.5 ± 0.9) | [2004ZAN/DIB] |
| | 25 | | | (48.2 ± 1.7) | |
| | 40 | | | (50 ± 2) | |
| | 55 | | | (53 ± 8) | |
| | 70 | | | (58 ± 3) | |
| | 85 | | | (61 ± 2) | |
| | 25-45 | pot | 1.0 M KCl | (85.0 ± 20.2) | [2009TEK/ACA] |
| | 25 | cal | 0.10 M TMA($NO_3$) [(b)] | (49.1 ± 0.9) | [2014ZAN/DIB] |
| 4:3 | 25 | cal | 0.10 M NaCl | (97.9 ± 0.5) | [2004CRE/DES] |
| | | | 0.50 M NaCl | (93 ± 1) | |
| | | | 1.00 M NaCl | (89.5 ± 0.6) | |
| | | | $I = 0$ | (98.9 ± 0.5) | [2004CRE/DES] |
| | 25 | cal | 0.10 M TMA($NO_3$) [(b)] | (94.2 ± 3.0) | [2014ZAN/DIB] |
| 5:3 | 25 | cal | 0.10 M NaCl | (118.8 ± 0.6) | [2004CRE/DES] |
| | | | 0.50 M NaCl | (112.1 ± 1.7) | |
| | | | 1.00 M NaCl | (108.5 ± 0.5) | |
| | | | 1.00 M $NaClO_4$ | (106.6 ± 0.5) | |
| | | | $I = 0$ | (119.5 ± 2.0) | [2004CRE/DES] |
| | 10 | cal | 0.10 M TEA($ClO_4$) [(a)] | (128.0 ± 0.5) | [2004ZAN/DIB] |
| | 25 | | | (120.1 ± 1.6) | |
| | 40 | | | (119 ± 2) | |
| | 55 | | | (113 ± 7) | |
| | 70 | | | (112 ± 3) | |
| | 85 | | | (110 ± 2) | |

(Continued on next page)

Table 9-3 (continued)

| *n*:*m* | *t* /°C | Method | *I* /medium | $\Delta H_{n,m}$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| | 25-45 | pot | 1.0 M KCl | (171.6 ± 5.1) | [2009TEK/ACA] |
| | 25 | cal | 0.10 M TMA($NO_3$ (b) | (123.5 ± 1.0) | [2014ZAN/DIB] |
| 6:3 | 25 | cal | 0.10 M TMA($NO_3$)(b) | (132.2 ± 4.0) | [2014ZAN/DIB] |
| 7:3 | 25 | cal | 0.10 M NaCl | (176 ± 6) | [2004CRE/DES] |
| | | | 0.50 M NaCl | (166 ± 6) | |
| | | | 1.00 M NaCl | (158 ± 6) | |
| | | | $I$ = 0 | (177 ± 7) | [2004CRE/DES] |
| | 25 | cal | 0.10 M TMA($NO_3$)(b) | (198.2 ± 2.1) | [2014ZAN/DIB] |
| 8:3 | 25 | cal | 0.10 M TMA($NO_3$)(b) | (230.2 ± 2.7) | [2014ZAN/DIB] |

(a) TEA($ClO_4$)—tetraethylammonium perchlorate.
(b) TMA($NO_3$)—tetramethylammonium nitrate.

#### 9.3.2.1.1 Monomeric hydrolysis species at 298.15 K

Most equilibrium constants for monomeric $UO_2(OH)_n^{2-n}$ species are based on potentiometric studies using test solutions in which polynuclear complexes, $(UO_2)_m(OH)_n^{2m-n}$, are predominant. Despite this, a consistent set of equilibrium constants for the monomers has been reported. Previous NEA reviews, [1992GRE/FUG] and [2003GUI/FAN], selected equilibrium constants for four monomeric hydrolysis species of U(VI), including (1,1), (2,1), (3,1), and (4,1), represented by Reactions (9.9), (9.10), (9.11), and (9.12):

$$UO_2^{2+} + H_2O(l) \rightleftharpoons UO_2OH^+ + H^+ \quad (9.9)$$

$$UO_2^{2+} + 2H_2O(l) \rightleftharpoons UO_2(OH)_2(aq) + 2H^+ \quad (9.10)$$

$$UO_2^{2+} + 3H_2O(l) \rightleftharpoons UO_2(OH)_3^- + 3H^+ \quad (9.11)$$

$$UO_2^{2+} + 4H_2O(l) \rightleftharpoons UO_2(OH)_4^{2-} + 4H^+ \quad (9.12)$$

The selection of equilibrium constants for the hydrolysis of U(VI) in previous reviews is based mainly on studies by potentiometry. However, information obtained by independent methods is important to validate the uniqueness of the hydrolysis model, in particular if this has been obtained under conditions where the concentration of polynuclear complexes is negligible. Since the previous NEA reviews, there have been nine new experimental studies that report equilibrium constants for the U(VI) monomeric hydrolysis species ([2002DES/GIA], [2004CRE/DES], [2004ZAN/DIB], [2005CRE/MIL], [2009TEK/ACA], [2012ZAN/DIB], [2014ZAN/DIB], [2016DRO/BAU], [2017ALT/YAL]). Among these, the first seven studies are based on potentiometry in conjunction with calorimetry, while the two most recent studies, [2016DRO/BAU] and [2017ALT/YAL], are based on the data from fluorescence spectroscopy and solubility measurements, respectively.

The study of [2016DRO/BAU] was conducted by using time-resolved fluorescence spectroscopy in a 1 M $NaClO_4$ ionic medium that allowed identification of separate emission bands for $UO_2(OH)_n^{2-n}$ ($n$ = 1-3) at a total concentration of U(VI) ≈ $10^{-8}$ M. The study in [2017ALT/YAL] used solubility measurements, where the low solubility made it possible to identify $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$. These studies, as well as the ones based on potentiometry/calorimetry, have been discussed in detail in the corresponding Appendix A entries. This review notes that there is a significant difference in the equilibrium constants in the alkaline range obtained in the potentiometric studies and by fluorescence spectroscopy and solubility measurements; the difference is most pronounced for the data obtained in tetra-alkylammonium media and the conclusion from this review is that the final selection should not be based on the potentiometric data, in which the concentrations of the (3,1) and (7,3) complexes are very low with a resulting difficulty to select a proper chemical model.

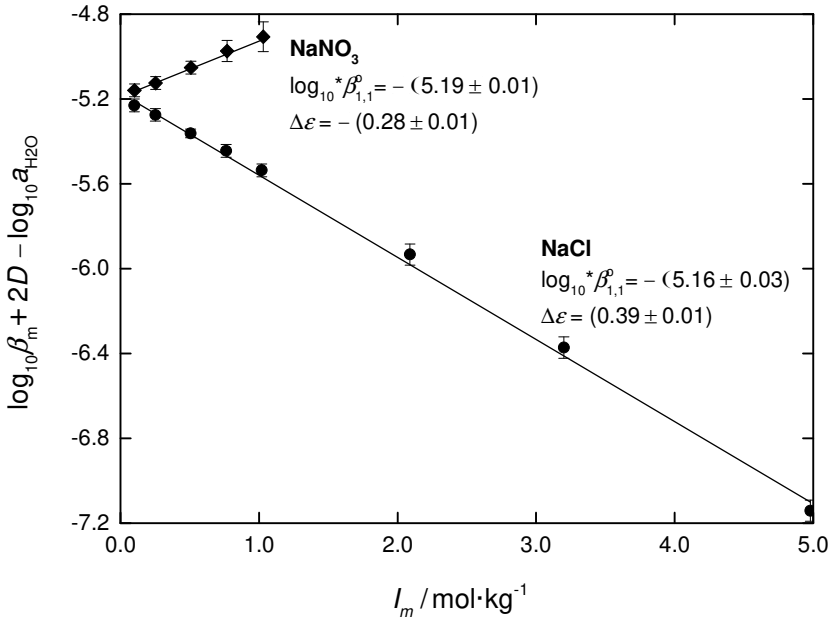
#### 9.3.2.1.1.1 $UO_2OH^+$

Using potentiometry, De Stefano *et al.* [2002DES/GIA] studied the hydrolysis of U(VI) in aqueous NaCl (0.1-4.5 M) and $NaNO_3$ (0.1-1 M) solutions with pH < 6 at $t$ = 25 °C. The model used to fit the data includes the (1,1) species, $UO_2OH^+$, and a number of polymeric species including $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, and $(UO_2)_3(OH)_7^-$. The equilibrium constants obtained for the NaCl and $NaNO_3$ media at different ionic strengths were then used to calculate those at infinite dilution by using a Debye-Hückel type equation using a polynomial expression of the ionic strength ($L(I) = CI + DI^{1.5} + EI^2$), where $C$, $D$ and $E$ are empirical parameters obtained by fitting. The value of $\log_{10} {}^*\beta^o_{n,m}$ for $UO_2OH^+$ was calculated to be – (5.19 ± 0.05), in good agreement with the value selected in [2003GUI/FAN], $\log_{10} {}^*\beta^o_{1,1}$ = – (5.25 ± 0.24).

The experimental data in [2002DES/GIA] were re-analysed with the standard SIT-method in this review by using the conditional equilibrium constants from [2002DES/GIA]. Hydrolysis equilibrium constants at infinite dilution and the associated ion interaction coefficients for the equilibrium ($\Delta\varepsilon$) were calculated as described below.

For the (1,1) species $UO_2OH^+$, the analysis of the data in [2002DES/GIA] is shown in the SIT plot in Figure 9-1. The value of $\log_{10} {}^*\beta^o_{1,1}$ was determined to be – (5.16 ± 0.03) and – (5.19 ± 0.01) from the data in NaCl and $NaNO_3$ ionic media, respectively. These values agree with the value – (5.25 ± 0.24) selected by [2003GUI/FAN].

Figure 9-1: SIT plots for the reaction $UO_2^{2+} + H_2O(l) \rightleftharpoons UO_2OH^+ + H^+$, with the data from [2002DES/GIA] without correction for the complexation of U(VI) with chloride or nitrate. The solid lines represent the best fits.




Several experimental values of $\log_{10}{}^{*}\beta_{1,1}$ at 298.15 K in other ionic media were reported in the literature, including – (5.2 ± 0.2) in 1.00 M $NaClO_4$ determined by calorimetry [2004CRE/DES], – (5.58 ± 0.24) in 0.10 M TEA($ClO_4$) by potentiometry [2004ZAN/DIB], – (5.79 ± 0.12) in 0.1 M $NaNO_3$ by potentiometry [2005CRE/MIL], – (5.54 ± 0.35) in 0.1 M KCl by potentiometry [2009TEK/ACA], and – (5.20 ± 0.10) in 0.10 M TMA($NO_3$) by potentiometry [2012ZAN/DIB]. Using the SIT approach, these values were converted to $\log_{10}{}^{*}\beta^{o}_{1,1}$ at 298.15 K using the SIT equation, $\log_{10}{}^{*}\beta^{o}_{1,1} - (\Delta Z^2 \times D) - (n \times \log_{10} a_{H_2O}) = \log_{10}{}^{*}\beta_{1,1} - \Delta\varepsilon \times I_m$, where $\Delta Z^2 = -2$ and $n = 1$ for Reaction (9.9), and summarised in Table 9-4.

In a recent study, Drobot *et al.* used laser-induced fluorescence spectroscopy to investigate the hydrolysis of U(VI) at an extremely low concentration ([U(VI)] = $1\times10^{-8}$ M) [2016DRO/BAU]. The equilibrium constant for Reaction (9.9), $\log_{10}{}^{*}\beta^{o}_{1,1}$ for $UO_2OH^+$, was determined to be – (4.6 ± 0.3) at $t$ = 1 °C and $I$ = 1.0 M $NaClO_4$, but revised to – (4.8 ± 0.2) when correlated data were excluded; the value extrapolated to $I$ = 0 and $t$ = 25 °C is $\log_{10}{}^{*}\beta^{o}_{1,1}$ = – (4.6 ± 0.3). The authors extrapolated their conditional equilibrium constants to $I$ = 0 using the SIT and corresponding interaction coefficients selected in [2003GUI/FAN]. The present review identified a

problem with the pH measurements in this study and corrected for this error (see Appendix A), which resulted in a significant change in the reported equilibrium constants. The value at zero ionic strength and 25 °C obtained after the correction is $\log_{10} {}^{*}\beta^{o}_{1,1} = -(5.2 \pm 0.3)$. As shown in Table 9-4, this value is in good agreement with the NEA selected value that is mainly based on potentiometry, thus confirming that accurate values of equilibrium constants for mononuclear complexes can be obtained by potentiometry, even in the presence of much larger amounts of polynuclear complexes.

Table 9-4 shows the values of $\log_{10} {}^{*}\beta^{o}_{1,1}$ from the new studies since the previous NEA reviews. The unweighted average of all values is $\log_{10} {}^{*}\beta^{o}_{1,1} = -(5.24 \pm 0.07)$, in excellent agreement with the value selected in [2003GUI/FAN], $\log_{10} {}^{*}\beta^{o}_{1,1}(298.15\ \text{K})$ **= – (5.250 ± 0.240)**, which is retained in this review.

Table 9-4: SIT treatment of experimental equilibrium constants ( $\log_{10} {}^{*}\beta^{o}_{1,1}$ ) at 298.15 K for the hydrolysis reaction: $UO_2^{2+} + H_2O(l) \rightleftharpoons UO_2OH^{+} + H^{+}$.

| Reference | *I* /medium | $\log_{10} {}^{*}\beta_{1,1}$ | $\log_{10} {}^{*}\beta^{o}_{1,1}$ | $\Delta\varepsilon$ |
|---|---|---|---|---|
| [2002DES/GIA] | 0.1-4.5 M NaCl | | – (5.16 ± 0.03) | (0.39 ± 0.02)[(a)] |
| | 0.1-1 M $NaNO_3$ | | – (5.19 ± 0.01) | – (0.28 ± 0.01)[(a)] |
| [2004CRE/DES] | 1.0 M $NaClO_4$ | – (5.2 ± 0.2) | – (5.19 ± 3.90) | – (0.4 ± 3.7)[(b)] |
| [2005CRE/MIL] | 0.16 M $NaNO_3$ | – (5.79 ± 0.12) | – (5.58 ± 0.12) | – (0.28 ± 0.01)[(a)] |
| [2004ZAN/DIB] | 0.1 M TEA($ClO_4$) | – (5.58 ± 0.24) | – (5.36 ± 0.24) | |
| [2009TEK/ACA] | 0.1 M KCl | – (5.54 ± 0.35) | – (5.28 ± 0.35) | (0.39 ± 0.02)[(a)] |
| [2012ZAN/DIB] | 0.1 M TMA($NO_3$) | – (5.20 ± 0.10) | – (4.98 ± 0.10) | |
| [2016DRO/BAU] | 1 M $NaClO_4$ | – | – (5.2 ± 0.3)[(c)] | – |
| Unweighted average | | | – (5.24 ± 0.08)[(d)] | |
| [2003GUI/FAN] | $I = 0$ | | – (5.250 ± 0.240) | |

(a) Derived from [2002DES/GIA], without including chloride/nitrate complexation.
(b) From [1992GRE/FUG], Table V.7, p. 107.
(c) Obtained by this review after correction of an error in pH measurement in [2016DRO/BAU].
(d) Unweighted average is calculated because the uncertainties of the data from [2002DES/GIA] are unrealistically small. The uncertainty of 0.08 for $\log_{10} {}^{*}\beta^{o}_{1,1}$ is obtained by using the method for estimation of uncertainty in Appendix C. However, the value from [2004CRE/DES] is not included when calculating the average value due to the unreasonably large uncertainty in Δε.

#### 9.3.2.1.1.2 $UO_2(OH)_2$(aq)

[2016DRO/BAU] is the only new experimental study that has reported the equilibrium constant for Reaction (9.10) for the $UO_2(OH)_2$(aq) complex: $\log_{10} {}^{*}\beta_{2,1}$ was determined to be – (12.2 ± 0.5) at $t$ = 1 °C and $I$ = 1.0 M $NaClO_4$. This value has been corrected by the present review, by taking into account a systematic error in the pH measurements and the revised value is $\log_{10} {}^{*}\beta^{o}_{2,1}(298.15\ \text{K}) = -(12.5 \pm 0.7)$, in good agreement with the value of $\log_{10} {}^{*}\beta^{o}_{2,1}(298.15\ \text{K}) = -(12.15 \pm 0.07)$ selected in [2003GUI/FAN]. Therefore this review retains the value of

$$\log_{10} {}^{*}\beta^{o}_{2,1}(298.15\ \text{K}) = \mathbf{-\ (12.150 \pm 0.070)}.$$

#### 9.3.2.1.1.3 $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$

In the studies of the ternary U(VI)-$OH^-$-$H_2O_2$ complexes in 0.1 M $TMA(NO_3)$, Zanonato *et al.*, [2012ZAN/DIB], [2014ZAN/DIB], also studied the binary U(VI)-$OH^-$ system and fitted the potentiometric titration data up to pH 11.5 by including the mononuclear $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ complexes. The equilibrium constants for Reactions (9.11) and (9.12) at $T = 298.15$ K and $I = 0.1$ M $TMA(NO_3)$, $\log_{10}{}^*\beta_{3,1}$ and $\log_{10}{}^*\beta_{4,1}$, were $-(18.81 \pm 0.17)$ and $-(31.25 \pm 0.50)$, respectively. As the ionic parameter, $\Delta\varepsilon$, for Reactions (9.11) and (9.12), is not known, we have assumed that an extrapolation to zero ionic strength can be made using only the Debye-Hückel term (*e.g.*, if $\Delta\varepsilon < 0.5$, then $\Delta\varepsilon \times I_m < 0.05$, which is much smaller than the uncertainty of the experimental values of $\log_{10}{}^*\beta_{3,1}$ and $\log_{10}{}^*\beta_{4,1}$). As a result, the values of $\log_{10}{}^*\beta^\circ_{3,1}$ and $\log_{10}{}^*\beta^\circ_{4,1}$ can be approximated by $\log_{10}{}^*\beta^\circ_{n,1} = \log_{10}{}^*\beta_{n,1} - \Delta Z^2 \times D - n \times \log_{10} a_{H_2O}$, where $n = 3$ and 4, $D$ is the Debye factor used in the SIT model ($D = 0.1092$ at 298.15 K and $I = 0.1$ m), and $a_{H_2O}$ is the activity of water in 0.1 M $TMA(NO_3)$. The value of $a_{H_2O}$ in 0.1 M $TMA(NO_3)$ is not known but expected to be close to 1. Using $\Delta Z^2 = 0$ and 4 for Reactions (9.11) and (9.12), respectively, $\log_{10}{}^*\beta^\circ_{3,1}$ and $\log_{10}{}^*\beta^\circ_{4,1}$ are calculated to be $-(18.81 \pm 0.17)$ and $-(31.71 \pm 0.50)$ in [2014ZAN/DIB]. It should be noted that the existence of $UO_2(OH)_4^{2-}$ has been demonstrated by EXAFS investigations, [1999WAH/MOL], [2000MOL/REI].

Drobot *et al.* [2016DRO/BAU] have determined the equilibrium constant for the formation of $UO_2(OH)_3^-$ by laser-induced fluorescence spectroscopy and reported $\log_{10}\beta_{3,1} = -(22.3 \pm 0.6)$ at $t = 1$ °C and $I = 1.0$ M $NaClO_4$. By using the Van't Hoff equation and the SIT parameters from [2003GUI/FAN], the value of $\log_{10}{}^*\beta^\circ_{3,1}$ (298.15 K) was calculated to be $-(20.7 \pm 0.7)$. This value has been revised by the present review after correction of a systematic error in pH measurements and the corrected value is $\log_{10}{}^*\beta^\circ_{3,1} = -(21.1 \pm 0.9)$, which is consistent with the NEA selected value, $\log_{10}{}^*\beta^\circ_{3,1} = -(20.25 \pm 0.42)$, but not with $\log_{10}{}^*\beta^\circ_{3,1} = -(18.81 \pm 0.17)$ obtained from [2014ZAN/DIB].

In a recent study by Altmaier *et al.,* the solubility of $Na_2U_2O_7{\cdot}H_2O$(cr) was measured in NaCl solutions of different concentrations [2017ALT/YAL]. From the solubility data, the equilibrium constants for the formation of $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ were obtained and extrapolated to zero ionic strength. They reported $\log_{10}{}^*\beta^\circ_{3,1} = -(20.7 \pm 0.4)$ and $\log_{10}{}^*\beta^\circ_{4,1} = -(31.9 \pm 0.2)$. The value of $\log_{10}{}^*\beta^\circ_{3,1}$ from solubility measurements in [2017ALT/YAL] is in good agreement with the value from fluorescence spectroscopy in [2016DRO/BAU].

The present review has no explanation for the significant difference between the value of $\log_{10}{}^*\beta^\circ_{3,1}$ obtained by potentiometry [2014ZAN/DIB] and those obtained by fluorescence and solubility experiments. We note, however, that the use of a tetra alkyl ammonium medium might result in a very different medium effect than in media with the smaller alkali-counter-ions. Some support for this is obtained by the fact that the $(UO_2)_3(OH)_6$(aq) complex could only be identified in the former ionic media. Therefore,

we have preferred to retain the value from the previous NEA TDB review [2003GUI/FAN], $\log_{10} {}^{*}\beta^{\circ}_{3,1}$ (298.15 K) = **– (20.250 ± 0.420)**.

For $\log_{10} {}^{*}\beta^{\circ}_{4,1}$, the value of – (31.71 ± 0.50) obtained in [2014ZAN/DIB] and the value of – (31.9 ± 0.2) obtained in [2017ALT/YAL] overlap with the one selected by the previous NEA review [2003GUI/FAN], $\log_{10} {}^{*}\beta^{\circ}_{4,1}$ = **– (32.400 ± 0.680)**, which is therefore retained by the present review.

This review selects also $\varepsilon(UO_2(OH)_3^-, Na^+)$ = – (0.24 ± 0.09) kg·mol$^{-1}$ and $\varepsilon(UO_2(OH)_4^{2-}, Na^+)$ = (0.01 ± 0.04) kg·mol$^{-1}$ determined in [2017ALT/YAL] from solubility experiments in alkaline NaCl systems.

#### 9.3.2.1.2 Polymeric hydrolysis species at 298.15 K

The hydrolysis of U(VI) in aqueous solutions is expressed by Reaction (9.13), with the equilibrium constants as ${}^{*}\beta_{n,m}$:

$$m UO_2^{2+} + n H_2O(l) \rightleftharpoons (UO_2)_m(OH)_n^{2m-n} + n H^+ \qquad (9.13)$$

$${}^{*}\beta_{n,m} = [(UO_2)_m(OH)_n^{2m-n}][H^+]^n / [UO_2^{2+}]^m$$

Thermodynamic data (equilibrium constants and enthalpy of hydrolysis) of polymeric U(VI) species, including (2,1), (2,2), (3,2), (3,3), (4,3), (5,3), (6,3), (7,3), (8,3), (6,4), and (7,4) species, have been reported in a number of papers since the previous review [2003GUI/FAN]. The new experimental equilibrium constants and enthalpies of hydrolysis are summarised in Table 9-2 and Table 9-3, respectively.

##### 9.3.2.1.2.1 Dimeric species, $(UO_2)_2(OH)_n^{(4-n)+}$

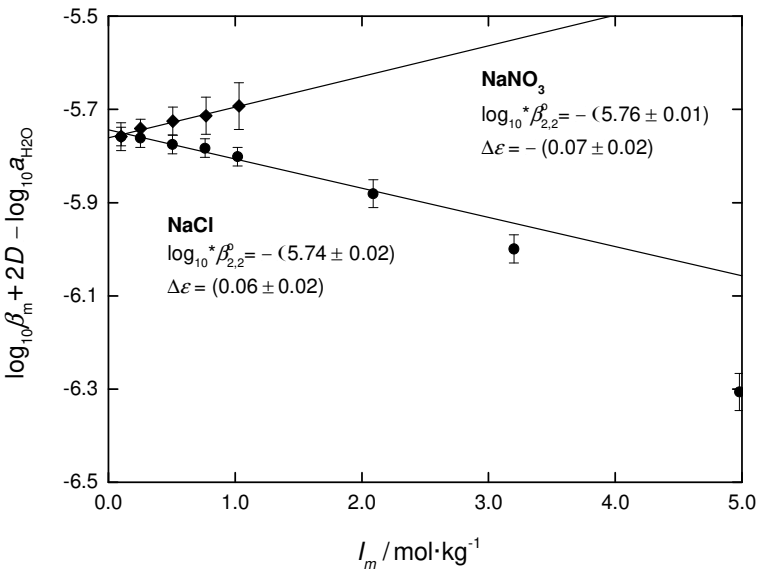
New data for the $(UO_2)_2(OH)_2^{2+}$ species are reported in [2002DES/GIA], [2004CRE/DES], [2003SAW/SHA], [2004GIA/MIL], [2004ZAN/DIB], [2005CRE/MIL], [2008AMO/GAM], [2009TEK/ACA], [2012ZAN/DIB], and [2014ZAN/DIB].

De Stefano *et al.* [2002DES/GIA] reported the hydrolysis constants for $(UO_2)_2(OH)_2^{2+}$ at 298.15 K in aqueous NaCl (0.1-4.5 M) and $NaNO_3$ (0.1-1 M) solutions. The equilibrium constants obtained for the NaCl and $NaNO_3$ media at different ionic strengths were used to calculate the constants at infinite dilution by using a Debye-Huckel type equation including a polynomial expression of the ionic strength ($L(I) = CI + DI^{1.5} + EI^2$), where $C$, $D$ and $E$ are empirical parameters obtained by fitting [2002DES/GIA]. The calculated value of $\log_{10} {}^{*}\beta^{\circ}_{2,2}$ was – (5.76 ± 0.04) in [2002DES/GIA], in fair agreement with the value selected by previous review, – (5.62 ± 0.04) [2003GUI/FAN].

The experimental data in [2002DES/GIA] were re-analysed using SIT and the result is shown in Figure 9-2.

The value of $\log_{10}{}^{*}\beta^{\circ}_{2,2}$ was determined to be $-(5.74 \pm 0.02)$ and $-(5.76 \pm 0.01)$ from the data in NaCl and $NaNO_3$ systems, respectively. From the slopes of the SIT plots in Figure 9-2, the specific ion interaction parameters, $\Delta\varepsilon$, were calculated to be $(0.06 \pm 0.02)$ kg·mol$^{-1}$ and $-(0.07 \pm 0.02)$ kg·mol$^{-1}$ for the NaCl and $NaNO_3$ systems, respectively. As stated in the beginning of Section 9.3.2.1 on the analysis of [2002DES/GIA] and [2004GIA/MIL], the $\Delta\varepsilon$ values are best considered as empirical parameters that cannot be used to obtain individual ion-interaction parameters. Nevertheless, the SIT type plots provide a good estimate of the equilibrium constants at zero ionic strength. The deviations at molalities larger than 2 m NaCl are presumably due to the formation of chloride compexes.

Figure 9-2: SIT plots with the data from [2002DES/GIA] for the hydrolysis reaction $2UO_2^{2+} + 2H_2O(l) \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$. The data points at $I$ = 3.0 M and 4.5 M NaCl are not included in the fit. The solid lines represent the best fits.




The experimental values of $\log_{10}{}^{*}\beta_{2,2}$ at 298.15 K in different ionic media from [2002DES/GIA], [2004CRE/DES], [2003SAW/SHA], [2004GIA/MIL], [2004ZAN/DIB], [2005CRE/MIL], [2008AMO/GAM], [2009TEK/ACA], [2012ZAN/DIB], and [2014ZAN/DIB], and the values at infinite dilution are summarised in Table 9-5. More discussion on these studies is provided in Appendix A.

Table 9-5: SIT treatment of experimental equilibrium constants ( $\log_{10}{}^{*}\beta_{2,2}$ ) at 298.15 K for the hydrolysis reaction: $2UO_2^{2+} + 2H_2O(l) \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$.

| Reference | $I$ /medium | $\log_{10}{}^{*}\beta_{2,2}$ | $\log_{10}{}^{*}\beta^{o}_{2,2}$ | $\Delta\varepsilon$ |
|---|---|---|---|---|
| [2002DES/GIA] | 0.1-4.5 M NaCl | | – (5.74 ± 0.02) | (0.06 ± 0.02)[(a)] |
| | 0.1-1 M $NaNO_3$ | | – (5.76 ± 0.01) | – (0.07 ± 0.02)[(a)] |
| [2003SAW/SHA] | 1.0 M $NaClO_4$ | – (6.15 ± 0.05) | – (5.78 ± 0.09) | – (0.07 ± 0.02)[(b)] |
| [2004CRE/DES] | 1.0 M $NaClO_4$ | – (5.95 ± 0.05) | – (5.58 ± 0.09) | – (0.07 ± 0.02)[(b)] |
| [2004GIA/MIL] | 0.5-3 M LiCl | | – (5.75 ± 0.02) | (0.12 ± 0.01)[(c)] |
| [2004ZAN/DIB] | 0.1M TEA($ClO_4$) | – (5.83 ± 0.02) | – (5.62 ± 0.02) | – (0.07 ± 0.02)[(b)] |
| [2005CRE/MIL] | 0.16 M $NaNO_3$ | – (5.932 ± 0.002) | – (5.73 ± 0.03) | – (0.07 ± 0.02)[(a)] |
| [2009TEK/ACA] | 0.1 M KCl | – (5.60 ± 0.24) | – (5.38 ± 0.24) | (0.06 ± 0.02)[(a)] |
| [2012ZAN/DIB] | 0.1 M TMA($NO_3$) | – (5.95 ± 0.03) | – (5.73 ± 0.03) | – (0.07 ± 0.02)[(a)] |
| [2014ZAN/DIB] | 0.1 M TMA($NO_3$) | – (5.94 ± 0.03) | – (5.72 ± 0.03) | – (0.07 ± 0.02)[(a)] |
| Unweighted average | $I$ = 0 | | – (5.68 ± 0.08)[(d)] | |
| [2003GUI/FAN] | $I$ = 0 | | – (5.62 ± 0.04) | |

(a) Derived from [2002DES/GIA], without including chloride/nitrate complexation;
(b) From [1992GRE/FUG], Table V.7, p. 107;
(c) From analysis of [2004GIA/MIL] as detailed in Appendix A;
(d) Unweighted average is calculated because the uncertainties of the data from [2002DES/GIA] are unrealistically small. The uncertainty of 0.08 for $\log_{10}{}^{*}\beta^{o}_{2,2}$ is obtained by assigning the largest uncertainty (0.24 from [2009TEK/ACA]) to all values of $\log_{10}{}^{*}\beta_{2,2}$ in Table 9-5 and following the method for estimation of uncertainty in Appendix C.

The unweighted average of the values of $\log_{10}{}^{*}\beta^{o}_{2,2}$ (298.15 K) from the studies shown in Table 9-5 is – (5.68 ± 0.08), in excellent agreement with the value selected by [2003GUI/FAN] and the new selected value is $\log_{10}{}^{*}\beta^{o}_{2,2}$ (298.15 K) = **– (5.620 ± 0.080)** where the uncertainty has been increased**.**

In a study of ternary U(VI)-Cu(II)-hydroxide and U(VI)-$(C_2H_5)_2Sn^{2+}$- hydroxide complexes [2005CRE/MIL], a hydrolysis constant (– (3.83 ± 0.05)) for the (1,2) complex $(UO_2)_2(OH)^{3+}$, was obtained at 298.15 K and $I$ = 0.16 M $NaNO_3$. The corresponding value at zero ionic strength is $\log_{10}{}^{*}\beta^{o}_{1,2}$ (298.15 K) = – (4.08 ± 0.05), calculated using only the Debye-Hückel term because of the low ionic strength). This value, is significantly lower than that – (2.7 ± 1.0), estimated by [1992GRE/FUG]. Since these experimental data are based on a single ionic strength, they have not been accepted by this review. The value of $\log_{10}{}^{*}\beta^{o}_{1,2}$ should be re-evaluated when more data become available. There is one study that reports the hydrolysis constant for $(UO_2)_2(OH)_3^+$ at 75 and 100 °C in 3.6 m $LiClO_4$ [2008AMO/GAM], but no attempt was made to recalculate these data to 298.15 K.

#### 9.3.2.1.2.2 Trimeric species, $(UO_2)_3(OH)_n^{6-n}$

Only one study reports the hydrolysis constant of the (3,3) species, $(UO_2)_3(OH)_3^{3+}$, at 75 and 100 °C in 3.6 m $LiClO_4$ [2008AMO/GAM]. No hydrolysis constants of the (3,3) species at 298.15 K were reported in the literature prior to this one.

A number of other trimeric hydrolysis species, including (4,3), (5,3), (6,3), (7,3), and (8,3), were reported in the literature [2002DES/GIA], [2004CRE/DES],

[2004GIA/MIL], [2004ZAN/DIB], [2005CRE/MIL], [2009TEK/ACA], [2012ZAN/DIB], and [2014ZAN/DIB]. Among these species, the values of hydrolysis constants at $I = 0$ for the (4,3), (5,3) and (7,3) species were selected in [2003GUI/FAN]. As noted in the introduction to Section 9.3, these stoichiometries are all consistent with a trinuclear core where the uranyl ions are linked by hydroxide bridges.

De Stefano *et al.* [2002DES/GIA] reported the hydrolysis constants for $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^{+}$, and $(UO_2)_3(OH)_7^{-}$, at 298.15 K in aqueous NaCl (0.1-4.5 M) and $NaNO_3$ (0.1-1 M) solutions. The conditional equilibrium constants obtained in the NaCl and $NaNO_3$ media at different ionic strengths were used to calculate the constants at infinite dilution by using a Debye-Huckel type equation including a polynomial expression of the ionic strength ($L(I) = CI + DI^{1.5} + EI^2$), where $C$, $D$ and $E$ are empirical parameters obtained by fitting and the resulting constants are: $\log_{10} {}^{*}\beta^{o}_{4,3} = -(11.82 \pm 0.08)$, $\log_{10} {}^{*}\beta^{o}_{5,3} = -(15.89 \pm 0.06)$, and $\log_{10} {}^{*}\beta^{o}_{7,3} = -(29.26 \pm 0.10)$, respectively.

The experimental data in [2002DES/GIA] were re-analysed with SIT and these plots are shown in Figure 9-3.

In addition to the data from [2002DES/GIA], the experimental values of $\log_{10} {}^{*}\beta_{n,3}$ at 298.15 K in different ionic media from other studies, including [2004CRE/DES], [2004GIA/MIL], [2004ZAN/DIB], [2005CRE/MIL], [2009TEK/ACA], [2012ZAN/DIB], and [2014ZAN/DIB], were recalculated to zero ionic strength and summarised in Table 9-6. The SIT analysis of the data of the LiCl media in [2004GIA/MIL] is shown in the Appendix A.

Figure 9-3: SIT plots for the hydrolysis reaction $3\ UO_2^{2+} + nH_2O(l) \rightleftharpoons (UO_2)_3(OH)_n^{6-n} + nH^+$, with the data from [2002DES/GIA]. The data points at $I > 1.5$ M NaCl are not included in the fit. The solid lines represent the best fits.

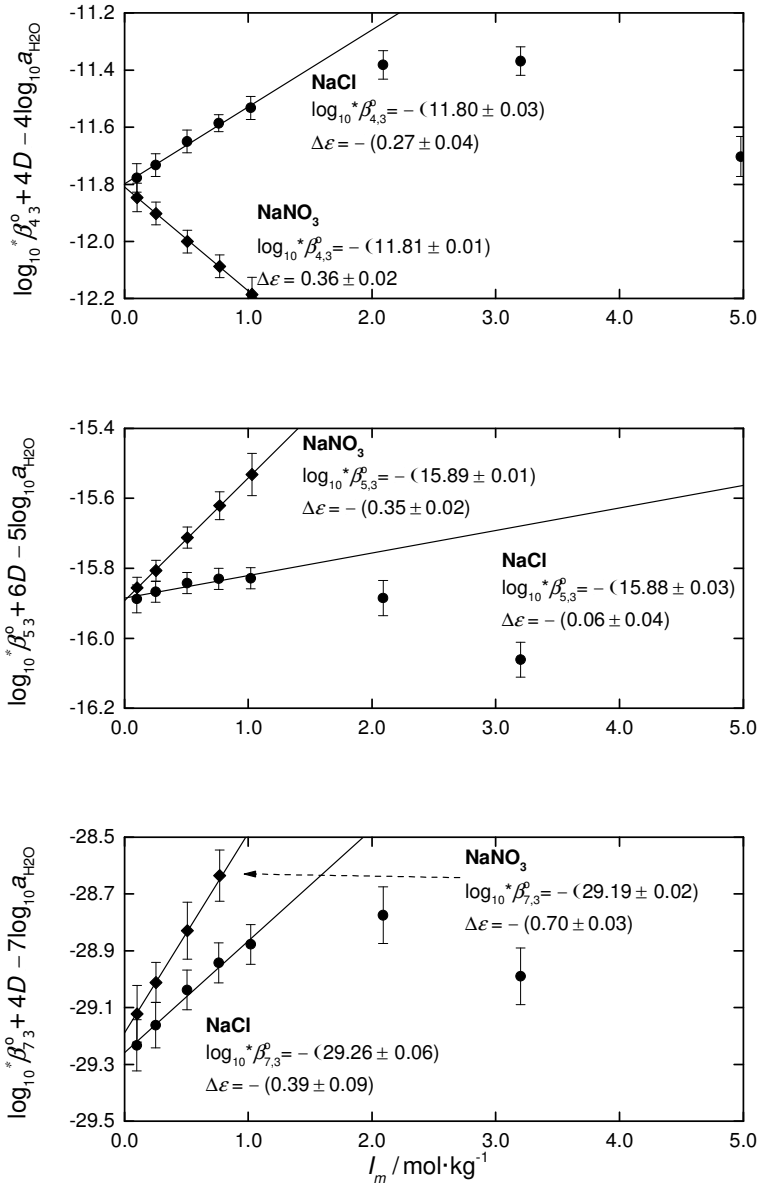


Table 9-6: SIT treatment of experimental equilibrium constants ( $\log_{10}{}^{*}\beta_{n,3}$ ) at 298.15 K for the hydrolysis reaction: $3UO_2^{2+} + nH_2O(l) \rightleftharpoons (UO_2)_3(OH)_n^{6-n} + nH^+$.

| Reference | $I$ /medium | $\log_{10}{}^{*}\beta_{4,3}$ | $\log_{10}{}^{*}\beta^{o}_{4,3}$ | $\Delta\varepsilon(4,3)$ |
|---|---|---|---|---|
| [2002DES/GIA] | 0.1-4.5 M NaCl | | – (11.80 ± 0.03) | – (0.27 ± 0.04)[a] |
| | 0.1-1 M $NaNO_3$ | | – (11.81 ± 0.01) | (0.36 ± 0.02)[a] |
| [2004GIA/MIL] | 0.5-3.0 M LiCl | | – (11.69 ± 0.11) | – (0.03 ± 0.07)[b] |
| [2005CRE/MIL] | 0.16 M $NaNO_3$ | – (12.79 ± 0.01) | – (12.31 ± 0.10) | (0.36 ± 0.02)[a] |
| [2009TEK/ACA] | 0.1 M KCl | – (11.21 ± 0.31) | – (10.79 ± 0.31) | – (0.27 ± 0.04)[a] |
| [2012ZAN/DIB] | 0.1 M TMA($NO_3$) | – (12.25 ± 0.08) | – (11.78 ± 0.08) | (0.36 ± 0.02)[a] |
| Unweighted average | $I$ = 0 | | – (11.70 ± 0.13)[c] | |
| [2003GUI/FAN] | $I$ = 0 | | – (11.9 ± 0.3) | |
| Reference | $I$ /medium | $\log_{10}{}^{*}\beta_{5,3}$ | $\log_{10}{}^{*}\beta^{o}_{5,3}$ | $\Delta\varepsilon(5,3)$ |
| [2002DES/GIA] | 0.1-4.5 M NaCl | | – (15.88 ± 0.03) | – (0.06 ± 0.04)[a] |
| | 0.1-1 M $NaNO_3$ | | – (15.89 ± 0.01) | – (0.35 ± 0.02)[a] |
| [2004CRE/DES] | 1.0 M $NaClO_4$ | – (16.2 ± 0.1) | – (15.13 ± 0.12) | – (0.23 ± 0.07)[d] |
| [2004GIA/MIL] | 0.5-3.0 M LiCl | | – (15.81 ± 0.13) | – (0.34 ± 0.07)[b] |
| [2004ZAN/DIB] | 0.1 M TEA($ClO_4$) | – (16.37 ± 0.02) | – (15.74 ± 0.02) | – (0.23 ± 0.07)[d] |
| [2005CRE/MIL] | 0.16 M $NaNO_3$ | – (16.457 ± 0.007) | – (15.60 ± 0.03) | – (0.35 ± 0.02)[a] |
| [2009TEK/ACA] | 0.1 M KCl | – (16.07 ± 0.16) | – (15.40 ± 0.16) | – (0.06 ± 0.04)[a] |
| [2012ZAN/DIB] | 0.1 M TMA($NO_3$) | – (16.43 ± 0.02) | – (15.67 ± 0.02) | – (0.35 ± 0.02)[a] |
| Unweighted average | $I$ = 0 | | – (15.67 ± 0.06)[c] | |
| [2003GUI/FAN] | $I$ = 0 | | – (15.55 ± 0.12) | |
| Reference | $I$ /medium | $\log_{10}{}^{*}\beta_{7,3}$ | $\log_{10}{}^{*}\beta^{o}_{7,3}$ | $\Delta\varepsilon(7,3)$ |
| [2002DES/GIA] | 0.1-4.5 M NaCl | | – (29.26 ± 0.06) | – (0.39 ± 0.09)[a] |
| | 0.1-1 M $NaNO_3$ | | – (29.19 ± 0.02) | – (0.70 ± 0.03)[a] |
| [2004GIA/MIL] | 0.5-3.0 M LiCl | | – (29.22 ± 0.08) | – (0.12 ± 0.03)[b] |
| [2005CRE/MIL] | 0.16 M $NaNO_3$ | – (28.58 ± 0.05) | – (28.16 ± 0.07) | – (0.70 ± 0.03)[a] |
| [2012ZAN/DIB] | 0.1 M TMA($NO_3$) | – (28.97 ± 0.07) | – (28.60 ± 0.07)[e] | |
| [2014ZAN/DIB] | 0.1 M TMA($NO_3$) | – (28.95 ± 0.12) | – (28.58 ± 0.12)[e] | |
| Unweighted average | $I$ = 0 | | – (28.84 ± 0.04)[c] | |
| [2003GUI/FAN] | $I$ = 0 | | – (32.2 ± 0.8) | |

(a) Derived from [2002DES/GIA], without including chloride/nitrate complexation.

(b) From analysis of [2004GIA/MIL], detailed in Appendix A.

(c) Unweighted average is calculated because the uncertainties of the data from [2002DES/GIA] are unrealistically small. The uncertainty is obtained by assigning the largest uncertainty among the values from the listed studies (0.31 from [2009TEK/ACA] for $\log_{10}\beta^{o}_{4,3}$, 0.16 from [2009TEK/ACA] for $\log_{10}{}^{*}\beta_{5,3}$ and 0.12 from [2014ZAN/DIB] for $\log_{10}\beta^{o}_{7,3}$) to all values and following the method for estimation of uncertainty in Appendix C.

(d) From Table V.7, p. 107 in [1992GRE/FUG].

(e) Estimated values by neglecting the ion interaction term ($\Delta\varepsilon \times I_m$) at the low ionic strength used in these studies; the ion-interaction coefficient $\varepsilon((UO_2)_3(OH)_7^-, M^+)$ is not known. Assuming $\Delta\varepsilon(7,3)$ for TMA($NO_3$) is < 1.0, the uncertainty introduced into the value of $\log_{10}{}^{*}\beta^{o}_{7,3}$ by ignoring the term ($\Delta\varepsilon \times I_m$) should be < ± 0.1.

The values of $\log_{10}{}^{*}\beta^{o}_{4,3}$ (298.15 K) derived from the new studies are all very close to the value selected by [2003GUI/FAN], – (11.9 ± 0.3), except the significantly lower value from [2009TEK/ACA], – (10.79 ± 0.31), (Table 9-6). The unweighted average of the values of $\log_{10}{}^{*}\beta^{o}_{4,3}$ (298.15 K) from the studies shown in Table 9-6 is – (11.70 ± 0.13), in good agreement with the value selected by [2003GUI/FAN]. Therefore, this review retains the value

$$\log_{10} {}^{*}\beta^{o}_{4,3}\,(298.15\ \text{K}) = \mathbf{-\ (11.900 \pm 0.300)}.$$

The unweighted average of the values of $\log_{10} {}^{*}\beta^{o}_{5,3}\,(298.15\ \text{K})$ from the studies shown in Table 9-6 is – (15.67 ± 0.06), in good agreement with the value selected by [2003GUI/FAN], which is therefore retained,

$$\log_{10} {}^{*}\beta^{o}_{5,3}\,(298.15\ \text{K}) = \mathbf{-\ (15.550 \pm 0.120)}.$$

The values of $\log_{10} {}^{*}\beta^{o}_{7,3}\,(298.15\ \text{K})$ from [2002DES/GIA], [2004GIA/MIL], [2005CRE/MIL], [2012ZAN/DIB], and [2014ZAN/DIB], all obtained by potentiometry, range from – 29.26 to – 28.16 (Table 9-6) with an unweigted average of – (28.84 ± 0.04) and are significantly higher than the value selected by [2003GUI/FAN], – (32.2 ± 0.8), which is mainly based on the solubility data from [1992SAN/BRU]. The problem with the potentiometric technique is that solid sodium or potassium uranates may precipitate in the $-\log_{10}[H^+]$ range where the (7,3) complex is formed, and that the concentration of this complex is small and sensitive to systematic errors. For example, De Stefano *et al.* [2002DES/GIA] made a careful analysis of the experimental data and demonstrated in their Table 2 that the concentration of the (7,3) complex is small and possibly dependent on the nitrate concentration. In other potentiometric studies such as [2012ZAN/DIB] and [2014ZAN/DIB], precipitation is avoided by using tetraalkyl ammonium ionic media, where the large cation prevents formation of uranates; however, the large cation may result in ionic medium effects that are quite different from the ones in media with alkali ions.

To further resolve the discrepancy between the values of $\log_{10} {}^{*}\beta^{o}_{7,3}$ determined from potentiometry and solubility measurements, the solubility data reported in [2017ALT/YAL] have been compared with thermodynamic calculations using $\log_{10} {}^{*}\beta^{o}_{7,3}$ selected in [2003GUI/FAN] or reported in potentiometric studies. The analysis indicates that the selected value in [2003GUI/FAN], $\log_{10} {}^{*}\beta^{o}_{7,3}\,(298.15\ \text{K})$ = **– (32.200 ± 0.800)**, did fit the solubility data from Altmaier *et al.* well and resulted in a value of $\log_{10} {}^{*}\beta^{o}_{3,1}$ = – (20.7 ± 0.4), which is in good agreement with the value derived from the spectroscopic data reported by Drobot *et al.* [2016DRO/BAU], $\log_{10} {}^{*}\beta^{o}_{3,1}$ = – (21.1 ± 0.9), and the value selected by NEA TDB review [2003GUI/FAN], $\log_{10} {}^{*}\beta^{o}_{3,1}\,(298.15\ \text{K})$ = **– (20.250 ± 0.420)**. The analysis of the solubility data in [2017ALT/YAL] is shown in Figure 9-4.

The dashed lines in Figure 9-4 show that the use of $\log_{10} {}^{*}\beta^{o}_{7,3}\,(298.15\ \text{K})$ = – 28.84 from the potentiometric studies results in a predicted solubility that is 1-2 orders of magnitude higher than the experimentally ones in the range of $-\log_{10}[H^+]$ from 7 to 8.5, where the (7,3) species is important.

Therefore, this review retains the value for the hydrolysis of (7,3) species selected by the previous NEA TDB review [2003GUI/FAN]:

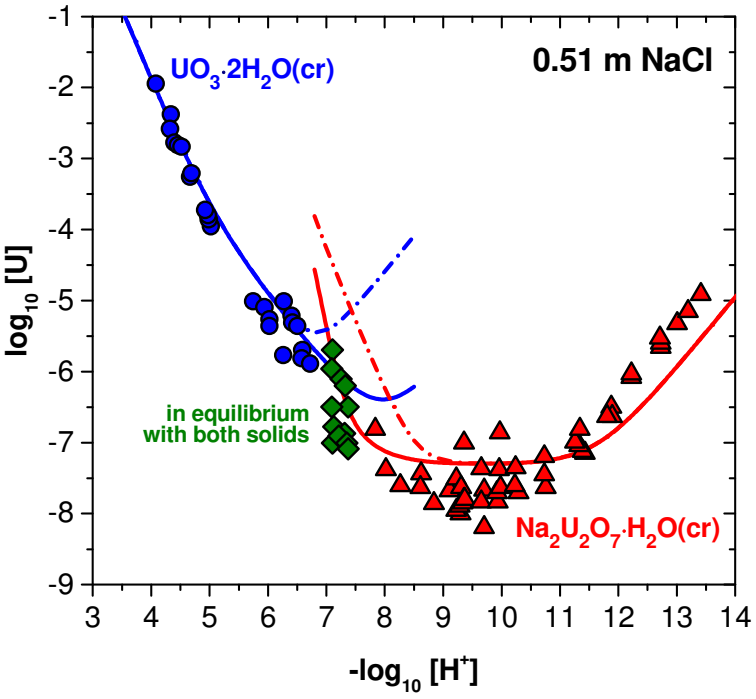
$$\log_{10} {}^{*}\beta^{o}_{7,3}\,(298.15\ \text{K}) = \mathbf{-\ (32.200 \pm 0.800)}.$$

Only two studies (from the same group) reported values of $\log_{10}{}^{*}\beta_{6,3}$ (298.15 K) and $\log_{10}{}^{*}\beta_{8,3}$ (298.15 K) in 0.1 M TMA($NO_3$) [2012ZAN/DIB] and [2014ZAN/DIB] (Table 9-2). The weighted average values of $\log_{10}{}^{*}\beta_{6,3}$ (298.15 K) and $\log_{10}{}^{*}\beta_{8,3}$ (298.15 K) are – (22.68 ± 0.16), and – (38.88 ± 0.11), respectively. The values of $\log_{10}{}^{*}\beta^{o}_{6,3}$ (298.15 K) and $\log_{10}{}^{*}\beta^{o}_{8,3}$ (298.15 K) are estimated to be – (22.0 ± 0.5), and – (38.9 ± 0.5), respectively, using SIT and ignoring the water activity term and the ion interaction term ($\Delta\varepsilon \times I_m$) because of the low ionic strength, 0.1 M; there is no data for $\varepsilon((UO_2)_3(OH)_8^{2-}, TMA^+)$. The uncertainties in the estimated $\log_{10}{}^{*}\beta^{o}_{6,3}$ (298.15 K) and $\log_{10}{}^{*}\beta^{o}_{8,3}$ (298.15 K) (± 0.5) are increased to account for the neglected ($\Delta\varepsilon \times I_m$) term.

It should be noted that the (6,3) species, $(UO_2)_3(OH)_6(aq)$, was observed only in the ionic media using tetramethylammonium ionic media (*e.g.*, TMA($NO_3$) in [2012ZAN/DIB] and [2014ZAN/DIB], but not in other ionic media, which raises the question if this species is actually present in the TMA($NO_3$) medium, or not. In fact, the analysis of the potentiometric data in TMA($NO_3$) in [2012ZAN/DIB] and [2014ZAN/DIB]) suggested that the equivalent point is located at a p[$H^+$] close to neutrality and must be interpreted as the formation of an uncharged species with the ratio (OH/U) = 2:1. This could of course be any of the complexes (2,1), (4,2) or (6,3). However, the model using (6,3) provided a better fit of the potentiometric data than (2,1) or (4,2) and was also independently confirmed by the calorimetric data in [2014ZAN/DIB]. Until more data in the TMA media are available, the question on the stoichiometry remains to be answered.

This review does not select values of $\log_{10}{}^{*}\beta^{o}_{6,3}$ (298.15 K) and $\log_{10}{}^{*}\beta^{o}_{8,3}$ (298.15 K) but points out that the values estimated from [2012ZAN/DIB] and [2014ZAN/DIB] seem to be reasonable when compared with the values of the other trimeric hydrolysis species and for this reason they are reported for information only.

Figure 9-4: Solubility of $UO_3{\cdot}2H_2O$(cr) and $Na_2U_2O_7{\cdot}H_2O$(cr) in 0.51 m NaCl as reported in [2017ALT/YAL] (blue, green and red symbols), or calculated using solubility and hydrolysis constants selected in this review (solid lines) and considering $\log_{10}{}^{*}\beta^{o}_{7,3}$ reported in potentiometric studies (dashed lines).




#### 9.3.2.1.2.3 Tetrameric species, $(UO_2)_4(OH)_n^{8-n}$

Values of $\log_{10}{}^{*}\beta_{6,4}$ (298.15 K) and $\log_{10}{}^{*}\beta_{8,4}$ (298.15 K) were determined by potentiometry in 1.0 M $NaClO_4$, using fluoride to supress the precipitation of U(VI) hydroxides [2003SAW/SHA]. It is to be noted that the model used in this study does not include the well-accepted (5,3) species, $(UO_2)_3(OH)_5^+$, that could be important in the pH region where the assumed (6,4) and (8,4) species may exist. Besides, the effect of fluoride on the data is not properly accounted for in that study. Even though the value, $\log_{10}{}^{*}\beta_{8,4}$ (298.15 K) = – (23.36 ± 0.07), in 1.0 M $NaClO_4$, seems reasonable in comparison with the value of $\log_{10}{}^{*}\beta^{o}_{7,4}$ (298.15 K) = – (21.9 ± 1.0) selected by [2003GUI/FAN], this review does not accept the values of $\log_{10}{}^{*}\beta_{6,4}$ (298.15 K) and $\log_{10}{}^{*}\beta_{8,4}$ (298.15 K) from [2003SAW/SHA]. There are no new experimental studies reporting thermodynamic data for the species (7,4), and this review retains the selection of $\log_{10}{}^{*}\beta^{o}_{7,4}$ in [2003GUI/FAN].

#### 9.3.2.1.3 Summary of selected equilibrium constants for the hydrolysis of U(VI)

The equilibrium constants of aqueous U(VI) hydrolysis at 298.15 K selected by this review (including those selected by [2003GUI/FAN] and retained by the present review), $\log_{10}{}^{*}\beta^{\circ}_{n,m}$ for the reaction $m\mathrm{UO_2^{2+}} + n\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{UO_2})_m(\mathrm{OH})_n^{2m-n} + n\mathrm{H^+}$, are summarised in Table 9-7.

Table 9-7: Summary of the equilibrium constants, $\log_{10}{}^{*}\beta^{\circ}_{n,m}$, and Gibbs energy of reaction, $\Delta_r G^{\circ}_m$ for the aqueous U(VI) hydrolysis, $m\mathrm{UO_2^{2+}} + n\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{UO_2})_m(\mathrm{OH})_n^{m-n} + n\mathrm{H^+}$, at 298.15 K selected by this review and [2003GUI/FAN].

| Species $n,m$ | $\log_{10}{}^{*}\beta^{\circ}_{n,m}$ | $\Delta_r G^{\circ}_m$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|
| 1,1 | **– (5.250 ± 0.240)** | **(29.967 ± 1.370)** | [2003GUI/FAN] |
| 2,1 | **– (12.150 ± 0.070)** | **(69.353 ± 0.400)** | [2003GUI/FAN] |
| 3,1 | **– (20.250 ± 0.420)** | **(115.588 ± 2.397)** | [2003GUI/FAN] |
| 4,1 | **– (32.400 ± 0.680)** | **(184.942 ± 3.882)** | [2003GUI/FAN] |
| 1,2 | **– (2.700 ± 1.000)** | **(15.412 ± 5.708)** | [1992GRE/FUG], [2003GUI/FAN] |
| 2,2 | **– (5.620 ± 0.080)** | **(32.079 ± 0.458)** | [1992GRE/FUG], [2003GUI/FAN] |
| 4,3 | **– (11.900 ± 0.300)** | **(67.926 ± 1.712)** | [1992GRE/FUG], [2003GUI/FAN] |
| 5,3 | **– (15.550 ± 0.120)** | **(88.760 ± 0.685)** | [1992GRE/FUG], [2003GUI/FAN] |
| 7,3 | **– (32.200 ± 0.800)** | **(183.799 ± 4.566)** | [2003GUI/FAN] |
| 7,4 | **– (21.900 ± 1.000)** | **(125.006 ± 5.708)** | [1992GRE/FUG], [2003GUI/FAN] |

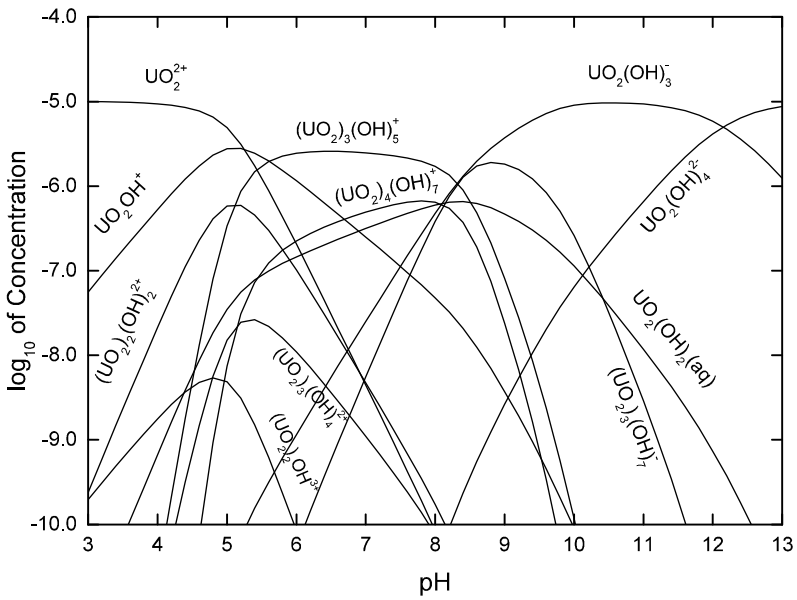
The corresponding standard Gibbs energies of formation for the hydrolysis species of U(VI) are calculated using the data in Table 9-7 and the auxiliary data in Chapter 14, and summarised in Table 9-8.

Table 9-8: Summary of selected $\Delta_f G^{\circ}_{n,m}$ at 298.15 K for the hydrolysis species of U(VI), $(\mathrm{UO_2})_m(\mathrm{OH})_n^{2m-n}$.

| $n,m$ | $\Delta_f G^{\circ}_{n,m}$ (298.15 K) /kJ·mol$^{-1}$ | Reference |
|---|---|---|
| 1,1 | **– (1159.724 ± 2.221)** | [2003GUI/FAN] |
| 2,1 | **– (1357.479 ± 1.794)** | [2003GUI/FAN] |
| 3,1 | **– (1548.384 ± 2.969)** | [2003GUI/FAN] |
| 4,1 | **– (1716.171 ± 4.260)** | [2003GUI/FAN] |
| 1,2 | **– (2126.830 ± 6.693)** | [1992GRE/FUG], [2003GUI/FAN] |
| 2,2 | **– (2347.303 ± 3.525)** | [1992GRE/FUG], [2003GUI/FAN] |
| 4,3 | **– (3738.288 ± 5.517)** | [1992GRE/FUG], [2003GUI/FAN] |
| 5,3 | **– (3954.594 ± 5.291)** | [1992GRE/FUG], [2003GUI/FAN] |
| 7,3 | **– (4333.835 ± 6.958)** | [2003GUI/FAN] |
| 7,4 | **– (5345.178 ± 9.028)** | [1992GRE/FUG], [2003GUI/FAN] |

Using the equilibrium constants of the hydrolysis of U(VI) in Table 9-7 at zero ionic strength and 298.15 K, we have calculated a distribution diagram in Figure 9-5 for the aqueous dioxouranium(VI) hydroxide system, between pH 3 and 12 and a total concentration of U(VI), $[U(VI)]_{total} = 1.0 \times 10^{-5}$ M. Care must be taken when using this distribution diagram because the calculation is based on the assumption that no solid U(VI) phases are formed.

Figure 9-5: Distribution diagram of the aqueous dioxouranium(VI) hydroxide system. $[U(VI)]_{total} = 1.0 \times 10^{-5}$ M, $I = 0$, 298.15 K. The precipitation of solid U(VI) phases is suppressed. Note that the speciation will change significantly at higher uranium concentrations.




### 9.3.2.1.4 Temperature dependence of the hydrolysis constants and the enthalpy of hydrolysis

Equilibrium constants of U(VI) hydrolysis at different temperatures were reported in three studies [2004ZAN/DIB], [2008AMO/GAM], [2009TEK/ACA] (Table 9-2). All data indicate that the hydrolysis is enhanced at higher temperatures. The studies of [2008AMO/GAM] and [2009TEK/ACA] were conducted at only two or three temperatures in narrow temperature ranges, *i.e.*, 75 and 100 °C in [2008AMO/GAM] and 25, 37, and 45 °C in [2009TEK/ACA] (Table 9-2). Because the temperature ranges in these two studies are too narrow and the numbers of data points few (two or three), this

review does not accept these data. The hydrolysis constants for the (1,1), (2,2) and (5,3) species were determined in the temperature range of 10-85 °C in [2004ZAN/DIB]. Using the Van't Hoff method, the "average" enthalpies of hydrolysis in the temperature range of 10-85 °C in 0.1 M TEA($ClO_4$) were calculated to be (46.5 ± 3.7) kJ·mol$^{-1}$, (47.6 ± 2.6) kJ·mol$^{-1}$, and (120.0 ± 3.7) kJ·mol$^{-1}$ for $UO_2OH^+$, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$ respectively. The values for $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ are in excellent agreement with those directly determined at 298.15 K by calorimetry in the same study, (48.2 ± 1.7) kJ·mol$^{-1}$ and (120.1 ± 1.6) kJ·mol$^{-1}$, respectively.

A few calorimetric studies including [2004CRE/DES], [2004ZAN/DIB] and [2014ZAN/DIB], were conducted to determine the enthalpies of hydrolysis for the (1,1), (3,1), (4,1), (2,2), (4,3), (5,3), (6,3), (7,3), and (8,3) species in different ionic media. To correct the experimentally determined enthalpies of hydrolysis at 298.15 K in the different ionic media and obtain the enthalpies of hydrolysis at 298.15 K and infinite dilution, the review uses only the data at low ionic strength (0.1 M) from [2004CRE/DES], [2004ZAN/DIB], and [2014ZAN/DIB], and adopts the method described in *Modelling in Aquatic Chemistry* [1997ALL/BAN], Section IX.10, Eqn. (IX. 72) on p. 412.

$$\Delta_r H_m - \mathrm{r}L_l = \Delta_r H_m^o + 3/4 \frac{A_L \Delta(Z_2)\sqrt{I_m}}{(1+1.5\sqrt{I_m})} - RT^2 \mathrm{m}\Delta\varepsilon_L \qquad (9.14)$$

The relative partial enthalpy of the solvent is obtained from Eq. (9.15)

$$L_l \approx \frac{M_w}{1000}\left[-\frac{3A_L}{2(1.5^3)}(t - 2\ln t - \frac{1}{t})\right] \qquad (9.15)$$

where $t = (1 + 1.5\sqrt{I_m})$. Because of the low ionic strength (0.1 M), $L_1$ is very close to zero and can be neglected. In addition, the third term on the right side of Eq. (9.14) is also neglected because it is most likely small, ≈ 10$^{-3}$ kg·mol$^{-1}$·K$^{-1}$ as discussed in *Modelling in Aquatic Chemistry* [1997ALL/BAN], p.421 and p.424. The corrections of the enthalpies of hydrolysis to $I = 0$ are shown in Table 9-9.

Table 9-9: Correction of experimental $\Delta_r H_{n,m}$ to $\Delta_r H_{n,m}^o$ at 298.15 K for the aqueous equilibria: $mUO_2^{2+} + nH_2O(l) \rightleftharpoons (UO_2)_m(OH)_n^{2m-n} + nH^+$. None of these corrected enthalpies of reaction were reported in [1992GRE/FUG] and [2003GUI/FAN].

| *n:m* | *t* /°C | Method | *I* /medium | $\Delta_r H_{n,m}$ /kJ·mol$^{-1}$ | $\Delta_r H_{n,m}^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|---|
| 1:1 | 25 | cal | 0.10 M NaCl | (42.7 ± 2.3) | (43.3 ± 2.3) | [2004CRE/DES] |
| | 10-85 | pot | 0.10 M TEA($ClO_4$) | (46.5 ± 3.7) | (47.1 ± 3.7)[(a)] | [2004ZAN/DIB] |
| | | | | | **(43.3 ± 2.3)** | This review |
| 3:1 | 25 | cal | 0.10 M TMA($NO_3$) | (93.7 ± 1.8) | (93.7 ± 1.8)[(a)] | [2014ZAN/DIB] |
| 4:1 | 25 | cal | 0.10 M TMA($NO_3$) | (167.6 ± 1.7) | (166.3 ± 1.7)[(a)] | [2014ZAN/DIB] |

(Continued on next page)

Table 9-9 (continued)

| *n:m* | *t* /°C | Method | *I* /medium | $\Delta_r H_{n,m}$ /kJ·mol$^{-1}$ | $\Delta_r H^o_{n,m}$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|---|
| 2:2 | 25 | cal | 0.10 M NaCl | (47.2 ± 0.5) | (47.8 ± 0.5) | [2004CRE/DES] |
| | 25 | cal | 0.10 M TEA($ClO_4$) | (48.2 ± 1.7) | (48.8 ± 1.7)[(a)] | [2004ZAN/DIB] |
| | 25 | cal | 0.10 M TMA($NO_3$) | (49.1 ± 0.9) | (49.7 ± 0.9)[(a)] | [2014ZAN/DIB] |
| | | | | | **(47.8 ± 0.5)** | This review |
| 4:3 | 25 | cal | 0.10 M NaCl | (97.9 ± 0.5) | (99.2 ± 0.5) | [2004CRE/DES] |
| | 25 | cal | 0.10 M TMA($NO_3$) | (94.2 ± 3.0) | (95.5 ± 3.0)[(a)] | [2014ZAN/DIB] |
| | | | | | **(99.2 ± 0.5)** | This review |
| 5:3 | 25 | cal | 0.10 M NaCl | (118.8 ± 0.6) | (120.7 ± 0.6) | [2004CRE/DES] |
| | 25 | cal | 0.10 M TEA($ClO_4$) | (120.1 ± 1.6) | (122.0 ± 1.6)[(a)] | [2004ZAN/DIB] |
| | 25 | cal | 0.10 M TMA($NO_3$) | (123.5 ± 1.0) | (125.4 ± 1.0)[(a)] | [2014ZAN/DIB] |
| | | | | | **(120.7 ± 0.6)** | This review |
| 6:3 | 25 | cal | 0.10 M TMA($NO_3$) | (132.2 ± 4.0) | (134.1 ± 4.0)[(a)] | [2014ZAN/DIB] |
| 7:3 | 25 | cal | 0.10 M NaCl | (176 ± 6) | (179 ± 6) | [2004CRE/DES] |
| | 25 | cal | 0.10 M TMA($NO_3$) | (198.2 ± 2.1) | (199.5 ± 2.1)[(a)] | [2014ZAN/DIB] |
| 8:3 | 25 | cal | 0.10 M TMA($NO_3$) | (230.2 ± 2.7) | (230.2 ± 2.7)[(a)] | [2014ZAN/DIB] |

(a) Enthalpy values from [2004ZAN/DIB] for hydroxide complexes with positive charge are in good agreement with those in NaCl media. The enthalpies of reaction for the (3,1), (4,1), (6,3), (7,3) and (8,3) complexes in TMA are given for information only because of the equilibrium constants are significantly different from those in perchlorate media.

No enthalpies of reaction for the aqueous hydrolysis of U(VI) were selected by previous reviews ([1992GRE/FUG], [2003GUI/FAN]). Based on the above discussions of the new studies that appeared since 2003, this review selects enthalpies of hydrolysis at 298.15 K and $I = 0$ for the reactions involving (1,1), (2,2), (4,3) and (5,3) species. The selected data are summarised in Table 9-10. The enthalpies of hydrolysis at 298.15 K and $I = 0$ for the reactions involving (6,3) and (8,3) species (Table 9-9), though reasonable, are not selected because further studies are needed to evaluate the equilibrium constants $\log_{10}{}^{*}\beta^{o}_{6,3}$ (298.15 K) and $\log_{10}{}^{*}\beta^{o}_{8,3}$ (298.15 K).

Table 9-10: Summary of $\Delta_r H^o_{n,m}$ values at 298.15 K for the aqueous equilibria: $m UO_2^{2+} + n H_2O(l) \rightleftharpoons (UO_2)_m (OH)_n^{2m-n} + n H^+$, selected by this review. In the third column, we have also included for information, some enthalpies of reaction estimated based on the Ryzhenko-Bryzgalin model, [1994GRE/PLY]. None of these values were reported in [1992GRE/FUG] and [2003GUI/FAN]. The selected values are in bold.

| *n:m* | $\Delta_r H^o_{n,m}$ /kJ·mol$^{-1}$ | $\Delta_r H^o_{n,m}$ /kJ·mol$^{-1}$ estimated |
|---|---|---|
| 1:1 | **(43.300 ± 2.300)** | (36 ± 20) |
| 2:1 | **–** | (65 ± 20) |
| 3:1 | **–** | (105 ± 25) |
| 4:1 | **–** | – |
| 2:2 | **(47.800 ± 0.500)** | (40 ± 10) |

(Continued on next page)

Table 9-10 (continued)

| *n:m* | $\Delta_r H^o_{n,m}$ /kJ·mol$^{-1}$ | $\Delta_r H^o_{n,m}$ /kJ·mol$^{-1}$ estimated |
|---|---|---|
| 4:3 | **(99.200 ± 0.500)** | – |
| 5:3 | **(120.700 ± 0.600)** | (108 ± 30) |
| 7:3 | **–** | – |

The present review has also noticed that Grenthe and Plyasunov [1994PLY/GRE] extended the Ryzhenko-Bryzgalin model in order to estimate equilibrium constants of mononuclear complexes at different temperatures between 273.15 and 523.15 K. The equilibrium constants at 273.15, 298.15 and 323.15 K were used by the present review to estimate the enthalpies of reaction for the complexes in Table 9-9 by using the experimental value of the equilibrium constants at 298.15 K and the entropy of reaction, $\Delta_r S^o_m$. The present review obtained the average enthalpy of reaction, $\Delta_r H^o_{n,m}$ (kJ·mol$^{-1}$), to be (36 ± 20) ($n$ = 1, $m$ = 1), (65 ± 20) ($n$ = 2, $m$ = 1), (105 ± 25) ($n$ = 3, $m$ = 1), (40 ± 10) ($n$ = 2, $m$ = 2), (108 ± 30) ($n$ = 5, $m$ = 3) kJ·mol$^{-1}$, respectively, values which, within the estimated uncertainty, are consistent with the ones obtained by calorimetry (Table 9-10). In a later fluorescence study [2000ELI/GRE], the authors used the enthalpy of reaction estimated by the Ryzhenko-Bryzgalin model to calculate the equilibrium constants and, accordingly, the speciation of U(VI) hydrolysis products for the determination of fluorescence lifetimes of U(VI) hydroxide complexes. The results from [1994PLY/GRE] and [2000ELI/GRE] suggest that the Ryzhenko-Bryzgalin model could be applicable for the estimation of both equilibrium constants at high temperatures and reaction enthalpies for mononuclear and polynuclear U(VI) hydrolysis reactions. Detailed discussions on the methodology are given in [1994PLY/GRE] and [2000ELI/GRE].

Using the data in Table 9-10 ($\Delta_r H^o_{n,m}$), Table 9-8 ($\Delta_f G^o_{n,m}$), and the auxiliary data in Chapter 14, the standard enthalpies of formation and the standard molar entropy for the hydrolysis species are calculated and are summarised in Table 9-11.

Table 9-11: Summary of $\Delta_f H^o_{n,m}$ and $S^o$ values at 298.15 K for the hydrolysis species of U(VI), $(UO_2)_m(OH)_n^{2m-n}$. The uncertainties are estimated by using the method for propagation of errors in Appendix C.6.2 in [2003GUI/FAN]. The selected values are in bold.

| *n:m* | Species | $\Delta_f H^o_{n,m}$ (298.15 K) /kJ·mol$^{-1}$ | $S^o$(298.15 K) /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|
| 1:1 | $UO_2OH^+$ | **– (1261.530 ± 2.746)** | **(16.468 ± 9.467)** |
| 2:2 | $(UO_2)_2(OH)_2^{2+}$ | **– (2561.860 ± 3.042)** | **– (3.772 ± 6.416)** |
| 4:3 | $(UO_2)_3(OH)_4^{2+}$ | **– (4101.120 ± 4.531)** | **(90.095 ± 10.808)** |
| 5:3 | $(UO_2)_3(OH)_5^{+}$ | **– (4365.450 ± 4.544)** | **(162.277 ± 9.505)** |

#### 9.3.2.1.5 Relevant solubility studies

This section deals with the selection of equilibrium constants for the dissolution of some U(VI) compounds including $UO_3 \cdot 2H_2O$(cr) (metaschoepite) and $Na_2U_2O_7 \cdot H_2O$(cr). The Section 9.3.3.1 deals with thermodynamic data for U(VI) oxides and hydroxides.

##### 9.3.2.1.5.1 Metaschoepite

Guillaumont *et al.*, [2003GUI/FAN], discussed experimental solubility constants for metaschoepite (listed in their Table 9-5, p. 168) and selected the weighted average, $\log_{10} {}^{*}K_s^{\circ}$ (9.16) = (5.19 ± 0.01). The present review considers the estimated uncertainty unrealistically small. We also note that the solubility constant is not listed in their Table 3-2 for *Selected thermodynamic data for reactions involving uranium compounds and complexes*. However, Guillaumont *et al.* have retained the selected thermodynamic data for $UO_3 \cdot 2H_2O$(cr) from [1992GRE/FUG].

$$UO_3 \cdot 2H_2O(cr) + 2H^+ \rightleftharpoons UO_2^{2+} + 3H_2O(l) \qquad (9.16)$$

Since the previous review, there are three additional solubility studies, [2005FUJ/YAM2], [2008CHO/JUN] and [2017ALT/YAL], see Table 9-12. Altmaier *et al.* give an authoritative review of previous studies and their study is the first one with an in-depth phase characterisation of $UO_3 \cdot 2H_2O$(cr) [2017ALT/YAL].

Table 9-12: Experimental solubility constants for the dissolution equilibria:
$UO_3 \cdot 2H_2O(cr) \rightleftharpoons UO_2^{2+} + 2OH^- + H_2O(l)$ and
$UO_3 \cdot 2H_2O(cr) + 2H^+ \rightleftharpoons UO_2^{2+} + 3H_2O(l)$.

| $t$ /°C | Method | Ionic medium | $\log_{10} K_{sp}^{\circ}$ | $\log_{10} {}^{*}K_s^{\circ}$ (9.16) | Reference |
|---|---|---|---|---|---|
| 25 | solubility | $I = 0$ | – (22.46 ± 0.10) | (5.54 ± 0.10) | [2005FUJ/YAM2] |
| | | | – (22.18 ± 0.12)[(b)] | (5.82 ± 0.13)[(b)] | |
| rt | solubility[(a)] | 0.1 M $NaClO_4$ | – (22.63 ± 0.04) | – | [2008CHO/JUN] |
| | | $I = 0$ | – (23.23 ± 0.04) | (4.77 ± 0.04)[(c)] | [2008CHO/JUN] |
| 25 | solubility | $I = 0$ | – (22.03 ± 0.14) | (5.97 ± 0.14) | [1992SAN/BRU] |
| | | | – (21.94 ± 0.13)[(b)] | (6.06 ± 0.13)[(b)] | |
| (22 ± 2) | solubility | $I = 0$ | – (22.65 ± 0.13) | (5.35 ± 0.13) | [2017ALT/YAL] |
| 25 | solubility | $I = 0$ | – (23.19 ± 0.43) | (4.81 ± 0.43) | [2003GUI/FAN] |
| 25 | solubility | $I = 0$ | **– (22.650 ± 0.130)** | **(5.350 ± 0.130)** | **Selected by this review** |

(a) LIBD—laser-induced breakdown technique was used to identify the point where precipitation was formed.
(b) Recalculated by this review.
(c) This value refers to solid phases with small (colloidal) particle size as shown by the X-ray powder pattern.

As pointed out in the Appendix A reviews, it is not straightforward to calculate the solubility constant for Reaction (9.16) because the value depends on the particle size of the solid, the speciation model and the hydrolysis constants used. Altmaier *et al.* [2017ALT/YAL] is the only study where the particle size has been properly estimated, the minimum particle size of the schoepite phase used by them is about 100 nm, which indicates that the particle size will only have a small effect on the measured solubility (*cf.*

[2008RAN/FUG], Section VII.4.2.3, pp. 197-194). The present review considers this as the most reliable and accurate study published so far and have therefore based our selected value, $\log_{10}{}^{*}K_{s}^{o}$ (9.16) = (**5.350 ± 0.130**), on this alone.

#### 9.3.2.1.5.2 $Na_2U_2O_7{\cdot}xH_2O$(cr)

The solubility of $Na_2U_2O_7{\cdot}H_2O$(cr) has been studied by Altmaier *et al.* [2017ALT/YAL], based on well-characterised samples. Solubility experiments were performed in 0.1-5.0 M NaCl solutions at 22 °C. The $Na_2U_2O_7{\cdot}H_2O$(cr) phase is only stable at pH > 8.5-9.0 and transforms at lower pH to metaschoepite, $UO_3{\cdot}2H_2O$(cr), Reaction (9.17).

The solubility constant reported in [2017ALT/YAL] for $Na_2U_2O_7{\cdot}H_2O$(cr) has been calculated from the solubility constant of $UO_3{\cdot}2H_2O$(cr), $\log_{10}{}^{*}K_{s,0}^{o} = (5.35 \pm 0.13)$ and the p[$H^+$] value where the two solids are in equilibrium. The variation in p[$H^+$] in the cross-over region between the solubility curves for the two phases suggests that equilibrium between them is not complete, but an average value of the p[$H^+$] in this region can nevertheless be used for a reliable location. Based on this, Altmaier *et al.* obtain the conditional equilibrium constants for Reaction (9.18), which recalculated to zero ionic strength and combined with the selected value for $\log_{10}{}^{*}K_{s}^{o} = (5.350 \pm 0.130)$ results in $\log_{10}{}^{*}K_{s}^{o}$ (9.18) = **(12.20 ± 0.20)**, which together with the corresponding $\Delta_r G_m^o$ (9.18) = **– (69.638 ± 1.142)** kJ·mol$^{-1}$ and $\Delta_f G_m^o$ ($Na_2U_2O_7{\cdot}H_2O$, cr) = **– (3238.292 ± 4.182)** kJ·mol$^{-1}$ are included among the selected values.

$$UO_3{\cdot}2H_2O(cr) + Na^+ \rightleftharpoons 1/2Na_2U_2O_7{\cdot}H_2O(cr) + H^+ + H_2O(l) \quad (9.17)$$

$$1/2Na_2U_2O_7{\cdot}H_2O(cr) + 3H^+ \rightleftharpoons Na^+ + UO_2^{2+} + 2H_2O(l) \quad (9.18)$$

This value is consistent with $\log_{10}{}^{*}K_{s,0}^{o}$ ($0.5Na_2U_2O_7{\cdot}xH_2O$, cr) recalculated from solubility data in [1998YAM/KIT]. Yamamura and co-workers investigated the solubility of $Na_2U_2O_7{\cdot}xH_2O$(cr) at $T$ = (25 ± 1) °C in alkaline carbonate solutions, and determined a solubility constant for the equilibrium reaction:

$$0.5Na_2U_2O_7{\cdot}xH_2O(cr) + 3CO_3^{2-} + (1.5 - 0.5x)H_2O(l) \rightleftharpoons UO_2(CO_3)_3^{4-} + 3OH^- + Na^+ \quad (9.19)$$

Combining this solubility constant with $\log_{10}K^{o}(UO_2(CO_3)_3^{4-}) = (21.84 \pm 0.04)$ selected in [2003GUI/FAN] and retained in the present review, results in $\log_{10}K_{s}^{o}$ ($0.5Na_2U_2O_7{\cdot}H_2O$, cr) = – (29.7 ± 1.0) or $\log_{10}{}^{*}K_{s}^{o}$ ($0.5Na_2U_2O_7{\cdot}H_2O$, cr) = (12.3 ± 1.0), in excellent agreement with the solubility constant determined in [2017ALT/YAL], demonstrating consistency with thermodynamics of the uranium(VI) carbonate system. Reaction (9.18) has also been studied by Devina *et al.* [1983DEV/YEF] at temperatures between 100 and 200 °C. Based on these, the present review has made an estimate of $\log_{10}{}^{*}K_{s,0}^{o}$ ($0.5Na_2U_2O_7{\cdot}H_2O$, cr) ≈ (13 ± 2) based on the assumption that the solid used was the monohydrate.

### 9.3.2.2 U(IV) hydroxide complexes

#### 9.3.2.2.1 Aqueous U(IV) hydroxide complexes

Some new studies have been published on the hydrolysis of U(IV), using different techniques including solvent extraction [2003FUJ/YAM2], solubility measurements [2003RAI/YUI] [2005FUJ/YAM], and emf measurements [2006MAN/CAR]. The experimental data from these studies are summarised in Table 9-13. Note that two different notations may be used to describe the hydrolysis reactions: $U^{4+} + nH_2O(l) \rightleftharpoons U(OH)_n^{4-n} + nH^+$ with the equilibrium constant ${}^*\beta_n$, and $U^{4+} + nOH^- \rightleftharpoons U(OH)_n^{4-n}$ with the equilibrium constant $\beta_n$.

Table 9-13: New experimental equilibrium constants for the aqueous U(IV) hydroxide system.

| $n$ | $t$ /°C | Method | $I$ /medium | $\log_{10}\beta_n$ | Reference |
|---|---|---|---|---|---|
| | | | $U^{4+} + nOH^- \rightleftharpoons U(OH)_n^{4-n}$ | | |
| 1 | rt | solv. ex. | $I = 0$ | (13.71 ± 0.31) | [2003FUJ/YAM2] |
| | 25 | | $I = 0$ | (13.46 ± 0.06) | [1992GRE/FUG] |
| 2 | rt | solv. ex. | $I = 0$ | (26.12 ± 0.21) | [2003FUJ/YAM2] |
| | 25 | | $I = 0$ | (26.9 ± 1.0)(a) | [2001NEC/KIM] |
| 3 | rt | solv. ex. | $I = 0$ | (36.85 ± 0.36) | [2003FUJ/YAM2] |
| | 25 | | $I = 0$ | (37.3 ± 1.0)(a) | [2001NEC/KIM] |
| 4 | rt | solv. ex. | $I = 0$ | (45.44 ± 0.40)(b) | [2003FUJ/YAM2] |
| | 25 | | $I = 0$ | (46.0 ± 1.4) | [2003GUI/FAN] |
| 5 | 25 | solubility | $I = 0$ | < 48.10 | [2005FUJ/YAM] |
| 6 | 25 | solubility | $I = 0$ | (48.95 ± 1.01) | [2005FUJ/YAM] |
| | | | $U^{4+} + nH_2O(l) \rightleftharpoons U(OH)_n^{4-n} + nH^+$ | | |
| 1 | 25 | emf | 3.0 M $NaClO_4$ | – (1.60 ± 0.02) | [2006MAN/CAR] |
| | | | $I = 0$ | – (0.49 ± 0.18) | |
| 4 | 22 | solubility | $I = 0$ | < – 11.6 | [2003RAI/YUI] |
| 4 | 25 | emf | 3.0 M $NaClO_4$ | – (7.67 ± 0.04) | [2006MAN/CAR] |
| | | | $I = 0$ | – (4.93 ± 0.35) | |

(a) Estimated value in [2001NEC/KIM].
(b) Estimated value in [2003FUJ/YAM2].

The study in [2003FUJ/YAM2] is an extended investigation following their previously published study on the hydrolysis of U(IV) and solubility of $UO_2$(am, hyd) [2002FUJ/YAM]. Solvent extraction was used with $^{233}U$ as radiotracer, covering the $-\log_{10}[H^+]$ region 1-4 and different ionic strengths ($I$ = 0.1, 0.5, and 1.0 M (H/Na)$ClO_4$) in the aqueous phase. The hydrolysis constants at $I = 0$ $\log_{10}\beta_n^o$, where $\beta_n = [U(OH)_n^{4-n}] / \{[U^{4+}][OH^-]^n\}$, were calculated to be: (13.71 ± 0.31) ($n$ = 1), (26.12 ± 0.21) ($n$ = 2), and (36.85 ± 0.36) ($n$ = 3) (Table 9-13), using the specific ion interaction parameters from [1992GRE/FUG]. The value of $\log_{10}\beta_4^o$ was estimated to be (45.44 ± 0.40), by using a semi-empirical "hard-core" model. The absence of reported values of $\log_{10}\beta_n$ at individual ionic strengths and details on the data fitting used in [2003FUJ/YAM2] precludes the validation by SIT calculations, however, the values of

$\log_{10}\beta_1^o$ and $\log_{10}\beta_4^o$ from [2003FUJ/YAM2] are consistent with those selected by [1992GRE/FUG] and [2003GUI/FAN], as shown in Table 9-13. The values of $\log_{10}\beta_2^o$ and $\log_{10}\beta_3^o$ from [2003FUJ/YAM2] are in good agreement with those estimated in [2001NEC/KIM] and discussed in [2003GUI/FAN].

In a carefully conducted solubility study with uranium dioxide [2003RAI/YUI], Rai *et al.* precipitated $UO_2$(cr) at 90 °C from low-pH U(IV) solutions, and equilibrated at 90 °C for 24 days and then at 22 °C for one day. Rigidly controlled redox conditions were maintained by adding $EuCl_2$ to avoid oxidation of U(IV). X-ray diffraction analyses of the solid phases in conjunction with the observed solubility behaviour indicated that $UO_2$(cr) and $UO_2$(am, hyd) were the dominant solid phases at pH < 1.2 and pH > 1.2, respectively. Based on these data, an upper limit of $\log_{10}{}^*\beta_4^o$ for the hydrolysis reaction ($U^{4+} + 4H_2O \rightleftharpoons U(OH)_4(aq) + 4H^+$) was estimated to be < – 11.6 (*i.e.*, $\log_{10}\beta_4^o < 44.4$). This upper limit is close to $\log_{10}\beta_4^o = (46.0 \pm 1.4)$ selected by [2003GUI/FAN] and the estimated in [2003FUJ/YAM2], (45.44 ± 0.40), taking into consideration that the uncertainties of the latter two values are ± 1.4 and ± 0.40, respectively.

In [2006MAN/CAR], the hydrolysis constants of U(IV) were determined by potentiometry in test solutions where no solid phase was present. The reaction cell contained inert Pd/Au metal sponge and glass electrodes and had the ionic strength $I$ = 3 mol·dm$^{-3}$ $NaClO_4$ and p$C_H$ = 0.5 to 1.8. The values of $\log_{10}{}^*\beta_1$ and $\log_{10}{}^*\beta_4$ were determined as – (1.62 ± 0.02) and – (7.70 ± 0.04), respectively at $I$ = 3 mol·dm$^{-3}$ $NaClO_4$, and converted by SIT to the values of $\log_{10}{}^*\beta_1^o$ = – (0.49 ± 0.18) and $\log_{10}{}^*\beta_4^o$ = – (4.93 ± 0.35). These values correspond to $\log_{10}\beta_1^o$ (13.51 ± 0.18) and $\log_{10}\beta_4^o$ (51.07 ± 0.35). The value of $\log_{10}\beta_1^o$ (13.51 ± 0.18) is consistent with that selected in [1992GRE/FUG], but the value of $\log_{10}\beta_4^o$ (51.07 ± 0.35) is significantly higher than the value obtained by solubility measurements ($\log_{10}\beta_4^o < 44.4$) in [2003RAI/YUI] and the value selected in [2003GUI/FAN], by the previous NEA review ($\log_{10}\beta_4^o = 46.0 \pm 1.4$).

Taking into consideration the recent data from [2003FUJ/YAM2], [2003RAI/YUI], [2006MAN/CAR], and the selection of previous NEA TDB reviews, this review retains the values of $\log_{10}\beta_1^o$ = **(13.460 ± 0.060)** and $\log_{10}\beta_4^o$ = **(46.000 ± 1.400)** from [2003GUI/FAN], and selects $\log_{10}\beta_2^o$ and $\log_{10}\beta_3^o$ from [2003FUJ/YAM2], **(26.100 ± 0.200)** for $\log_{10}\beta_2^o$ and **(36.800 ± 0.400)** for $\log_{10}\beta_3^o$, respectively. These values correspond to – (1.9 ± 0.2) for $\log_{10}{}^*\beta_2^o$ and – (5.2 ± 0.4) for $\log_{10}{}^*\beta_3^o$.

Fujiwara *et al.* [2005FUJ/YAM], also measured the solubility of $UO_2$(am, hyd) from oversaturation at high pH (12-14) using $Na_2S_2O_4$ as a reducing agent. They obtained hydrolysis constants, $\log_{10}\beta_n^o$, for the complexes $U(OH)_n^{4-n}$ by modeling the solubility data using the solubility product obtained in a previous study ($\log_{10}K_{sp}^o$ = – 53.93 [2003FUJ/YAM2]). The values of $\log_{10}\beta_5^o$ (< 48.10) and $\log_{10}\beta_6^o$ (48.95 ± 1.01), have been obtained using the ion interaction parameters: $\varepsilon(Na^+, U(OH)_5^-)$

< 0.63 kg·mol$^{-1}$, and $\varepsilon(Na^+, U(OH)_6^{2-})$ = (1.01 ± 0.712) kg·mol$^{-1}$. Taking into consideration the extreme difficulty to maintain the U(IV) oxidation state in solutions of very high pH, the present review considers both the stoichiometry and the ion-interaction coefficients as tentative. It should also be pointed out that the ion interaction parameters $\varepsilon(Na^+, U(OH)_5^-)$ and $\varepsilon(Na^+, U(OH)_6^{2-})$ reported in [2005FUJ/YAM] seem too high for the interactions of $Na^+$ with anions of – 1 or – 2 charges. Fujiwara *et al.* also mentioned that the solubility of tetravalent oxides of Th, Np, or Pu remains constant in the pH region up to 13-14, which is a strong indication that anionic hydroxide complexes are not formed for these elements. As a result, the values of $\log_{10}\beta_5^o$ and $\log_{10}\beta_6^o$ from [2005FUJ/YAM] are not selected by this review.

#### 9.3.2.2.2 Solubility studies of $UO_2$(am) and $UO_2$(cr)

The measurement of the equilibrium constants for the dissolution reaction, $UO_2(s) + 2H_2O \rightleftharpoons U^{4+} + 4OH^-$, is complicated by the difficulty in maintaining the tetravalent U(IV) state in solutions of high pH as well as the uncertainty in the nature of the solid (crystalline *vs.* amorphous), particle size and equilibration time considered in the study. Values of $\log_{10}K_{sp}$ were reported in two studies [2003FUJ/YAM2]
and [2007OPE/WEI]. The study of [2003RAI/YUI] that was mentioned in the previous review by [2003GUI/FAN] and discussed in Section 9.3.2.2.1 is also included in Table 9-14.

Fujiwara *et al.* used the hydrolysis constants ($\log_{10}\beta_n^o$, $n$ = 1-4) from [2003FUJ/YAM2] to re-evaluate the solubility data of a previous study [2002FUJ/YAM] and determined $\log_{10}K_{sp}$ at $I$ = 0.1, 0.5, 1.0, and 2.0 M $NaClO_4$ for the reaction $UO_2(s) + 2H_2O \rightleftharpoons U^{4+} + 4OH^-$ [2003FUJ/YAM2]. Using SIT and ion interaction parameters selected by NEA [1992GRE/FUG], the value of $K_{sp}^o$ ($I$ = 0) was calculated to be – (54.61 ± 0.05), which agrees very well with the value of – (54.5 ± 1.0) selected for $UO_2$(am, hyd) by [2003GUI/FAN].

The value of $\log_{10}K_{sp}^o$ obtained by the laser-induced breakdown technique for $UO_2$(am, hyd), – (54.1 ± 1.0) [2007OPE/WEI], is also consistent with the one from [2003FUJ/YAM2] and that selected by [2003GUI/FAN]. Therefore, this review retains the value of $\log_{10}K_{sp}^o$ = **– (54.500 ± 1.000)** for $UO_2$(am, hyd).

Table 9-14: New experimental solubility constants for the dissolution equilibria: $UO_2(s) + 2H_2O(l) \rightleftharpoons U^{4+} + 4OH^-$.

| Solid | $t$ /°C | Method | $I$ /medium | $\log_{10} K_{sp}$ | $\log_{10} K_{sp}^{\circ}$ | Reference |
|---|---|---|---|---|---|---|
| $UO_2$(am, hyd) | 25 | solubility | 0.1 M $NaClO_4$ | – (51.63 ± 0.10) | – (53.84 ± 0.10)[(a)] | [2003FUJ/YAM2] |
| | | | 0.5 M $NaClO_4$ | – (50.94 ± 0.06) | – (54.56 ± 0.06)[(a)] | |
| | | | 1.0 M $NaClO_4$ | – (50.16 ± 0.16) | – (54.40 ± 0.17)[(a)] | |
| | | | 2.0 M $NaClO_4$ | – (50.21 ± 0.17) | – (55.34 ± 0.20)[(a)] | |
| | 25 | | $I$ = 0 | | – (54.61 ± 0.05)[(b)] | this review |
| | rt | LIBD | $I$ = 0 | – (54.1 ± 1.0) [(c)] | – (54.1 ± 1.0)[(c)] | [2007OPE/WEI] |
| | 25 | | $I$ = 0 | | – (54.5 ± 1.0) | [2003GUI/FAN] |
| $UO_2$(cr) | 25 | solubility | $I$ = 0 | | – (60.20 ± 0.24) | [2003RAI/YUI] |
| | rt | LIBD | $I$ = 0 | – (59.6 ± 1.0) [(d)] | – (59.6 ± 1.0)[(d)] | [2007OPE/WEI] |
| | 25 | | $I$ = 0 | | – (60.86 ± 0.36) | [1992GRE/FUG] |

(a) Calculated using SIT by this review.
(b) Weighted average of $\log_{10} K_{sp}^{\circ}$ values from different $I$. The uncertainty was estimated by using the method in Appendix C.
(c) $UO_2$(am, hyd), not corrected for particle size.
(d) $UO_2$(cr), corrected for particle size.

As discussed in a previous section on aqueous U(IV) hydroxide complexes (Section 9.3.2.2.1), Rai *et al.* [2003RAI/YUI] conducted a solubility study with $UO_2$(cr) and $UO_2$(am, hyd) covering a wide pH region [2003RAI/YUI], using $EuCl_2$ to maintain strongly reducing conditions. $UO_2$(cr) was identified as the dominant solid phase at pH < 1.2 by X-ray diffraction (XRD). The upper limit for $\log_{10} K_{sp}^{\circ}$ ($UO_2(cr) + 2H_2O(l) \rightleftharpoons U^{4+} + 4OH^-$) was established as – (60.2 ± 0.24).

The value of $\log_{10} K_{sp}^{\circ}$ for $UO_2$(cr) was determined to be – (59.6 ± 1.0) by the laser-induced breakdown technique [2007OPE/WEI]. This value overlaps with that obtained by solubility measurements in [2003RAI/YUI], – (60.20 ± 0.24), and is close to that obtained from the CODATA values, which gives – (60.86 ± 0.36) reported in [1992GRE/FUG]. Accepting the two experimentally determined values from [2007OPE/WEI] and [2003RAI/YUI], this review retains the value of $\log_{10} K_{sp}^{\circ}$ for $UO_2$(cr) from the previous review [1992GRE/FUG], but with enlarged uncertainty in order to overlap with the data from [2007OPE/WEI] and [2003RAI/YUI]: $\log_{10} K_{sp}^{\circ}$ ($UO_2$, cr, 298.15 K) = **– (60.860 ± 1.000).**

#### 9.3.2.2.3 Summary of selected equilibrium constants for U(IV) hydrolysis and dissolution of $UO_2$(s)

Based on the discussions in this review and the selections by previous NEA TDB reviews [1992GRE/FUG], [2003GUI/FAN], equilibrium constants for the hydrolysis of U(IV) and the dissolution of $UO_2$(s) are selected and summarised in Table 9-15.

Table 9-15: Summary of the equilibrium constants, $\log_{10}{}^{*}\beta_n^{\circ}$, and Gibbs free energy of the hydrolysis of U(IV), $U^{4+} + nH_2O(l) \rightleftharpoons U(OH)_n^{(4-n)} + nH^+$, and the $\log_{10}K_{sp}^{\circ}$ of the dissolution reaction $UO_2(s) + 2H_2O(l) \rightleftharpoons U^{4+} + 4OH^-$ at 298.15 K retained or selected by this review. The uncertainties of $\Delta_r G_m^{\circ}$ are estimated by using the method for propagation of errors in Appendix C.

| $n$ | $\log_{10}{}^{*}\beta_n^{\circ}$ | $\Delta_r G_m^{\circ}$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|
| 1 | **– (0.540 ± 0.060)** | **(3.082 ± 0.342)** | [1992GRE/FUG], [2003GUI/FAN] |
| 2 | **– (1.900 ± 0.200)** | **(10.845 ± 1.142)** | This review |
| 3 | **– (5.200 ± 0.400)** | **(29.682 ± 2.283)** | This review |
| 4 | **– (10.000 ± 1.400)**[(a)] | **(57.081 ± 7.991)** | [2003GUI/FAN] |

| Solid | $\log_{10}K_{sp}^{\circ}$ | | Reference |
|---|---|---|---|
| | $UO_2(s) + 2H_2O(l) \rightleftharpoons U^{4+} + 4OH^-$ | | |
| $UO_2$(am, hyd) | **– (54.500 ± 1.000)** | **– (311.088 ± 5.708)** | [2003GUI/FAN] |
| $UO_2$(cr) | **– (60.860 ± 1.000)** | **– (347.389 ± 5.708)** | This review |

(a) Converted from the value of $\log_{10}\beta_4^{\circ}$ = (46.000 ± 1.400) in [2003GUI/FAN]

The standard Gibbs energies of formation for the hydrolysis species of U(IV) are calculated using the data in Table 9-15 and the auxiliary data in Chapter 14 and Table 9-16.

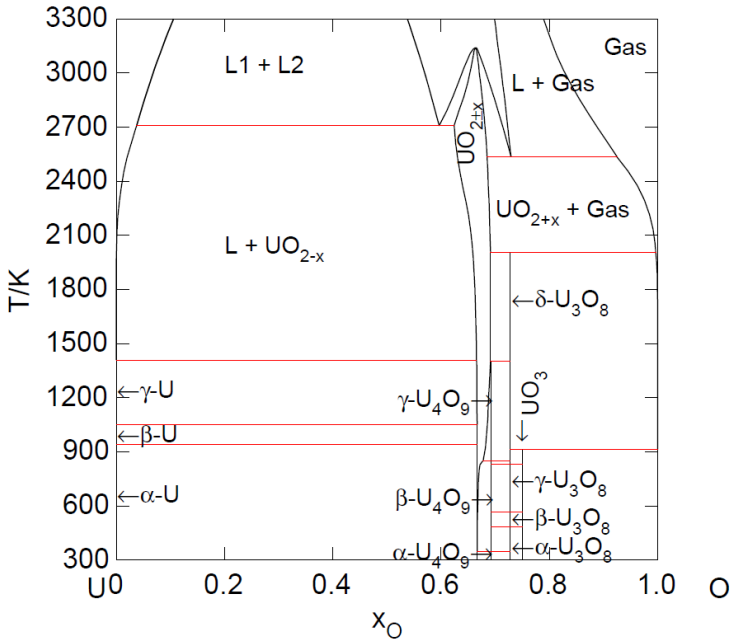
Table 9-16: Summary of $\Delta_f G_m^{\circ}$ at 298.15 K for the hydrolysis species of U(IV), $U(OH)_n^{4-n}$. The uncertainties of $\Delta_f G_m^{\circ}$ are estimated by using the method for propagation of errors in Appendix C.

| $n$ | $\Delta_f G_m^{\circ}$ (298.15 K) /kJ·mol$^{-1}$ | Reference |
|---|---|---|
| 1 | **– (763.918 ± 1.798)** | [1992GRE/FUG], [2003GUI/FAN] |
| 2 | **– (993.295 ± 2.102)** | This review |
| 3 | **– (1211.598 ± 2.886)** | This review |
| 4 | **– (1421.309 ± 8.189)** | [2003GUI/FAN] |

### 9.3.3 Crystalline uranium oxides and hydroxides

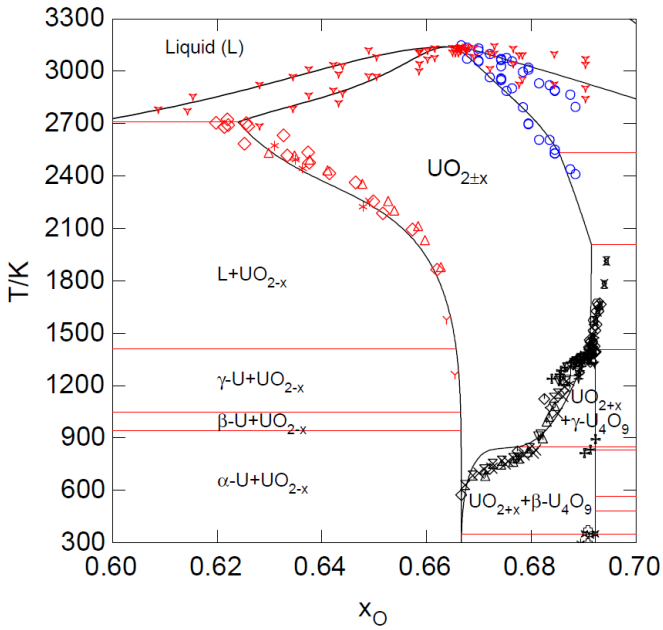
The uranium oxygen system has been extensively investigated both experimentally and theoretically, which is well represented in the CALPHAD assessment of [2011GUE/DUP] (depicted in Figure 9-6) as well as the review of [2014KON/BEN].

Figure 9-6: U-O phase diagram calculated using the CALPHAD model reported in [2011GUE/DUP].




The main phases considered in the U-O system are $UO_2$, $U_4O_9$, $U_3O_8$, and $UO_3$. The dioxide $UO_{2\pm x}$ evidently exhibits both under- and over-stoichiometric ranges from $1.66 < O/U < 2.25$. The hypo-stoichiometric composition $UO_{2-x}$ exists only at temperatures above 1500 K. The deviation from stoichiometry in $UO_{2+x}$ increases with temperature up to a maximum oxygen content of O/U = 2.25 at ~ 2006 K. $U_4O_9$ exists in three different crystallographic forms α, β, and γ. The γ-$U_4O_9$ form has a crystal structure similar to that of $UO_2$. It is stable up to 1400 K, where it decomposes into $UO_{2+x}$ and $U_3O_8$. At low temperatures, α-$U_4O_9$ undergoes a transition into the β-$U_4O_9$ phase around 340 K. A further transition occurs at temperatures higher than 850 K at which it transforms to γ-$U_4O_9$. Also $U_3O_8$ exhibits four different crystallographic modifications, α, β, γ and δ. Both $U_4O_9$ and $U_3O_8$ exhibit a small understoichiometric deviation in oxygen composition, which are not represented in the CALPHAD assessment of [2011GUE/DUP]. The $UO_3$ phase has five crystallographic forms and does not exhibit any deviation from stoichiometry; it is in equilibrium with $U_3O_8$ and the gas phase at temperatures above 912 K.

Figure 9-7: U-O phase diagram in the composition range 60 to 70 at % O (1.5 < O/U < 2.33) calculated using the CALPHAD model by [2011GUE/DUP], and comparison with the experimental data in the literature. The data in the $UO_2$-$U_3O_8$ composition range are from the critical review by Labroche *et al.* [2003LAB/DUG2], the data in the U-$UO_2$ composition range from Baichi *et al.* [2006BAI/CHA2], and the blue points from the work by Manara *et al.* [2005MAN/RON].




### 9.3.3.1 α, β and γ-phases of $UO_2(OH)_2$(cr) and $UO_3{\cdot}2H_2O$(cr)

The thermodynamics of hydrous uranium(VI) oxide and its hydrates have been discussed in [1992GRE/FUG] and [2003GUI/FAN]. The selected enthalpy of formation and molar entropy at 298.15 K in [1992GRE/FUG] for $UO_3{\cdot}2H_2O$(s) were based on calorimetric data and the corresponding Gibbs energy of formation obtained from the Gibbs-Helmholtz equation.

Equilibria in the $UO_3$-$CO_2$(g)-$H_2O$(l) system has been investigated by Sergeyeva *et al.* [1972SER/NIK] that studied Reaction (9.20) over the temperature range 25-200 °C.

$$UO_2CO_3(cr) + H_2O(l) \rightleftharpoons UO_2(OH)_2(cr,\alpha) + CO_2(g) \qquad (9.20)$$

From the temperature dependence of the equilibrium constant they report, $\Delta_r H_m^o$ (9.20) = (55.65 ± 7.5) kJ·mol$^{-1}$, and the selected enthalpies of formation of $UO_2CO_3$(cr), $UO_2^{2+}$, $H_2O$(l) and $CO_2$(g) this review finds, $\Delta_f H_m^o$ ($UO_2(OH)_2$, cr, 298.15 K) = – (1528.0 ± 7.7) kJ·mol$^{-1}$. The thermodynamics of hydrated $UO_3$ phases was discussed in [2003GUI/FAN] that suggest an

enthalpy of formation for $UO_3 \cdot H_2O \equiv UO_2(OH)_2$, $\Delta_f H_m^o(UO_2(OH)_2, cr, \alpha, 298.15\ K)$ = – (1536.4 ± 1.9) kJ·mol$^{-1}$, $\Delta_f H_m^o(UO_2(OH)_2, cr, \beta, 298.15\ K)$= – (1533.8 ± 1.3) kJ·mol$^{-1}$ and $\Delta_f H_m^o(UO_2(OH)_2, cr, \gamma, 298.15\ K)$ = – (1531.4 ± 1.3) kJ·mol$^{-1}$; all these values agree within the estimated uncertainty, confirming the reliability of the studies and the consistency of the enthalpies of formation of $UO_2CO_3$(cr) and $UO_2(OH)_2$(cr).

The present review retains the thermodynamic data for the α, β and γ-phases of $UO_2(OH)_2$(cr) from [2003GUI/FAN] and also the thermodynamic data for $UO_3 \cdot 2H_2O$(cr). The present review has accepted the practice in previous reviews to base the selected solubility constant on the solubility experiments and selects, $\log_{10} {}^*K_s^o(9.16)$ = (**5.350 ± 0.130**).

#### 9.3.3.2 U(IV) oxides

##### 9.3.3.2.1 Crystalline $UO_2$ (uraninite)

A number of review papers have been published concerning the O-U system [2003LAB/DUG2] and [2006BAI/CHA], [2006BAI/CHA2], most of which touch on the oxygen potential within the non-stoichiometry range of the uranium dioxide phase and data for phase diagram evaluation. The notable findings of these studies include the discussion of the λ-transition at high temperature and the evaluation of the liquid heat capacity of $UO_2$, discussed by [2007MAN/RON] and [2014KON/BEN]. The heat capacity function suggested by [2014KON/BEN] for solid $UO_2$(cr) is based on the data of [1987INA/NAI] and [2001AMA/UNE] in addition to the previously considered data by [2000FIN], as discussed in [2003GUI/FAN]. This leads to a more complete fit that is in relatively good agreement with [2000FIN] until 1300 K, and with deviations up to 3 % in the range (1300 K < $T$ < 2250 K). We therefore select the more complete dataset of [2014KON/BEN] for the $UO_2$ heat capacity in this review, valid for the temperature range 298.15 to 3000 K:

$$C_p(UO_2, cr, T) = 66.7437 + 43.1393\times10^{-3}\,(T/K) - 35.640\times10^{-6}\,(T/K)^2 + 11.655\times10^{-9}\,(T/K)^3 - 1.16863\times10^{6}\,(T/K)^{-2} \quad \text{for } T = (298.15\text{-}3000\,K)$$

The papers dealing with thermodynamic properties at high temperatures are discussed in Appendix A, including new measurements for the solidus/liquidus temperatures of $UO_{2+x}$ for the U-O phase diagram by laser-pulse methods.

#### 9.3.3.3 Mixed valence oxides

##### 9.3.3.3.1 $UO_{2.6667} = 1/3 \cdot U_3O_8$

The only discrepancy between [2014KON/BEN] and [2003GUI/FAN] concerns the heat capacity of the mixed oxides $U_3O_8$ or $UO_{2.66667}$. The heat capacity data reported in the literature were discussed by [1992GRE/FUG] but their fitting function, $C_{p,m}(T)$ has been replaced in [2014KON/BEN], which provides a slightly better fit, *cf.* Appendix A.

The improvement goes from 3 % deviation of the data from [1977INA/SHI] and [1968GIR/WES] in [1992GRE/FUG], to within 0.5 %, and the present review therefore selects the fit by [2014KON/BEN] as it more accurately represents the experimental data.

$$C_p(\mathrm{UO_{2.6667}}, \mathrm{cr}, T) = 93.089 + 9.16\times10^{-3}\ (T/\mathrm{K}) - 1.4372\times10^{6}\ (T/\mathrm{K})^{-2}$$
$$\text{for } T = (298.15 - 2000\ \mathrm{K})$$

#### 9.3.3.4 U(VI) peroxides

##### 9.3.3.4.1 Aqueous uranium peroxide complexes

###### 9.3.3.4.1.1 Ternary U(VI)-peroxide-hydroxide complexes

Experimental thermodynamic equilibrium constants for the formation of aqueous ternary U(VI)-peroxide-hydroxide complexes are reported in four publications [2011MEC/MAR], [2012ZAN/DIB], [2013MAR/MEC], and [2014ZAN/DIB]. The techniques used for these studies include potentiometry, spectrophotometry, and fluorescence spectroscopy. The reported constants are summarised in Table 9-17.

Zanonato *et al.* [2012ZAN/DIB] described their potentiometric titration data using two ternary complexes, $[UO_2(O_2)(OH)]^-$ and $[(UO_2)_2(O_2)_2(OH)]^-$, in which the molar ratio of $O_2^{2-}/UO_2^{2+}$ is one. No ternary complexes with the molar ratio of $O_2^{2-}/UO_2^{2+}$ larger than one were found. The equilibrium constants at 25 °C and $I = 0.1$ M $(TMA)NO_3$ were determined to be $-(2.67 \pm 0.07)$ and $(7.16 \pm 0.16)$ for the reactions of $UO_2^{2+} + HO_2^- + H_2O(l) \rightleftharpoons [UO_2(O_2)(OH)]^- + 2H^+$ and $2UO_2^{2+} + 2HO_2^- + H_2O(l) \rightleftharpoons [(UO_2)_2(O_2)_2(OH)]^- + 3H^+$, respectively. In a later study by calorimetry, [2014ZAN/DIB], the equilibrium constants were re-evaluated and slightly modified to be $-(2.56 \pm 0.07)$ and $(7.34 \pm 0.16)$, respectively, in conjunction with the enthalpy of reaction.

The formation of ternary U(VI)-peroxide-hydroxide complexes was also studied by spectrophotometry in [2011MEC/MAR] and fluorescence spectroscopy [2013MAR/MEC] in alkaline conditions. Both studies provide similar equilibrium constants for the reaction $UO_2^{2+} + H_2O_2(l) + 4OH^- \rightleftharpoons [UO_2(O_2)(OH)_2]^{2-} + 2H_2O(l)$, $(28.1 \pm 0.1)$ in [2011MEC/MAR] and $(28.7 \pm 0.4)$ in [2013MAR/MEC] at 25 °C and $I = 0$. In addition to the $[UO_2(O_2)(OH)_2]^{2-}$ complex, a ternary species with the molar ratio of $O_2^{2-}/UO_2^{2+} = 2$ was also included when modelling the spectrophotometric data in [2011MEC/MAR]. In both [2011MEC/MAR] and [2013MAR/MEC], it seems incorrect to assume $H_2O_2$ as the reactant since its concentration is much lower than that of $HO_2^-$ at pH > 12. The mass balance equation for total $H_2O_2$ includes only the $[H_2O_2]^0$ species and the uranyl-peroxide-hydroxide complex (equation 14 on p. 7978 in [2011MEC/MAR]), which is incorrect. In addition, it is not clear how sensitive the equilibrium constants are to the fluorescence spectra and lifetime in the fluorescence study [2013MAR/MEC]. Due to these concerns, this review does not accept the equilibrium constants from [2011MEC/MAR] and [2013MAR/MEC].

Table 9-17: Experimental equilibrium constants and enthalpies for the U(VI)-peroxide-hydroxide system reported in the literature and corrected to $I = 0$ in this review.

| $t$ /°C | Method | $I$ /medium | $\log_{10} K$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| | $UO_2^{2+} + HO_2^- + H_2O(l) \rightleftharpoons [UO_2(O_2)(OH)]^- + 2H^+$ | | | | |
| 25 | Pot | 0.1 M (TMA)$NO_3$ [(a)] | – (2.67 ± 0.07) | | [2012ZAN/DIB] |
| | | | – (2.56 ± 0.07) | – (43.4 ± 1.5) | [2014ZAN/DIB] |
| | | 0 | – (2.340 ± 0.070) | – (42.700 ± 1.500) | This review |
| | $2UO_2^{2+} + 2HO_2^- + H_2O(l) \rightleftharpoons [(UO_2)_2(O_2)_2(OH)]^- + 3H^+$ | | | | |
| 25 | Pot | 0.1 M (TMA)$NO_3$ [(a)] | (7.16 ± 0.16) | | [2012ZAN/DIB] |
| | | | (7.34 ± 0.16) | – (91 ± 9) | [2014ZAN/DIB] |
| | | 0 | (7.990 ± 0.160) | – (89.000 ± 9.000) | This review |
| | $UO_2^{2+} + H_2O_2(l) + 4OH^- \rightleftharpoons [UO_2(O_2)(OH)_2]^{2-} + 2H_2O(l)$ | | | | |
| 25 | Sp | 0.01 M (TMA)OH [(a)] | (27.9 ± 0.1) | | [2011MEC/MAR] |
| | | $I = 0$ | (28.1 ± 0.1) | | |
| 25 | TRLFS | 0.1 M (TMA)Cl [(a)] | (28.4 ± 0.4) | | [2013MAR/MEC] |
| | | $I = 0$ | (28.7 ± 0.4) | | |
| | $UO_2^{2+} + 2H_2O_2(l) + 6OH^- \rightleftharpoons [UO_2(O_2)_2(OH)_2]^{4-} + 4H_2O(l)$ | | | | |
| 25 | Sp | 0.01 M (TMA)OH [(a)] | (37.1 ± 0.2) | | [2011MEC/MAR] |
| | | $I = 0$ | (36.8 ± 0.2) | | |

(a) TMA—tetramethylammonium cation.

This review accepts the equilibrium constants and enthalpy of reactions for the ternary complexes, $[UO_2(O_2)(OH)]^-$ and $[(UO_2)_2(O_2)_2(OH)]^-$ (Reactions (9.21) and (9.22)) from [2014ZAN/DIB]. The equilibrium constants have been corrected to $I = 0$ by neglecting the ion interaction term, $\Delta\varepsilon \times I_m$ due to the low ionic strength used in the study. The enthalpy of reaction has been corrected according to the method described in the Appendix B. Both the hydroxide and the peroxide systems studied in the tetraalkylammonium medium are the only ones available and they are also consistent with one another. The experiments are satisfactory, but there is a medium effect that is difficult to account for. For this reason the data below are given for information only.

$$UO_2^{2+} + HO_2^- + H_2O(l) \rightleftharpoons [UO_2(O_2)(OH)]^- + 2H^+ \quad (9.21)$$

$$\log_{10} K^o((9.21), 298.15\ K) = -(2.340 \pm 0.070)$$

$$\Delta_r H_m^o((9.21), 298.15\ K) = -(42.700 \pm 1.500)\ kJ \cdot mol^{-1}$$

$$\Delta_r G_m^o((9.21), 298.15\ K) = (13.357 \pm 0.400)\ kJ \cdot mol^{-1}$$

$$\Delta_r S_m^o((9.21), 298.15\ K) = -(188.016 \pm 5.206)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$2UO_2^{2+} + 2HO_2^- + H_2O(l) \rightleftharpoons [(UO_2)_2(O_2)_2(OH)]^- + 3H^+ \quad (9.22)$$

$$\log_{10} K^\circ ((9.22), 298.15\ K) = (7.990 \pm 0.160)$$

$$\Delta_r H_m^\circ ((9.22), 298.15\ K) = -(89.000 \pm 9.000)\ kJ \cdot mol^{-1}$$

$$\Delta_r G_m^\circ ((9.22), 298.15\ K) = -(45.607 \pm 0.913)\ kJ \cdot mol^{-1}$$

$$\Delta_r S_m^\circ ((9.22), 298.15\ K) = -(145.541 \pm 30.341)\ J \cdot K^{-1} \cdot mol^{-1}.$$

#### 9.3.3.4.1.2 Ternary U(VI)-peroxide-carbonate complexes

Two experimental studies reporting thermodynamic equilibrium constants of ternary U(VI)-peroxide-carbonate complexes were conducted using UV/VIS absorption spectroscopy [2008GOF/BRO] and the combination of potentiometry and absorption spectroscopy [2012ZAN/DIB2]. The reported constants are summarised in Table 9-18.

Under the experimental conditions of [2008GOF/BRO], only one ternary species, $UO_2(O_2)(CO_3)_2^{4-}$, was observed. The authors did not use the p$K_a$ value of $H_2O_2$, and described the data with an apparent formation constant of $\log_{10} K' = (4.70 \pm 0.02)$, where $K' = ([UO_2(O_2)(CO_3)_2^{4-}][CO_3^{2-}])/([UO_2(CO_3)_3^{4-}][H_2O_2]_{total})$. The data of this study were re-analysed by this review as follows. Using the p$K_{a1}$ of $H_2O_2$ (11.5) measured in [2012ZAN/DIB] and the experimental conditions in this work (pH ~ 11.6 ± 0.05), we determined the equilibrium constant for the reaction $UO_2(CO_3)_3^{4-} + HO_2^- \rightleftharpoons [UO_2(O_2)(CO_3)_2]^{4-} + CO_3^{2-} + H^+$ to be – (6.6 ± 0.1). This value is reasonably close to the one obtained in [2012ZAN/DIB2], – (6.3 ± 0.1).

The apparent equilibrium $\log_{10} K'$ in [2008GOF/BRO] can also be converted to the equilibrium constant for the reaction $UO_2^{2+} + H_2O_2(l) + 2CO_3^{2-} \rightleftharpoons [UO_2(O_2)(CO_3)_2]^{4-} + 2H^+$ by using the experimental conditions in [2008GOF/BRO], the p$K_{a1}$ of $H_2O_2$ (11.5) measured in [2012ZAN/DIB], and the equilibrium constant for $UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$ from [2003GUI/FAN]. The value obtained by this review is (3.74 ± 0.10), in fair agreement with the value of (4.03 ± 0.05) in [2012ZAN/DIB2].

Zanonato *et al.* [2012ZAN/DIB2] determined the equilibrium constants of the formation of a series of ternary U(VI)-peroxide-carbonate complexes in 0.5 M $Na^+(ClO_4^-, CO_3^{2-})$, using the notation (*p, q, r*, –2*q*) for the reactions:

$$pUO_2^{2+} + qH_2O_2(l) + rCO_3^{2-} \rightleftharpoons [(UO_2)_p(O_2)_q(CO_3)_r]^{(2p-2q-2r)} + 2qH^+$$

Using the p$K_{a1}$ of $H_2O_2$ determined in [2012ZAN/DIB], the authors calculated the equilibrium constants for the reactions of (1,1,1,– 2), (1,1,2,– 2), (2,1,2,– 2), (2,1,4,– 2), (2,2,1,– 4), and (5,5,5,– 10) for the ionic media of 0.5 M $Na^+(ClO_4^-, CO_3^{2-})$. The value for the (1,1,2, – 2) species from [2012ZAN/DIB2] agrees well with the value from [2008GOF/BRO], taking into consideration that the two studies were conducted in different ionic media (Table 9-18).

The experimental techniques in both [2008GOF/BRO] and [2012ZAN/DIB2] are satisfactory and the analysis of the data seems reasonable. Also, the equilibrium constants of the ternary species that are observed in both studies compare fairly well with each other. Therefore, this review accepts the conditional equilibrium constants from [2012ZAN/DIB2] for the formation of the (1,1,1,– 2), (1,1,2,– 2), (2,1,2,– 2), (2,1,4,– 2), (2,2,1,– 4), and (5,5,5,– 10) complexes in 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ). However, the constants are given for information only because they have not been extrapolated to $I = 0$, which requires additional studies.

Table 9-18: Experimental equilibrium constants for the ternary U(VI)-peroxide-carbonate system. The ternary species are denoted as (*p,q,r*), these values are not selected by the present review and are reported for information only.

| Species | $t$ /°C | Method | $I$ /medium | $\log_{10}K$ | Reference |
|---|---|---|---|---|---|
| 1,1,1 | $UO_2^{2+} + H_2O_2(l) + CO_3^{2-} \rightleftharpoons [UO_2(O_2)(CO_3)]^{2-} + 2H^+$ | | | | |
| | 0 | Pot | (0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ )) | (1.47 ± 0.09) | [2012ZAN/DIB2] |
| 1,1,2 | $UO_2(CO_3)_3^{4-} + HO_2^- \rightleftharpoons [UO_2(O_2)(CO_3)_2]^{4-} + CO_3^{2-} + H^+$ | | | | |
| | 24.4 | Sp | 1.5 M (0.5 M $K_2CO_3$) | – (6.6 ± 0.1)[a] | [2008GOF/BRO] |
| | 25 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | – (6.3 ± 0.1)[b] | [2012ZAN/DIB2] |
| 1,1,2 | $UO_2^{2+} + H_2O_2(l) + 2CO_3^{2-} \rightleftharpoons [UO_2(O_2)(CO_3)_2]^{4-} + 2H^+$ | | | | |
| | 24.4 | Sp | 1.5 M (0.5 M $K_2CO_3$) | (3.74 ± 0.1)[c] | [2008GOF/BRO] |
| | 0 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (4.37 ± 0.07) | [2012ZAN/DIB2] |
| | 25 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (4.03 ± 0.05) | [2012ZAN/DIB2] |
| 2,1,2 | $2UO_2^{2+} + H_2O_2(l) + 2CO_3^{2-} \rightleftharpoons [(UO_2)_2(O_2)(CO_3)_2]^{2-} + 2H^+$ | | | | |
| | 0 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (18.31 ± 0.16) | [2012ZAN/DIB2] |
| | 25 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (17.87 ± 0.13) | [2012ZAN/DIB2] |
| 2,1,4 | $2UO_2^{2+} + H_2O_2(l) + 4CO_3^{2-} \rightleftharpoons [(UO_2)_2(O_2)(CO_3)_4]^{6-} + 2H^+$ | | | | |
| | 0 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (27.69 ± 0.14) | [2012ZAN/DIB2] |
| | 25 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (26.32 ± 0.11) | [2012ZAN/DIB2] |
| 2,2,1 | $2UO_2^{2+} + 2H_2O_2(l) + CO_3^{2-} \rightleftharpoons [(UO_2)_2(O_2)_2(CO_3)]^{2-} + 4H^+$ | | | | |
| | 0 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (1.98 ± 0.15) | [2012ZAN/DIB2] |
| | 25 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (1.87 ± 0.12) | [2012ZAN/DIB2] |

(Continued on next page)

Table 9-18 (continued)

| Species | $t$ /°C | Method | $I$ /medium | $\log_{10}K$ | Reference |
|---|---|---|---|---|---|
| 5,5,5 | $5UO_2^{2+} + 5H_2O_2(l) + 5CO_3^{2-} \rightleftharpoons [(UO_2)_5(O_2)_5(CO_3)_5]^{10-} + 10H^+$ | | | | |
| | 0 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (19.40 ± 0.39) | [2012ZAN/DIB2] |
| | 25 | Pot | 0.5 M $Na^+$( $ClO_4^-$, $CO_3^{2-}$ ) | (17.52 ± 0.35) | [2012ZAN/DIB2] |

(a) Estimated value from the apparent equilibrium constant, $\log_{10}K' = (4.70 \pm 0.02)$, where $K' = ([UO_2(O_2)(CO_3)_2^{4-}][CO_3^{2-}]) / [H_2O_2]_{total}$, using the p$K_{a1}$ of $H_2O_2$ (11.5) measured in [2012ZAN/DIB] and the experimental conditions in [2008GOF/BRO] (pH ~ 11.6 ± 0.05).

(b) Converted value from the equilibrium constant, $\log_{10}K = (4.03 \pm 0.05)$ for the reaction $UO_2^{2+} + H_2O_2(l) + 2CO_3^{2-} \rightleftharpoons [UO_2(O_2)(CO_3)_2]^{4-} + 2H^+$, using the p$K_{a1}$ of $H_2O_2$ (11.5) measured in [2012ZAN/DIB] and the equilibrium constant for $UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$ from [2003GUI/FAN].

(c) Estimated value from the apparent equilibrium constant, $\log_{10}K' = (4.70 \pm 0.02)$, where $K' = ([UO_2(O_2)(CO_3)_2^{4-}][CO_3^{2-}])\ ([UO_2(O_2)(CO_3)_2^{4-}][(CO_3)_3^{2-}]) / [H_2O_2]_{total}$, using the p$K_{a1}$ of $H_2O_2$ (11.5) measured in [2012ZAN/DIB] and the equilibrium constant for $UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$ from [2003GUI/FAN].

#### 9.3.3.4.1.3 Ternary U(VI)-peroxide-fluoride complexes

Zanonato *et al.* [2013ZAN/DIB] determined the equilibrium constants of the formation of ternary U(VI)-peroxide-fluoride complexes in 0.1 M $NaClO_4$, using $H^+$- and $F^-$-potentiometry. Several chemical models were tested and two of them provided the best agreement with the potentiometric data, one includes $[(UO_2)_4(O_2)_4F]^-$ and $[(UO_2)_4(O_2)_4F_2]^{2-}$, the other $[(UO_2)_4(O_2)_4F]^-$ and $[(UO_2)_5(O_2)_5F_3]^{3-}$. Zanonato *et al.* selected the second as the best one. The results are shown in Table 9-19. The technique is satisfactory and the data analysis seems reasonable. However, since this is the only such study and at least two models fit the data fairly well, the present review has not accepted equilibrium constants for the ternary U(VI)-peroxide-fluoride complexes. More studies of the system are recommended.

Table 9-19: Experimental equilibrium constants for the ternary U(VI)-peroxide-fluoride reactions: $pUO_2^{2+} + qH_2O_2(l) + rF^- \rightleftharpoons [(UO_2)_p(O_2)_qF_r]^{(2p-2q-2r)} + 2qH^+$. The ternary species are denoted as ($p$,$q$,$r$). These values are not selected by the present review and are reported for information only.

| Species | $t$ /°C | Method | $I$ /medium | $\log_{10}K$ | Reference |
|---|---|---|---|---|---|
| 4,4,1 | $4UO_2^{2+} + 4H_2O_2(l) + F^- \rightleftharpoons [(UO_2)_4(O_2)_4F]^- + 8H^+$ | | | | |
| | 0 | Pot | 0.100 M $NaClO_4$ | (1.78 ± 0.12) | [2013ZAN/DIB] |
| 5,5,3 | $5UO_2^{2+} + 5H_2O_2(l) + 3F^- \rightleftharpoons [(UO_2)_5(O_2)_5F_3]^{3-} + 10H^+$ | | | | |
| | 0 | Pot | 0.100 M $NaClO_4$ | (6.71 ± 0.12) | [2013ZAN/DIB] |

#### 9.3.3.4.1.4 Related solubility data

Experimental solubility data for studtite, $UO_4{\cdot}4H_2O$(cr), reported in [2003HUG/HEL] and [2005DJO/CUC] are summarised in Table 9-20.

Table 9-20: Experimental solubility data for the U(VI)-peroxide system.

| $t$ /°C | Method | $I$ /medium | $\log_{10}K$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| $(UO_2)O_2(H_2O)_4(cr) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2(aq) + 4H_2O(l)$ | | | | | |
| 25 | sol. cal | $I \rightarrow 0$ | $-(2.87 \pm 0.02)$[a] | $-8.79$[b] | [2003HUG/HEL] |
| $UO_4{\cdot}4H_2O(s) \rightleftharpoons UO_2^{2+} + O_2^{2-} + 4H_2O(l)$ | | | | | |
| 22 ± 1 | | 0.7 M $LiClO_4$ | $-35.88$[c] | | [2005DJO/CUC] |

(a) Calculated from the average of five $K$ values in [2003HUG/HEL]: $(1.32, 1.35, 1.34, 1.34, 1.37) \times 10^{-3}$.
(b) Calculated by this review from the $\Delta_f H_m^o(UO_4{\cdot}4H_2O(cr), 298\ K)$ in [2003HUG/HEL], and the $\Delta_f H_m^o$ values for $UO_2^{2+}$, $H_2O_2$, $H_2O$ (l) from [2003GUI/FAN].
(c) The solid phase was checked by powder X-ray diffraction, but the crystallinity of the solid is unknown. No uncertainty was reported for this phase.

The solubility product of $UO_4{\cdot}4H_2O(cr)$ for the reaction:

$$(UO_2)O_2(H_2O)_4(\text{crystalline}, 298\ K) + 2H^+(\text{aqueous}, 298\ K) \rightleftharpoons UO_2^{2+}(\text{aqueous}, 298\ K) + H_2O_2(\text{aqueous}, 298\ K) + 4H_2O(l, 298\ K) \quad (9.23)$$

was determined to be $\log_{10}K_s^o = -2.87$ in [2003HUG/HEL], based on data where the concentration of $H_2O_2$ varied from $7.57 \times 10^{-7}$ to $9.99 \times 10^{-3}$ M over a pH range 2.91-3.37. Using high-temperature oxide-melt solution calorimetry, they determined the standard enthalpy of formation of studtite, $\Delta_f H_m^o(UO_4{\cdot}4H_2O, cr, 298\ K) = -(2344.7 \pm 4.0)$ kJ·mol$^{-1}$. The thermodynamic cycle used in [2003HUG/HEL] includes $H_2O_2$(l), which was not evaluated in previous NEA books. For this reason, the value of $\Delta_f H_m^o(UO_4{\cdot}4H_2O, cr, 298\ K)$ reported in [2003HUG/HEL] is not selected by this review.

The measurements by solubility seem to be well conducted and the data reliable. This review accepts the value of $\log_{10}K_s^o$ (298.15 K) from [2003HUG/HEL] but retains $\Delta_f H_m^o(UO_4{\cdot}4H_2O, cr, 298\ K)$ selected in [2003GUI/FAN].

$$(UO_2)O_2(H_2O)_4(cr) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2(aq) + 4H_2O(l) \quad (9.24)$$

$$\log_{10}K_s^o((9.24), 298.15\ K) = \mathbf{-(2.870 \pm 0.020)}$$

$$\Delta_r G_m^o((9.24), 298.15\ K) = \mathbf{(16.382 \pm 0.114)}\ \text{kJ·mol}^{-1}$$

$$\Delta_f H_m^o(UO_4{\cdot}4H_2O, cr, 298.15\ K) = \mathbf{-(2384.700 \pm 2.100)}\ \text{kJ·mol}^{-1}.$$

Djogić *et al.* reported the solubility product of studtite, $UO_4{\cdot}4H_2O(s)$ [2005DJO/CUC] by the precipitation of U(VI) peroxide in $LiClO_4$. The solid phase was checked by powder X-ray diffraction and identified as $UO_4{\cdot}4H_2O(s)$; this phase was then converted to $UO_4{\cdot}2H_2O(s)$ after drying. The crystallinity of the solid phase was unknown. The authors claimed, by using a deprotonation constant of $10^{-36.65}$ for the reaction $H_2O_2 \rightleftharpoons 2H^+ + O_2^{2-}$ reported in [1949EVA/URI], that the solubility product of

$[UO_2^{2+}][O_2^{2-}]$ was $\log_{10} K_s = 1.32 \times 10^{-36}$. By checking ref. 28 of the paper, this review could not find the reported deprotonation constant of $H_2O_2$. In fact, it is impossible to determine the second protonation constant of $H_2O_2$ in aqueous solution. As the deprotonation constant is not confirmed in [2005DJO/CUC], the present review has reanalysed the experimental solubility data. At the experimental pH of 4.8, the concentration of $[H_2O_2(l)]$ can be considered as identical to $[H_2O_2(l)]_{total}$, which allows a calculation of the solubility constant for the reaction $(UO_2)(O_2)(s) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2$, which can be compared with the zero ionic strength and 25 °C one from [2003HUG/HEL]. Details of the calculation are shown in Appendix A.

The calculation shows that the logarithm of the solubility product ($\log_{10} {}^*K_{sp}$) for the reaction $(UO_2)(O_2)(s) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2$ ranges from 0.75 to 0.93 in [2005DJO/CUC], substantially higher than the value of – 2.87 from [2003HUG/HEL]. Such discrepancy could be due to the difference in the degree of crystallinity of the solid phases in the two studies. It is noted that the solid phase was checked by powder X-ray diffraction, but the crystallinity of the solid is unknown in [2005DJO/CUC].

Due to the unsubstantiated use of an unknown equilibrium constant for the reaction $H_2O_2 \rightleftharpoons 2H^+ + O_2^{2-}$ and the lack of information on the crystallinity of the solid phase, data from [2005DJO/CUC] are not accepted by the present review.

## 9.3.4 Uranium hydrides

A short discussion of uranium hydrides is given in [1992GRE/FUG] that reports Gibbs energies, enthalpies of formation, molar entropies and isobaric heat capacities of $UH_3$(cr, β), $UD_3$(cr, β) and $UT_3$(cr, β) and no new data have been published since this review. Grenthe *et al.* [2006GRE/DRO] give a short review of the properties of uranium hydrides in Chapter 5 in *The Chemistry of the Actinide and Transactinide Elements*, (eds. L.R. Morss, N. M. Edelstein and J. Fuger, Springer, 2006), [2006MOR/EDE]. The thermodynamic data reported are the same as in [1992GRE/FUG]. In addition there is information on the phase diagram in the uranium-hydrogen system in the range H/U = 2.3-3.0 from [1984FLO/HAS], a discussion on magnetic properties and bonding and information on uranium(IV) borohydride, $U(BH_4)_4$(s). This information has not been discussed in the present review and [2006MOR/EDE] should be consulted for details.

## 9.4 Uranium group 17 (halogen) compounds and complexes

### 9.4.1 General

Since the review by Guillaumont *et al.* [2003GUI/FAN], a large number of quantum chemical studies of uranium halides have been published. These compounds have been studied both at the *ab initio* and DFT levels ([2002PRI/SCH], [2006GAR/WIL], [2007SHA/SCH], [2008ZHA/LI], [2013JOH/BHA]) and using Car-Parrinello molecular dynamics simulations ([2008BUH/SIE], [2009BUH/SIE]). In general the different quantum chemistry methods give concordant results on the geometry (structure, interatomic distances and angles) that are in good agreement with the molecular parameters reported in Table 9-9 in [2003GUI/FAN]. The quantum chemistry calculations also provide information on vibrational frequencies, but these can vary significantly depending on the different approximation methods used; in the best ones the agreement with experimental observations is quite good [2013JOH/BHA]. The electronic and vibration spectra allow calculations of gas-phase entropies and heat capacities and there are several examples of good agreement between experimental and calculated values ([2007SHA/SCH], [2002PRI/SCH]). Johnson *et al.* [2013JOH/BHA] have used the most advanced coupled-cluster calculations, CCSD(T), to calculate the Gibbs energy and enthalpy of formation of $UF_4(g)$ and $UCl_4(g)$ that are in good agreement with the selected data in [2003GUI/FAN]. One should note that quantum chemistry calculations for reactions in solution are much less accurate than those in gas phase. As the selected thermodynamic data in the NEA reviews are based on experimental information this review has not selected the values from quantum chemistry data, which are reported for information only. The comparison with theory is, however, of interest because it indicates that quantum chemistry methods can be useful for the estimation of thermodynamic data where no experimental information is available; examples of reaction energies studied by quantum chemistry methods and corresponding experimental data are given in Table 9-21.

Table 9-21: Comparison of enthalpies of reaction in gas phase obtained using quantum chemistry methods with the corresponding values obtained from the selected enthalpies of formation in [2003GUI/FAN].

| Reaction | Reaction enthalpy in kJ·mol$^{-1}$ | Experimental reaction enthalpy in kJ·mol$^{-1}$ from [2003GUI/FAN] | Reference |
|---|---|---|---|
| $UF_6 + 2UO_3 \rightleftharpoons 3UO_2F_2$ | – 303.5 | – 310.5 | [2007SHA/SCH] |
| $UF_6 + UO_2F_2 \rightleftharpoons 2UOF_4$ | 19.3 | 24.9 | “ |
| $UOF_4 + UO_3 \rightleftharpoons 2UO_2F_2$ | – 160.4 | – 141.8 | “ |
| $UF_6 \rightleftharpoons UF_5 + F$ | 319.5 | 315.0 | “ |
| $UF_5 \rightleftharpoons UF_4 + F$ | 417.8 | 387.2 | “ |
| $UOF_4 \rightleftharpoons UOF_3 + F$ | 391.0 | – | “ |

(Continued on next page)

Table 9-21 (continued)

| Reaction | Reaction enthalpy in kJ·mol$^{-1}$ | Experimental reaction enthalpy in kJ·mol$^{-1}$ from [2003GUI/FAN] | Reference |
|---|---|---|---|
| $UOF_4 \rightleftharpoons UOF_2 + 2F$ | 909.8 | – | " |
| $UOF_4 \rightleftharpoons UF_4 + O$ | 407.8 | 407.0 | " |
| $UO_2F_2 \rightleftharpoons UO_2F + F$ | 479.0 | – | " |
| $UO_2F_2 \rightleftharpoons UO_2 + 2F$ | 1040.8 | – | " |
| $UO_2F_2 \rightleftharpoons UOF_2 + O$ | 596.6 | – | " |
| $UO_3 \rightleftharpoons UO_2 + O$ | 567.7 | 570.6 | " |
| $UF_6 + H_2O \rightleftharpoons UOF_4 + 2HF$ | 191.3 | 80.8 | " |
| $UF_6 + 2H_2O \rightleftharpoons UO_2F_2 + 4HF$ | 251.2 | 186.6 | " |
| $UF_6 + 3H_2O \rightleftharpoons UO_3 + 6HF$ | 528.4 | – | " |
| $2UO_3 + UF_6 \rightleftharpoons 3UO_2F_2$ | – 329 | – 310.5 | [2002PRI/SCH] |
| $UO_2F_2 + 2H_2O \rightleftharpoons UO_2(OH)_2 + 2HF$ | 72 | 64 | " |
| $UF_6 + 2H_2O \rightleftharpoons UO_2F_2 + 4HF$ | 187 | 187 | " |
| $UO_3 + H_2O \rightleftharpoons UO_2(OH)_2$ | – 186 | – | " |
| $UF_6 + 3H_2O \rightleftharpoons UO_3 + 6HF$ | 444 | 435 | " |

Information on the structure and composition of complexes in gas phase is of interest also for solutions, because they provide additional and often more detailed structure information than those from experimental methods such as Large Angle X-ray scattering (LAXS) and Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS), [2005HEN/TUT], [2011UEH/FUJ]. Recently, Soderholm, Wilson *et al.* have used High-Energy X-ray Scattering (HEXS), [2011SOD/SKA], [2011WIL/SKA], which provides information on pair-correlation functions in the form of radial distribution functions that are more precise than those obtained by LAXS; the information value of these structure methods increases significantly if they are combined with quantum chemistry data.

Reaction dynamics, with identification of transition states and intermediates have been studied in [2002VAL/WAH], [2003TOR/PRI], [2008BUH/SIE] and [2008GAR/BEC].

#### 9.4.1.1 Molecular parameters of the gaseous uranium halide species

As indicated in the previous section, a number of quantum chemical studies have been conducted since the previous update, [2003GUI/FAN], and as these data are consistent with those given in Table 9-9 in [2003GUI/FAN] the latter have been retained also in the present review.

### 9.4.2 Fluorine compounds and complexes

#### 9.4.2.1 Gaseous uranium fluorides

There are no new experimental thermodynamic data, only information from a number of quantum chemical studies of chemical reactions that are reported in Table 9-21; these are

given for information only, but are often consistent with experimental data. The selected data for gaseous fluorides from [1992GRE/FUG] and [2003GUI/FAN] are retained by the present review.

#### 9.4.2.2 Aqueous uranium fluorides

##### 9.4.2.2.1 Aqueous U(VI) fluorides

###### 9.4.2.2.1.1 Binary complexes

There are two new experimental studies of fluoride complex formation in aqueous solution, [2004KIR/KIM2] and [2009TIA/RAO]. The first one, as discussed in Appendix A, is a Raman investigation that does not provide information on equilibrium constants. This study refers to uranyl(VI) phosphate and fluoride systems studied between pH = 0 and 3 over the temperature range 20-150 °C. The focus is on fluorescence life-times and not on equilibrium data.

Only the study by Tian and Rao [2009TIA/RAO] provides new experimental information on the equilibrium constants and enthalpies of reaction for (9.25) studied in 1.00 M $NaClO_4$ and 25-70 °C.

$$UO_2^{2+} + nF^- \rightleftharpoons UO_2F_n^{2-n} \; ; n = 1\text{-}4 \qquad (9.25)$$

The equilibrium constants and estimated uncertainties (see Table 9-22) are very similar to those in [1992GRE/FUG] and [2003GUI/FAN], when extrapolated to $I = 0$ using SIT with interaction parameters from NEA. The values reported in [2009TIA/RAO] agree within the uncertainty range with those selected in [2003GUI/FAN], and this review finds no reason to change the selected values and the Gibbs energies. The corresponding enthalpies and entropies of reaction have been determined by Tian *et al.* using microcalorimetry and this method is different from the "traditional" solution calorimetry used in [1971AHR/KUL]. The two methods result in surprisingly large differences, but, as discussed in Appendix A, we can find no reason to prefer one study to the other and have therefore selected the weighted average of the enthalpies of reaction in 1.00 M $NaClO_4$, which have been extrapolated to zero ionic strength as described in Appendix B. The equilibrium constants, $\log_{10}\beta_n^\circ$, the average enthalpies of reaction, $\Delta_{r,aver}H_m$ (298.15 K) and $\Delta_{r,aver}H_m^\circ$ (298.15 K), and $\Delta_r S_m^\circ$ are listed in Table 9-22. The enthalpies of reaction in [1992GRE/FUG] and [2003GUI/FAN] were not extrapolated to zero ionic strength; this correction is significant, which is the reason for the revised values of the enthalpies of formation and the molar entropies selected in the present review.

Chi [2007CHI] has used electro-spray mass spectroscopy to study reactions in gas-phase between the uranyl-ion and a number of different ligands, A, where A = hydroxide, nitrate, perchlorate and the halides, which are of interest for this review. Using water as spray solvent, Chi could identify the complexes $UO_2A(OH_2)^+$, $UO_2A(OH_2)_2^+$ and $UO_2A(OH_2)_3^+$, where the last was the most stable one.

Table 9-22: Equilibrium constants from [2009TIA/RAO] and weighted enthalpies of reaction, $\Delta^{r,aver}H^{m}(298.15\,K)$ in kJ·mol$_{-1}$ in 1.00 M $NaClO_4$ for the reactions $UO_2^{2+} + nF^- \rightleftharpoons UO_2F_n^{2-n}$, $n$ = 1-4 from [2009TIA/RAO] and [1971AHR/KUL]; the corresponding values at zero ionic strength are denoted as $\Delta_{r,aver}H_m^o(298.15\,K)$. Selected values from [2003GUI/FAN] are denoted with a hashtag, #. Selected values in this review are marked in bold.

| Reaction | $t$/°C | $\log_{10}\beta_n$ $I$ = 1.0 M | $\log_{10}\beta_n^o$ | $\Delta_{r\text{-}aver}H_m$ (298.15 K) /kJ·mol$^{-1}$ | $\Delta_{r\text{-}aver}H_m^o$ (298.15 K) /kJ·mol$^{-1}$ | $\Delta_rS_m^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| $UO_2^{2+} + F^- \rightleftharpoons UO_2F^+$ | 25 | (4.60 ± 0.02) | (5.20 ± 0.07) | (1.87 ± 0.26) | **– (0.540 ± 0.260)** | **(96.976 ± 1.441)** |
| | | | **(5.160 ± 0.060)**$^{\#}$ | (1.700 ± 0.080)$^{\#}$ | | |
| $UO_2^{2+} + 2F^- \rightleftharpoons UO_2F_2(aq)$ | 25 | (8.07 ± 0.04) | (8.74 ± 0.07) | (2.27 ± 0.18) | **– (1.340 ± 0.180)** | **(164.554 ± 1.648)** |
| | | | **(8.830 ± 0.080)**$^{\#}$ | (2.100 ± 0.190)$^{\#}$ | | |
| $UO_2^{2+} + 3F^- \rightleftharpoons UO_2F_3^-$ | 25 | (10.62 ± 0.04) | (11.25 ± 0.02) | (2.43 ± 0.31) | **– (1.180 ± 0.300)** | **(204.719 ± 2.163)** |
| | | | **(10.900 ± 0.100)**$^{\#}$ | (2.350 ± 0.310)$^{\#}$ | | |
| $UO_2^{2+} + 4F^- \rightleftharpoons UO_2F_4^{2-}$ | 25 | (11.92 ± 0.14) | (12.01 ± 0.18) | (0.2 ± 3.3) | **– (2.120 ± 0.470)** | **(219.563 ± 2.631)** |
| | | | **(11.840 ± 0.110)**$^{\#}$ | (0.29 ± 0.47)$^{\#}$ | | |



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There is no thermodynamic information but the observation that $UO_2(OH_2)_3(NO_3)^+$ is formed in aqueous solution.

The following values of Gibbs energy, enthalpy and entropy of formation together with the ion entropy $S^o_m(UO_2F^{2-n}_n, aq, 298.15\ K)$ have been selected by this review. The values of $\Delta_f H^o_m$ and $S^o_m$ differ slightly from those in [2003GUI/FAN].

$$\Delta_f G^o_m(UO_2F^+, aq, 298.15\ K) = \mathbf{-\ (1263.527 \pm 1.911)}\ kJ\cdot mol^{-1};$$

$$\Delta_f H^o_m(UO_2F^+, aq, 298.15\ K) = \mathbf{-\ (1354.890 \pm 1.655)}\ kJ\cdot mol^{-1};$$

$$S^o_m(UO_2F^+, aq, 298.15\ K) = \mathbf{-\ (15.024 \pm 3.423)}\ J\cdot K^{-1}\cdot mol^{-1};$$

$$\Delta_f G^o_m(UO_2F_2, aq, 298.15\ K) = \mathbf{-\ (1565.999 \pm 2.276)}\ kJ\cdot mol^{-1};$$

$$\Delta_f H^o_m(UO_2F_2, aq, 298.15\ K) = \mathbf{-\ (1691.040 \pm 1.993)}\ kJ\cdot mol^{-1};$$

$$S^o_m(UO_2F_2, aq, 298.15\ K) = \mathbf{(38.755 \pm 3.778)}\ J\cdot K^{-1}\cdot mol^{-1};$$

$$\Delta_f G^o_m(UO_2F_3^-, aq, 298.15\ K) = \mathbf{-\ (1859.338 \pm 2.774)}\ kJ\cdot mol^{-1};$$

$$\Delta_f H^o_m(UO_2F_3^-, aq, 298.15\ K) = \mathbf{-\ (2026.230 \pm 2.478)}\ kJ\cdot mol^{-1};$$

$$S^o_m(UO_2F_3^-, aq, 298.15\ K) = \mathbf{(65.119 \pm 4.409)}\ J\cdot K^{-1}\cdot mol^{-1};$$

$$\Delta_f G^o_m(UO_2F_4^{2-}, aq, 298.15\ K) = \mathbf{-\ (2146.226 \pm 3.334)}\ kJ\cdot mol^{-1};$$

$$\Delta_f H^o_m(UO_2F_4^{2-}, aq, 298.15\ K) = \mathbf{-\ (2362.520 \pm 3.038)}\ kJ\cdot mol^{-1};$$

$$S^o_m(UO_2F_4^{2-}, aq, 298.15\ K) = \mathbf{(66.163 \pm 5.115)}\ J\cdot K^{-1}\cdot mol^{-1};$$

Bühl *et al.* [2009BUH/SCH], have studied the reaction:

$$UO_2(OH_2)_5^{2+} + F^- \rightleftharpoons UO_2F(OH_2)_4^+ + H_2O; \qquad (9.26)$$

using Car-Parrinello molecular dynamics simulation and note a satisfactory agreement between the calculated Gibbs energy, – (27 ± 10) kJ·mol$^{-1}$ (MD) and the experimental value, – (29.453 ± 0.342) kJ·mol$^{-1}$. Using "static" DFT with the aqueous solvent described as a dielectric continuum, Bühl *et al.* also studied the reactions:

$$UO_2(OH_2)_5^{2+} + nF^- \rightleftharpoons UO_2F_n(OH_2)_{5-n}^{2-n} + nH_2O;\ n = 1\text{-}5 \qquad (9.27)$$

The corresponding Gibbs energies of reaction deviate significantly, up to 100 kJ·mol$^{-1}$ from experimental values, demonstrating the problems encountered when using quantum chemistry in combination with simplistic models for the water solvent. Toraishi *et al.* [2003TOR/PRI] have compared the experimental and quantum chemistry equilibrium constants/Gibbs energy of reaction for the Reaction (9.28) by using a thermodynamic cycle where this reaction is divided into several steps and taking possible systematic errors in the models into account; even so there is a significant difference

between experimental $\Delta_r G_m^o$ (9.28) = – 11 kJ·mol$^{-1}$, and the quantum chemistry value, $\Delta_r G_m^o$ (9.28) = – 25 kJ·mol$^{-1}$.

$$UO_2^{2+}(aq) + HF(aq) \rightleftharpoons UO_2F^+(aq) + H^+(aq) \quad (9.28)$$

Toraishi *et al.* have also studied the mechanism for Reaction (9.28) using quantum chemistry modeling; their multi-step mechanism has an activation energy that is in good agreement with experiment, but these data are of minor interest for the current review.

Vallet *et al.* [2001VAL/WAH] and Tian and Rao [2009TIA/RAO] have identified the complex $[UO_2F_4(OH_2)]^{2-}$ in solution using EXAFS information, but quantum chemistry calculations from Bühl *et al.* suggest that this structure is less stable than $UO_2F_4^{2-}$ without coordinated water. At the highest fluoride concentration, 3 M, used by Vallet *et al.* the EXAFS data provide evidence for the formation of $UO_2F_5^{3-}$ and this review has estimated an equilibrium constant $K$ = 0.3 M$^{-1}$ and $\Delta_r G_m^o$ = 3.0 kJ·mol$^{-1}$ for Reaction (9.29).

$$UO_2F_4^{2-} + F^- \rightleftharpoons UO_2F_5^{3-} \quad (9.29)$$

Bühl *et al.* have studied the same reaction and find the Helmholtz energy of reaction (not significantly different from the Gibbs energy of reaction) $\Delta A$ = – 8 kJ·mol$^{-1}$, with an estimated uncertainty of ± 10 kJ·mol$^{-1}$ which spans the experimental value. This value is reported for information only.

#### 9.4.2.2.2 Aqueous U(IV) fluorides

Kovalenko *et al.* [2012KOV/RYZ] studied the solubility of $UO_2$(cr) in HF solutions at 500 °C and 1000 bar and reported the formation of the complexes $U(OH)_3F$(aq), $U(OH)_2F_2$(aq), $U(OH)F_3$(aq) and $UF_4$(aq).

$$UO_2(cr) + nHF + (2-n)H_2O(l) \rightleftharpoons U(OH)_{4-n}F_n(aq) \quad (9.30)$$

The analysis in Appendix A, points out several shortcomings in this study and the proposed stoichiometry of the complexes and their equilibrium constants have not been accepted.

Johnson *et al.* [2013JOH/BHA] have made a quantum chemistry calculation of the Gibbs energy of formation, $\Delta_f G_m^o(UF_4, aq, 298.15\ K)$ = – 1822.0 kJ·mol$^{-1}$, which is in fair agreement with the selected value in [2003GUI/FAN], $\Delta_f G_m^o(UF_4, aq, 298.15\ K)$ = – (1806.302 ± 6.388) kJ·mol$^{-1}$. As discussed in the corresponding review in Appendix A, this agreement is probably fortuitous and the present review retains the experimental value selected in [2003GUI/FAN].

#### 9.4.2.3 Solid uranium fluorides

##### 9.4.2.3.1 Binary uranium fluorides and their hydrates

###### 9.4.2.3.1.1 $UF_3$(cr)

Since the previous review [2003GUI/FAN], one new study of the low-temperature heat capacity of $UF_3$(cr) has been reported by Beneš *et al.* [2011BEN/GRI] in which two different techniques (adiabatic and relaxation calorimetry) were employed to obtain data from 0.5 to 300 K. The derived heat capacity and entropy values differ from those selected previously, based on unpublished work of Westrum, cited in [1989COR/KON]. The new study takes into account the ferromagnetic transition at 1.5 K, which was not considered by Westrum. As a result a somewhat higher standard entropy was obtained, which is selected here:

$$S^{o}_{m}(UF_3, cr, 298.15\ K) = \mathbf{(126.800 \pm 2.500)}\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

The value of $C^{o}_{p,m}(298.15\ K)$ is:

$$C^{o}_{p,m}(UF_3, cr, 298.15\ K) = \mathbf{(94.010 \pm 0.400)}\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

As a result of the change in entropy, the present review has selected a new value for the Gibbs energy of formation of $UF_3$(cr), $\Delta_f G^{o}_{m}$ ($UF_3$, cr, 298.15 K) = **– (1433.545 ± 4.759)** kJ·mol$^{-1}$, very close to the value – (1432.531 ± 4.702) kJ·mol$^{-1}$ selected in [2003GUI/FAN].

The selected $C^{o}_{p,m}$ equation for $UF_3$(cr) in [2003GUI/FAN] has been replaced by a new polynomial to fit the unpublished enthalpy increment data from 377 to 867 K by Cordfunke [1989COR/KON] and the low temperature data from [2011BEN/GRI] from 250 to 300 K:

$$C^{o}_{p,m}(UF_3, cr, T) = 107.3920 + 0.8878\times10^{-3}T - 1.2131\times10^{6}T^{-2}\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

from 298.15 to 1768 K.

### 9.4.3 Chlorine compounds and complexes

#### 9.4.3.1 Uranium chlorides

##### 9.4.3.1.1 Gaseous uranium chlorides

There are no new experimental thermodynamic data, only information from a number of quantum chemical studies of chemical reactions that are discussed in Appendix A, [2006GAR/WIL], [2013JOH/BHA]. The quantum chemical studies contain chemical information of interest, but the present review has not discussed their technical details as this is outside the scope of the NEA reviews. The selected data for gaseous chlorides from [1992GRE/FUG] and [2003GUI/FAN] are retained by the present review.

#### 9.4.3.1.2 Aqueous uranium chlorides

##### 9.4.3.1.2.1 Aqueous U(VI) chlorides

Uranyl(VI) chloride complexes are weak and it is therefore difficult to distinguish between complex formation and activity factor variations that result from the large change in the ionic medium necessary to study these complexes. The ambiguity between activity factor variations and complex formation can, however, be resolved from structure determinations in aqueous solution. Hennig *et al.* [2005HEN/TUT] have used EXAFS to study uranyl chloride solutions with chloride concentrations of 0, 3, 6 and 9 M. These results give conclusive evidence that several chloride complexes are formed; the average coordination numbers in the test solutions are 1.1, 2.3 and 3.1, respectively with an uncertainty of at least 10 %. By using high-intensity X-ray scattering, Soderholm *et al.* [2011SOD/SKA] were able to increase the accuracy of the structure determination and also to determine concentration equilibrium constants at an ionic strength of 5 m in solutions where the chloride concentration varied from 0 to 4.8 m. They report the following conditional equilibrium constants, $\beta_1 = (1.5 \pm 1.0)\ m^{-1}$; $\beta_2 = (0.8 \pm 0.4)\ m^{-2}$ and $\beta_3 = (0.4 \pm 0.1)\ m^{-3}$, for Reaction (9.31).

$$UO_2^{2+} + n\mathrm{Cl}^- \rightleftharpoons [UO_2\mathrm{Cl}_n]^{2-n}\ ;\ n = 1\text{-}3 \tag{9.31}$$

Using SIT, we have calculated $\log_{10}\beta_1^o = (0.0 \pm 0.3)$, which is consistent with the value selected in [1992GRE/FUG] and [2003GUI/FAN], $\log_{10}\beta_1^o = (0.170 \pm 0.020)$. However, the high ionic strength makes the use of SIT-extrapolation uncertain. The equilibrium constant from [1992GRE/FUG] and [2003GUI/FAN], $\log_{10}\beta_1^o$ = **(0.170 ± 0.020)**, obtained from data in mixed chloride/perchlorate media, and the corresponding thermodynamic data have been retained by the present review, but we note that additional complexes $UO_2\mathrm{Cl}_2(aq)$ and $UO_2\mathrm{Cl}_3^-$ cannot be neglected in brine systems where the equilibrium constants from Soderholm *et al.* can be used for estimates.

Dargent *et al.* [2013DAR/DUB] have studied the uranyl(VI) chloride system between 21 and 350 °C and saturation pressure using Raman spectroscopy to determine equilibrium constants for the formation of $UO_2\mathrm{Cl}_n^{2-n}$, $n$ = 1-5. For the reasons given in Appendix A, these equilibrium constants have not been included among the selected values.

Uehara *et al.* [2006UEH/FUJ] report from EXAFS studies that the number of coordinated chloride ions increases from 1.8 to 2.2 in $CaCl_2$ solutions when the concentration increases from 4.7 and 6.9 M.

Bühl *et al.* [2008BUH/SIE] have studied the Reactions (9.32) and (9.33) using Car-Parrinello molecular dynamics simulation in an aqueous solvent:

$$UO_2(OH_2)_5^{2+} + n\mathrm{Cl}^- \rightleftharpoons [UO_2\mathrm{Cl}_n(OH_2)_{5-n}]^{2-n} + nH_2O \tag{9.32}$$

$$[UO_2\mathrm{Cl}_n(OH_2)_{5-n}]^{2-n} \rightleftharpoons [UO_2\mathrm{Cl}_n(OH_2)_{4-n}]^{2-n} + H_2O \tag{9.33}$$

The calculated Helmholtz energy of reaction differs significantly from the experimental Gibbs energy of reaction.

The present review concludes that there is very strong experimental evidence for the formation of $UO_2Cl_n^{2-n}$ complexes and that the selected thermodynamic data for formation of $UO_2Cl^+$ and $UO_2Cl_2(aq)$ from [1992GRE/FUG] and [2003GUI/FAN] can be retained.

In the hydrolysis section, there are many studies using high Cl concentrations (> 3 M), in which chloride complexes have been disregarded, *cf.* Section 9.3.2.1. It is feasible that ternary U(VI)-$OH^-$-$Cl^-$ might form, but in the opinion of this review they will be difficult to identify using equilibrium measurements; a better approach would be to use EXAFS that should give direct structure information if U-$Cl^-$ interactions occur.

#### 9.4.3.1.2.2 Aqueous U(IV) chlorides

Uehara *et al.* [2011UEH/FUJ] have studied the complex formation in the U(IV) and Th(IV)-chloride systems in $CaCl_2$ solutions by EXAFS spectroscopy using test solutions where the chloride concentration varies from 4 to 6.9 M. Their data analysis of the two test solutions suggests that the number of coordinated chloride ions increases from (1.3 ± 0.2) to (3.4 ± 0.5), in the U(IV) complexes, while the number of coordinated water decreases from (6.7 ± 1.0) to (4.5 ± 0.7), suggesting a constant coordination number of eight. In the Th(IV) system the change in the number of coordinated chloride ions is much smaller, from 1.5 to 1.9, this difference is surprisingly large because the equilibrium constants for formation of $UCl^{3+}$ and $ThCl^{3+}$ selected in [2003GUI/FAN] and [2008RAN/FUG] are identical, $\log_{10}\beta_1^o$ ($UCl^{3+}$) = (1.72 ± 0.13), and $\log_{10}\beta_1^o$ ($ThCl^{3+}$) = (1.70 ± 0.10).

Kovalenko *et al.* [2012KOV/RYZ] studied the solubility of $UO_2$(cr) in chloride solutions at 500 °C and 1000 bar. This review has not made a detailed analysis of the experimental data but notes that there is no discussion of the chemical model used and we find it unlikely that, as the authors suggest, only uncharged complexes are formed in Reactions (9.34) and (9.35):

$$UO_2(cr) + 2HF \rightleftharpoons U(OH)_2F_2 ;\ \log_{10}K = -3.15 \quad (9.34)$$

$$UO_2(cr) + 2HCl \rightleftharpoons U(OH)_2Cl_2 ;\ \log_{10}K = -3.56 \quad (9.35)$$

Johnson *et al.* [2013JOH/BHA] have used quantum chemistry to calculate the Gibbs energy of formation for $UCl_4$(aq) and report $\Delta_f G_m^o$ ($UCl_4$, aq, 298.15 K) = – 1127.6 kJ·mol$^{-1}$; there is no experimental value reported for this reaction, but the quantum chemistry value will result in Gibbs energy of reaction $\Delta_r G_m^o$ (9.36) = – 75.9 kJ·mol$^{-1}$, which corresponds to an equilibrium constant $\log_{10}K$ (9.36) = 13. This is not consistent with the experimental observations that U(IV) chloride complexes are weak.

$$U^{4+} + 4Cl^- \rightleftharpoons UCl_4(aq) \quad (9.36)$$

The present review retains the equilibrium constants and the other thermodynamic data selected in [2003GUI/FAN].

#### 9.4.3.1.3 Solid uranium chlorides

A large number of binary and ternary uranium chloride compounds and an overview of their structure and physical properties, including some thermodynamic data from [2003GUI/FAN] and other sources, are described in "*The Chemistry of the Actinide and Transactinide elements*", (Eds. L. R. Morss, N. M. Edelstein and J. Fuger), Vol. 1, I. Grenthe, J. Drożdżyński, T. Fujino, E. C. Buck, T. E. Albrecht-Schmitt and S. F. Wolf, Chapter five, *Uranium.*

##### 9.4.3.1.3.1 $UCl_3$(cr)

Since the previous review [2003GUI/FAN], no new studies on this compound have been reported. However, Konings [2001KON] argued that the low-temperature heat capacity data of $UCl_3$(cr) reported by Cordfunke *et al.* [1989COR/KON] does not take into account the contribution of the ferromagnetic transition below 10 K, which was shown to be the case for $UF_3$ in [2011BEN/GRI]. Therefore the $R\ln(2)$ term has been added to the experimental value, and the uncertainty has been increased to reflect this, to give the new selected value:

$$S^{o}_{m}(UCl_3, cr, 298.15\ K) = \mathbf{(163.900 \pm 2.000)}\ J\cdot K^{-1}\cdot mol^{-1}$$

The value of $C^{o}_{p,m}(298.15\ K)$ from [2003GUI/FAN] is retained:

$$C^{o}_{p,m}(UCl_3, cr, 298.15\ K) = \mathbf{(102.520 \pm 0.500)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

##### 9.4.3.1.3.2 UNCl(cr)

The thermodynamic properties of UNCl(cr) have been reported in a series of papers [2002HUN/BOO], [2002AKA/KOB], [2005NAK/AKA]. The enthalpy of formation was measured by the enthalpy of dissolution in (0.76 $mol\cdot dm^{-3}$ HCl + 0.03 $mol\cdot dm^{-3}$ $FeCl_3$) [2002HUN/BOO], [2002AKA/KOB]:

$$UNCl(cr) + 4HCl(aq) \rightleftharpoons UCl_4 + NH_4Cl(aq) \qquad (9.37)$$

The enthalpy of formation was derived from a thermochemical cycle that includes the experimental enthalpies of solution in the same solvent. The enthalpy of formation remains unchanged using the auxiliary data from the present review and the selected value is:

$$\Delta_f H^{o}_{m}(UNCl, cr, 298.15\ K) = \mathbf{-\ (559.000 \pm 4.000)}\ kJ\cdot mol^{-1}.$$

The low temperature heat capacity of UNCl(cr) was measured by adiabatic calorimetry from 5 to 430 K, revealing an antiferromagnetic anomaly with Néel temperature at 30.8 K. The standard entropy derived from the measurements in [2002HUN/BOO] is:

$$S^{o}_{m}\,(\text{UNCl, cr, 298.15 K}) = \mathbf{(96.540 \pm 0.100)}\ \text{J·K}^{-1}\text{·mol}^{-1}$$

and the value of $C^{o}_{p,m}$ (298.15 K) is:

$$C^{o}_{p,m}\,(\text{UNCl, cr, 298.15 K}) = \mathbf{(68.080 \pm 0.100)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

Both values are new and selected by the present review.

The heat capacity equation for UNCl(cr) is based on the DSC (300-1100 K) and drop calorimetry (399-933 K) measurements reported by [2002HUN/BOO], and two different equations have been reported. Since the experimental DSC data have not been reported in detail, we select the $C^{o}_{p,m}$ equation reported by [2002HUN/BOO] based on the average of the two equations:

$$C^{o}_{p,m}\,(\text{UNCl, cr}, T) = 80.238 + 1.872\times10^{-3}\,T + 1.10558\times10^{6}\,T^{-2}\ \text{J·K}^{-1}\text{·mol}^{-1}$$

from 298.15 to 1100 K.

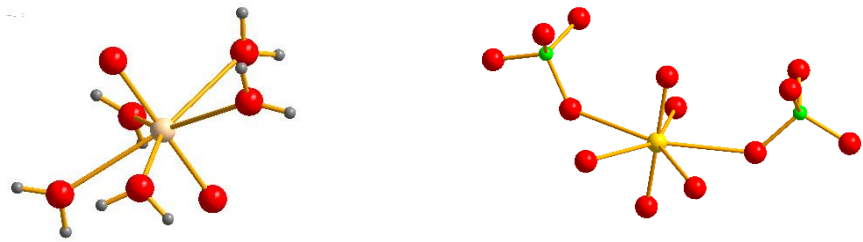
It should be noticed that the equation has been corrected for a typing error in the original paper.

#### 9.4.3.1.4 Solid uranium perchlorates

There are two X-ray crystallographic studies [2003FIS] and [2010GRI/KRO] that illustrate the relative affinities between the uranyl(VI) ion, water and perchlorate. Fisher has determined the X-ray structure of three different phases, $[UO_2(OH_2)_3(ClO_4)_2]$(cr); $[UO_2(OH_2)_5](ClO_4)_2$(cr) and $[UO_2(OH_2)_5](ClO_4)_2\cdot 2H_2O$(cr), Figure 9-8. The first one contains coordinated perchlorate ions and three coordinated water, while the following two contain $[UO_2(OH_2)_5]^{2+}$ with perchlorate in the second coordination sphere. A more detailed study of the second phase was made by Grigor'ev and Krot that confirmed the structure from Fischer, but added information on the position of the hydrogen atoms in the coordinated water. This was possible by performing the X-ray study at 100 K; in addition they also determined the structures of the corresponding Np and Pu compounds. The solid phases were prepared by crystallisation from aqueous solution under very similar conditions and these observations imply that the relative affinities between the actinyl(V/VI) ions and perchlorate and water are very similar, despite the difference in charge, and also a strong indication that the interactions between $UO_2^{2+}$ and $ClO_4^{-}$ are of the outer-sphere type.

Figure 9-8: (a) Structure of $[UO_2(OH_2)_5](ClO_4)_2$(cr) based on data from Grigor´ev and Krot, [2010GRI/KRO]. (b) Structure of $[UO_2(OH_2)_3(ClO_4)_2]$(cr) based on data from Fischer [2003FIS].

(a) (b)



## 9.4.4 Bromine compounds and complexes

### 9.4.4.1 Gaseous uranium bromides

There are no new experimental studies and the thermodynamic data from [1992GRE/FUG] and [2003GUI/FAN] are retained.

### 9.4.4.2 Aqueous U(VI) bromides

Wilson *et al.* [2011WIL/SKA] studied the formation and structure of uranyl(VI) bromide complexes in aqueous solution using high-intensity X-ray scattering. In 11 m HBr they found the coordination of $(1.9 \pm 0.2)$ bromide ions and $(2.0 \pm 0.5)$ water ligands, suggesting a slightly smaller number of coordinated water ligands than in the corresponding chloride complex ([2011SOD/SKA]) and also that the coordination of bromide is weaker than that of chloride. The present review concludes that there is strong experimental evidence for the formation of inner-sphere complexes and based on this retains the equilibrium constant and Gibbs energy of formation $UO_2Br^+$ (aq, 298.15 K) from [1992GRE/FUG] and [2003GUI/FAN], but notes that higher complexes are formed at high bromide concentrations.

### 9.4.4.3 Aqueous U(IV) bromides

There are no new thermodynamic data published since the [2003GUI/FAN] review, and the values selected there for $UBr^{3+}$ are retained in the present review.

## 9.4.5 Iodide compounds and complexes

### 9.4.5.1 Gaseous uranium iodides

There are no new experimental studies since the review by Guillaumont *et al.* and the selected values in [1992GRE/FUG] and [2003GUI/FAN] are retained.

#### 9.4.5.2 Solid uranium iodides and periodate

Crawford and Mayer [2005CRA/MAY] have made a single-crystal X-ray study of the adduct $(Ph_4P)_2(UO_2I_4)\cdot 2NCCH_3(cr)$, where $Ph_4P^+$ is the tetra-phenyl phosphonium ion and $CH_3CN$ is methyl cyanide. The complex has octahedral geometry with a linear uranyl-unit and four iodide ions coordinated in the equatorial plane. They have also measured Raman spectra of the solid and solutions and in this way validated quantum chemistry calculations. Bray *et al.* [2006BRA/BEI] determined the structure of $Na_2[UO_2(IO_3)_4(OH_2)](cr)$ that contains coordinated water and four uni-dentate coordinated iodate ions, resulting in the common pentagonal bi-pyramid coordination around uranium. Sullens *et al.* [2004SUL/JEN] describe U(VI)-U(VI) cation interactions in an open framework uranyl-periodate structure, $M[(UO_2)(HIO_6)(OH)(O)(OH_2)]\cdot 1.5H_2O(cr)$, $M = Na^+$-$Cs^+$. There is no thermodynamic information in these studies.

#### 9.4.5.3 Aqueous uranium iodate and periodate

Two experimental studies dealing with aqueous U(VI) complexes with iodate and periodate have been published since the last Update book, [2003KAR/FOU] and [2004KAR/HUB]. Both studies use the same experimental methods, time-resolved laser induced fluorescence spectroscopy (TRLFS) and capillary zone-electrophoresis (CZE). [2003KAR/FOU] and [2004KAR/HUB] give concordant equilibrium constants for the Reactions (9.38) and (9.39) *cf.* Table 9-23.

$$UO_2^{2+} + nIO_3^- \rightleftharpoons UO_2(IO_3)_n^{2-n};\ n = 1, 2 \tag{9.38}$$

$$UO_2^{2+} + IO_4^- \rightleftharpoons UO_2IO_4^+ \tag{9.39}$$

Table 9-23: Equilibrium constants for the formation of uranyl(VI) iodate and periodate complexes from [2003KAR/FOU] and [2004KAR/HUB].

| Reaction | $\log_{10}\beta_1$ (TRLFS) | $\log_{10}\beta_1$ (CZE) | $\log_{10}\beta_2$ (TRLFS) | $\log_{10}\beta_2$ (CZE) |
|---|---|---|---|---|
| $UO_2^{2+} + IO_3^- \rightleftharpoons UO_2(IO_3)^+$ | (1.5 ± 0.2) | (1.62 ± 0.1) | | |
| $UO_2^{2+} + 2IO_3^- \rightleftharpoons UO_2(IO_3)_2(aq)$ | | | (3.6 ± 0.2) | (3.05 ± 0.1) |
| $UO_2^{2+} + IO_4^- \rightleftharpoons UO_2IO_4^+$ | (1.8 ± 0.2) | (2.0 ± 0.2) | | |

The iodate equilibria have been studied in a 0.05 M $NaClO_4$ ionic medium and recalculation of the measured equilibrium constants to zero ionic strength using the interaction coefficients in Appendix B, gives $\log_{10}\beta_1^o = (1.9 \pm 0.2)$ as an average of the two values and $\log_{10}\beta_2^o = (3.67 \pm 0.20)$, where the value from the TRLFS study has been rejected based on the arguments in Appendix A. These values are in good agreement with those selected in [1992GRE/FUG] but their uncertainty is much larger and we have therefore retained the selected equilibrium constants for the iodate complexes from [1992GRE/FUG] and [2003GUI/FAN].

$$\log_{10}\beta_1^o\ ((9.38),\ n = 1,\ 298.15\ K) = \mathbf{(2.000 \pm 0.020)}$$

$$\log_{10}\beta_2^{o}((9.38), n = 2, 298.15\ \text{K}) = \mathbf{(3.590 \pm 0.150)}$$

and

$$\Delta_r G_m^{o}(\ UO_2IO_3^{+}, \text{aq}, 298.15\ \text{K}) = \mathbf{-\ (11.416 \pm 0.114)},$$

$$\Delta_r G_m^{o}(\ UO_2(IO_3)_2, \text{aq}, 298.15\ \text{K}) = \mathbf{-\ (20.492 \pm 0.856)}.$$

There is no previous information on the equilibrium constants in the uranyl periodate system and the present review has accepted the equilibrium constant for the Reaction (9.39), which recalculated to zero ionic strength gives $\log_{10}\beta_1^{o} = (2.35 \pm 0.20)$. For the extrapolation to zero ionic strength we used $\varepsilon(\ IO_4^-, Na^+) = \varepsilon(\ ClO_4^-, Na^+) = 0.01$ kg·mol$^{-1}$ and $\varepsilon(\ UO_2IO_4^+, ClO_4^-) = \varepsilon(\ UO_2IO_3^+, ClO_4^-) = 0.33$ kg·mol$^{-1}$.

The selected equilibrium constant and Gibbs energy of reaction are:

$$\log_{10}\beta_1^{o}((9.39), 298.15\ \text{K}) = \mathbf{(2.350 \pm 0.200)}$$

and

$$\Delta_r G_m^{o}(\ UO_2IO_4^{+}, \text{aq}, 298.15\ \text{K}) = \mathbf{-\ (13.414 \pm 1.142)}.$$

Wagman *et al.* [1982WAG/EVA] report the Gibbs energy of formation, $\Delta_f G_m^{o}(IO_4^-, \text{aq}, 298.15\ \text{K}) = -58.2$ kJ·mol$^{-1}$. From this value the present review obtains $\Delta_f G_m^{o}(UO_2IO_4^+, 298.15\ \text{K}) = -(1024.165 \pm 2.891)$ kJ·mol$^{-1}$, which is provided for information only. The uncertainy has been estimated assuming an uncertainty of 2 kJ·mol$^{-1}$ in the Gibbs energy of formation of $IO_4^-(\text{aq})$.

# 9.5 Uranium group 16 (chalcogens) compounds and complexes

## 9.5.1 Aqueous uranium sulfate

### 9.5.1.1 Aqueous U(VI) sulfates

#### 9.5.1.1.1 Binary complexes

There are two new experimental studies of uranyl(VI) sulfate complexes. Vercouter *et al.* [2008VER/VIT] have determined equilibria in the temperature range 10-75 °C in a 0.10 M $Na^+(ClO_4^-/SO_4^{2-})$ ionic medium, using time resolved laser fluorescence spectroscopy and from the temperature dependence of the equilibrium constants they have calculated the corresponding reaction enthalpies and entropies, as reported in Table 9-24 and Table 9-25. Tian and Rao [2009TIA/RAO] used spectrophotometry in the temperature range 25-70 °C, and microcalorimentry at 25 °C, to determine equilibrium constants and enthalpies of reaction in a 1 M $Na^+(ClO_4^-/SO_4^{2-})$ ionic medium, as reported in Table 9-24 and Table 9-25. The equilibrium constants are not significantly

different and the present review retains the values selected in [2003GUI/FAN], but with a larger uncertainty.

Table 9-24: Equilibrium constants for the binary complexes $UO_2(SO_4)_r^{2-2r}$ from [2008VER/VIT] and [2009TIA/RAO], the selected values from the present review in bold. The uncertainty in the equilibrium constants has been increased compared to the ones selected in [2003GUI/FAN].

| Species | $\log_{10}\beta$ ; $I$ = 0.10 M | $\log_{10}\beta^o$ | Reference |
|---|---|---|---|
| $UO_2SO_4$(aq) | (2.45 ± 0.05) | (3.29 ± 0.10) | [2008VER/VIT] |
| | | (3.15 ± 0.02) | [2003GUI/FAN] |
| $UO_2(SO_4)_2^{2-}$ | (3.48 ± 0.06) | (4.33 ± 0.14) | [2008VER/VIT] |
| | | (4.14 ± 0.07) | [2003GUI/FAN] |
| Species | $\log_{10}\beta$ ; $I$ = 1.00 M | $\log_{10}\beta^o$ | Reference |
| $UO_2SO_4$(aq) | (1.96 ± 0.06) | (3.23 ± 0.08) | [2009TIA/RAO] |
| $UO_2(SO_4)_2^{2-}$ | (2.97 ± 0.03) | (4.32 ± 0.15) | [2009TIA/RAO] |
| Species | $\log_{10}\beta$ ; $I$ = 3.0 M | $\log_{10}\beta^o$ | Reference |
| $UO_2(SO_4)_3^{4-}$ | (4.24 ± 0.16) | – | [2008VER/VIT] |
| $UO_2(SO_4)_3^{4-}$ | | (3.02 ± 0.38) | [2003GUI/FAN] |
| $UO_2SO_4$(aq) | | **(3.150 ± 0.100)** | This review |
| $UO_2(SO_4)_2^{2-}$ | | **(4.140 ± 0.150)** | This review |
| $UO_2(SO_4)_3^{4-}$ | | **(3.020 ± 0.380)** | This review |

The high ionic strength, 3 M, and the high concentration of sulfate in the $Na^+(ClO_4^-/SO_4^{2-})$ ionic medium used by Vercouter *et al.* do not allow an accurate extrapolation to zero ionic strength of the conditional equilibrium constant for the formation of $UO_2(SO_4)_3^{4-}$. Geipel *et al.* [1996GEI/BRA] reported an equilibrium constant for formation of $UO_2(SO_4)_3^{4-}$, $\log_{10}\beta_3 = (3.2 \pm 0.25)$ at $I = 1$ M, and extrapolated this value to zero ionic strength using an estimated interaction coefficient $\varepsilon(UO_2(SO_4)_3^{4-}, Na^+) = -0.24$ kg·mol$^{-1}$, based on $\varepsilon(P_2O_7^{4-}, Na^+)$. In agreement with [2003GUI/FAN], the present review considers that $\varepsilon(UO_2(CO_3)_3^{4-}, Na^+) = -(0.01 \pm 0.11)$ provides a better estimate, which results in a change of $\log_{10}\beta_3^o = (2.62 \pm 0.45)$ from Geipel *et al.* to $\log_{10}\beta_3^o = (3.02 \pm 0.38)$. Based on the discussion in Appendix A, this review finds no reason to question the equilibrium constants data from the previous reviews, especially as the uncertainty in the selected value of $\log_{10}\beta_1^o = (3.15 \pm 0.02)$ is significantly lower than those in the more recent studies. The estimates of the individual uncertainty in $\log_{10}\beta_1^o$ in Table V.34 of [1992GRE/FUG] are all larger than 0.05 $\log_{10}$ units and for this reason the present review considers 0.10 $\log_{10}$ units as a better estimate. For the same reason we have increased the uncertainty to ± 0.15 in $\log_{10}\beta_2^o$ compared with the one selected in [2003GUI/FAN]. With these changes, also the equilibrium constant from of Vercouter *et al.* and Tian and Rao, fall within the estimated uncertainty ranges. The present review has retained the selected values in [2003GUI/FAN], but increased their uncertainty.

This review has listed reaction enthalpies from previous studies in Table 9-25 and extrapolated them to zero ionic strength using only the Debye-Hückel term. It is not

straightforward to select a weighted average of the enthalpies of reaction at zero ionic strength because of the fairly large Debye-Hückel term that varies from 1 to 4.8 kJ·mol$^{-1}$ and for this reason the present review has reported the unweighted averages in Table 9-25, which are in good agreement with the ones selected in [2003GUI/FAN] and these, given in bold, have therefore been retained in the present review.

Vercouter *et al.* also report $\Delta_r H_m^o(UO_2(SO_4)_3^{4-}) = (57 \pm 10)$ kJ·mol$^{-1}$ in 3.0 M $Na^+(ClO_4^-/SO_4^{2-})$ but this value is not selected because it cannot accurately be extrapolated to zero ionic strength.

Table 9-25: Experimental enthalpies of reaction, $\Delta_r H_m$, in kJ·mol$^{-1}$ for the formation of binary complexes $UO_2(SO_4)_r^{2-2r}$ and the corresponding standard enthalpies of reaction, $\Delta_r H_m^o$, obtained by using only the Debye-Hückel term of the SIT (Appendix B and Grenthe *et al.* [1997ALL/BAN], p. 424).

| Reaction | Ionic strength /M | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4(aq)$ | ≈ 0.05 | (21 ± 2) | (19 ± 2) | [1967WAL] |
| | ≈ 0 | (20.8 ± 0.3) | (20.8 ± 0.3) | [1971BAI/LAR] |
| | 1.0 | (18.2 ± 0.2) | (13.4 ± 0.2) | [1971AHR/KUL] |
| | ≈ 0.01 | (19.6 ± 0.7) | (18.6 ± 0.7) | [1986ULL/SCH] |
| | 0.1 | (29.1 ± 4.0) | (26.5 ± 4.0) | [2008VER/VIT] |
| | 1.0 | (17.7 ± 0.3) | (12.9 ± 0.3) | [2009TIA/RAO] |
| | | | (18.5 ± 6.0) | Average value |
| | | | **(19.500 ± 1.600)** | [2003GUI/FAN] |
| $UO_2^{2+} + 2SO_4^{2-} \rightleftharpoons UO_2(SO_4)_2^{2-}$ | ≈ 0.05 | (29 ± 4) | (27 ± 4) | [1967WAL] |
| | 1.0 | (35.1 ± 4) | (30.3 ± 4) | [1971AHR/KUL] |
| | ≈ 0.01 | (37.8 ± 2.0) | (36.7 ± 2.0) | [1986ULL/SCH] |
| | 0.1 | (45.7 ± 6.0) | (43.2 ± 6.0) | [2008VER/VIT] |
| | | | (34.3 ± 9.0) | Average value |
| | | | **(35.100 ± 1.000)** | [2003GUI/FAN] |
| $UO_2^{2+} + 3SO_4^{2-} \rightleftharpoons UO_2(SO_4)_3^{4-}$ | 3 | (57 ± 10) | – | [2008VER/VIT] |

Table 9-26: Selected values of the Gibbs energy, enthalpy and entropy of reaction, and standard molar entropy for the formation of $UO_2SO_4(aq)$ and $UO_2(SO_4)_2^{2-}$. The Gibbs energy of reaction, the entropy of reaction and the molar entropies are the same as in [2003GUI/FAN], but their uncertainties have been increased compared to the ones reported there.

| Reaction | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4(aq)$ | **– (17.980 ± 0.571)** | **(19.500 ± 1.600)** | **(125.709 ± 5.698)** | **(46.009 ± 6.452)** |
| $UO_2^{2+} + 2SO_4^{2-} \rightleftharpoons UO_2(SO_4)_2^{2-}$ | **– (23.631 ± 0.856)** | **(35.100 ± 1.000)** | **(196.985 ± 4.415)** | **(135.786 ± 5.397)** |

There are a number of additional studies of the uranyl(VI) sulfate system that are of interest. Meinrath *et al.* [2006MEI/LIS] discuss the influence of errors resulting from the selection of different models in the analysis of experimental data, which are based mainly on their own spectrophotometric studies of systems containing sulfate and hydroxide complexes. This study provides no new thermodynamic information. The coordination and geometry of $UO_2SO_4(aq)$ and $UO_2(SO_4)_2^{2-}$ have been studied experimentally using new EXAFS experiments, [2007HEN/SCH], [2007HEN/SCH2], [2008HEN/IKE], [2008HEN/TSU], High-energy X-ray Scattering (HEXS), [2004NEU/SKA] and different quantum chemical methods [2007VAL/GRE], [2008HEN/TSU]. The EXAFS study in [2007HEN/SCH2] is of particular interest, because it provides no evidence for the formation of a complex $UO_2(SO_4)_3^{4-}$ in the test solution with the highest sulfate concentration (0.05 M $UO_2SO_4$ + 0.6 M $H_2SO_4$ + 2.35 M $(NH_4)_2SO_4$), where the free sulfate concentration is ≈ 1 M). These experimental findings also demonstrate that sulfate is coordinated to a single oxygen donor in $UO_2SO_4(aq)$. Quantum chemical calculations, on the other hand, indicate that bi-dentate coordination in $UO_2SO_4(aq)$ is more stable than the monodentate coordination by about 17 kJ·mol$^{-1}$; this energy difference, however, is of about the same magnitude as the expected error in this type of quantum chemistry calculations.

#### 9.5.1.2 Aqueous uranium(IV) sulfate

There are no new experimental determinations of equilibrium constants and the thermodynamic data for the aqueous complexes in [1992GRE/FUG] and [2003GUI/FAN] are therefore retained. There are two EXAFS studies by Hennig *et al.*, [2007HEN/SCH] and [2008HEN/KRA], of the structure of uranium(IV) sulfate complexes at high sulfate concentrations, in addition the same authors have published a review article [2008HEN/TSU] on the same subject.

The U(IV) and Th(IV) sulfate systems were studied in acid test solutions with high total concentrations of sulfate. The EXAFS analysis indicates four U-S distances, corresponding to the stoichiometry $U(SO_4)_4^{4-}$, with mono and bidentate coordination of sulfate, where the ratio mono:bi decreases with increasing total concentration of sulfate. The EXAFS analysis suggests nine oxygen donors in the first coordination shell, which is consistent with the structure $U(SO_{4,bid})_x(SO_{4,mono})_y(OH_2)_3^{4-}$, where (x + y) ≈ 4. There is no thermodynamic information in this study, but the observation that the evidence for formation of anionic U(IV) sulfate complexes at high total concentrations of sulfate is weak, is important.

### 9.5.2 Solid uranium sulfate compounds

Schnaars and Wilson [2012SCH/WIL] have prepared a number of different U(IV) sulfate compounds, $[U(SO_4)_2(H_2O)_7]\cdot 2H_2O(cr)$; $[U(SO_4)_2(H_2O)_4]\cdot H_2O(cr)$, $K_8[U_2(SO_4)_8]\cdot 6H_2O(cr)$; $Rb_8[U_2(SO_4)_8]\cdot 2.5H_2O(cr)$ and $Cs_2[U(SO_4)_3(H_2O)_2](cr)$; these structures contain both mono- and bi-dentate coordinated sulfate. Schnaars and Wilson

note that "there appears to be three primary phases of the neutral An(IV) sulfate complexes with the formula $An(SO_4)_2(H_2O)_x$ that occur within the actinides, β-$An(SO_4)_2(H_2O)_4$, An = U, Np, Pu; $[An(SO_4)_2(H_2O)_7]\cdot H_2O$(cr), An = Th, U and $An(SO_4)_2$(cr), An = Th, U". This paper contains IR and Raman spectra of the various compounds but no thermodynamic information.

Karyakin *et al.* [2003KAR/KNY], [2004KAR/KNY] and [2005KAR/KNY] have determined the standard enthalpy, entropy and Gibbs energy of formation of $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr), and $M[UO_2(SO_4)_2]$(s, amorph) (M = Mn, Fe, Co, Ni, Cu, Zn) using dissolution calorimetry and adiabatic low-temperature calorimetry in the range 7-300 K. $M[UO_2(SO_4)_2]$(s, amorph) is the completely dehydrated phase, for which there is no additional structure information. This review does not consider formation data of amorphous phases, and thus only information for $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) crystalline phases is discussed hereafter. The calorimetric studies are based on a cycle of dissolution reactions that results in the enthalpy of reaction for:

$$\begin{aligned} &UO_2(SO_4)\cdot 3H_2O(cr) + M(SO_4)\cdot nH_2O(cr) \rightleftharpoons \\ &M[UO_2(SO_4)_2]\cdot 5H_2O(cr) + (n-2)H_2O(l) \end{aligned} \qquad (9.40)$$

The calculation of the enthalpy of formation of $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr), requires information of the enthalpies of formation of $H_2O$(l), $UO_2(SO_4)\cdot 3H_2O$(cr) and $M(SO_4)\cdot nH_2O$(cr), that are listed in Chapter 14 and the corresponding reviews in Appendix A.

The present review has recalculated the thermodynamic data reported by Karyakin *et al.* using the selected data from [2003GUI/FAN] and [2005GAM/BUG] and these data are reported in Table 9-27. The relative partial molal enthalpy of water in 2 M HCl, $L_1 = -0.07$ kJ·mol$^{-1}$ is small but has been considered for the correction of the enthalpy of formation of $H_2O$(l) in the conditions of the experiments. Note that the enthalpies of formation reported in [2005KAR/KNY] are the same as in [2003KAR/KNY] and [2004KAR/KNY].

Table 9-27: Standard enthalpies of formation, $\Delta_f H_m^o$, of 3d transition metal uranyl sulfates, $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) at 298.15 K, reported in [2003KAR/KNY] and [2004KAR/KNY], which have been recalculated as described in Appendix A and then selected by this review. Selected values of molar entropy $S_m^o$ (298.15 K) and molar heat capacity $C_{p,m}^o$ (298.15 K) are as reported in [2003KAR/KNY], [2004KAR/KNY] and [2005KAR/KNY]. The Gibbs energy of formation for the $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) compounds have been obtained from the listed enthalpies of formation and the molar entropies in [2003KAR/KNY] and [2005KAR/KNY]. All reported data are new.

| M | $\Delta_f H_m^o$ ($M[UO_2(SO_4)_2]\cdot 5H_2O$,cr) /kJ·mol$^{-1}$ | $S_m^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S^o(M[UO_2(SO_4)_2]\cdot 5H_2O,cr)$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G^o(M[UO_2(SO_4)_2]\cdot 5H_2O,cr)$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| Mn | **– (4426.160 ± 5.058)** | **(607.3 ± 2.1)** | **(591.9 ± 1.5)** | **– (1731.058 ± 2.116)** | **– (3910.045 ± 5.097)** |
| Fe | **– (4285.562 ± 4.649)** | **(574.6 ± 2.1)** | **(548.2 ± 1.5)** | **– (1758.833 ± 2.118)** | **– (3761.166 ± 4.692)** |

(Continued on next page)

Table 9-27 (continued)

| M | $\Delta_f H_m^o$ ($M[UO_2(SO_4)_2]\cdot 5H_2O$,cr) /kJ·mol$^{-1}$ | $S_m^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S^o(M[UO_2(SO_4)_2]\cdot 5H_2O,cr)$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G^o(M[UO_2(SO_4)_2]\cdot 5H_2O,cr)$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| Co | **– (4243.140 ± 5.033)** | **(600.7 ± 2.1)** | **(590.6 ± 1.5)** | **– (1735.688 ± 2.119)** | **– (3725.645 ± 5.072)** |
| Ni | **– (4253.057 ± 4.719)** | **(581.4 ± 2.1)** | **(535.4 ± 1.5)** | **– (1754.818 ± 2.122)** | **– (3729.858 ± 4.761)** |
| Cu | **– (4119.110 ± 4.785)** | **(514.2 ± 2.1)** | **(483.3 ± 1.5)** | **– (1825.298 ± 2.114)** | **– (3574.897 ± 4.827)** |
| Zn | **– (4332.260 ± 4.736)** | **(477.1 ± 2.1)** | **(447.5 ± 1.5)** | **– (1870.878 ± 2.118)** | **– (3774.458 ± 4.778)** |

The molar isobaric heat capacity was determined by low-temperature calorimetry ($T$ = 5-300 K) for the penta-hydrates $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) ([2003KAR/KNY], [2005KAR/KNY]). The values of $C_{p,m}^o$ reported at $T$ = 298.15 K have been selected in this review and are included in Table 9-27. For $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) with M = Ni, Cu, Zn, the heat capacities increase monotonically without apparent anomalies in the temperature range below 240 K (M = Ni), below 300 K (M = Cu) and below 260 K (M = Zn). Extrapolation of the experimental heat capacities to 0 K were made using the following functions:

$$C_{p,m}(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 1.97\times10^{-1}T(\text{K})^{1.53} \quad \text{for} \quad \text{Ni}[UO_2(SO_4)_2]\cdot 5H_2O(\text{cr})$$

$$C_{p,m}(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 5.66\times10^{-3}T(\text{K})^{2.73} \quad \text{for} \quad \text{Cu}[UO_2(SO_4)_2]\cdot 5H_2O(\text{cr})$$

$$C_{p,m}(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 7.37\times10^{-3}T(\text{K})^{2.58} \quad \text{for} \quad \text{Zn}[UO_2(SO_4)_2]\cdot 5H_2O(\text{cr}).$$

Because of the long temperature extrapolation, the uncertainty in the reported entropies is possibly underestimated, but they have nevertheless been accepted by the present review.

The heat capacities and their temperature dependence in the range where no anomalies appear, can within the experimental errors be described as:

$$C_{p,m}(\text{Ni}[UO_2(SO_4)_2]\cdot 5H_2O,\text{cr}) = -28.886 + 2.9064T - 0.0034T^2 \quad \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}(\text{Zn}[UO_2(SO_4)_2]\cdot 5H_2O,\text{cr}) = 34.664 + 1.8600T - 0.0016T^2 \quad \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Above 150 K, Karyakin *et al.* [2005KAR/KNY], report an anomalous increase in the isobaric heat capacity as a result of phase transitions in $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr), M = Mn, Fe, Co, and the values of the enthalpy and entropy of transition are given in Table 9-28 and are accepted by this review.

Table 9-28: Enthalpy and entropy of transition for the $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) phases with M = Mn, Fe and Co. All these data are new.

| Compound | Transition temperature /K | $\Delta_{tr}H_m$ /J·mol$^{-1}$ | $\Delta_{tr}S_m$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|
| $Mn[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | 176 | **(510.000 ± 3.000)** | **(2.900 ± 0.020)** |
| | 238 | **(190.000 ± 3.000)** | **(0.800± 0.020)** |
| $Fe[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | 182 | **(200.000 ± 3000)** | **(1.100 ± 0.020)** |
| $Co[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | 237 | **(1920.000 ± 3.000)** | **(8.100 ± 0.020)** |

Karyakin *et al.* [2004KAR/KNY] have reported the enthalpy of dehydration of $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) phases as reported in Table 9-29, these values are also accepted by this review.

Table 9-29: The total enthalpy of dehydration and the average enthalpy of dehydration per water in kJ·mol$^{-1}$ for $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) at 298.15 K. There was no information on these reactions in [1992GRE/FUG] and [2003GUI/FAN].

| M | $\Delta_{dehyd}H_m^o$ /kJ·mol$^{-1}$ | $\Delta_{dehyd}H_m^o$ /kJ·mol$^{-1}$ (per water) |
|---|---|---|
| Mn | **(82.350 ± 0.640)** | **16.5** |
| Fe | **(101.400 ± 0.300)** | **20.5** |
| Co | **(113.000 ± 0.800)** | **22.5** |
| Ni | **(105.600 ± 0.500)** | **21.0** |
| Cu | **(90.490 ± 0.310)** | **18.0** |
| Zn | **(84.740 ± 0.330)** | **17.0** |

## 9.5.3 Aqueous uranium selenite

There are two new experimental studies of the equilibria in the uranyl(VI)-selenite system. In one of them Sladkov *et al.* [2009SLA/FOU] have used TRLFS and UV/VIS spectrophotometry to determine the equilibrium constant $\log_{10}\beta_1^o = (3.62 \pm 0.15)$ for the formation of $UO_2HSeO_3^+$ based on experiments at 20 °C and $I = 0.05$ M. $HSeO_3^-$ is a weak acid with a p$K$ value of 7.22 and in the pH range 1-2 used in these experiments, the concentration of $SeO_3^{2-}$ is too low for formation of significant amounts of $UO_2SeO_3$(aq), which could influence the analysis of the experimental data. In a second study, Sladkov [2010SLA] studied the Reactions (9.41) using capillary electrophoresis and identified complexes with $n$ = 1, 2.

$$UO_2^{2+} + nHSeO_3^- \rightleftharpoons UO_2(HSeO_3)_n^{2-n};\ n = 1, 2 \qquad (9.41)$$

The equilibrium constants at 20 and 25 °C in the 0.05 M ionic medium used and their values extrapolated to zero ionic strength using SIT are given in Table 9-30.

Table 9-30: Equilibrium constants for the formation of uranyl(VI)-selenite complexes from [2009SLA/FOU] and [2010SLA].

| Reaction | $\log_{10}\beta_n$ $I$ = 0.05 M | $\log_{10}\beta_n^o$ | Reference |
|---|---|---|---|
| $UO_2^{2+} + HSeO_3^- \rightleftharpoons UO_2HSeO_3^+$ | (3.35 ± 0.12)[(a)] | (3.62 ± 0.15) | [2009SLA/FOU] |
| | (2.93 ± 0.13) | (3.27 ± 0.15) | [2010SLA] |
| $UO_2^{2+} + 2HSeO_3^- \rightleftharpoons UO_2(HSeO_3)_2$(aq) | (5.04 ± 0.11) | (5.51 ± 0.11) | [2010SLA] |

(a) Experiments at 20 °C.

This review has selected the equilibrium constants from [2010SLA]. The corresponding Gibbs energy of reaction has been also included among the selected values.

$\log_{10}\beta_1^o$ = **(3.270 ± 0.150)**; $\Delta_r G_m^o(UO_2HSeO_3^+)$ = **– (18.665 ± 0.856)** kJ·mol$^{-1}$.

$\log_{10}\beta_2^o$ = **(5.510 ± 0.110)**; $\Delta_r G_m^o(UO_2(HSeO_3)_2, aq)$ = **– (31.451 ± 0.628)** kJ·mol$^{-1}$.

Using the Gibbs energy of formation, $\Delta_f G_m^o(HSeO_3^-) = -(410.112 \pm 1.166)$ kJ·mol$^{-1}$, from [2005OLI/NOL] we obtain the following selected Gibbs energies of formation

$$\Delta_f G_m^o(UO_2HSeO_3^+) = \mathbf{-(1381.328 \pm 2.268)}\ \text{kJ·mol}^{-1}$$

$$\Delta_f G_m^o(UO_2(HSeO_3)_2, aq) = \mathbf{-(1804.226 \pm 2.981)}\ \text{kJ·mol}^{-1}.$$

### 9.5.4 Aqueous uranium selenate

Equilibria in the uranyl(VI)-selenate system have been discussed in the review by Olin *et al.* [2005OLI/NOL], where the selected equilibrium constant, $\log_{10}\beta_1^o(UO_2SeO_4, aq) = (2.74 \pm 0.25)$, was based on equilibrium data in a 3.0 M $Na^+(ClO_4^-/SeO_4^{2-})$ ionic medium; as noted in [2005OLI/NOL] the extrapolation of this value to zero ionic strength is very uncertain and the uncertainty might therefore be larger than reported. Sladkov has published three studies of complex formation in the uranyl(VI)-selenate system, [2010SLA], [2012SLA] and [2013SLA] using capillary electrophoresis (Table 9-31); based on these the present review has selected the following thermodynamic data for the complex formation reactions, Table 9-32.

Table 9-31: Equilibrium constants for the formation of uranyl(VI) selenate complexes from [2010SLA] and [2012SLA], the extrapolation to zero ionic strength has been made by this review.

| Reaction | $\log_{10}\beta_n$ $I$ = 0.05 M | $\log_{10}\beta_n^o$ | Reference |
|---|---|---|---|
| $UO_2^{2+} + SeO_4^{2-} \rightleftharpoons UO_2SeO_4(aq)$ | (2.27 ± 0.06) | (2.93 ± 0.06) | [2010SLA] |
| | (2.26 ± 0.03) | (2.93 ± 0.04) | [2012SLA] |
| $UO_2^{2+} + 2SeO_4^{2-} \rightleftharpoons UO_2(SeO_4)_2^{2-}$ | (3.24 ± 0.10) | (4.03 ± 0.18) | [2010SLA] |
| | (3.24 ± 0.06) | (4.03 ± 0.06)[(a)] | [2012SLA] |

(a) recalculated by this review.

Table 9-32: Selected equilibrium constants, Gibbs energies, enthalpies and entropies of reaction for formation of $UO_2SeO_4(aq)$ and $UO_2(SeO_4)_2^{2-}$, where the enthalpies of reaction are from [2013SLA] and the Gibbs energies and entropies of reaction recalculated by the present review.

| Complex | $\log_{10}\beta_1^o$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2(SeO_4)(aq)$ | **(2.930 ± 0.040)** | **−(16.725 ± 0.228)** | **(20.000 ± 2.000)** | **(123.176 ± 6.751)** |
| $UO_2(SeO_4)_2^{2-}$ | **(4.030 ± 0.090)** | **−(23.003 ± 0.514)** | **(31.000 ± 4.000)** | **(181.127 ± 13.526)** |

The enthalpies of reaction in [2013SLA] were determined from the temperature dependence of the equilibrium constants in the range 15-55 °C, reported in [2012SLA]. Sladkov identified two complexes and $\log_{10}\beta_1^o(UO_2SeO_4, aq) = (2.95 \pm 0.08)$ and $\log_{10}\beta_2^o(UO_2(SeO_4)_2^{2-})$ (the first one in good agreement with the value, $\log_{10}\beta_1^o(UO_2SeO_4, aq) = (2.74 \pm 0.25)$ selected in [2005OLI/NOL] that was based

on the study by Lubal and Havel [1997LUB/HAV]). Using SIT this review obtained $\log_{10}\beta_2^{\circ}(UO_2(SeO_4)_2^{2-}) = (4.03 \pm 0.18)$ at zero ionic strength from [2010SLA]. These constants have very near the same value as the corresponding ones for sulfate, $\log_{10}\beta_1^{\circ}(UO_2SO_4, aq) = (3.15 \pm 0.02)$, and $\log_{10}\beta_2^{\circ}(UO_2(SO_4)_2^{2-}) = (4.14 \pm 0.07)$, which is not unexpected because of the chemical similarity between the ligands. We note that enthalpies of reaction reported in [2013SLA] for the formation of $UO_2SeO_4$(aq) and $UO_2(SeO_4)_2^{2-}$ are in excellent agreement with enthalpy data selected in [2003GUI/FAN] for the analogous sulfate complexe, $\Delta_r H_m^{\circ}(UO_2SO_4, aq) = (19.5 \pm 1.6)$ kJ·mol$^{-1}$ and $\Delta_r H_m^{\circ}(UO_2(SO_4)_2^{2-}) = (35.1 \pm 1.0)$ kJ·mol$^{-1}$. Using the selected Gibbs energy and enthalpy of formation of selenate $SeO_4^{2-}$ from [2005OLI/NOL], $\Delta_f G_m^{\circ}(SeO_4^{2-}) = -(439.485 \pm 1.431)$ kJ·mol$^{-1}$, $\Delta_f H_m^{\circ}(SeO_4^{2-}) = -(603.500 \pm 3.500)$ kJ·mol$^{-1}$ and $S_m^{\circ}(SeO_4^{2-}) = (32.965 \pm 12.687)$ J·K$^{-1}$·mol$^{-1}$, the present review has selected the following thermodynamic values for the uranyl(VI) selenate complexes:

$$\Delta_f G_m^{\circ}(UO_2SeO_4, aq) = \mathbf{-\ (1408.761 \pm 2.270)}\ \text{kJ·mol}^{-1};$$

$$\Delta_f H_m^{\circ}(UO_2SeO_4, aq) = \mathbf{-\ (1602.500 \pm 4.301)}\ \text{kJ·mol}^{-1};$$

$$S_m^{\circ}(UO_2SeO_4, aq) = \mathbf{(57.941 \pm 14.681)}\ \text{J·K}^{-1}\text{·mol}^{-1};$$

$$\Delta_f G_m^{\circ}(UO_2(SeO_4)_2^{2-}, aq) = \mathbf{-\ (1854.524 \pm 3.392)}\ \text{kJ·mol}^{-1};$$

$$\Delta_f H_m^{\circ}(UO_2(SeO_4)_2^{2-}, aq) = \mathbf{-\ (2195.000 \pm 8.201)}\ \text{kJ·mol}^{-1}$$

$$S_m^{\circ}(UO_2(SeO_4)_2^{2-}, aq) = \mathbf{(148.857 \pm 28.910)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

### 9.5.5 Solid uranium(VI) selenate compounds

Krivovichev [2008KRI] reports the X-ray structure of $(H_3O)_2[UO_2(SeO_4)_2(OH_2)]\cdot(H_2O)_2$(cr) and $(H_3O)_2[UO_2(SeO_4)_2(OH_2)]\cdot(H_2O)$(cr), and finds that the uranyl-ion is coordinated by four mono-dentate selenate ions and one water ligand, which is the same coordination as in $K_2[UO_2(SO_4)_2(OH_2)]\cdot(H_2O)_2$(cr) from Niinistö *et al.* [1979NII/TOI].

## 9.6 Uranium group 15 compounds and complexes

### 9.6.1 Nitrogen compounds and complexes

#### 9.6.1.1 Uranium nitrates

##### 9.6.1.1.1 Aqueous U(VI) nitrates

Marcantonatos *et al.* [1980MAR/DES], Suleimenov *et al.*, [2007SUL/SEW], Smith [2010SMI] and Smith and Czerwinski [2013SMI/CZE] have determined equilibrium

constants in the aqueous uranyl(VI)-nitrate system by using spectrophotometric methods. Information on enthalpies and entropies of reaction obtained from the temperature dependence of equilibrium constant and the Van't Hoff equation are reported in [1980MAR/DES] and [2007SUL/SEW] for Reaction (9.42):

$$UO_2^{2+} + NO_3^- \rightleftharpoons UO_2NO_3^+ \quad (9.42)$$

$$UO_2^{2+} + 2NO_3^- \rightleftharpoons UO_2(NO_3)_2(aq) \quad (9.43)$$

$$UO_2NO_3^+ + NO_3^- \rightleftharpoons UO_2(NO_3)_2(aq) \quad (9.44)$$

This review has made a new evaluation of the equilibrium data in [1992GRE/FUG]. In the spectrophotometric studies the measured molar absorptivity, $E_j$, is equal to:

$$E_j = \frac{\varepsilon_o + \varepsilon_1 \beta_1 [NO_3^-]}{1 + \beta_1 [NO_3^-]} \quad (9.45)$$

where $\varepsilon_o$ is the molar absorptivity of $UO_2^{2+}$, $\varepsilon_1$ the molar absorptivity of $UO_2NO_3^+$ and $\beta_1$ the corresponding equilibrium constant. In systems, like the present one, where the absorption bands of the different species overlap, there is a strong correlation between $\varepsilon_1$ and $\beta_1$, which leads to difficulty to select the individual values. In [1992GRE/FUG] the selected value of $\beta_1$ was based on the potentiometric study of Ahrland [1951AHR] and the distribution data of [1954DAY/POW], which were recalculated to zero ionic strength giving $\log_{10}\beta_1^o = (0.38 \pm 0.18)$ and $\log_{10}\beta_1^o = (0.01 \pm 0.26)$, respectively. Based on these [1992GRE/FUG] and [2003GUI/FAN] selected, $\log_{10}\beta_1^o = (0.30 \pm 0.15)$. The present review has reconsidered this choice and selected the value from [2007SUL/SEW], $\log_{10}\beta_1^o(UO_2NO_3^+)$ = **– (0.190 ± 0.150)**.

All equilibrium constants and enthalpies of reaction are reported in Table 9-33. Only the values of $\log_{10}\beta_1^o$ and the reaction enthalpy, reported in [2007SUL/SEW] have been accepted by this review, but with an increased uncertainty. Only the value reported by Ahrland [1951AHR] and the previous selection in [2003GUI/FAN] are outside the estimated uncertainty range.

Table 9-33: Equilibrium constants and enthalpies of reaction in kJ·mol$^{-1}$ for the formation of $UO_2NO_3^+$ at zero ionic strength, the selected values in bold.

| $\log_{10}\beta_1^o$ | $\Delta_r H_1^o$ /kJ·mol$^{-1}$ | $\log_{10}\beta_2^o$ | Reference |
|---|---|---|---|
| – 0.19 | – | – | [1949BET/MIC] |
| – 0.13 | – | – | [1954DAY/POW] |
| (0.38 ± 0.18) | – | – | [1951AHR] |
| (0.00 ± 0.17)[(a)] | – | – | [1967OHA/MOR] |
| – 0.09[(b)] | 3.1[(b)] | – | [1980MAR/DES] |
| – (0.19 ± 0.02) | (18.5 ± 3.5) | – | [2007SUL/SEW] |
| | (20.9 ± 3.5) at $I$ = 0[(c)] | | |
| – 0.1 | – | (3.67 ± 0.02)[(d)] | [2013SMI/CZE] |
| No complex assumed | | (3.14 ± 0.02)[(e)] | |
| (0.30 ± 0.15) | – | – | [2003GUI/FAN] |
| **– (0.190 ± 0.150)** | **(20.900 ± 3.500)** | – | Selected by this review |

(a) Recalculated, but not accepted, by this review
(b) Recalculated by this review from data at $I$ = 2 M
(c) Recalculated by this review
(d) Assuming that the light absorbing species are $UO_2NO_3^+$ and $UO_2(NO_3)_2$(aq)
(e) Assuming that the light absorbing species are $UO_2^{2+}$ and $UO_2(NO_3)_2$(aq)

The equilibrium constants from [2010SMI] and [2013SMI/CZE] have been rejected for reasons given in the Appendix A entries. We have no problem with the study by Ahrland, but note that the experimental method results in a large uncertainty. It is clear that additional experimental studies of the uranyl(VI)-nitrate system would be helpful, but until new data have been obtained we have selected $\log_{10}\beta_1^o$ = – (0.190 ± 0.150) in Table 9-33, where the estimated uncertainty is substantially larger than the experimenal value in [2007SUL/SEW]. The enthalpy and entropy of reaction from [2007SUL/SEW] valid at $I$ = 0 M, have been accepted by this review. The new selected values for formation of $UO_2NO_3^+$ are:

$$\log_{10}\beta_1^o = \mathbf{-\ (0.190 \pm 0.150)};$$

$$\Delta_r G_m^o(UO_2NO_3^+, \text{aq}) = \mathbf{(1.085 \pm 0.856)}\ \text{kJ·mol}^{-1};$$

$$\Delta_r H_m^o(UO_2NO_3^+, \text{aq}) = \mathbf{(20.900 \pm 3.500)}\ \text{kJ·mol}^{-1};$$

$$\Delta_r S_m^o(UO_2NO_3^+, \text{aq}) = \mathbf{(66.460 \pm 12.085)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

$$\Delta_f G_m^o(UO_2NO_3^+, \text{aq}) = \mathbf{-\ (1062.260 \pm 1.990)}\ \text{kJ·mol}^{-1};$$

$$\Delta_f H_m^o(UO_2NO_3^+, \text{aq}) = \mathbf{-\ (1204.950 \pm 3.829)}\ \text{kJ·mol}^{-1};$$

$$S_m^o(UO_2NO_3^+, \text{aq}) = \mathbf{(114.960 \pm 12.458)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

The reported enthalpy and entropy of reaction from [1980MAR/DES] are not accepted in this review for the reasons given in Appendix A.

Tsierkezos *et al.* [2009TSI/ROI] discuss if electrospray mass spectroscopy can be used to study speciation in aqueous uranyl(VI) nitrate solutions. The composition of the complexes are detected in gas-phase: aqua-ions, hydroxide and nitrate complexes are

identified, but their concentrations do not match those expected in the aqueous phase. Accordingly, these data do not provide thermodynamic information of use for the present review.

The uranyl(VI)-nitrate system has been studied by using molecular dynamics simulations both at the Car-Parrinello level by Bühl *et al.* [2007BUH/GOL], [2007BUH/DIS] and by using interatomic potentials by Ye *et al.* [2010YE/SMI]. The MD studies provide structures, in particular the mode of coordination of the nitrate ion, and also reaction energies. The results of the two simulations in water differ somewhat. In [2007BUH/DIS], $\eta^1$ coordination of nitrate in the complex $UO_2(NO_3)(OH_2)_4^+$ is somewhat more stable than $\eta^2$ coordination. In [2010YE/SMI], on the other hand, nitrate is found to be coordinated in $\eta^2$ configuration. These studies provide insights into structures, but also on the limitations of this type of modelling. There are no thermodynamic data in these quantum chemistry studies that can be used in the present review.

Ikeda-Ohno *et al.* [2009IKE/HEN] have investigated uranyl(VI) and uranium(IV) nitrate complexes using EXAFS. This study is important, even if no thermodynamic data are reported, because it gives direct structure information that allows estimate of the predominant complexes at different nitrate concentrations. The EXAFS data confirm the constitution of a number of U(VI)/U(IV)-nitrate complexes and of the aqua-ions, $[UO_2(OH_2)_5]^{2+}$ and $[U(OH_2)_{9\text{-}10}]^{4+}$. In the uranyl(VI) system they propose the formation of $[UO_2(OH_2)_4(\eta_2\text{-}NO_3)]^+$, $[UO_2(OH_2)_2(\eta_2\text{-}NO_3)_2]$ and a complex with three coordinated nitrate, possibly $[UO_2(OH_2)(NO_3)_3]$, where the mode of coordination of nitrate is not clear. The $[UO_2(OH_2)_2(\eta_2\text{-}NO_3)_2]$ coordination is not consistent with the modelling in [2007BUH/GOL] and [2007BUH/DIS]. It should be noted that complexes with two and three coordinated nitrate are formed at high nitrate concentrations $3 < [NO_3^-] / M < 14.5$.

#### 9.6.1.1.2 Aqueous U(IV) nitrates

There are no new thermodynamic data since the review by Guillaumont *et al.* [2003GUI/FAN]. Ikeda-Ohno *et al.* [2009IKE/HEN] have made an EXAFS study of the U(IV)-$HNO_3$ system and note that the coordination of nitrate is stronger than in the corresponding U(VI) system and that bidentate coordination is observed at the highest nitrate concentration; the authors suggest the formation of $[U(OH_2)_x(NO_3)_5]^-$ in 9 M $HNO_3$, and $[UO_2(NO_3)_3]^-$ in 14.5 M $HNO_3$, where most of the nitrate ions are coordinated in $\eta_2$ fashion. These observations are important as they provide independent information on the chemical models that can be used in the analysis of equilibrium data in aqueous solutions. The quantum chemical data in [2009IKE/HEN] provide useful information on structures but not on reaction energies.

The present review retains the thermodynamic data for the U(IV)-nitrate system selected in [2003GUI/FAN].

#### 9.6.1.1.3 Solid uranium nitrates

##### 9.6.1.1.3.1 $UO_2(NO_3)_2{\cdot}6H_2O$(cr)

The enthalpy of formation of $UO_2(NO_3)_2{\cdot}6H_2O$(cr), $\Delta_f H_m^o$ ($UO_2(NO_3)_2{\cdot}6H_2O$, cr) = – (3167.5 ± 1.5) kJ·mol$^{-1}$, selected in [1992GRE/FUG] is based on the calorimetric heat of dissolution of $UO_2(NO_3)_2{\cdot}6H_2O$(cr) in water, $\Delta_r H_m^o$ = (19.35 ± 0.20) kJ·mol$^{-1}$, from Fuger and Oetting, [1976FUG/OET] and Devina *et al.* [1982DEV/YEF]. This value is retained by the current review.

In a later calorimetric study, Devina *et al.* [1983DEV/YEF] have determined the enthalpy of reaction:

$$UO_2(NO_3)_2{\cdot}6H_2O(cr) + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} + 2NO_3^- + 6H_2O(l) \qquad (9.46)$$

at different temperatures and ionic strengths, information that provides a check on the consistency of the thermodynamic data for U(VI) nitrate and carbonate systems. The experimental enthalpies of reaction extrapolated to zero ionic strength, $\Delta_r H_m^o$ (9.46) = – (21.44 ± 0.13) kJ·mol$^{-1}$ can be used to calculate the enthalpy of formation of $UO_2(NO_3)_2{\cdot}6H_2O$(cr), *cf.* 9.7.1.1.1 A consistency check of uranyl(VI) carbonate, nitrate and hydroxide data.

### 9.6.1.2 Uranium nitrides

#### 9.6.1.2.1 UN(cr)

Since the review of [2003GUI/FAN], the only new experimental measurement reported for uranium nitride is by [2002NAK/ARA], who measured the heat capacity in the temperature range 323-1023 K by Differential Scanning Calorimetry. The calculated data are 2.4 % higher than recommended by [1992GRE/FUG] and [2003GUI/FAN] at 1000 K, and 5 % lower at room temperature, which does not satisfy the necessary constraint on $C_{p,m}^o$ (UN, cr, 298.15 K). We therefore prefer to retain the equation recommended in [1992GRE/FUG], [2003GUI/FAN] based on the data of Matsui and Ohse [1987MAT/OHS] for the temperature range 298.15 < $T$ /K < 1000:

$$C_{p,m}^o(\text{UN, cr}, T) = 50.54 + 1.066\times10^{-2}T - 5.238\times10^{5}T^{-2} \text{ J·K}^{-1}\text{·mol}^{-1}.$$

Although the value generated by this function at 298.15 K is not identical to the value of $C_{p,m}^o$ (UN, cr, 298.15 K) selected in [1992GRE/FUG], [2003GUI/FAN] based on low temperature heat capacity measurements, the function is consistent within the stated uncertainties.

[2005KUR/ADA] reported a molecular dynamics (MD) study of the thermophysical properties of UN(cr) in the temperature range 300-2500 K and the pressure range 0.1 MPa-1.5 GPa. The calculated ($C_V + C_d$) values (heat capacity at constant volume plus lattice dilatation term) were found to be lower than the literature data, the difference being of the order of 11 J·K$^{-1}$·mol$^{-1}$ at 1800 K, which the authors

attributed to the neglect of electronic contributions. We refer the reader to the Appendix A for further details. [2005SED/KON] performed *ab initio* calculations of the enthalpies of formation of the actinide mononitrides AnN(cr) (An = Ac, Th, Pa, U, Np, Pu, Am) using the full potential linearised augmented plane wave technique modified for local orbitals (APW + lo), yielding the difference in cohesive energies between the actinide mononitrides and the actinide metals An(cr) plus $1/2N_2$(g). The calculated cohesive energies showed a steep decrease from Ac towards Th-Pa and a progressive increase from Pa towards Am, which was related to the covalent/ionic character of the An-5f chemical bonds. The minimum around ThN and PaN was interpreted in terms of increased hybridisation with 5f and 6d states due to covalent mixing, hence stabilising the bonding states of the valence band. The calculated enthalpies of formation showed a linear decrease from UN towards AmN, which can be extrapolated to AcN. This decrease was related to the stabilising effect of the Madelung term, when the bonding becomes more ionic. The values calculated for ThN and PaN were found to be much lower due to covalent stabilisation. The calculated enthalpy of formation for UN(cr), *i.e.*, $\Delta_f H_m^o$ (UN, cr, 298.15 K) = – 291.0 kJ·mol$^{-1}$, is in very good agreement with the selected value in [2003GUI/FAN]. The same is true for NpN(cr), but large deviations are found for ThN(cr) and PuN(cr). The uncertainty in the calculated values is estimated to be around 15 kJ·mol$^{-1}$ by the present review. First principles calculations of the lattice parameters, thermal expansion, electronic structure, phonon dispersion and heat capacity at constant pressure were reported by [2007WEC/KIM] and [2010LU/WAN]. The electronic density of states calculations revealed a large degree of d-f hybridisation near the Fermi level, and a marked f-orbital character in the conduction band [2007WEC/KIM], [2010LU/WAN]. The lattice contribution to the heat capacity was found to be much lower than the literature data [1966COU/DEL], [1987MAT/OHS], and the result was improved when adding the contribution from the conduction electrons, the difference being of the order of 3-4 %, which illustrates the importance played by the itinerant 5f-electrons.

This review retains the data selected in [1992GRE/FUG] and [2003GUI/FAN]:

$$\Delta_f H_m^o \text{ (UN, cr, 298.15 K)} = \mathbf{-\ (290.000 \pm 3.000)} \text{ kJ·mol}^{-1}$$

$$C_{p,m}^o \text{ (UN, cr, 298.15 K)} = \mathbf{(47.570 \pm 0.400)} \text{ J·K}^{-1}\text{·mol}^{-1}$$

$$S_m^o \text{ (UN, cr, 298.15 K)} = \mathbf{(62.430 \pm 0.220)} \text{ J·K}^{-1}\text{·mol}^{-1}$$

$$\Delta_f G_m^o \text{ (UN, cr, 298.15 K)} = \mathbf{-\ (265.082 \pm 3.001)} \text{ kJ·mol}^{-1}.$$

## 9.6.2 Uranium phosphorus compounds and complexes

### 9.6.2.1 Aqueous uranium phosphorus species

#### 9.6.2.1.1 The uranium-phosphoric acid system

##### 9.6.2.1.1.1 Complex formation in the U(VI)-$H_3PO_4$ system

A detailed overview of the complex formation in the U(VI)-$H_3PO_4$ system has been presented in [1992GRE/FUG], where equilibrium stability constants were selected for the following species: $UO_2PO_4^-$, $UO_2HPO_4(aq)$, $UO_2H_2PO_4^+$, $UO_2H_3PO_4^{2+}$, $UO_2(H_2PO_4)_2(aq)$, $UO_2(H_2PO_4)(H_3PO_4)^+$, for most of which equilibrium constants have been measured in acid solutions. The study by Mathur [1991MAT] reported a somewhat different speciation scheme and corresponding equilibrium constants, but these data are disregarded for the reasons given in Appendix A. The review by Guillaumont *et al.* [2003GUI/FAN] confirmed both the speciation and the equilibrium constants selected in [1992GRE/FUG].

There are some new experimental studies of the complex formation in the U(VI)-$H_3PO_4$ system. [2004KIR/KIM2] investigated fluorescence lifetimes at pH = 1 in test solutions with total concentrations of phosphate, $0.003 \le [P] \le 0.3$ M, and a uranyl concentration of $5 \times 10^{-5}$ M in 0.50 M $NaClO_4$ at 20-150 °C. However, the equilibrium constants used in their speciation calculation were not measured, but taken from [1992GRE/FUG] and their study only provides confirmation of these. In an important study Rai *et al.* [2005RAI/XIA] investigated the solubility of $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$ over a wide range of pH (2.5-10.5) and found that the contribution of the $UO_2PO_4^-$ species, the main species at pH > 6, is strongly overestimated when using the equilibrium constant from [1992GRE/FUG] and [2003GUI/FAN]. Based on their solubility data and considering equilibrium constants for U(VI) hydrolysis species and phosphate complexes as reported in [2003GUI/FAN] (except for $UO_2PO_4^-$), the authors determined the stability constant for this species, $\log_{10}\beta^\circ = (11.01 \pm 0.48)$. This value differs significantly from the one in [1992GRE/FUG] and [2003GUI/FAN], $\log_{10}\beta^\circ = (13.23 \pm 0.15)$, but the present review considers it more reliable and therefore selects for the Reaction (9.47) the following equilibrium constant and Gibbs energy of reaction:

$$UO_2^{2+} + PO_4^{3-} \rightleftharpoons UO_2PO_4^- \qquad (9.47)$$

$$\log_{10}\beta^\circ = (\mathbf{11.010 \pm 0.480})$$

$$\Delta_r G_m^\circ = \mathbf{-\ (62.845 \pm 2.740)}\ \text{kJ}\cdot\text{mol}^{-1}.$$

Using the values of $\Delta_f G_m^\circ$ for $UO_2^{2+}$ and $PO_4^{3-}$ from [2003GUI/FAN], we have selected the Gibbs energy of formation of $UO_2PO_4^-$:

$$\Delta_f G_m^\circ = \mathbf{-\ (2040.887 \pm 3.611)}\ \text{kJ}\cdot\text{mol}^{-1}.$$

#### 9.6.2.1.1.2 Complex formation in the U(IV)-$H_3PO_4$ system

As indicated in the previous reviews [1992GRE/FUG] and [2003GUI/FAN], the results of [1955SCH] on the solubility of $U(HPO_4)_2 \cdot 6H_2O$(cr) in solutions of phosphoric acid, and of [1956BAE2] and [1987LOU/BES] on the reduction of U(VI) by Fe(II) in phosphate solutions, indicate the formation of stable uranium(IV) phosphate complexes, although no quantitative information can be obtained from these studies. The need of additional investigations was emphasised by Grenthe *et al.* [1992GRE/FUG].

New results were presented by Lehman *et al.* [2010LEH/GEI], who used time-resolved laser fluorescence spectroscopy (TRLFS) to study the complex formation between U(IV) and phosphate at various pH below 2 in $I = 0.1$ M (NaCl). The results indicate the formation of the species $UH_2PO_4^{3+}$ with the equilibrium constant $\log_{10}\beta^o$ = (**6.800 ± 0.700**), for Reaction (9.48), (see discussion in Appendix A).

$$U^{4+} + H_2PO_4^- \rightleftharpoons UH_2PO_4^{3+} \tag{9.48}$$

This review selects this value for the equilibrium constant, and the corresponding Gibbs energy of reaction:

$$\Delta_r G_m^o = -\ (\mathbf{38.815 \pm 3.996})\ \text{kJ·mol}^{-1}.$$

Using the Gibbs energy of formation, $\Delta_f G_m^o$, for $U^{4+}$ and $H_2PO_4^-$ from [2003GUI/FAN], the present reviews selects the Gibbs energy of formation of $UH_2PO_4^{3+}$:

$$\Delta_f G_m^o = \mathbf{-\ (1705.826 \pm 4.641)}\ \text{kJ·mol}^{-1}.$$

### 9.6.2.2 Solid uranium phosphorus compounds

#### 9.6.2.2.1 Uranium orthophosphates

##### 9.6.2.2.1.1 U(VI) orthophosphates

Previous NEA uranium reviews [1992GRE/FUG] and [2003GUI/FAN] selected thermodynamic data for dioxouranium(VI) orthophosphate hydrates, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr) and $(UO_2)_3(PO_4)_2 \cdot 6H_2O$(cr). Grenthe *et al.* [1992GRE/FUG] presented a review of the solubility studies for $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr), see Table 9-34. Thermodynamic data from solubility studies of the tetrahydrate were recalculated into the equilibrium constant for Reaction (9.49):

$$(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr) \rightleftharpoons 3UO_2^{2+} + 2PO_4^{3-} + 4H_2O(l) \tag{9.49}$$

When necessary, the reported equilibrium constants were recalculated to the value of $\log_{10} K_s^o$ (9.49) using protonation constants for the phosphate ion selected in [2003GUI/FAN].

In [1992GRE/FUG], the selected values refer to the reaction:

$$4H_2O + 3UO_2^{2+} + 2H_3PO_4(aq) \rightleftharpoons (UO_2)_3(PO_4)_2 \cdot 4H_2O(cr) + 6H^+ \quad (9.50)$$

for which the selected solubility constant $\log_{10} {}^{*}K_s^o$ (9.50) is (5.960 ± 0.300), which gives – (49.312 ± 0.300) when recalculated to Reaction (9.49).

Table 9-34: Values of $\log_{10} K_s^o$ for Reaction (9.49). In bold the values selected in [1992GRE/FUG] after recalculation to correspond to Reaction (9.49), and in this review.

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| [1961KAR] | Various | Recalculated in [1992GRE/FUG]. The hexahydrate[(a)] | – (48.82 ± 0.30) |
| [1965VES/PEK] | 0.3 M $NaNO_3$ | $t$ = (20 ± 1) °C. Recalculated in [1992GRE/FUG]. | **– (49.360 ± 0.300)** |
| [1983MAR/PAV] | $I$ < 0.01 M | Authors' value | – (49.00 ± 0.80) |
| [1992SAN/BRU] | 0.5 M $NaClO_4$ | | – (53.32 ± 0.17) |
| [2005RAI/XIA] | Various | Authors' value, selected in this review | **– (49.080 ± 0.480)** |
| [2009GOR/SHV] | $I$ < 0.01 M | | – (49.36 ± 0.04) |
| [2010ARM/FEL] | 0.1 M $NaClO_4$ | $t$ = (23 ± 1) °C. Authors' value based on one data point | – 49.7 |
| [2011NIP/CHE] | $I$ < 0.02 M | | – (50.39 ± 0.47) |
| [2003GUI/FAN] | | | – (49.312 ± 0.300) |

(a) As discussed in [1992GRE/FUG], the solubility of the tetra- and hexahydrate are very similar.

Four new studies reporting solubility products for $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr) have appeared since the previous reviews, see Table 9-34. All values, excluding the ones from [1992SAN/BRU], are in good agreement. Averaging these values (except the one from [1992SAN/BRU], identified as an outlier), and using weights equal to 2 for results given in bold that are judged to be the most reliable, this review obtains $\log_{10} K_s^o$ = – (49.35 ± 0.36), the uncertainty is for the confidence level 0.95. The value for Reaction (9.50) is $\log_{10} K_s^o$ = (5.946 ± 0.36). This result is practically identical to the value selected in [1992GRE/FUG], which is retained by this review as well as the value of the selected Gibbs energy of formation of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr).

The first calorimetric determination of the enthalpy of formation of this phase was reported by Gorman-Lewis *et al.* [2009GOR/SHV]. However, as discussed in Appendix A, this value is likely to be in error, and this review retains the values of $\Delta_f H_m^o$ and $S_m^o$ selected in [1992GRE/FUG] and [2003GUI/FAN]. An experimental determination of the entropy of this phase by means of a low-temperature calorimetry would be helpful to decrease the uncertainties of the entropy and enthalpy of formation of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr).

#### 9.6.2.2.2 U(VI) phosphates

The thermodynamic properties of U(VI) phosphates are based mostly on solubility data. Significant contributions were made by Vochten with coworkers, who

have performed extensive studies of structures, thermogravimetry, IR-spectra, solubility and electro-kinetic properties of a number of different uranyl(VI) phosphate and arsenate minerals: $M[UO_2PO_4]_2 \cdot nH_2O$, M = Cu, Ni, Co, [1981VOC/PIR]; bassetite, $Fe^{II}_{1-x}Fe^{III}_x[UO_2PO_4]_2(OH)_x \cdot nH_2O$, [1984VOC/GRA]; chernikovite, $(H_3O)_2[UO_2PO_4]_2 \cdot 6H_2O$; parsonite, $Pb_2[UO_2(PO_4)_2] \cdot 0.5H_2O$, [1991VOC/HAV2]; meta-uranocircite, $Ba[(UO_2)(PO_4)_2] \cdot 6H_2O$, [1992VOC/HAV]; meta-zeunerite and meta-kirchenerite, $M[UO_2AsO_4]_2 \cdot nH_2O$; M = Cu, Co, Ni, [1984VOC/GOE]; metakhalerite, $Fe[UO_2PO_4]_2 \cdot 8H_2O$; manganese uranylarsenate $Mn[UO_2AsO_4]_2 \cdot 8H_2O$, [1986VOC/GRA]. Only the solubility products are of interest for this review. In the discussion of the different papers we point out that the solubility products often cannot be selected, because the conditional constants have not been obtained using the NEA auxiliary data and that the corrections to zero ionic strength are uncertain. However, these data are sufficiently accurate to be used for scoping calculations of stability ranges for minerals and for modeling of transport in aqueous solutions.

In addition, many uranyl-bearing compounds, including phosphates and arsenates, were synthesised and investigated by the group from the University of Nizhny Novgorod, Russia (Chernorukov and co-workers). Solubility products obtained at the conditions of congruent dissolution were selected in this review. It should be noted that this group has often not given a detailed characterisation of studied samples: the authors did not report the exact stoichiometry and only idealised compositions, in addition they give no exact analytical data for the water content (reporting compositions, for example, as $Ni[(UO_2)(PO_4)]_2 \cdot 12H_2O$). A number of discrepancies in the low temperature calorimetric data for uranyl phosphates and uranyl arsenates reported by this group have been noticed by the review team. For example, values of $S^{\circ}_m$ (298.15 K) for $M[(UO_2)(AsO_4)]$ (M = Li, Na, K, Rb, and Cs) were reported in [1998KAR/CHE4] and [2000KAR/CHE], both from the same research group, and the differences between the two studies for Li-, Na- and K-uranyl arsenates are 3-5 %, which increases to ~ 8 % for $Rb[(UO_2)(AsO_4)]$ and ~ 15 % for $Cs[(UO_2)(AsO_4)]$. This fact and the lack of data on the exact composition of the phases make calorimetric data from this group at best semi-quantitative and for this reason the results are not accepted by this review, but we have reported them for information. The uranyl phosphate compounds can crystallise with different amounts of water and accurate analyses of this water content are very important, especially in low temperature calorimetric measurements of heat capacity and entropy, as these are strongly affected by the water content. The same is true for the enthalpy of solution data, reported by the same research group.

The calculations of the enthalpies of formation of alkali metal uranyl phosphates require values of $\Delta_f H^{\circ}_m$ of the reaction participants. Of particular concern is the enthalpy of formation for $KH_2PO_4$(cr). The Nizhny Novgorod group used the value from [1981GLU/MED], in which $\Delta_f H^{\circ}_m = -(1568.0 \pm 1.3)$ kJ·mol$^{-1}$ for $KH_2PO_4$(cr). However, the values of $\Delta_f H^{\circ}_m$ for all phosphate phases from that handbook have to be

corrected, because they are based on the enthalpy of formation of $P_4O_{10}$(cr) equal to $\Delta_f H_m^o = -(2984.0 \pm 4.2)$ kJ·mol$^{-1}$, see [1968GLU/MED]. This value was later revised, when preparing the handbook "Thermodynamic properties of individual substances" [1978GLU/GUR]. By the analysis of relevant data for solid compounds, and aqueous solutions, the authors of [1978GLU/GUR] selected two key values: for $P_4O_{10}$(cr) $\Delta_f H_m^o = -(3010.1 \pm 3.2)$ kJ·mol$^{-1}$ and for aqueous $H_3PO_4$ $\Delta_f H_m^o$ ($H_3PO_4 \cdot 100H_2O$, sln) $= -(1296.2 \pm 1.0)$ kJ·mol$^{-1}$. For the aqueous solution the identical value was accepted by CODATA [1989COX/WAG], and despite the fact that the CODATA team did not endorse the $\Delta_f H_m^o$ value for $P_4O_{10}$(cr), we do not expect a large difference from the reported value, $\Delta_f H_m^o = -(3010.1 \pm 3.2)$ kJ·mol$^{-1}$. The difference between the "new" and "old" values of the enthalpy of formation of $P_4O_{10}$(cr) is about 26 kJ·mol$^{-1}$. Therefore, the values of $\Delta_f H_m^o$ for phosphate phases from the Glushko/Medvedev Tables have to be made more negative by 6.5 kJ·mol$^{-1}$ per P atom in the chemical formula of a compound. As an example, such a procedure gives for $KH_2PO_4$(cr) $\Delta_f H_m^o = -1574.5$ kJ·mol$^{-1}$ with an expected uncertainty of ± 2 kJ·mol$^{-1}$. A check can be made using the value of $\Delta_r H_m^o$ = 19.69 kJ·mol$^{-1}$ [1966EGA/LUF] for the reaction $KH_2PO_4(cr) \rightleftharpoons K^+ + H_2PO_4^-$. Applying for $K^+$ $\Delta_f H_m^o = -(252.14 \pm 0.08)$ kJ·mol$^{-1}$ and for $H_2PO_4^-$ $\Delta_f H_m^o = -(1302.6 \pm 1.5)$ kJ·mol$^{-1}$ (both from the NEA database), we calculate for $KH_2PO_4$(cr) $\Delta_f H_m^o = -1574.43$ kJ·mol$^{-1}$, in good agreement with the corrected value from [1981GLU/MED].

The selected values in this review are usually based on experiments from different groups or by different methods, but such data do not exist for a number of solid phosphate, arsenate, silicate, borate and vanadate phases, which are discussed in Appendix A and the conclusions drawn there motivates whether the data are selected or not; we conclude that it is highly desirable that new experiments are performed on these important systems.When the quality of the published studies does not allow a selection of thermodynamic properties using NEA criteria, the results are included for information and can probably be used in scoping calculations or preliminary thermodynamic modeling.

#### 9.6.2.2.3 $UO_2HPO_4 \cdot 4H_2O$(cr)

The thermodynamic properties of the phase $UO_2HPO_4 \cdot 4H_2O$(cr) were discussed by Grenthe *et al.* [1992GRE/FUG]. The properties of this phase were considered identical to those of the mineral chernikovite $(H_3O)_2(UO_2)_2(PO_4)_2 \cdot 6H_2O$(cr), often written as $(H_3O)(UO_2)(PO_4) \cdot 3H_2O$(cr) or $H(UO_2)(PO_4) \cdot 4H_2O$(cr). Reported equilibrium constants of dissolution of $UO_2HPO_4 \cdot 4H_2O$(cr) were recalculated in the present review into the values of $\log_{10} {}^*K_s^o$ of Reaction (9.51) using protonation constants for phosphate selected in [2003GUI/FAN]:

$$UO_2HPO_4 \cdot nH_2O(cr) \rightleftharpoons UO_2^{2+} + H^+ + PO_4^{3-} + nH_2O(l) \qquad (9.51)$$

see Table 9-35.

Table 9-35: Values of $\log_{10}{}^{*}K^{o}$ for Reaction (9.51), with the one in bold selected in [1992GRE/FUG].

| Reference | Medium | Comments | $\log_{10}{}^{*}K^{o}$ |
|---|---|---|---|
| [1965VES/PEK] | 0.32 M $NaNO_3$ | $t$ = (20 ± 1) °C. Recalculated in [1992GRE/FUG] | – (24.120 ± 0.070) |
| [1967MOS/SHE] | Various | Recalculated in [1992GRE/FUG] | – (24.290 ± 0.070) |
| [1983MAR/PAV] | $I$ < 0.05 M | Recalculated in [1992GRE/FUG] | – (24.230 ± 0.130) |
| | | Selected in [1992GRE/FUG] | **– (24.202 ± 0.090)**[(b)] |
| [1985MAG/JES] | 0.093 M $HClO_4$ | One data point | – (24.57 ± 0.05) |
| [1985ZHI/POL] | $I$ < 0.10 M HCl | Two data points | – (24.18 ± 0.21) |
| [1996HAV/VOC] | $I$ < 0.11 M | Recalculated in this review | – (24.53 ± 0.21) |
| [2003CHE/SUL3] | $I$ < 0.02 M $H_2SO_4$ | | – (25.9 ± 1.0) |
| [2009GOR/SHV] | | For $UO_2HPO_4{\cdot}3H_2O$(cr)[(a)] | – (25.52 ± 0.03) |
| [2011CHE/NIP] | $I$ < 0.1 M | | – (25.15 ± 0.50) |

(a) By its XRD data (the reference file card 75-1106 from the Joint committee on Powder Diffraction Standards-International Centre for Diffraction Data, see Supporting materials to the paper) $UO_2HPO_4{\cdot}3H_2O$(cr) is identical to mineral chernikovite $UO_2HPO_4{\cdot}4H_2O$(cr).

(b) This value is recalculated from $\log_{10}{}^{*}K^{o}$ = (2.500 ± 0.090) that refers to the reaction $UO_2^{2+} + H_3PO_4(aq) + 4H_2O(l) \rightleftharpoons UO_2HPO_4{\cdot}4H_2O(cr) + 2H^{+}$.

The average of data for $\log_{10}{}^{*}K_s^{o}$ of the Reaction (9.51) (excluding the data from [2003CHE/SUL3], [1985MAG/JES] because the value is based on a single data point, [2011CHE/NIP] (excluded because of disagreement with [2003CHE/SUL3] from the same laboratory), and [2009GOR/SHV] (excluded because of the different stoichiometry)):

$$\log_{10}{}^{*}K_s^{o} = -(24.570 \pm 0.500),$$

where the uncertainty refers to the confidence level of 0.95. This value is overlapping with the older selection [1992GRE/FUG]:

$$\log_{10}{}^{*}K_s^{o} = \mathbf{-(24.202 \pm 0.090)},$$

and the older value is therefore retained. Accordingly, for Reaction (9.51) we have:

$$\Delta_r G_m^{o} = \mathbf{(138.146 \pm 0.514)}\ \text{kJ}\cdot\text{mol}^{-1}$$

The Gibbs energy of formation of $UO_2HPO_4{\cdot}4H_2O$(cr):

$$\Delta_f G_m^{o} = \mathbf{-(3064.749 \pm 2.414)}\ \text{kJ}\cdot\text{mol}^{-1}$$

from [1992GRE/FUG] is retained.

Low-temperature measurements of the heat capacity of $(H_3O)(UO_2)(PO_4){\cdot}3H_2O$(cr) by Karyakin *et al.* [2000KAR/CHE] led to the values of the heat capacity and the entropy of this phase at 298.15 K (the uncertainty is estimated in this review by taking into account the lack of data on the exact stoichiometry of the studied sample and the fact that data between 0-80 K were extrapolated):

$$C^{o}_{p,m} = (317 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1},$$
$$S^{o}_{m} = (328 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}.$$

Using the entropies of elements in their standard states from [2003GUI/FAN], this review calculates $\Delta_f S^{o}_{m} = -(1377.110 \pm 10.005)$, and combining this value with $\Delta_f G^{o}_{m}$, one obtains using the Gibbs-Helmholtz relation:

$$\Delta_f H^{o}_{m} = -(3475.334 \pm 3.838)\ kJ \cdot mol^{-1}.$$

Formally, this $\Delta_f H^{o}_{m}$ is in good agreement with the value of $-(3473 \pm 8)$ kJ·mol$^{-1}$ obtained in [1994KAR/CHE], however, as discussed in Appendix A, the reported value requires a number of corrections, and the agreement is most likely fortuitous. Within the uncertainties, the new value is consistent with the value of $\Delta_f H^{o}_{m} = -(3470.0 \pm 7.8)$ kJ·mol$^{-1}$ given in [2003GUI/FAN].

Therefore, the current review selects the following thermodynamic values for $UO_2HPO_4 \cdot 4H_2O$(cr):

$$\Delta_f G^{o}_{m}\ (UO_2HPO_4 \cdot 4H_2O, cr, 298.15\ K) = \mathbf{-\ (3064.749 \pm 2.414)}\ kJ \cdot mol^{-1};$$
$$\Delta_f H^{o}_{m}\ (UO_2HPO_4 \cdot 4H_2O, cr, 298.15\ K) = \mathbf{-\ (3475.334 \pm 3.838)}\ kJ \cdot mol^{-1};$$
$$S^{o}_{m}\ (UO_2HPO_4 \cdot 4H_2O, cr, 298.15\ K) = \mathbf{(328.000 \pm 10.000)}\ J \cdot K^{-1} \cdot mol^{-1};$$
$$C^{o}_{p,m}\ (UO_2HPO_4 \cdot 4H_2O, cr, 298.15\ K) = \mathbf{(317.000 \pm 10.000)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

There are also data for the anhydrous compound, $UO_2HPO_4$(cr), all from the same laboratory, [1994KAR/CHE]. First, for the reaction:

$$UO_2HPO_4 \cdot 4H_2O(cr) \rightleftharpoons UO_2HPO_4(cr) + 4H_2O(l) \qquad (9.52)$$

$\Delta_r H^{o}_{m}$ (9.52) $= (57.2 \pm 2.9)$ kJ·mol$^{-1}$, as determined in this review from the heats of solution in 18 m·dm$^{-3}$ HF in [1994KAR/CHE]. Combining this value with $\Delta_f H^{o}_{m}$ for $UO_2HPO_4 \cdot 4H_2O$(cr) given above and $\Delta_f H^{o}_{m}$ for liquid water from the NEA database, this review calculates for $UO_2HPO_4$(cr) $\Delta_f H^{o}_{m} = -(2274.814 \pm 4.812)$ kJ·mol$^{-1}$. Formally, this value is in good agreement with the result of $-(2275 \pm 7)$ kJ·mol$^{-1}$ obtained in [1994KAR/CHE], however, as discussed in Appendix A, the value requires a number of corrections which were not made, and in addition, it was based on the auxiliary $\Delta_f H^{o}_{m}$ for $KH_2PO_4$(cr), not analysed in the NEA database, see the review of [1993KAR/CHE] in Appendix A. The low-temperature measurements of the heat capacity [1999KAR/CHE] resulted at 298.15 K in $C^{o}_{p,m} = 145.9$ J·K$^{-1}$·mol$^{-1}$ and $S^{o}_{m} = 167.2$ J·K$^{-1}$·mol$^{-1}$ (the Latimer method [1951LAT], see Appendix D, gives a similar value, $S^{o}_{m} = (158 \pm 12)$ J·K$^{-1}$·mol$^{-1}$). Accepting these results, the current review selects the following thermodynamic values for $UO_2HPO_4$(cr):

$$\Delta_f G^{o}_{m}\ (UO_2HPO_4, cr, 298.15\ K) = \mathbf{-\ (2094.408 \pm 5.660)}\ kJ \cdot mol^{-1};$$
$$\Delta_f H^{o}_{m}\ (UO_2HPO_4, cr, 298.15\ K) = \mathbf{-\ (2274.814 \pm 4.812)}\ kJ \cdot mol^{-1};$$
$$S^{o}_{m}\ (UO_2HPO_4, cr, 298.15\ K) = \mathbf{(167.000 \pm 10.000)}\ J \cdot K^{-1} \cdot mol^{-1};$$
$$C^{o}_{p,m}\ (UO_2HPO_4, cr, 298.15\ K) = \mathbf{(146.000 \pm 10.000)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

The value of $\Delta_f G_m^o$ is calculated from the Gibbs-Helmholtz relation.

#### 9.6.2.2.4 M[(UO₂)(PO₄)]·*x*H₂O(cr), where M=Li, Na, K, Rb, Cs, NH₄

All these phases belong to the autunite mineral group, and are, according to Locock *et al.* [2004LOC/BUR], characterised by the presence of corrugated sheets of composition $[(UO_2)(XO_4)]^-$, where X = P or As, in which uranyl square bipyramids share equatorial vertices with phosphate or arsenate tetrahedra and in this way forming infinite sheets where the interlayer region contains mono- or divalent cations and $H_2O$. Thermodynamic data for these compounds, in addition to the ones discussed in [2003GUI/FAN], are based on the following studies: [1961KLY/ZAV], [1968PEK/VES], [1985MAG/JES], [1993KAR/CHE], [1994KAR/CHE2], [1996HAV/VOC], [1998KAR/CHE3], [1999KAR/CHE], [2002ERM], [2000KAR/CHE], [2002SUL/KAR], [2003CHE/SUL3], [2005FEL/XIA], [2006CHE/NIP], [2010ARM/FEL], [2011CHE/NIP]. Dissolution kinetics is discussed in [2007WEL/GUN] and [2008MAT/WEL] and phase transformations in [2008REY/GIM] and [2010ARM/FEL]. Shvareva *et al.* [2012SHV/FEI] have published a review on thermodynamic properties of uranyl minerals, emphasising the role of constraints given by calorimetric and solubility data. Detailed reviews of these publications are given in Appendix A.

*a)* $\Delta_f G_m^o$ *of alkali metal uranyl phosphates*

Solubility products of these compounds, reported in various studies, were recalculated, when necessary, into $\log_{10} K_s^o$ for Reaction (9.53) are reported in Table 9-36.

$$M[(UO_2)(PO_4)]\cdot xH_2O(cr) \rightleftharpoons UO_2^{2+} + M^+ + PO_4^{3-} + xH_2O(l) \qquad (9.53)$$

The varying water content has, as a rule, only a small effect on the value of $\log_{10} K_s^o$, however, the composition is important for interpreting the calorimetric measurements.

Table 9-36: Values of $\log_{10} K^o$ for Reaction (9.53) for various $M[UO_2PO_4]\cdot xH_2O(cr)$.

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| | | Li[(UO₂)(PO₄)]·*x*H₂O(cr) | |
| [1985MAG/JES] | $H_2O$ | One data point | – (24.95 ± 0.10) |
| [2003CHE/SUL3] | $I$ < 0.15 M $H_2SO_4$ | | – (25.4 ± 0.1) |
| [2011CHE/NIP] | $I$ < 0.1 M | | – (25.70 ± 0.40) |
| | | Na[(UO₂)(PO₄)]·*x*H₂O(cr) | |
| [1965VES/PEK] | 0.2 M $NaNO_3$ | $t$ = 20 °C. Recalculated in [1992GRE/FUG] | – (23.36 ± 0.10) |
| [1985MAG/JES] | $H_2O$ | One data point | – (24.85 ± 0.10) |
| [2003CHE/SUL3] | $I$ < 0.15 M $H_2SO_4$ | | – (25.8 ± 0.3) |
| [2005FEL/XIA] | 0.5 M $NaNO_3$ | $t$ = 23 °C. Recalculated in this review | – (23.33 ± 0.38) |
| [2011CHE/NIP] | $I$ < 0.1 M | | – (26.19 ± 0.40) |

(Continued on next page)

Table 9-36 (continued)

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| | | $K[(UO_2)(PO_4)]\cdot xH_2O$(cr) | |
| [1965VES/PEK] | 0.2 M $NaNO_3$ | $t$ = 20 °C. Recalculated in [1992GRE/FUG] | – (24.70 ± 0.15) |
| [1985MAG/JES] | $H_2O$ | One data point | – (25.55 ± 0.10) |
| [1996HAV/VOC] | $I$ < 0.0.3 M | Recalculated in this review | – (24.74 ± 0.80) |
| [2003CHE/SUL3] | $I$ < 0.15 M $H_2SO_4$ | | – (26.2 ± 0.5) |
| [2011CHE/NIP] | $I$ < 0.1 M | | – (26.47 ± 0.40) |
| | | $Rb[(UO_2)(PO_4)]\cdot xH_2O$(cr) | |
| [1965VES/PEK] | 0.2 M $NaNO_3$ | $t$ = 20 °C. Recalculated in [1992GRE/FUG] | – (24.93 ± 0.20) |
| [2003CHE/SUL3] | $I$ < 0.15 M $H_2SO_4$ | | – (26.2 ± 0.5) |
| [2011CHE/NIP] | $I$ < 0.1 M | | – (26.53 ± 0.40) |
| | | $Cs[(UO_2)(PO_4)]\cdot xH_2O$(cr) | |
| [1965VES/PEK] | 0.2 M $NaNO_3$ | $t$ = 20 °C. Recalculated in [1992GRE/FUG] | – (24.60 ± 0.20) |
| [2003CHE/SUL3] | $I$ < 0.15 M $H_2SO_4$ | | – (26.4 ± 0.7) |
| [2011CHE/NIP] | $I$ < 0.1 M | | – (26.73 ± 0.40) |
| | | $NH_4[(UO_2)(PO_4)]\cdot xH_2O$(cr) | |
| [1961KLY/ZAV] | $I$ < 0.3 M | Extrapolated to $I$ = 0 in this review | – (27.1 ± 0.9) |
| [1965VES/PEK] | 0.2 M $NaNO_3$ | $t$ = 20 °C. Recalculated in [1992GRE/FUG] | – (25.52 ± 0.10) |
| [2011CHE/NIP] | $I$ < 0.1 M | | – (25.69 ± 0.40) |

The data in Table 9-36 have been used to select the values of $\log_{10} K_s^o$ for Reaction (9.53) for the alkali metal uranyl phosphates, see Table 9-37. The selected equilibrium constants are based on the unweighted average values, except for $Na[(UO_2)(PO_4)]\cdot xH_2O$(cr). For the sodium phase, we noted that the $\log_{10} K_s^o$ values, determined in media with excess $Na^+$ ([1965VES/PEK] and [2005FEL/XIA]), are systematically, at least 1.5 $\log_{10}$ units, larger than the values obtained on dissolution of this phase in sodium-free media. This fact cannot be checked for other alkali metal uranyl phosphates, because the effect of variations of the cation concentrations was not studied. For $Na[(UO_2)(PO_4)]\cdot xH_2O$(cr), the results of [1965VES/PEK] and [2005FEL/XIA] were given weights 2 in the averaging procedure, while weights equal to one were used for all other data. The estimated uncertainties are 1.3 $\log_{10}$ units for the cesium phase and 1.0 $\log_{10}$ for all other phases. This review emphasises the need for additional, more precise studies of solubility of alkali metal uranyl phosphates in solutions with varying amounts of alkali metal cations and phosphates.

Table 9-37 also lists the values of $\Delta_r G_m^o$ for Reaction (9.53), and the last column of the Table reports the Gibbs energy of formation of alkali metal uranyl phosphates, $\Delta_f G_m^o$. The numerical values of $\Delta_f G_m^o$ strongly depend on the amount of water of hydration in crystalline solid hydrates, and different studies do not agree on this value. This review accepts, based mainly on results by Locock *et al.* [2004LOC/BUR], the compositions of the solid phases as given in Table 9-37.

Table 9-37: Selected values of $\log_{10} K^{o}$ for Reaction (9.53) for various $M[(UO_2)(PO_4)]\cdot xH_2O$(cr) at 298.15 K.

| $M[(UO_2)(PO_4)]\cdot xH_2O$(cr) | $\log_{10} K_s^{o(a)}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Li[(UO_2)(PO_4)]\cdot 4H_2O$(cr) | **– (25.500 ± 1.000)** | **(145.554 ± 5.708)** | **– (3365.074 ± 6.177)** |
| $Na[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | **– (24.300 ± 1.000)** | **(138.705 ± 5.708)** | **– (3090.120± 6.176)** |
| $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | **– (25.500 ± 1.000)** | **(145.554 ± 5.708)** | **– (3117.526 ± 6.176)** |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | **– (25.800 ± 1.000)** | **(147.267 ± 5.708)** | **– (3120.738 ± 6.177)** |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O$(cr) | **– (25.900 ± 1.300)** | **(147.837 ± 7.420)** | **– (3010.185 ± 7.804)** |
| $NH_4[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | **– (26.100 ± 1.000)** | **(148.979 ± 5.708)** | **– (2917.839 ± 6.181)** |

(a) Uncertainties are estimated in this review

*b) $S_m^o$ and $\Delta_f H_m^o$ of alkali metal uranyl phosphates*

Enthalpies of formation of these compounds have been experimentally determined in a number of studies, see Table 9-39. A common problem with the data published by the Nizhny Novgorod group is that the exact stoichiometry of the studied samples has not been reported, and accordingly variations of the water content may have noticeable effects on the final $\Delta_f H_m^o$ value.

The uranyl phosphate compounds can crystallise with different amounts of water, and low temperature calorimetric measurements of the heat capacity are strongly affected by the water content. The analysis of such data is facilitated by the use of an approximate estimation of the entropy of solid substances using the Latimer [1951LAT] method, see Appendix D, which provides an independent way to detect unlikely experimental values and to estimate the uncertainties.

Table 9-38 presents the experimentally determined values of the heat capacity, $C_{p,m}^o$, and the entropy, $S_m^o$, of alkali metal uranyl phosphates, together with $S_m^o$ estimated by the Latimer method. Note the non-monotonous change of $C_{p,m}^o$ and $S_m^o$ for Na, K, and Rb trihydrates of the uranyl phosphates, for which the most likely explanation is a higher hydration of the sodium phase. For Li-, K-, Rb-, and Cs-compounds the estimates by the Latimer [1951LAT] method are within (10-15) J·K$^{-1}$·mol$^{-1}$ of the experimental values, while for the Na-phase this difference exceeds 35 J·K$^{-1}$·mol$^{-1}$. Taking into account these observations, this review prefers, for scoping calculations, the experimental values for all phases except the Na- and $NH_4$-compounds, for which the Latimer [1951LAT] estimates are considered more reliable, see Table 9-39. However, these values are not selected and given for information only.

Table 9-38: Experimental and estimated values of $C_{p,m}^o$ and $S_m^o$ for various $M[(UO_2)(PO_4)]\cdot xH_2O$(cr) at 298.15 K; these values are reported for information only.

| Compound | $C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ / J·K$^{-1}$·mol$^{-1}$ | Estim. $S_m^{o\,(a)}$ / J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Li[(UO_2)(PO_4)]\cdot 4H_2O$(cr) | 332.1 | 336.1 | (351 ± 25) | [2000KAR/CHE] |
| $Na[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | 371.6 | 358.5 | (323 ± 19) | [2000KAR/CHE] |

(Continued on next page)

Table 9-38 (continued)

| Compound | $C^{o}_{p,m}$ / J·K$^{-1}$·mol$^{-1}$ | $S^{o}_{m}$ / J·K$^{-1}$·mol$^{-1}$ | Estim. $S^{o}_{m}$ [(a)], / J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | 304.2 | 342.4 | (330 ± 19) | [1998KAR/CHE2] |
| | 308.4 | 343.9 | | [2000KAR/CHE] |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | 300.3 | 348.0 | (341 ± 19) | [2000KAR/CHE] |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O$(cr) | 269.8 | 337.7 | (326 ± 17) | [2000KAR/CHE] |
| $NH_4[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | | | (350 ± 19) | |

(a) Estimated by the Latimer [1951LAT] method, see Appendix D

Using the selected $\Delta_f G^{o}_{m}$ and estimated $S^{o}_{m}$ values, this review calculated the enthalpy of formation, $\Delta_f H^{o}_{m}$, of alkali metal uranyl phosphates, and Table 9-39 presents these in the third column, to be compared with $\Delta_f H^{o}_{m}$ obtained in calorimetric measurements, in the fourth column of the Table. The agreement is within the combined uncertainties of experimental and estimated results, except for $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O$(cr), where the difference between the measured and estimated values exceeds 30 kJ·mol$^{-1}$.

Table 9-39: Enthalpy data calculated with the Gibbs-Helmholtz relation and comparison with the experimentally determined values of $\Delta_f H^{o}_{m}$ (298.15 K) for various $M[(UO_2)(PO_4)]\cdot xH_2O$(cr) at 298.15 K; these data are reported for information only.

| Compound | $S^{o}_{m}$ [(a)] /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f H^{o}_{m}$ [(b)] /kJ·mol$^{-1}$ | $\Delta_f H^{o}_{m}$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Li[(UO_2)(PO_4)]\cdot 4H_2O$(cr) | (336 ± 20) | – (3762.5 ± 8.6) | – (3741.7 ± 4.3)[(c)] | [2002ERM] |
| $Na[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | (323 ± 20) | – (3428.5 ± 8.6) | – (3422.4 ± 3.6)[(c,d)] | [1993KAR/CHE] |
| | | | – (3423.4 ± 5.2)[(c)] | [2002SUL/KAR] |
| $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | (343 ± 15) | – (3453.9 ± 7.6) | – (3457.0 ± 3.9)[(c,d)] | [1993KAR/CHE] |
| | | | – (3455.0 ± 4.7)[(c)] | [2002SUL/KAR] |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | (348 ± 15) | – (3459.2 ± 7.6) | – (3450.8 ± 3.8)[(c)] | [2002ERM] |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O$(cr) | (338 ± 15) | – (3319.4 ± 9.0) | – (3281.3 ± 4.0)[(c)] | [2002ERM] |
| $NH_4[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | (350 ± 20) | – (3337.0 ± 8.6) | | |

(a) Values considered most reliable in this review.

(b) Calculated in this review using the Gibbs-Helmholtz relation from values of $S^{o}_{m}$ (this Table) and $\Delta_f G^{o}_{m}$ (from Table 9-37).

(c) Numerical values are recalculated in this review as described in Appendix A.

(d) Values are obtained by combining $\Delta_f H^{o}_{m}$ of anhydrous uranyl phosphates with enthalpies of hydration of these phases from [2002SUL/KAR].

This review has only selected the Gibbs energy of formation for alkali metal uranyl phosphates, see Table 9-37. Values of $S^{o}_{m}$ and $\Delta_f H^{o}_{m}$ of the other compounds in Table 9-39 are given for information only.

In order to reduce the uncertainty of $\Delta_f G^{o}_{m}$ values, it would be helpful to investigate the solubility of $M[(UO_2)(PO_4)]\cdot xH_2O$(cr) in solutions with varying amounts of alkali metal cations and phosphates. In order to reduce the uncertainty of calorimetric

data, new measurements of the low-temperature heat capacity of well-characterised samples with carefully controlled water content are necessary.

*c) Thermodynamic properties of anhydrous alkali metal uranyl phosphates*

The thermodynamic properties of the anhydrous alkali metal uranyl phosphates are determined mostly from calorimetric measurements (low-temperature heat capacity data to calculate $S^{o}_{m}$, and the enthalpy of dissolution in water-acid mixtures to determine $\Delta_f H^{o}_{m}$) performed by the same research group ([1993KAR/CHE], [1994KAR/CHE], [1999KAR/CHE], [2000KAR/CHE]). Solubility data are absent for these compounds as they are unstable in the presence of water. Therefore, another strategy was chosen to evaluate the thermodynamic properties of these compounds where $S^{o}_{m}$ and $\Delta_f H^{o}_{m}$ were used to calculate $\Delta_f G^{o}_{m}$. An independent check of the Gibbs energies of these phases can be made using measurements of the water vapor pressure over monovariant associations of the anhydrous and hydrated compounds ([2002ERM], [2002SUL/KAR]).

Values of $C^{o}_{p,m}$ and $S^{o}_{m}$ at 298.15 K, based on low-temperature calorimetric measurements between 80-300 K, reported in two studies from the same laboratory, are reported in Table 9-40. The difference in $C^{o}_{p,m}$ (298.15 K) values is within (1.5-5.2) %, while the difference in tabulated $S^{o}_{m}$ can be as high as 15 %. These discrepancies in the $S^{o}_{m}$ values could be due to different procedures for extrapolation to 0 K, in the numerical integration of $C^{o}_{p,m}(T)$ data, and to variations in the composition of the studied samples (no data on the exact stoichiometry of the investigated phosphates are reported). It is worth noting that both sets of data do not show the regular increase in $S^{o}_{m}$ from Li to Cs, expected in isostructural compounds. The transition from the Li- to the Cs isostructural compound typically increases the entropy by (40-45) $J \cdot K^{-1} \cdot mol^{-1}$, see the handbook [1982GLU/GUR] for numerous examples. The estimates by the Latimer method show the expected trend, in contrast to the experimental data, which demonstrate an increase of about 60 $J \cdot K^{-1} \cdot mol^{-1}$. A check of the internal consistency of $S^{o}_{m}$ data for uranyl phosphates and arsenates, reported in [2000KAR/CHE], suggests that their uncertainty is often ± 20-30 $J \cdot K^{-1} \cdot mol^{-1}$, see Appendix A. Based on these arguments, this review considers the values estimated with the Latimer method [1951LAT] to be more reliable.

Table 9-40: Experimental ($C^{o}_{p,m}$ and $S^{o}_{m}$) and estimated ($S^{o}_{m}$ and $\Delta_f S^{o}_{m}$) values (in $J \cdot K^{-1} \cdot mol^{-1}$) for various M[$(UO_2)(PO_4)$](cr) phases at 298.15 K; these data are reported for information only.

| Compound | $C^{o}_{p,m}$ | $S^{o}_{m}$ | Reference | Estim. $S^{o}_{m}$ [(a)] | $\Delta_f S^{o}_{m}$ |
|---|---|---|---|---|---|
| Li[$(UO_2)(PO_4)$](cr) | 157.1 | 169.3 | [1999KAR/CHE] | (172 ± 12) | – (563.9 ± 12) |
| | 154.7 | 177.9 | [2000KAR/CHE] | | |
| Na[$(UO_2)(PO_4)$](cr) | 161.0 | 202.6 | [1999KAR/CHE] | (189 ± 12) | – (569.0 ± 12) |
| | 159.7 | 216.9 | [2000KAR/CHE] | | |

(Continued on next page)

Table 9-40 (continued)

| Compound | $C^{o}_{p,m}$ | $S^{o}_{m}$ | Reference | Estim. $S^{o}_{m}$ (a) | $\Delta_f S^{o}_{m}$ |
|---|---|---|---|---|---|
| K[$(UO_2)(PO_4)$](cr) | 164.0 | 194.0 | [1999KAR/CHE] | (196 ± 12) | – (575.4 ± 12) |
| | 163.5 | 221.8 | [2000KAR/CHE] | | |
| Rb[$(UO_2)(PO_4)$](cr) | 162.6 | 219.8 | [1999KAR/CHE] | (207 ± 12) | – (576.5 ± 12) |
| | 169.8 | 247.1 | [2000KAR/CHE] | | |
| Cs[$(UO_2)(PO_4)$](cr) | 168.8 | 230.7 | [1999KAR/CHE] | (214 ± 12) | – (578.0 ± 12) |
| | 160.5 | 236.7 | [2000KAR/CHE] | | |

(a) Estimated by the Latimer [1951LAT] method, see Appendix D.

Experimentally determined values of the enthalpies of formation of anhydrous alkali metal uranyl phosphates ([1993KAR/CHE], [2002ERM], [2002SUL/KAR]) were combined with the values of $\Delta_f S^{o}_{m}$ of these phases from Table 9-40 to calculate their Gibbs energies of formation, see Table 9-41. The resulting values of $\Delta_f G^{o}_{m}$ can be compared with the Gibbs energy of formation, calculated from $\Delta_r G^{o}_{m}$ dehydration reactions ([2002ERM], [2002SUL/KAR]), see the last two columns of Table 9-41. For Li-, Na-, K, and Rb phases the agreement is within combined uncertainties of two values (although for Rb[$(UO_2)(PO_4)$](cr) barely so), however, for Cs[$(UO_2)(PO_4)$](cr) the difference between the two values exceeds 20 kJ·mol$^{-1}$.

Table 9-41: Experimental $\Delta_f H^{o}_{m}$, and calculated values of $\Delta_f G^{o}_{m}$ for various M[$(UO_2)(PO_4)$](cr) phases at 298.15 K.

| Compound | $\Delta_f H^{o}_{m}$ /kJ·mol$^{-1}$ | Reference | $\Delta_f G^{o}_{m}$ (a) /kJ·mol$^{-1}$ | $\Delta_r G^{o}_{m}$ (b) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G^{o}_{m}$ (c) /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| Li[$(UO_2)(PO_4)$](cr) | – (2539.9 ± 4.5) | [2002ERM] | – (2371.8 ± 5.7) | – (71.0 ± 5.7) | – (2379.7 ± 8.4) |
| Na[$(UO_2)(PO_4)$](cr) | – (2517.2 ± 3.0) | [1993KAR/CHE] | – (2347.6 ± 4.7) | – (48.0 ± 5.7) | – (2356.4 ± 8.4) |
| | – (2518.2 ± 5.5) | [2002SUL/KAR] | – (2348.6 ± 6.6) | | |
| K[$(UO_2)(PO_4)$](cr) | – (2543.5 ± 3.9) | [1993KAR/CHE] | – (2372.3 ± 5.3) | – (43.1 ± 5.7) | – (2388.7 ± 8.4) |
| | – (2553.1 ± 4.7) | [2002SUL/KAR] | – (2381.5 ± 5.9) | | |
| Rb[$(UO_2)(PO_4)$](cr) | – (2542.6 ± 3.2) | [1993KAR/CHE] | – (2370.7 ± 4.8) | – (39.2 ± 5.7) | – (2395.8 ± 8.4) |
| | – (2554.8 ± 3.9) | [2002ERM] | – (2382.9 ± 5.3) | | |
| Cs[$(UO_2)(PO_4)$](cr) | – (2556.4 ± 4.2) | [1993KAR/CHE] | – (2384.1 ± 5.5) | – (34.7 ± 5.7) | – (2404.0 ± 9.7) |
| | – (2541.2 ± 4.1) | [2002ERM] | – (2368.9 ± 5.4) | | |

(a) Calculated using experimental $\Delta_f H^{o}_{m}$ and accepted $\Delta_f S^{o}_{m}$ values.
(b) Values of the Gibbs energy changes for reactions of the type $M[(UO_2)(PO_4)]\cdot nH_2O(cr) \rightleftharpoons M[(UO_2)(PO_4)](cr) + nH_2O(g)$, calculated in this review from water vapor pressure data reported in [2002ERM] and [2002SUL/KAR], uncertainties are estimated.
(c) Calculated using $\Delta_r G^{o}_{m}$ values together with $\Delta_f G^{o}_{m}$ of $H_2O(g)$ and hydrated phases from Table 9-37.

These values have not been selected as the number of experimental data and their precision do not correspond to the NEA criteria. The calculated properties for these compounds are reported for information only. Figure 9-9 and Figure 9-10 below show the phase relations in the systems U(VI)-P(V)-Na-$H_2O$ and U(VI)-P(V)-K-$H_2O$ at 298.15 K and 0.1 MPa. The diagrams are built using the Gibbs energies of solid phases and aqueous ions from the NEA database, or selected in the current review. These diagrams should be

of help when designing new experimental studies of solubilities and phase relations of uranyl phosphates in aqueous solutions.

Figure 9-9: Phase relations in the U(VI)-P(V)-Na-H-O system in aqueous solutions at 298.15 K and 0.1 MPa.

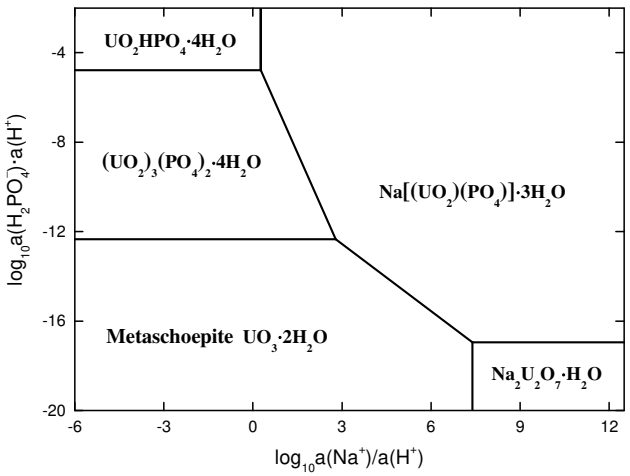
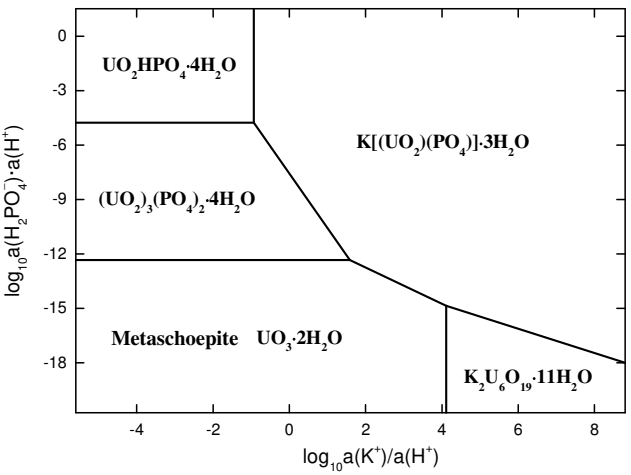



Figure 9-10: Phase relations in the U(VI)-P(V)-K-H-O system in aqueous solutions at 298.15 K and 0.1 MPa.



#### 9.6.2.2.5 M[(UO2)(PO4)]2·xH2O(cr), where M = Mg, Ca, Sr, Ba

These phases belong to the autunite mineral group, the name autunite itself designates the hydrated calcium uranyl phosphate of the general formula $Ca[(UO_2)(PO_4)]_2 \cdot 10\text{-}12H_2O(cr)$, which at dehydration transforms into meta-autunite $Ca[(UO_2)(PO_4)]_2 \cdot 2\text{-}6H_2O(cr)$.

In these phases there is a large variation of the degree of hydration that is still compatible with the autunite structure and it is not always clear which hydrate is stable in water at ambient conditions. Most probably, the difference in the thermodynamic stability of various hydrates is small. For example, the dioxouranium(VI) orthophosphate hydrates, $(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$ and $(UO_2)_3(PO_4)_2 \cdot 6H_2O(cr)$, have practically the same aqueous solubility [1992GRE/FUG]. These observations suggest that, as a first approximation, one can ignore the difference in the degree of hydration when comparing the solubility products reported in the literature. The large variation of the number of water of crystallisation in natural minerals is also an indirect indication that their stability in aqueous solutions is similar, see for example data in Table 9-42 for the Ca-phases with different water contents.

*a)* $\Delta_f G_m^o$ *of alkaline earth metal uranyl phosphates*

Values of solubility products, reported in the literature, have been recalculated, when necessary, into $\log_{10} K_s^o$ for Reaction (9.54).

$$M[(UO_2)(PO_4)]_2 \cdot xH_2O(cr) \rightleftharpoons 2UO_2^{2+} + M^{2+} + 2PO_4^{3-} + xH_2O(l) \quad (9.54)$$

(see Table 9-42).

Table 9-42: Values of $\log_{10} K_s^o$ for Reaction (9.54) for various $M[(UO_2)(PO_4)]_2 \cdot xH_2O(cr)$ phases.

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| | | $Mg[(UO_2)(PO_4)]_2 \cdot xH_2O(cr)$ | |
| [1985MAG/JES] | $H_2O$ | $x$ = 10.25. One data point | – (47.0 ± 1.0) |
| [2011NIP/PYK] | $I$ < 0.1 M | $x$ = 8.0 | – (50.3 ± 0.4) |
| | | $Ca[(UO_2)(PO_4)]_2 \cdot xH_2O(cr)$ | |
| [1968PEK/VES] | $I$ = 0.2 M ($Ca(NO_3)_2$) | $x$ = 6.0. No primary data. Extrapolated to $I$ = 0 in this review | – 50.83 |
| [1985MAG/JES] | 0.0931 M $HClO_4$ | $x$ = 6.96. One data point | – (51.4 ± 1.0) |
| [1985ZHI/POL] | $I$ < 0.1 M (HCl) | $x$ = 8.5. Two data points | – (49.61 ± 0.25) |
| [2009GOR/SHV] | $I$ < 0.01 M | $x$ = 3.0. From both under- and oversaturation | – (48.36 ± 0.03) |
| [2011NIP/PYK] | $I$ < 0.1 M | $x$ = 8.0 | – (50.4 ± 0.4) |
| | | $Sr[(UO_2)(PO_4)]_2 \cdot xH_2O(cr)$ | |
| [1968PEK/VES] | $I$ = 0.2 M ($Sr(NO_3)_2$) | $x$ = 7.5. No primary data. Extrapolated to $I$ = 0 in this review | – 51.91 |
| [2011NIP/PYK] | $I$ < 0.1 M | $x$ = 8.0 | – (50.7 ± 0.4) |

(Continued on next page)

Table 9-42 (continued)

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| | | $Ba[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr) | |
| [1968PEK/VES] | $I$ = 0.2 M ($Ba(NO_3)_2$) | $x$ = 6.0. No primary data. Extrapolated to $I$ = 0 in this review | – 53.17 |
| [1992VOC/HAV] | $I$ < 0.05 M | $x$ = 6.0. Extrapolated to $I$ = 0 in this review | – (53.2 ± 1.6) |
| [2011NIP/PYK] | $I$ < 0.1 M | $x$ = 7.0 | – (51.3 ± 0.4) |

These data have been used to select the values of $\log_{10} K_s^o$ for Reaction (9.54). For the Mg and Ba phases, the result of [2011NIP/PYK] were used with the weight 2, as they were considered more reliable than other data for these phases. For autunite $Ca[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr), results of [1968PEK/VES] and [2009GOR/SHV] were taken with the weight 2 in the averaging procedure. Uncertainties are estimated in this review and taken equal to 1.2 $\log_{10}$ units for the Mg phase and 1.0 $\log_{10}$ units for all other phases. Table 9-43 also lists the values of $\Delta_r G_m^o$ for Reaction (9.54), in which the last column provides the Gibbs energy of formation, $\Delta_f G_m^o$, of these phases. The numerical values of $\Delta_f G_m^o$ depend strongly on the amount of water of hydration, which differs in the various studies. The stoichiometry of the solid phases, given in Table 9-43, corresponds to meta-phases, *i.e.* to phases with the smallest number of hydration water per formula unit. For example, the Mg phase saleeite has the composition $Mg(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr), while meta-saleeite is composition $Mg(UO_2)_2(PO_4)_2 \cdot 8H_2O$(cr), the examples of autunite and meta-autunite were discussed above. The Ba-mineral uranocircite has the composition $Ba(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr), meta-uranocircite I, $Ba(UO_2)_2(PO_4)_2 \cdot 8H_2O$(cr) and meta-uranocircite II, the composition $Ba(UO_2)_2(PO_4)_2 \cdot 6H_2O$(cr). The sources of compositions and water content for alkaline-earth metal uranyl phosphates are mineralogical websites http://www.handbookofmineralogy.org, http://www.mindat.org or other publications, for example [2005LOC/BUR]. The Gibbs energies of formation for other hydrates with a different water content can be estimated by adding the value of $\Delta_f G_m$ of liquid water to the values of $\Delta_f G_m^o$, tabulated for selected phases.

Table 9-43: Selected values of $\log_{10} K_s^o$ for Reaction (9.54) for various $M[(UO_2)(PO_4)] \cdot xH_2O$(cr) at 298.15 K.

| Compound | $\log_{10} K_s^{o(a)}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr) | **– (49.200 ± 1.200)** | **(280.834 ± 6.850)** | **– (6589.413 ± 8.423)** |
| $Ca[(UO_2)(PO_4)]_2 \cdot 6H_2O$(cr) | **– (50.000 ± 1.000)** | **(285.400 ± 5.708)** | **– (6217.131 ± 7.476)** |
| $Sr[(UO_2)(PO_4)]_2 \cdot 6H_2O$(cr) | **– (51.300 ± 1.000)** | **(292.821 ± 5.708)** | **– (6235.609 ± 7.443)** |
| $Ba[(UO_2)(PO_4)] \cdot 6H_2O$(cr) | **– (52.200 ± 1.000)** | **(297.958 ± 5.708)** | **– (6234.538 ± 7.839)** |

(a) Uncertainties are estimated in this review.

*b) $S^\circ_m$ and $\Delta_f H^\circ_m$ of alkaline-earth metal uranyl phosphates*

As in the case of alkali metal uranyl phosphates, the evaluation of thermodynamic properties of alkaline-earth metal uranyl phosphates is based on the entropies of these compounds. Experimentally determined $S^\circ_m$ data, and corresponding results estimated by the Latimer [1951LAT] method, see Appendix D, are given in Table 9-44. For the Mg phase an experimental value is given for the decahydrate $Mg(UO_2)_2(PO_4)_2 \cdot 10H_2O(cr)$ and this was recalculated to correspond to the octahydrate as discussed in Appendix D, assuming the contribution of 44.7 $J \cdot K^{-1} \cdot mol^{-1}$ per water of hydration. Similarly, for the Sr phase the experimental value for octahydrate was recalculated to correspond to that of the hexahydrate.

As seen from data in Table 9-44, the agreement between experimental values and the Latimer estimates is within 40 $J \cdot K^{-1} \cdot mol^{-1}$ (which corresponds to one water of hydration), suggesting errors in the water content of the studied samples and a strong dependence of measured $C^\circ_{p,m}$ and $S^\circ_m$ on the water content. Therefore, these experimental data are judged to be of low reliability. Indeed, numerous reliable calorimetric data for alkaline-earth metal compounds [1981GLU/GUR] show that in the series of isostructural Ca-Sr-Ba compounds the difference in entropy between adjacent alkaline-earth compounds increases by approximately 10-12 $J \cdot K^{-1} \cdot mol^{-1}$. Certainly, experimental data for hexahydrates do not follow this trend, although it can be seen in the Latimer-type estimates. Therefore, this review uses the values estimated with the Latimer method, with uncertainties taken to be ± 20 $J \cdot K^{-1} \cdot mol^{-1}$ for the Sr phase and ± 40 $J \cdot K^{-1} \cdot mol^{-1}$ for all other compounds, see Table 9-44. These data are reported for information only, but might be used for scoping calculations.

Table 9-44: Experimental and estimated values of $C^\circ_{p,m}$ and $S^\circ_m$ for various $M[(UO_2)(PO_4)]_2 \cdot xH_2O(cr)$ at 298.15 K. These data are given for information only.

| Compound | $C^\circ_{p,m}$ /$J \cdot K^{-1} \cdot mol^{-1}$ | $S^\circ_m$, /$J \cdot K^{-1} \cdot mol^{-1}$ | Estim. $S^\circ_m$ [(a)] /$J \cdot K^{-1} \cdot mol^{-1}$ | Reference |
|---|---|---|---|---|
| $Mg[(UO_2)(PO_4)]_2 \cdot 10H_2O(cr)$ | 802.1 | 756 | (794 ± 63) | [2006SUL/CHE] |
| $Mg[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$ | | 667[(b)] | (704 ± 52) | |
| $Ca[(UO_2)(PO_4)]_2 \cdot 6H_2O(cr)$ | 620.2 | 667 | (622 ± 41) | [2006SUL/CHE] |
| $Sr[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$ | 707.8 | 717.4 | (723 ± 52) | [2003SUL/KAR] |
| $Sr[(UO_2)(PO_4)]_2 \cdot 6H_2O(cr)$ | | 628[(b)] | (633 ± 41) | |
| $Ba[(UO_2)(PO_4)]_2 \cdot 6H_2O(cr)$ | 655.3 | 686.4 | (641 ± 41) | [2006SUL/CHE2] |

(a) Estimated by the Latimer [1951LAT] method, see Appendix D.

(b) Recalculated from the experimental value of a higher hydrate assuming the contribution of 44.7 $J \cdot K^{-1} \cdot mol^{-1}$ per water of hydration.

The selected values for $\Delta_f G^\circ_m$ and estimated $S^\circ_m$ allow calculation of the enthalpy of formation, $\Delta_f H^\circ_m$, for alkaline-earth metal uranyl phosphates, see the third column of Table 9-45. These values can be compared with $\Delta_f H^\circ_m$ obtained in calorimetric measurements from [1998KAR/CHE4] for hexahydrates of Ca, Sr, and Ba phases. The

difference of about (13-20) kJ·mol$^{-1}$ is close to the combined uncertainties of the two sets of data.

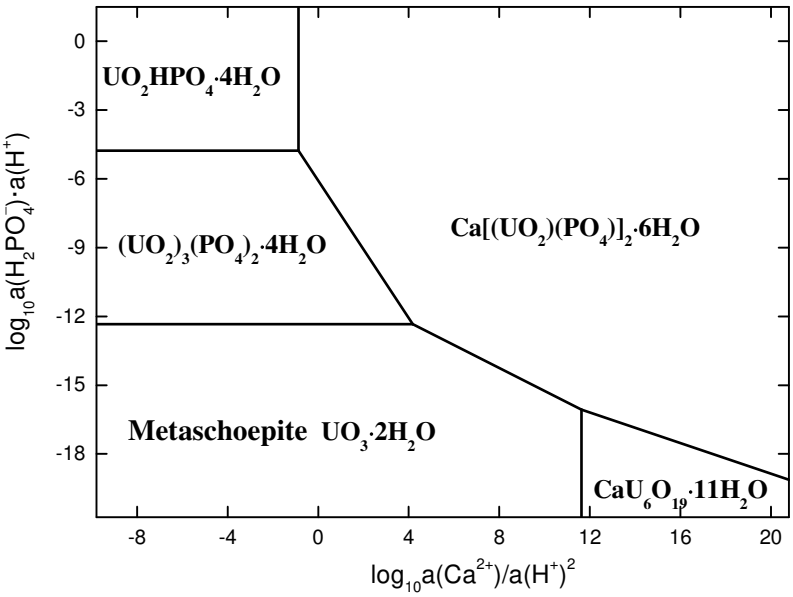
Table 9-45: The entropy and enthalpy of formation at 298.15 K calculated from $\Delta_f G_m^o$ and $S_m^o$ values and the experimentally determined $\Delta_f H_m^o(298.15\ K)$ for various $M[(UO_2)(PO_4)]_2 \cdot xH_2O(cr)$. These data are given for information only.

| Compound | $\Delta_f S_m^o$ [(a)] /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f H_m^o$ [(b)] /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Mg[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$ | – (2608.21 ± 40.0) | – (7367.1 ± 14.6) | | |
| $Ca[(UO_2)(PO_4)]_2 \cdot 6H_2O(cr)$ | – (2232.62 ± 40.0) | – (6882.8 ± 14.1) | – (6863.9 ± 5.0)[(c)] | [1998KAR/CHE4] |
| $Sr[(UO_2)(PO_4)]_2 \cdot 6H_2O(cr)$ | – (2235.73 ± 20.0) | – (6902.2 ± 9.5) | – (6887.8 ± 6.7)[(c)] | [1998KAR/CHE4] |
| $Ba[(UO_2)(PO_4)]_2 \cdot 6H_2O(cr)$ | – (2234.45 ± 40.0) | – (6900.7 ± 14.3) | – (6885.5 ± 6.6)[(c)] | [1998KAR/CHE4] |

(a) Calculated using the estimated with the Latimer method values of $S_m^o$ of uranyl phosphates from Table 9-44 and $S_m^o$ of elements in their standard states from NEA database.
(b) Calculated in this review from values of $\Delta_f S_m^o$ (this Table) and $\Delta_f G_m^o$ (Table 9-43).
(c) Numerical values are recalculated in this review.

This review has only selected the Gibbs energy of formation for alkaline-earth metal uranyl phosphates, see Table 9-43. Values of $S_m^o$ and $\Delta_f H_m^o$ of these compounds are given for information only. Alkaline-earth metal uranyl phosphates is a group of compounds where few accurate studies have been made. Whereas the solubility products of these phases are known with a reasonable accuracy, the situation for calorimetric data is not satisfactory. New measurements of the low-temperature heat capacity of well-characterised samples with carefully controlled water content would be of value. Figure 9-11 below shows the phase relations in the U(VI)-P(V)-Ca-H-O system in aqueous solutions. The diagram is built using the Gibbs energies of solid phases and aqueous ions from the NEA data base or selected in the current review. The location of boundaries, especially for becquerelite, $CaU_6O_{19} \cdot 11H_2O(cr)$, has significant uncertainties (up to 2 $\log_{10}$ units) and new experimental studies would be helpful.

Figure 9-11: Phase relations in the U(VI)-P(V)-Ca-H-O system in aqueous solutions at 298.15 K and 0.1 MPa.




#### 9.6.2.2.6 M[(UO2)(PO4)]2·xH2O(cr), where M = Cu, Zn, Co, Ni

The experimental, mostly solubility data, have been reported for a number of transition metal uranyl phosphates, which all belong to the autunite mineral group. This section presents data only for compounds, for which consistent $\Delta_f G_m^o$ data were reported by at least two research groups. Other similar compounds are considered in Section 9.6.2.2.7.

a) $\Delta_f G_m^o$ of some transition metal uranyl phosphates

Values of solubility products, reported in the literature, see Table 9-47 and Appendix A, have been recalculated, when necessary, into $\log_{10} K_s^o$ of Reaction (9.55).

$$M[(UO_2)(PO_4)]_2 \cdot xH_2O(cr) \rightleftharpoons 2UO_2^{2+} + M^{2+} + 2PO_4^{3-} + xH_2O(l) \quad (9.55)$$

Table 9-46: Values of $\log_{10} K_s^o$ for Reaction (9.55) for various $M[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr). The values considered the most reliable in this review are underlined.

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| | | $Cu[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr) | |
| [1968PEK/VES] | $I$ = 0.2 M ($Cu(NO_3)_2$) | $x$ = 9.0. No primary data. Extrapolated to $I$ = 0 in this review | – 55.65 |
| [1981VOC/PIR] | $I$ < 0.09 M | $x$ = 8.0. Extrapolated to $I$ = 0 in this review | – (52.4 ± 1.1) |
| [1985MAG/JES] | 0.0931 M $HClO_4$ | $x$ = 8.96. One data point | – (54.7 ± 1.0) |
| [1985ZHI/POL] | $I$ < 0.1 M (HCl) | $x$ = 7.73. Two data points | – (52.61 ± 0.18) |
| [2010ILT/ZAC] | $I$ < 0.03 M ($HNO_3$ or $H_3PO_4$) | $x$ = 8.0. t = 22ºC. From both under- and oversaturation. | <u>– (52.7 ± 0.3)</u> |
| [2012NIP/CHE] | $I$ < 0.1 M | $x$ = 8.0 | – (48.85 ± 0.40) |
| [2013CRE/SZE] | 1 M ($HNO_3$, or HCl, or $H_2SO_4$) | $x$ = 7.6. From both under- and oversaturation. | <u>– (52.9 ± 0.3)</u> |
| | | $Zn[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr) | |
| [1968PEK/VES] | $I$ = 0.2 M ($Zn(NO_3)_2$) | $x$ = 7.5. No primary data. Extrapolated to $I$ = 0 in this review | – 50.32 |
| [2012NIP/CHE] | $I$ < 0.1 M | $x$ = 12.0 | – (49.28 ± 0.40) |
| | | $Co[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr) | |
| [1968PEK/VES] | $I$ = 0.2 M ($Co(NO_3)_2$) | $x$ = 7.0. No primary data. Extrapolated to $I$ = 0 in this review | – 50.35 |
| [1981VOC/PIR] | $I$ < 0.02 M | $x$ = 7.0. Extrapolated to $I$ = 0 in this review | – (49.36 ± 0.33) |
| [2012NIP/CHE] | $I$ < 0.1 M | $x$ = 12.0 | – (49.08 ± 0.40) |
| | | $Ni[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr) | |
| [1968PEK/VES] | $I$ = 0.2 M ($Ni(NO_3)_2$) | $x$ = 10.0. No primary data. Extrapolated to $I$ = 0 in this review | – 50.41 |
| [1981VOC/PIR] | $I$ < 0.02 M | $x$ = 7.0. Extrapolated to $I$ = 0 in this review | – (48.96 ± 0.25) |
| [1985MAG/JES] | $H_2O$ | $x$ = 9.16. One data point | – (50.9 ± 1.0) |
| [2012NIP/CHE] | $I$ < 0.1 M | $x$ = 12.0 | – (49.34 ± 0.40) |

As in the case of alkaline-earth uranyl phosphate hydrates, we have assumed that the solubility of the various hydrates is similar and that data can be averaged, ignoring the difference in the amount of water of crystallisation. The selected $\log_{10} K_s^o$ values are reported in Table 9-47, they were obtained by averaging the experimental data in Table 9-46. For the Cu phase the selected value of $\log_{10} K_s^o = -(52.8 \pm 0.3)$ is the average of results of [2010ILT/ZAC] and [2013CRE/SZE], which, in the opinion of the current review, stand out in quality. The composition of most solid phases, given in Table 9-48, correspond to octahydrates, however, hydrates, containing between 6 and 12 molecules of water are known for these phases in mineralogical publications (http://www.handbookofmineralogy.org, [2004LOC/BUR2], *etc.*). In order to make a direct comparison between experimental thermodynamic data of these phases, we also included $Zn[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr), $Co[(UO_2)(PO_4)]_2 \cdot 7H_2O$(cr) and $Ni[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr), for which $S_m^o$ and $\Delta_f H_m^o$ are reported in the literature. The last column of Table 9-47 presents values of the Gibbs energy of formation, $\Delta_f G_m^o$, of phases, calculated using the selected $\Delta_r G_m^o$ results for Reaction (9.55) and $\Delta_f G_m^o$ of ions from the NEA database, except for $Co^{2+}$, for which $\Delta_f G_m^o = -(53.64 \pm 0.38)$ kJ·mol$^{-1}$ is taken from the Glushko *et al.*, 1965-1981 handbook, v.6.

Table 9-47: Selected values of $\log_{10} K_s^o$ and Gibbs energies of reaction for Reaction (9.55) for various $M[(UO_2)(PO_4)]\cdot xH_2O(cr)$ at 298.15 K, these values are all new.

| Compound | $\log_{10} K_s^o$ (a) | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Cu[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ | **– (52.800 ± 0.300)** | **(301.383 ± 1.712)** | **– (6089.547 ± 5.254)** |
| $Zn[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$ | **– (49.800 ± 1.000)** | **(284.259 ± 5.708)** | **– (6758.946 ± 7.413)** |
| $Zn[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ | **– (49.800 ± 1.000)** | **(284.259 ± 5.708)** | **– (6284.666 ± 7.409)** |
| $Co[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ | **– (49.600 ± 1.000)** | **(283.118 ± 5.708)** | **– (6189.961 ± 7.415)** |
| $Co[(UO_2)(PO_4)]_2\cdot 7H_2O(cr)$ | **– (49.600 ± 1.000)** | **(283.118 ± 5.708)** | **– (5952.821 ± 7.413)** |
| $Ni[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$ | **– (49.900 ± 1.000)** | **(284.830 ± 5.708)** | **– (6658.087 ± 7.449)** |
| $Ni[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ | **– (49.900 ± 1.000)** | **(284.830 ± 5.708)** | **– (6183.807 ± 7.445)** |

(a) Uncertainties are estimated in this review.

### *b) $S_m^o$ and $\Delta_f H_m^o$ of some transition metal uranyl phosphates*

Experimentally determined $S_m^o$ values are available only for the Cu- and Ni-phases, see Table 9-48. However, due to the lack of data on the exact compositions these results are considered semi-quantitative. The estimated entropy [1951LAT] for $Ni[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$ is in reasonable agreement with the experimental result, while the estimate for $Cu[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ is more than 60 J·K$^{-1}$·mol$^{-1}$ larger than the experimental value. We note that the Latimer method predicts very similar values for Cu, Ni, Zn and Co phases containing the same amounts of water of crystallisation. This review recommends the same value $S_m^o = (686 \pm 30)$ J·K$^{-1}$·mol$^{-1}$, for all octahydrates. This value is based on experimental result for the Ni-phase, recalculated to the octahydrate form as discussed in Appendix D, *i.e.*, assuming the contribution of 44.7 J·K$^{-1}$·mol$^{-1}$ per water of hydration. Correspondingly, the $S_m^o$ value for $Zn[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$ is taken equal to that of $Ni[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$, and the value for $Co[(UO_2)(PO_4)]_2\cdot 7H_2O(cr)$ is obtained by decreasing the value for $Ni[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$ by three times the contribution of water of hydration, see Table 9-48.

Table 9-48: Experimental and estimated values of $C_{p,m}^o$ and $S_m^o$ for various $M[(UO_2)(PO_4)]_2\cdot xH_2O(cr)$ at 298.15 K. These data are given for information only.

| Compound | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | Estim. $S_m^o$ (a) /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Cu[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ | 627.3 | 644.3 | (718 ± 52) | [2002KAR/CHE3] |
| $Zn[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$ | | | (808 ± 63) | |
| $Zn[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ | | | (718 ± 52) | |
| $Co[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ | | | (717 ± 52) | |
| $Co[(UO_2)(PO_4)]_2\cdot 7H_2O(cr)$ | | | (672 ± 46) | |
| $Ni[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$ | 799.9 | 774.9 | (806 ± 63) | [2002KAR/CHE3] |
| $Ni[(UO_2)(PO_4)]_2\cdot 8H_2O(cr)$ | | 686 (b) | (717 ± 52) | |

(a) Estimated by the Latimer [1951LAT] method, see Appendix D.

(b) Recalculated from the experimental value of a higher hydrate assuming the contribution of 44.7 J·K$^{-1}$·mol$^{-1}$ per water of hydration, see text.

The selected $\Delta_f G_m^o$ and the estimated $S_m^o$ results have been used to calculate the enthalpy of formation, $\Delta_f H_m^o$, of transition earth metal uranyl phosphates, see the third column of Table 9-49. These values can be compared with $\Delta_f H_m^o$ reported in the literature. For the Co and Ni phases the agreement is satisfactory, within 7 kJ·mol$^{-1}$, *i.e.* within the combined errors of experimental and calculated values. For the Zn and Cu phases the experimental calorimetric results ([2003KAR/CHE3], [2003CHE/SUL]) are more negative (by 24 and 30 kJ·mol$^{-1}$, respectively), while the result of [2013CRE/SZE] for the Cu phase obtained from the temperature dependence of the solubility, practically coincides with the value of $\Delta_f H_m^o$ for $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr) calculated in this review.

Table 9-49: Entropy and enthalpy of formation at 298.15 K calculated from selected $\Delta_f G_m^o$ and estimated $\Delta_f S_m^o$ and the experimentally determined values of $\Delta_f H_m^o(298.15\ \text{K})$ for various $M[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr). These data are given for information only.

| Compound | $\Delta_f S_m^o$ [(a)] /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f H_m^o$ [(b)] /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr) | – (2618.0 ± 30.0) | – (6870.1 ± 10.4) | – (6900.8 ± 7.4)[(c)] | [2002KAR/CHE3] |
| | | | – (6900.7 ± 7.5)[(c)] | [2003CHE/SUL] |
| | | | – (6869 ± 12)[(c,d)] | [2013CRE/SZE] |
| $Zn[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr) | – (2618.9 ± 30.0) | – (7065.5 ± 11.6) | | |
| $Zn[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr) | – (2996.4 ± 30.0) | – (7652.3 ± 11.6) | – (7674.3 ± 8.0)[(c)] | [2003CHE/SUL] |
| $Co[(UO_2)(PO_4)]_2 \cdot 7H_2O$(cr) | – (2430.1 ± 30.0) | – (6677.4 ± 11.6) | – (6670.8 ± 5.0)[(c)] | [2000KIR/CHE] |
| | | | – (6674.4 ± 7.6)[(c)] | [2003CHE/SUL] |
| $Co[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr) | – (2618.4 ± 30.0) | – (6970.6 ± 11.6) | | |
| $Ni[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr) | – (2623.4 ± 30.0) | – (6966.0 ± 11.6) | | |
| $Ni[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr) | – (3000.9 ± 30.0) | – (7552.8 ± 11.6) | – (7545.7 ± 4.7)[(c)] | [2000KIR/CHE] |
| | | | – (7549.9 ± 7.4)[(c)] | [2002KAR/CHE3] |
| | | | – (7549.6 ± 7.4)[(c)] | [2003CHE/SUL] |

(a) Calculated using the estimated values of $S_m^o$ of uranyl phosphates, see text, and $S_m^o$ of elements in their standard states from NEA database, except for Co(cr), for which $S_m^o$ = (24.81 ± 0.21) J·K$^{-1}$·mol$^{-1}$ is from the Glushko *et al.*, 1965-1981 handbook, v.6.

(b) Calculated in this review from estimated values of $\Delta_f S_m^o$ (this Table) and $\Delta_f G_m^o$ (from Table 9-47).

(c) Numerical values are recalculated in this review.

(d) It was assumed that the reported $\Delta_r H_m^o$ value is valid for the reaction of dissolution of a compound of the idealised composition: $Cu[(UO_2)(PO_4)] \cdot 8H_2O(cr) \rightleftharpoons Cu^{2+} + 2UO_2^{2+} + 2PO_4^{3-} + 8H_2O(l)$

Only values of the Gibbs energy of formation are selected for $M[(UO_2)(PO_4)]_2 \cdot xH_2O$(cr), where M = Cu, Zn, Co and Ni, see Table 9-47.

#### 9.6.2.2.7 Other phosphate minerals and solid compounds

Experimental results, mostly solubility and calorimetric measurements, are available for a few additional uranyl phosphates. Data for these compounds were not selected in this review, because they do not meet the NEA criteria: often too few details of experimental procedures were provided, or the results were obtained from a single study without the

possibility for an independent verification. Still, published results can be used for scoping calculations or for planning additional, more detailed, experimental investigations.

a) Vochten and Pelsmaekers [1983VOC/PEL] studied the solubility of the synthetic mineral sabugalite, $HAl[(UO_2)(PO_4)]_4 \cdot 16H_2O(cr)$. Data are only presented in a plot in the paper, nevertheless, the current review, see Appendix A, evaluated the data to give $\log_{10} {}^{*}K^{o} = -(13.1 \pm 1.2)$ for Reaction (9.56):

$$HAl[(UO_2)(PO_4)]_4 \cdot 16H_2O(cr) + 7H^+ \rightleftharpoons Al^{3+} + 4UO_2^{2+} + 4H_2PO_4^- + 16H_2O(l) \qquad (9.56)$$

b) The solubility of the compound $Pb_2(UO_2)(PO_4)_2 \cdot 0.5H_2O(cr)$ was studied by Vochten *et al.* [1991VOC/HAV2]. This compound is known as the mineral parsonite, although the mineralogical sources usually give its formula as $Pb_2(UO_2)(PO_4)_2 \cdot 2H_2O(cr)$, see for example, http://www.handbookofmineralogy.org/pdfs/parsonsite.pdf. Vochten *et al.* [1991VOC/HAV2] reported equilibrium constants for Reaction (9.57):

$$Pb_2(UO_2)(PO_4)_2 \cdot 0.5H_2O(cr) \rightleftharpoons 2Pb^{2+} + UO_2^{2+} + 2PO_4^{3-} + 0.5H_2O(l) \qquad (9.57)$$

From these values of $\log_{10} K$, the current review (see Appendix A) has evaluated $\log_{10} K_s^o = -(52.2 \pm 0.8)$.

c) In addition to the uranyl phosphates discussed above, Nipruk *et al.* [2012NIP/CHE], also studied the solubility of $Mn[(UO_2)(PO_4)]_2 \cdot 10H_2O(cr)$, $Cd[(UO_2)(PO_4)]_2 \cdot 10H_2O(cr)$ and $Pb[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$, and determined the following values of $\log_{10} K_s^o$, corresponding to Reaction (9.55): $-(50.22 \pm 0.40)$, $-(50.34 \pm 0.30)$ and $-(49.85 \pm 0.50)$, respectively. These values were not selected because they are the only experimental results available for these compounds, but they are included for information and may be used for scoping calculations. The uncertainty was increased by this review to 1.5 $\log_{10}$ units (a conservative estimate, based on agreement of results of this group with data of other researchers, see Table 9-47).

d) There are $\Delta_f H_m^o$ data for several uranyl phosphates (for some of them $S_m^o$ were also experimentally measured), studied by Chernorukov and coworkers ([1996KAR/CHE], [2000KIR/CHE], [2002CHE/KAR], [2002KAR/CHE5], [2003CHE/SUL]). These results, combined in several instances with $S_m^o$, either experimental or estimated using the Latimer method, were employed to calculate the Gibbs energy of formation of related compounds; these data are reported in Appendix A for information only. As a rule, the uncertainties of the experimental $\Delta_f H_m^o$ values are estimated in this review to be $\pm$ 20 kJ·mol$^{-1}$. (It should be noted that the agreement of $\Delta_f H_m^o$ data for the same compounds, reported, for example in [2000KIR/CHE] and [2003CHE/SUL], is much better, within 3-4 kJ·mol$^{-1}$. However, both studies were made in the same laboratory employing identical thermochemical cycles, therefore, this smaller difference may reflect random instrumental errors only, without taking into account possible undetected systematic errors. Our selection of the expected uncertainty (accuracy, rather than precision) is based on variations of $\Delta_f H_m^o$ data in Table 9-49).

## 9.6.3 U(VI) arsenates

### 9.6.3.1 Aqueous U(VI) arsenates

An overview of the complex formation in the U(VI)-$H_3AsO_4$ system with the selection of the equilibrium constants and related thermodynamic data has been reported in Guillaumont *et al.* [2003GUI/FAN]. The following aqueous species have been identified: $UO_2HAsO_4(aq)$, $UO_2H_2AsO_4^+$ and $UO_2(H_2AsO_4)_2(aq)$. It was pointed out that all equilibrium constants agree within the uncertainty with those in the corresponding phosphate systems.

There are no new studies reporting thermodynamic properties of U(VI) arsenate complexes, but their structures have been discussed in [2012GEZ/HEN] on the basis of EXAFS measurements and DFT quantum chemistry calculations. The same research group [2012GEZ/HEN2] discussed experimental methods, mainly based on fluorescence spectroscopy used to study uranyl(VI)-arsenate complex formation. This review retains the selected values in [2003GUI/FAN] and the auxiliary data for the aqueous arsenic species from [1992GRE/FUG].

### 9.6.3.2 Solid uranium arsenate compounds

Available solubility ([2011NIP/CHE] and others) and structure data ([2004LOC/BUR], for example) demonstrate a strong similarity between phosphate and arsenate U(VI) compounds, although uranyl arsenates typically have higher solubility compared to the corresponding phosphate phases.

The auxiliary thermodynamic data for aqueous arsenates selected by Grenthe *et al.* [1992GRE/FUG] for the NEA database were taken from the NBS compilation [1982WAG/EVA]. As was discussed in [1992GRE/FUG], a complete re-analysis of the thermodynamic data for arsenic species is needed due to existing discrepancies in the values of key arsenic species in various compilations. Specifically, they pointed out that the uncertainties per arsenic atom in the formulae could be up to ± 0.6 $J \cdot K^{-1} \cdot mol^{-1}$ in $S_m^o$ values and ± 4 $kJ \cdot mol^{-1}$ in $\Delta_f H_m^o$.

The thermochemistry of uranyl arsenates is based on calorimetric measurements by Chernorukov and coworkers, see [1994KAR/CHE2], [1994KAR/CHE3], [1996KAR/CHE2], [1998KAR/CHE4], [2002CHE/KAR], [2002CHE/SUL], [2002KAR/CHE3], [2002KAR/CHE5], [2003SUL/CHE]. In these studies the authors report the heats of solution of solid phases, including $KH_2AsO_4$(cr), in aqueous mixtures of inorganic acids. Their thermochemical cycles involve the enthalpy of formation of $KH_2AsO_4$(cr), which was not reported in the NBS tables. They accepted the value $\Delta_f H_m^o = -(1183.36 \pm 0.46)$ $kJ \cdot mol^{-1}$ for $KH_2AsO_4$(cr) from the Glushko (1965-1981) handbook. However, this value cannot be directly used in combination with data from the NBS compilation, as the key value for As(V), the enthalpy of formation of $As_2O_5$(cr), in the NBS work ($\Delta_f H_m^o = -924.87$ $kJ \cdot mol^{-1}$) and in the Glushko handbook ($\Delta_f H_m^o = -(926.4 \pm 1.7)$ $kJ \cdot mol^{-1}$) are not identical. This review, therefore decided to proceed as follows: for the reaction $KH_2AsO_4(cr) \rightleftharpoons K^+ + H_2AsO_4^-$ we obtained $\Delta_r H_m^o = (19.6 \pm 1.4)$ $kJ \cdot mol^{-1}$ from the values of $\Delta_f H_m^o$ of the reaction participants tabulated in the Glushko/Medvedev handbooks [1968GLU/MED]-[1982GLU/MED]. This result is in good agreement with $\Delta_r H_m^o = 20.1$ $kJ \cdot mol^{-1}$ from [1944STE] based on unspecified calorimetric measurements (this value is given in the handbook of Bichowsky F.R., Rossini F.D. *Thermochemistry of the chemical substances*, Reinholf Publishing Corp., N.Y., 1936 with a reference to work of Graham in *Ann. Chim. Phys.* (3) 13, 188 (1845)). By combining, $\Delta_r H_m^o = (19.6 \pm 1.4)$ $kJ \cdot mol^{-1}$, with the corresponding data from the NEA database for $K^+$ and $H_2AsO_4^-$, this review obtains for $KH_2AsO_4$(cr) $\Delta_f H_m^o = -(1181.3 \pm 4.2)$ $kJ \cdot mol^{-1}$, which was used for recalculating the calorimetric results reported for uranyl arsenates.

Solubility studies for uranyl arsenates are not as numerous as those for uranyl phosphates. In many cases only a single measurement was used to determine the solubility product for each phase. The solubility of uranyl arsenates have in general been investigated by the same research groups which reported reliable data for uranyl phosphates. In such cases, the results for arsenates have been judged to be reliable.

#### 9.6.3.2.1 U(VI) orthoarsenates

Grenthe *et al.* [1992GRE/FUG] selected data for the anhydrous uranyl arsenate, $(UO_2)_3(AsO_4)_2(cr)$. No other arsenate phases have been considered in the NEA reviews for uranium ([1992GRE/FUG], [2003GUI/FAN]).

Recently, data on solubility and stability of the uranyl orthoarsenate hydrate were reported by Nipruk *et al.* [2011NIP/CHE]. According to them, $(UO_2)_3(AsO_4)_2\cdot 4H_2O(cr)$, the analogue of the corresponding phosphate phase $(UO_2)_3(PO_4)_2\cdot 4H_2O(cr)$, has a very narrow field of existence, between pH 1.8-2.0, in aqueous solution at 25 °C, and transforms at lower pH into $H_3O[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ and at pH > 2 into $(UO_2)_3(AsO_4)_2\cdot 12H_2O(cr)$ (the latter phase, according to mineralogical websites http://www.mindat.org/min-4013.html and http://www.handbookofmineralogy.org/pdfs/trogerite.pdf, is recognised as the mineral trögerite). This system is not sufficiently well studied, and it is not clear if the tetrahydrate is a stable phase, or if its formation is kinetically driven. In any case, the solubility products of both phases must be practically identical. The solubility product of $(UO_2)_3(AsO_4)_2\cdot 12H_2O(cr)$ according to the reaction:

$$(UO_2)_3(AsO_4)_2\cdot 12H_2O(cr) \rightleftharpoons 3UO_2^{2+} + 2AsO_4^{3-} + 12H_2O(l) \qquad (9.58)$$

was determined by Nipruk *et al.* [2011NIP/CHE] from solubility data at pH 2.28-6.20 (seven points), *i.e.,* in the stability field of the compound: $\log_{10}K_s^o((UO_2)_3(AsO_4)_2\cdot 12H_2O, cr) = -(45.33 \pm 0.32)$. This study also reported the solubility product of the uranyl phosphate tetrahydrate ($\log_{10}K_s^o((UO_2)_3(PO_4)_2\cdot 4H_2O, cr) = -(50.39 \pm 0.47)$) in reasonable agreement with the value selected in this review ($\log_{10}K_s^o((UO_2)_3(PO_4)_2\cdot 4H_2O, cr) = -(49.35 \pm 0.36)$), therefore, the $\log_{10}K_s^o$ for the arsenate phase was also accepted. Thus, this review selected for the Reaction (9.58):

$$\log_{10}K_s^o((UO_2)_3(AsO_4)_2\cdot 12H_2O, cr)) = \mathbf{-(45.330 \pm 1.000)},$$

here the uncertainty is estimated.

Correspondingly, for the Reaction (9.58)

$$\Delta_r G_m^o = \mathbf{(258.744 \pm 5.708)}\ kJ\cdot mol^{-1}$$

and the Gibbs energy of formation of $(UO_2)_3(AsO_4)_2\cdot 12H_2O(cr)$ is:

$$\Delta_f G_m^o = \mathbf{-(7258.797 \pm 11.160)}\ kJ\cdot mol^{-1}.$$

##### 9.6.3.2.1.1 $UO_2HAsO_4\cdot 4H_2O(cr)$

The phase with the composition $UO_2HAsO_4\cdot 4H_2O(cr)$ is called hydrogen uranospinite in the mineralogical literature, and is the As analog of the well-studied chernikovite, $UO_2HPO_4\cdot 4H_2O(cr)$, which was discussed in Section 9.6.2.2.3.

Values of the solubility product of $UO_2HAsO_4 \cdot 4H_2O(cr)$ according to the reaction

$$UO_2HAsO_4 \cdot 4H_2O(cr) \rightleftharpoons UO_2^{2+} + H^+ + AsO_4^{3-} + 4H_2O(l) \qquad (9.59)$$

were reported in three studies, see Table 9-50, and found to be in good agreement. The underlined values are considered more reliable by this review (note that both of these research groups provided reliable data for the corresponding uranyl phosphate).

Table 9-50: Values of $\log_{10} K_s^o$ for the Reaction (9.59). The values considered more reliable are underlined.

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| [1956CHU/SHA] | $I < 0.01$ M | Extrapolated to $I = 0$ in this review | – (22.3 ± 0.6) |
| [1987ZHI/POL] | $I < 0.01$ M | Two data points, averaged in this review | <u>– (22.8 ± 0.2)</u> |
| [2006CHE/SUL] | $I < 0.1$ M ($HClO_4$) | | <u>– (23.1 ± 0.4)</u> |

This review has selected $\log_{10} K_s^o$ = **– (23.000 ± 0.300)** for the Reaction (9.59).

The corresponding Gibbs energy of reaction and formation are:

$$\Delta_r G_m^o = (\mathbf{131.284 \pm 1.713})\ kJ \cdot mol^{-1}$$

$$\Delta_f G_m^o = \mathbf{-\ (2680.755 \pm 4.698)}\ kJ \cdot mol^{-1}.$$

Low-temperature heat capacity measurements of $UO_2HAsO_4 \cdot 4H_2O(cr)$ by Karyakin *et al.* [2000KAR/CHE] led to the values of the heat capacity and the entropy of this phase at 298.15 K (the uncertainty is estimated in this review by taking into account the lack of data on the exact stoichiometry of the studied sample and the fact that data between 0-80 K were extrapolated):

$$C_{p,m}^o = (326 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1},$$

$$S_m^o = (349 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}.$$

Using the entropies of elements in their standard states from [2003GUI/FAN], this review calculates $\Delta_f S_m^o = -\ (1350.12 \pm 10.02)\ J \cdot K^{-1} \cdot mol^{-1}$, and combining this value with $\Delta_f G_m^o$ obtains:

$$\Delta_f H_m^o = -\ (3083.293 \pm 5.567)\ kJ \cdot mol^{-1}.$$

$\Delta_f H_m^o$ is in good agreement with the value of $-\ (3086 \pm 7)\ kJ \cdot mol^{-1}$ obtained in [1994KAR/CHE], however, as discussed in Appendix A, the reported value requires a number of corrections, and the agreement is most likely fortuitous.

Thus, the current review selects the following thermodynamic values of $UO_2HAsO_4 \cdot 4H_2O(cr)$ :

$$\Delta_f G^o_m = \mathbf{-\ (2680.755 \pm 4.698)}\ \text{kJ}\cdot\text{mol}^{-1};$$

$$\Delta_f H^o_m = \mathbf{-\ (3083.293 \pm 5.567)}\ \text{kJ}\cdot\text{mol}^{-1};$$

$$S^o_m = \mathbf{(349.000 \pm 10.000)}\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1};$$

$$C^o_{p,m} = \mathbf{(326.000 \pm 10.000)}\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

#### 9.6.3.2.1.2 M[$(UO_2)(AsO_4)$]$\cdot x H_2O$(cr), where M=Li, Na, K, Rb, Cs, $NH_4$

*a) $\Delta_f G^o_m$ of alkali metal uranyl arsenates*

Solubility products of these compounds according to Reaction (9.60):

$$M[(UO_2)(AsO_4)]\cdot x H_2O(cr) \rightleftharpoons UO_2^{2+} + M^+ + AsO_4^{3-} + x H_2O(l) \quad (9.60)$$

were reported in two studies, see Table 9-51. The agreement of the reported values is generally satisfactory, and it is worth noting that the data from Chernorukov's group for the corresponding phosphate phases are within 1 $\log_{10}$ unit from the values selected in the present review.

Table 9-51: Values of $\log_{10} K^o_s$ for the Reaction (9.60) for various $M[UO_2AsO_4]\cdot x H_2O$(cr) compounds.

| Reference | Medium | Comments | $\log_{10} K^o_s$ |
|---|---|---|---|
| | | $Li[(UO_2)(AsO_4)]\cdot 4H_2O$(cr) | |
| [1956CHU/SHA] | $I$ < 0.01 M | Extrapolated to $I$ = 0 in this review | – (19.30 ± 0.64) |
| [2006CHE/SUL] | $I$ < 0.1 M $HClO_4$ | | – (21.0 ± 0.2) |
| | | $Na[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | |
| [1956CHU/SHA] | $I$ < 0.01 M | Extrapolated to $I$ = 0 in this review | – (22.28 ± 0.65) |
| [2006CHE/SUL] | $I$ < 0.1 M $HClO_4$ | | – (23.0 ± 0.2) |
| | | $K[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | |
| [1956CHU/SHA] | $I$ < 0.01 M | Extrapolated to $I$ = 0 in this review | – (22.99 ± 0.51) |
| [2006CHE/SUL] | $I$ < 0.1 M $HClO_4$ | | – (23.4 ± 0.2) |
| | | $Rb[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | |
| [2006CHE/SUL] | $I$ < 0.1 M $HClO_4$ | | – (24.6 ± 0.2) |
| | | $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O$(cr) | |
| [2006CHE/SUL] | $I$ < 0.1 M $HClO_4$ | | – (25.2 ± 0.8) |
| | | $NH_4[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | |
| [1956CHU/SHA] | $I$ < 0.01 M | Extrapolated to $I$ = 0 in this review | – (24.22 ± 0.46) |
| [2006CHE/SUL] | $I$ < 0.1 M $HClO_4$ | | – (24.9 ± 0.3) |

Table 9-52 gives the selected $\log_{10} K^o_s$ values, the values of $\Delta_r G^o_m$ for the Reaction (9.60) and the Gibbs energy of formation of alkali metal uranyl arsenates, $\Delta_f G^o_m$. Note that there is a controversy about the stoichiometry of the Cs-phase. Some studies from the Chernorukov laboratory ([1994KAR/CHE2], [2006CHE/SUL]) reported its water content as $3H_2O$ per formula unit, although other studies from the same group ([2000KAR/CHE], [2002ERM], [2003SUL/CHE]) gave its composition as $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O$(cr). A careful structural study of the compounds of the meta-autunite groups, containing monovalent cations [2004LOC/BUR], also reported the

formula of the cesium uranyl arsenate hydrate as $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr)$. The current review has accepted the phase composition with $2.5H_2O$ and based the thermodynamic properties for cesium uranyl arsenate on this, recalculating data where necessary.

Table 9-52: Selected values, all new, of $\log_{10}K_s^o$ for the Reaction (9.60) for various $M[(UO_2)(AsO_4)]\cdot xH_2O(cr)$ compounds at 298.15 K.

| $M[(UO_2)(AsO_4)]\cdot xH_2O(cr)$ | $\log_{10}K_s^o$ (a) | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr)$ | **– (20.400 ± 1.000)** | **(116.443 ± 5.708)** | **– (2958.832 ± 7.193)** |
| $Na[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | **– (22.800 ± 1.000)** | **(130.143 ± 5.708)** | **– (2704.427 ± 7.192)** |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | **– (23.300 ± 1.000)** | **(132.997 ± 5.708)** | **– (2727.838 ± 7.192)** |
| $Rb[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | **– (24.600 ± 1.000)** | **(140.417 ± 5.708)** | **– (2736.757 ± 7.193)** |
| $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr)$ | **– (25.200 ± 1.000)** | **(143.842 ± 5.708)** | **– (2629.059 ± 7.211)** |
| $NH_4[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | **– (24.700 ± 1.000)** | **(140.988 ± 5.708)** | **– (2532.717 ± 7.197)** |

(a) Uncertainties are estimated in this review.

*b) $S_m^o$ and $\Delta_f H_m^o$ of hydrated alkali metal uranyl arsenates*

Table 9-53 presents the experimentally determined values of the entropy, $S_m^o$, and the heat capacity, $C_{p,m}^o$, of alkali metal uranyl arsenates, together with $S_m^o$ estimated by the Latimer method. Except for the Li-phase, the agreement is poor and the differences range between 25 and 63 J·K$^{-1}$·mol$^{-1}$. This is notably worse than for alkali uranyl phosphate hydrates. The regular pattern of changes from the Li- to the Cs-phases, expected for isostructural compounds, is not observed. The reason could be variable hydration states of the uranyl arsenates. In this situation this review prefers the $S_m^o$ values estimated using the Latimer (1951) method, see the Appendix D, but the resulting values of $S_m^o$ and $\Delta_f H_m^o$ are not selected and reported for information only.

Table 9-53: Experimental [2000KAR/CHE] and estimated values of $S_m^o$ for various $M[(UO_2)(AsO_4)]\cdot xH_2O(cr)$ at 298.15 K. The values are reported for information only.

| Compound | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | Estim. $S_m^o$ (a) /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr)$ | 354.0 | 364.8 | (367 ± 25) |
| $Na[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | 376.5 | 402.7 | (339 ± 19) |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | 323.4 | 371.9 | (346 ± 19) |
| $Rb[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | 338.4 | 383.5 | (358 ± 19) |
| $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr)$ | 306.2 | 372.7 | (342 ± 17) |
| $NH_4[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | | | (366 ± 19) |

(a) Estimated by the Latimer [1951LAT] method, see Appendix D.

The selection of $\Delta_f G_m^o$ and the choice of $S_m^o$ values allows calculation of the enthalpy of formation $\Delta_f H_m^o$ of alkali metal uranyl arsenates, see the third column of Table 9-54. These values can be compared with $\Delta_f H_m^o$ obtained from calorimetric measurements in the fourth column of Table 9-54. It is, however, worth noting that the results from [1994KAR/CHE2] and [2003SUL/CHE], both from the same laboratory, differ by up to 36 kJ·mol$^{-1}$, where the latter set of results is in a better agreement with

values calculated from $\Delta_f G_m^o$ and $S_m^o$. However, taking into account the questionable accuracy of the experimental $S_m^o$ values and the large scatter of the $\Delta_f H_m^o$ data, this review did not select any of the calorimetric properties of the alkali metal uranyl arsenates. The values of $S_m^o$ from the last column of Table 9-53 and the $\Delta_f H_m^o$ values from the third column of Table 9-54 are given for information only, but might be used for scoping calculations.

Table 9-54: Calculated and experimentally determined values (at 298.15 K) of $\Delta_f H_m^o$ for various $M[(UO_2)(AsO_4)]\cdot xH_2O(cr)$; these data are given for information only.

| Compound | $\Delta_f S_m^o$ (a) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f H_m^o$ (b) /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr)$ | – (1298.1 ± 25) | – (3345.2 ± 10.4) | – (3328.1 ± 5.2)(c) | [1994KAR/CHE2], |
| | | | – (3348.0 ± 5.0)(c) | [2003SUL/CHE] |
| $Na[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | – (1049.1 ± 19) | – (3036.2 ± 9.2) | – (2991.5 ± 5.1)(c) | [1994KAR/CHE2], |
| | | | – (3021.6 ± 4.9)(c) | [2003SUL/CHE] |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | – (1093.3 ± 19) | – (3061.5 ± 9.2) | – (3015.0 ± 5.3)(c) | [1994KAR/CHE2], |
| | | | – (3045.9 ± 5.2)(c) | [2003SUL/CHE] |
| $Rb[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | – (1093.8 ± 19) | – (3070.5 ± 9.2) | – (3016.5 ± 4.9)(c) | [1994KAR/CHE2], |
| | | | – (3052.2 ± 5.1)(c) | [2003SUL/CHE] |
| $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr)$ | – (996.4 ± 17) | – (2935.3 ± 8.8) | – (2880.0 ± 4.7)(c) | [1994KAR/CHE2], |
| | | | – (2907.2 ± 5.0)(c) | [2003SUL/CHE] |
| $NH_4[(UO_2)(AsO_4)]\cdot 3H_2O(cr)$ | – (1391.7 ± 19) | – (2947.7 ± 9.2) | | |

(a) Calculated using the selected values of $S_m^o$ of uranyl arsenates from Table 9-53 and $S_m^o$ of elements in their standard states from the NEA database.
(b) Calculated in this review from selected values of $\Delta_f S_m^o$ (this Table) and $\Delta_f G_m^o$ (Table 9-52).
(c) Numerical values are recalculated in this review as described in Appendix A.

This review selects only values of $\log_{10} K_s^o$, $\Delta_r G_m^o$ and $\Delta_f G_m^o$ of hydrated alkali metal uranyl arsenates, given in Table 9-52.

The enthalpies of formation of anhydrous uranyl arsenates of alkali metals from heats of solution in concentrated HF have been reported in [1994KAR/CHE3], see App. A. These results have not been selected in the current review.

The figures below show the phase relations in the systems U(VI)-As(V)-Na-$H_2O$ and U(VI)-As(V)-K-$H_2O$ at 298.15 K and 0.1 MPa, calculated using the Gibbs energies of solid phases and aqueous ions from the NEA database, or selected in the current review.

Figure 9-12: Phase relations in the U(VI)-As(V)-Na-H-O system in aqueous solutions at 298.15 K and 0.1 MPa.

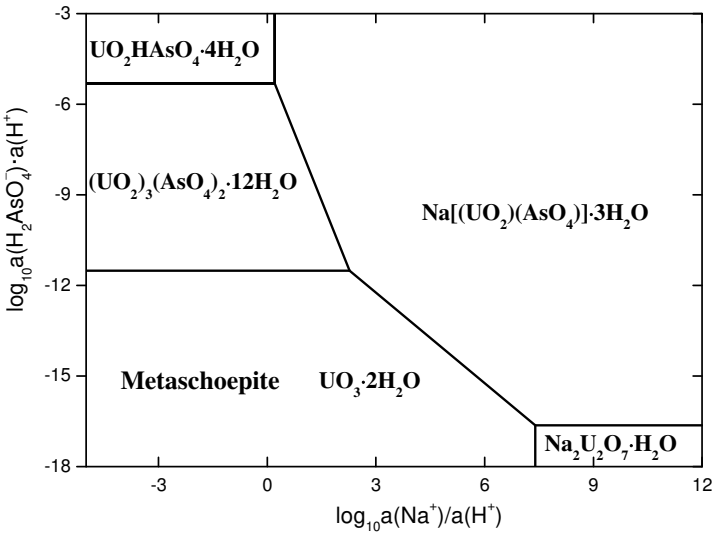
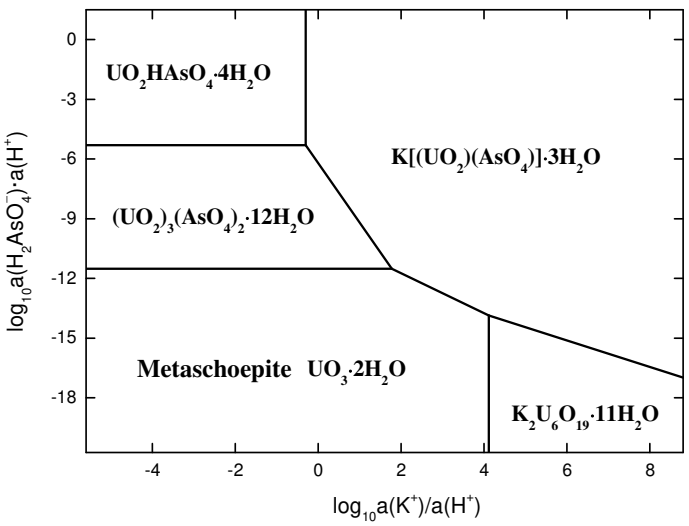



Figure 9-13: Phase relations in the U(VI)-As(V)-K-H-O system in aqueous solutions at 298.15 K and 0.1 MPa.



#### 9.6.3.2.1.3 M[(UO₂)(AsO₄)]₂·*x*H₂O(cr), where M=Mg, Ca, Sr, Ba

*a)* $\Delta_f G_m^o$ *of alkaline-earth metal uranyl arsenate hydrates*

The solubility products reported in the literature for these compounds have been recalculated when necessary into $\log_{10} K_s^o$ of Reaction (9.61):

$$M[(UO_2)(AsO_4)]_2 \cdot xH_2O(cr) \rightleftharpoons 2UO_2^{2+} + M^{2+} + 2AsO_4^{3-} + xH_2O(l) \quad (9.61)$$

(see Table 9-55). As was the case for the corresponding phosphate analogues, we assume that phases differing in the amount of water of hydration have practically identical solubility products. Data are provided by two research groups, and their agreement is satisfactory. Note that neither study provided analytical data on the composition of studied phases and one cannot exclude phase impurities and small amounts of phases with different water content.

Table 9-55: Values of $\log_{10} K_s^o$ for Reaction (9.61) for various $M[(UO_2)(AsO_4)]_2 \cdot xH_2O(cr)$ phases. The selected values are shown in Table 9-56.

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| | | $Mg[(UO_2)(AsO_4)]_2 \cdot xH_2O(cr)$ | |
| [1987ZHI/POL] | $I$ < 0.01 M | $x$ = 8.0. Recalculated in this review | – (44.44 ± 0.29) |
| [2009CHE/NIP] | $I$ < 0.01 M | $x$ = 10.0. From both over- and undersaturation | – (44.7 ± 0.3) |
| | | $Ca[(UO_2)(AsO_4)]_2 \cdot xH_2O(cr)$ | |
| [1987ZHI/POL] | $I$ < 0.01 M | $x$ = 8.0. Recalculated in this review | – (45.76 ± 0.14) |
| [2009CHE/NIP] | $I$ < 0.01 M | $x$ = 10.0. From both over- and undersaturation | – (44.4 ± 0.3) |
| | | $Sr[(UO_2)(AsO_4)]_2 \cdot xH_2O(cr)$ | |
| [2009CHE/NIP] | $I$ < 0.01 M | $x$ = 8.0. From both over- and undersaturation | – (45.1 ± 0.3) |
| | | $Ba[(UO_2)(AsO_4)]_2 \cdot xH_2O(cr)$ | |
| [2009CHE/NIP] | $I$ < 0.01 M | $x$ = 7.0. From both over- and undersaturation | – (44.7 ± 0.3) |

The data in Table 9-55 have been used to select $\log_{10} K^o$ for the Reaction (9.61) for the different alkaline-earth metal uranyl arsenates, see Table 9-56, together with the values of $\Delta_r G_m^o$ for the Reaction (9.61) and the Gibbs energy of formation of these compounds. Note that, as was the case for the corresponding phosphates, alkaline-earth metal uranyl arsenates crystallise with variable content of water. This review has chosen the stoichiometry of phases shown in Table 9-55, but it had been desirable to have analytical data of the phase composition, in addition to the X-ray powder data. Again, as was the case for corresponding phosphates, we assume that the solubility products are about the same for the different hydrates, and that the Gibbs energies of formation for other hydrates with a different composition than the ones in Table 9-56 can be estimated by adding the value of $\Delta_f G_m^o$ of liquid water to the values of $\Delta_f G_m^o$, tabulated for selected phases.

Table 9-56: Selected values, all new, of $\log_{10} K_s^o$ for the Reaction (9.61) for various $M[(UO_2)(AsO_4)]\cdot xH_2O(cr)$ compounds.

| Compound | $\log_{10} K_s^{o\ (a)}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$ | **– (44.600 ± 0.500)** | **(254.577 ± 2.855)** | **– (6283.174 ± 9.304)** |
| $Ca[(UO_2)(AsO_4)]_2\cdot 6H_2O(cr)$ | **– (45.100 ± 1.000)** | **(257.431 ± 5.708)** | **– (5434.899 ± 10.498)** |
| $Ca[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$ | **– (45.100 ± 1.000)** | **(257.431 ± 5.708)** | **– (6383.459 ± 10.503)** |
| $Sr[(UO_2)(AsO_4)]_2\cdot 8H_2O(cr)$ | **– (45.100 ± 1.000)** | **(257.431 ± 5.708)** | **– (5920.237 ± 10.477)** |
| $Ba[(UO_2)(AsO_4)]\cdot 7H_2O(cr)$ | **– (44.700 ± 1.000)** | **(255.148 ± 5.708)** | **– (5674.606 ± 10.761)** |

(a) Uncertainties are estimated in this review.

*b) $S_m^o$ and $\Delta_f H_m^o$ of alkaline-earth metal uranyl arsenates*

Experimentally determined $S_m^o$ data, as well as corresponding values estimated by the Latimer [1951LAT] method, see Appendix D, are given in Table 9-57. For all compounds, except $Mg[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$, the agreement between experimental and estimated $S_m^o$ is satisfactory. This review notes that the difference in entropy between $Mg[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$ and $Ca[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$ exceeds 100 J·K$^{-1}$·mol$^{-1}$, which appears unrealistic: according to the Glushko handbook [1982GLU/GUR], the difference is about 15 J·K$^{-1}$·mol$^{-1}$ for most solid compounds of Mg and Ca. This review accepts experimentally determined $S_m^o$ for all phases, except $Mg[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$, for which the value of $S_m^o$ is taken to be 15 J·K$^{-1}$·mol$^{-1}$ smaller than that for calcium decahydrate, *i.e.* equal to 859 J·K$^{-1}$·mol$^{-1}$, which is provided for information only.

Table 9-57: Experimental and estimated values of $C_{p,m}^o$ and $S_m^o$ for various $M[(UO_2)(AsO_4)]_2\cdot xH_2O(cr)$ at 298.15 K.

| Compound | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | Estim. $S_m^{o\ (a)}$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Mg[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$ | 765.4 | 766 | (827 ± 63) | [2006SUL/CHE] |
| $Ca[(UO_2)(AsO_4)]_2\cdot 6H_2O(cr)$ | | (695)[(b)] | (655 ± 41) | |
| $Ca[(UO_2)(AsO_4)]_2\cdot 10H_2O(cr)$ | 939.7 | 874 | (834 ± 63) | [2006SUL/CHE] |
| $Sr[(UO_2)(AsO_4)]_2\cdot 8H_2O(cr)$ | 720.9 | 758.4 | (756 ± 52) | [2003SUL/KAR] |
| $Ba[(UO_2)(AsO_4)]_2\cdot 7H_2O(cr)$ | 700.8 | 738.3 | (718 ± 47) | [2006SUL/CHE2] |

(a) Estimated by the Latimer [1951LAT] method, see Appendix D.

(b) Recalculated from the experimental value of a decahydrate assuming the contribution of 44.7 J·K$^{-1}$·mol$^{-1}$ per water of hydration.

The selected $\Delta_f G_m^o$ and chosen $S_m^o$ values allow calculation of the enthalpy of formation, $\Delta_f H_m^o$, of alkaline-earth metal uranyl arsenates, see the third column of Table 9-58. These values can be compared with $\Delta_f H_m^o$ obtained in calorimetric measurements [1998KAR/CHE4] for hydrates of Ca, Sr, and Ba phases. The differences are about (7-15) kJ·mol$^{-1}$, which is within the combined uncertainties of the two sets of data; for $Ca[(UO_2)(AsO_4)]_2\cdot 6H_2O(cr)$ this difference is larger, 24 kJ·mol$^{-1}$.

Table 9-58: Experimentally determined values of $\Delta_f H_m^o$ (298.15 K) and values calculated from the entropy and Gibbs energy of formation using the Gibbs-Helmholtz relation for various $M[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) at 298.15 K; these data are reported for information only.

| Compound | $\Delta_f S_m^o$ (a) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f H_m^o$ (b) /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Mg[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | – (2907.7 ± 40) | – (7150 ± 15) | | |
| $Ca[(UO_2)(AsO_4)]_2 \cdot 6H_2O$(cr) | – (2147.6 ± 30) | – (6075 ± 14) | – (6052.5 ± 9.0)(c) | [1998KAR/CHE4] |
| $Ca[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | – (2901.7 ± 30) | – (7249 ± 14) | – (7242.9 ± 9.0)(c) | [1998KAR/CHE4] |
| $Sr[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | – (2565.3 ± 20) | – (6685 ± 12) | – (6691.6 ± 9.5)(c) | [1998KAR/CHE4] |
| $Ba[(UO_2)(AsO_4)]_2 \cdot 7H_2O$(cr) | – (2358.7 ± 30) | – (6378 ± 14) | – (6393.5 ± 9.4)(c) | [1998KAR/CHE4] |

(a) Calculated using the chosen values of $S_m^o$ of uranyl arsenates, see text and $S_m^o$ of elements in their standard states from the NEA database;

(b) Calculated in this review using the Gibbs-Helmholtz relation from values of $\Delta_f S_m^o$ (this Table) and $\Delta_f G_m^o$ (Table 9-56);

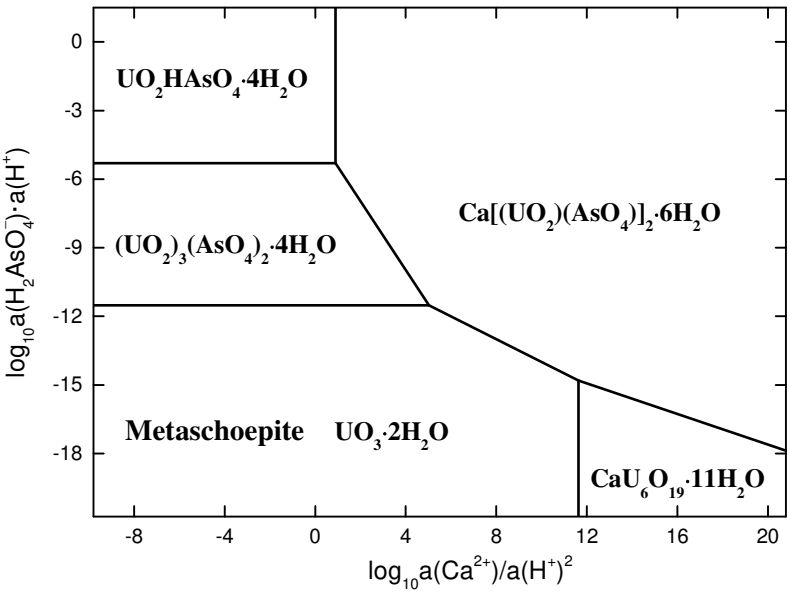
(c) Numerical values are recalculated in this review.

Only $\log_{10} K_s^o$ and Gibbs energies of reaction and formation for alkaline-earth uranyl arsenates are selected in this review, see Table 9-56. The experimental calorimetric data leading to $\Delta_f H_m^o$ and $S_m^o$ are not sufficiently accurate to allow inclusion among the selected thermodynamic data and are reported for information only.

We note that the enthalpies of formation of anhydrous uranyl arsenates of alkaline-earth metals from enthalpy of solution in concentrated HF have been reported in [1996KAR/CHE4], see App. A. These results have not been selected in the current review.

New calorimetric measurements of both the low-temperature heat capacity and enthalpies of solution of well-characterised samples of alkaline-earth metal uranyl arsenates with carefully controlled water content would be useful. Figure 9-14 below shows the phase relations in the U(VI)-As(V)-Ca-H-O system in aqueous solutions. The diagrams are built using the Gibbs energies of solid phases and aqueous ions from the NEA database or selected in the current review.

Figure 9-14: Phase relations in the U(VI)-As(V)-Ca-H-O system in aqueous solutions at 298.15 K and 0.1 MPa.




#### 9.6.3.2.1.4 M[(UO₂)(AsO₄)]₂·*x*H₂O(cr), where M=Cu, Co, Ni, Fe, Mn, Zn, Cd, Pb

*a)* $\Delta_f G_m^o$ *of some transition metal uranyl arsenates*

Solubility data are obtained for some transition metal uranyl arsenates. Values of solubility products reported in the literature (see Appendix A) have been recalculated when necessary into $\log_{10} K_s^o$ for Reaction (9.62).

$$M[(UO_2)(AsO_4)]_2 \cdot xH_2O(cr) \rightleftharpoons 2UO_2^{2+} + M^{2+} + 2AsO_4^{3-} + xH_2O(l) \quad (9.62)$$

(see Table 9-59).

Table 9-59: Values of $\log_{10} K_s^o$ at 298.15 K for the Reaction (9.62) for various $M[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) compounds.

| Reference | Medium | Comments | $\log_{10} K_s^o$ |
|---|---|---|---|
| | | $Cu[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) | |
| [1984VOC/GOE] | $I < 0.10$ M | $x = 8.0$. Extrapolated to $I = 0$ in this review | – (50.9 ± 1.6) |
| [1987ZHI/POL] | $I < 0.05$ M | $x = 10.0$. Recalculated in this review | – (46.33 ± 0.37) |
| [2012CHE/NIP] | $I < 0.10$ M | $x = 8.0$ | – (44.97 ± 0.40) |
| | | $Co[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) | |
| [1984VOC/GOE] | $I < 0.10$ M | $x = 7.0$. Extrapolated to $I = 0$ in this review | – (47.5 ± 1.8) |
| [2012CHE/NIP] | $I < 0.10$ M | $x = 12.0$ | – (45.52 ± 0.40) |
| | | $Ni[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) | |
| [1984VOC/GOE] | $I < 0.06$ M | $x = 7.0$. Extrapolated to $I = 0$ in this review | – (46.3 ± 0.8) |
| [2012CHE/NIP] | $I < 0.10$ M | $x = 12.0$ | – (45.56 ± 0.40) |
| | | $Fe[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) | |
| [1986VOC/GRA] | $I < 0.10$ M | $x = 8.0$. Extrapolated to $I = 0$ in this review | – (46.1 ± 2.2) |
| | | $Mn[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) | |
| [1986VOC/GRA] | $I < 0.10$ M | $x = 8.0$. Extrapolated to $I = 0$ in this review | – (43.6 ± 2.2) |
| [2012CHE/NIP] | $I < 0.10$ M | $x = 12.0$ | – (45.14 ± 0.40) |
| | | $Zn[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) | |
| [2012CHE/NIP] | $I < 0.10$ M | $x = 12.0$ | – (45.05 ± 0.40) |
| | | $Cd[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) | |
| [2012CHE/NIP] | $I < 0.10$ M | $x = 10.0$ | – (45.42 ± 0.40) |
| | | $Pb[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) | |
| [2012CHE/NIP] | $I < 0.10$ M | $x = 8.0$ | – (46.25 ± 0.40) |

As in the case of the alkaline-earth uranyl phosphate hydrates, we have assumed that the solubility of various hydrates is similar and that data for phases with different water of crystallisation can be averaged, see Table 9-60 in the selection of $\log_{10} K_s^o$. This review has in general used the stoichiometry corresponding to less hydrated meta-phases, known as the minerals metazeunerite, $Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$(cr), metakirchheimerite, $Co(UO_2)_2(AsO_4)_2 \cdot 8H_2O$(cr), metakahlerite, $Fe(UO_2)_2(AsO_4)_2 \cdot 8H_2O$(cr), *etc.* [1984VOC/GOE]. The Ni phase, $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr), is known as the mineral rauchite. When selecting $\log_{10} K_s^o$ values for the Cu phase, the result reported in [1984VOC/GOE] was not accepted, as it is more than 3 $\log_{10}$ units lower than all other data for transition metal uranyl arsenates; the selected values for the other phases were calculated as the unweighted average of the published data. The last column of Table 9-60 reports the Gibbs energy of formation, $\Delta_f G_m^o$, of the phases, calculated using the selected $\Delta_r G_m^o$ results for the Reaction (9.62) and $\Delta_f G_m^o$ of ions from the NEA database, except for $Co^{2+}$ and $Mn^{2+}$ for which $\Delta_f G_m^o = -(53.64 \pm 0.38)$ and $-(230.96 \pm 1.26)$ kJ·mol$^{-1}$, respectively, were taken from Glushko *et al.*, the 1965-1981 handbook, v.6 and v.7, respectively.

Table 9-60: Selected values, all new, of $\log_{10} K_s^o$ for the Reaction (9.62) for various $M[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) compounds at 298.15 K.

| Compound | $\log_{10} K_s^o$ (a) | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | **– (45.700 ± 1.000)** | **(260.856 ± 5.708)** | **– (5294.758 ± 10.563)** |
| $Co[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | **– (46.500 ± 1.000)** | **(265.422 ± 5.708)** | **– (5418.004 ± 10.455)** |
| $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | **– (45.900 ± 1.000)** | **(261.998 ± 5.708)** | **– (5880.993 ± 10.479)** |
| $Fe[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | **– (46.100 ± 2.200)** | **(263.139 ± 12.558)** | **– (5452.800 ± 15.319)** |
| $Mn[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | **– (44.400 ± 1.000)** | **(253.436 ± 5.708)** | **– (5583.338 ± 10.523)** |
| $Zn[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | **– (45.100 ± 1.000)** | **(257.431 ± 5.708)** | **– (5503.576 ± 10.451)** |
| $Cd[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | **– (45.400 ± 1.000)** | **(259.144 ± 5.708)** | **– (5435.819 ± 10.475)** |
| $Pb[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | **– (46.300 ± 1.000)** | **(264.281 ± 5.708)** | **– (5861.741 ± 10.458)** |

(a) Uncertainties are estimated in this review

*b) $S_m^o$ and $\Delta_f H_m^o$ of some transition metal uranyl arsenates*

Experimentally determined $S_m^o$ values are available only for the Cu- and Ni-phases, see Table 9-61, however, due to lack of data on the exact compositions of the solids, they are considered semi-quantitative. The estimated entropy by the Latimer [1951LAT] method, see Appendix D, for $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr), $S_m^o = (839 \pm 63)$ J·K$^{-1}$·mol$^{-1}$, is not in good agreement with the experimental result, $S_m^o = 782.9$ J·K$^{-1}$·mol$^{-1}$, and the same is true for $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr), where the experimental value $S_m^o = 660.7$ J·K$^{-1}$·mol$^{-1}$ differs even more from the Latimer estimate $S_m^o = (751 \pm 52)$ J·K$^{-1}$·mol$^{-1}$. We note that the Latimer method predicts very similar contributions to the entropies of the solid phases for the transition metals Cu, Ni, Zn, Mn, Fe and Co, whereas the values for the Cd and Pb phases are about ~ 15 and ~ 20 J·K$^{-1}$·mol$^{-1}$ higher. This review has used the experimental value for $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr), $S_m^o = (783 \pm 30)$ J·K$^{-1}$·mol$^{-1}$, as an anchor, and based the estimated $S_m^o$ for other phases on this value, using the Latimer method to evaluate the $S_m^o$ changes between the Ni- and other uranyl arsenate phases. The results are shown in the fourth column of Table 9-61. As discussed in Appendix D, the contribution of $S_m^o$ per water of hydration was taken as 44.7 J·K$^{-1}$·mol$^{-1}$. These estimated values are given for information only.

Table 9-61: Experimental and estimated values of $C_{p,m}^o$ and $S_m^o$ for various $M[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) compounds.

| Compound | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | Estim. $S_m^o$ (a) /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | 629.6 | 660.7 | (695 ± 30) | [2002KAR/CHE3] |
| $Co[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | | | (694 ± 30) | |
| $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | 773.8 | 782.9 | (783 ± 30) | [2002KAR/CHE3] |
| $Fe[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | | | (693 ± 30) | |
| $Mn[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | | | (693 ± 30) | |
| $Zn[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | | | (695 ± 30) | |
| $Cd[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | | | (710 ± 30) | |
| $Pb[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | | | (804 ± 30) | |

(a) Estimated in this review using the value for $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) as an anchor, see text.

The selected $\Delta_f G_m^o$ and the estimated $S_m^o$ values have been used to calculate the enthalpy of formation, $\Delta_f H_m^o$, of transition metal uranyl arsenates, see the third column of Table 9-62. These values can be compared with $\Delta_f H_m^o$ reported in the literature, in the fourth column of Table 9-62.

For all phases, except $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr), the agreement is satisfactory and within the combined errors of experimental and calculated values. For the copper phase the difference is between 38 and 50 kJ·mol$^{-1}$, compared with experimental results in [2002KAR/CHE3] and [2002CHE/SUL], respectively. In order to provide an agreement between both experimental $\Delta_f G_m^o$ and $\Delta_f H_m^o$ for $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr), the "correct" $S_m^o$ value should be at least 127 J·K$^{-1}$·mol$^{-1}$ smaller than the accepted value, which is highly unlikely.

Table 9-62: Experimentally determined values of $\Delta_f H_m^o$ (298.15 K) and values calculated from the entropy and Gibbs energy of formation at 298.15 K using the Gibbs-Helmholtz relation for various $M[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr) compounds.

| Compound | $\Delta_f S_m^o$ [(a)] /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f H_m^o$ [(b)] /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | – (2597.0 ± 30) | – (6069.1 ± 13.8) | – (6120.5 ± 10.5)[(c)] | [2002CHE/SUL] |
| | | | – (6108.1 ± 10.4)[(c)] | [2002KAR/CHE3] |
| $Co[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | – (2598.4 ± 30) | – (6192.7 ± 13.8) | – (6175.8 ± 10.5)[(c)] | [2002CHE/SUL] |
| $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | – (2980.9 ± 30) | – (6769.8 ± 13.8) | – (6757.9 ± 10.5)[(c)] | [2002CHE/SUL] |
| | | | – (6759.2 ± 10.8)[(c)] | [2002KAR/CHE3] |
| $Fe[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | – (2601.7 ± 30) | – (6228.5 ± 17.7) | – (6234.0 ± 10.4)[(c)] | [2002CHE/SUL] |
| $Mn[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | – (2606.6 ± 30) | – (6360.5 ± 13.8) | | |
| $Zn[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | – (2598.0 ± 30) | – (6278.2 ± 13.8) | – (6289.5 ± 10.9)[(c)] | [2002CHE/SUL] |
| $Cd[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | – (2609.4 ± 30) | – (6213.8 ± 13.8) | – (6206.1 ± 10.4)[(c)] | [2002CHE/SUL] |
| $Pb[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | – (2994.9 ± 30) | – (6754.7 ± 13.8) | | |

(a) Calculated using the values of $S_m^o$ of uranyl arsenates from Table 9-61 and $S_m^o$ of elements in their standard states from the NEA database, except for Co(cr) and Mn(cr), for which $S_m^o$ = (24.81 ± 0.21) and (32.01 ± 0.13) J·mol$^{-1}$ K$^{-1}$, respectively, are taken from the Glushko *et al*., 1965-1981 handbook, v.6 and v.7, correspondingly.

(b) Calculated in this review from estimated values of $\Delta_f S_m^o$ (this Table) and selected results for $\Delta_f G_m^o$ (Table 9-60).

(c) Numerical values are recalculated in this review.

Using the values of the Gibbs energy of formation for the auxiliary species, this review has selected the Gibbs energy of formation for $M[(UO_2)(AsO_4)]_2 \cdot xH_2O$(cr), where M = Cu, Ni, Fe, Zn, Cd, and Pb, reported in Table 9-60. As the evaluation of calorimetric properties is based on estimated $S_m^o$ values, the $S_m^o$ and $\Delta_f H_m^o$ of these compounds are not selected, but reported for information only.

New measurements of the low-temperature heat capacity of well-characterised samples with a carefully controlled water content would be helpful to reduce the uncertainties of calorimetric properties of these compounds.

## 9.6.4 Bismuth compounds

### 9.6.4.1 Bismuth uranates

#### 9.6.4.1.1 α-$Bi_2UO_6$

[2015POP/BEN] reported for the first time measurements of the low temperature heat capacity of α-$Bi_2UO_6$ in the temperature range 1.85 to 270 K using hybrid adiabatic relaxation calorimetry, and the enthalpy increments in the temperature range 430.3 to 1088.8 K using drop calorimetry. α-$Bi_2UO_6$ has a monoclinic structure in space group *C2* [1999VAN/THE], [2015POP/BEN]. It undergoes a reversible phase transition to β-$Bi_2UO_6$ (trigonal space group $P\bar{3}$) between 873 and 1073 K [1975KOS/REN], [2016POP/PRI], the α and β structures being closely related.

We agree with the derivation of [2015POP/BEN] for the heat capacity and entropy values at 298.15 K, but the errors have been estimated in this review:

$$C^{\circ}_{p,\mathrm{m}}(\alpha\text{-}Bi_2UO_6, \mathrm{cr}, 298.15\ \mathrm{K}) = \mathbf{(185.100 \pm 5.600)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\alpha\text{-}Bi_2UO_6, \mathrm{cr}, 298.15\ \mathrm{K}) = \mathbf{(238.800 \pm 7.700)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The equation for the enthalpy increment, and thereafter the heat capacity at high temperatures reported in the study of [2015POP/BEN] contains a typographical error. The correct equation for the temperature range 298.15 to 1088.8 K is:

$$C^{\circ}_{p,\mathrm{m}}(\alpha\text{-}Bi_2UO_6, \mathrm{cr}, T) = 230.912 + 1.812\times10^{-2}T - 4.5526\times10^{6}T^{-2}\ \ \mathrm{J\cdot K\cdot mol^{-1}}$$

It should be pointed out that the enthalpy increment data did not show any sign of a transition around 873-1073 K. We conclude that the enthalpy of transition between the two related structures is too small to be detected by drop calorimetry.

# 9.7 Uranium group 14 compounds and complexes

## 9.7.1 The aqueous uranium carbonate system

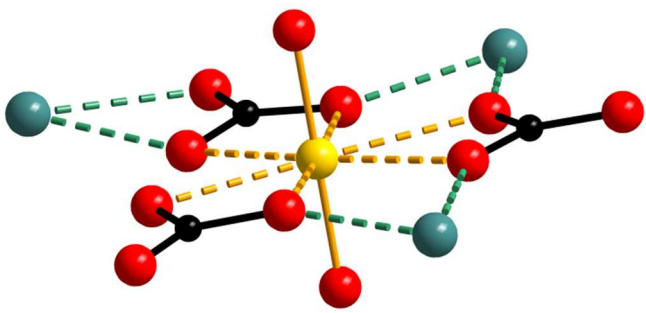
A number of publications dealing with various aspects of the chemistry of the aqueous uranium(VI)-carbonate system have appeared since the [2003GUI/FAN] review. These include quantum chemical studies, [2003MAJ/ROS], [2003VAZ/BO], [2009KUB/HAL], spectrophotometric studies [2008GEI/AMA], [2011GOT/GEI], one EXAFS study, [2010HEN/IKE], and a number of calorimetric studies, [2003DEV/SER], [2004KAR/CHE], [2005KAR/CHE3], [2005KAR/CHE] and [2005KUB/HEL]. The equilibria between M(II) ions and $UO_2(CO_3)_3^{4-}$ have been studied in [2002AMA], [2006DON/BRO], [2008DON/BRO], [2008GEI/AMA], [2009KIM/KIM], [2013LEE/YUN], [2014END/RAO] and [2017LEE/VES]. Additional studies include carbonate exchange kinetics [2005MIZ/GRE], a preparative study [2009CHE/KNY] and studies of complex formation in the ternary U(VI)-carbonate-peroxide system

[2008GOF/BRO], [2009KIM/KIM], [2012ZAN/DIB], [2013WAT/IKE], [2014ZAN/DIB].

#### 9.7.1.1 Binary U(VI) carbonate complexes

Majdumar *et al.* [2003MAJ/ROS] used quantum chemical methods to study the solvation of $UO_2CO_3$ to form $UO_2(CO_3)(OH_2)_n$; $n$ = 1-3, using a continuum model of water. The average binding energy of water is surprisingly constant and equal to – 135, – 119 and – 117 kJ·mol$^{-1}$ for $n$ = 1-3. As these thermodynamic data do not refer to an experimental aqueous system they are not used in the current review. Vázquez *et al.* [2003VAZ/BO] have used quantum chemistry to determine structures and mode of coordination of acetate, carbonate and malonate in the corresponding U(VI) complexes; only the carbonate system is relevant for the present review, we note that the geometry of the tris-carbonato complex, $UO_2(CO_3)_3^{4-}$ is in good agreement with experimental X-ray data. The authors also discuss the mode of coordination of $Ca^{2+}$ in $Ca_2[UO_2(CO_3)_3]$ and identify a geometry with $Ca^{2+}$ in the same plane as the "$U(CO_3)_3$"-unit where it acts as a bridge between two adjacent carbonate ligands; a structure motif that is very similar to the one in the mineral liebigite, $Ca_2[UO_2(CO_3)_3]\cdot 11H_2O$(cr), Figure 9-15. Kubicki *et al.* [2009KUB/HAL] have discussed structures of $UO_2(CO_3)_2(OH_2)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ and $Ca_2[UO_2(CO_3)_3]$ and note a good agreement with EXAFS data; more details are given in Appendix A. The general structure information is of interest for this review, but there are no thermodynamic data.

Figure 9-15: Coordination geometry in the mineral liebigite, $Ca_2[UO_2(CO_3)_3]\cdot 11H_2O$(cr).



##### 9.7.1.1.1 A consistency check of uranyl(VI) carbonate, nitrate and hydroxide data

The study of Devina *et al.* [1983DEV/YEF] was discussed in [1992GRE/FUG], but with no detailed review. This is an important study as detailed in our Appendix A, in which the equilibrium constant for the formation of $UO_2(CO_3)_3^{4-}$ between 25 and 200 °C, was determined. Devina *et al.* also measured the enthalpy of reaction for the reactions:

$$UO_2(NO_3)_2\cdot 6H_2O(cr) + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} + 2NO_3^- + 6H_2O(l) \quad (9.63)$$

$$UO_2(NO_3)_2\cdot 6H_2O(cr) \rightleftharpoons UO_2^{2+} + 2NO_3^- + 6H_2O(l) \quad (9.64)$$

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \quad (9.65)$$

Combination of the enthalpies of reaction for (9.63) and (9.64) allows the determination of the enthalpy of reaction $\Delta_r H_m^o$ (9.65) = – (40.620 ± 0.130) kJ·mol$^{-1}$, which is in good agreement with the value obtained by direct reaction calorimetry, $\Delta_r H_m^o$ (9.65) = – (39.20 ± 4.10) kJ·mol$^{-1}$ selected in [2003GUI/FAN]. The experimental data for Reactions (9.63), (9.64) and (9.65) form a thermodynamic cycle, which requires that $\Delta_r H_m^o(9.63) - \Delta_r H_m^o(9.64) - \Delta_r H_m^o(9.65) \equiv 0$, and from the experimental values we find, – (1.6 ± 4.1) kJ·mol$^{-1}$. This demonstrates the internal consistency between the selected enthalpies of formation for reactants and products.

Based on the entropy change for Reaction (9.65), Devina *et al.* [1983DEV/YEF] also discuss the standard molar entropy of $UO_2(CO_3)_3^{4-}$(aq). Based on the value, $\log_{10}\beta_3 = 21.2$, they report $\Delta_r G_m^o(9.65)$ = – (121.03 ± 0.14) kJ·mol$^{-1}$, which together with $\Delta_r H_m^o(9.65)$ = – (40.62 ± 0.13) kJ·mol$^{-1}$ gives $\Delta_r S_m^o((9.65), 298.15\ K)$ = – (269.70 ± 0.64) J·K$^{-1}$·mol$^{-1}$ as compared to – (286.6 ± 13.8) J·K$^{-1}$·mol$^{-1}$ selected in [2003GUI/FAN]. The molar entropy $S_m^o(UO_2(CO_3)_3^{4-}, aq)$ = (24.5 ± 6.8) J·K$^{-1}$·mol$^{-1}$ was obtained from the data in [1983DEV/YEF] as compared to $S_m^o(UO_2(CO_3)_3^{4-}, aq)$ = (38.4 ± 14.4) J·K$^{-1}$·mol$^{-1}$ in [2003GUI/FAN]. The two sets of data agree within the estimated uncertainties, but the present review prefers to base our selected values on the Gibbs energy of reaction in [2003GUI/FAN] that is based on a larger number of calorimetric studies, see the corresponding discussion in [1992GRE/FUG], and the present review has for this reason retained this, despite its larger estimated uncertainty.

$$\Delta_f G_m^o(UO_2(CO_3)_3^{4-}, aq, 298.15\ K) = \mathbf{-\ (2660.914 \pm 2.116)}\ kJ\cdot mol^{-1};$$

$$\Delta_f H_m^o(UO_2(CO_3)_3^{4-}, aq, 298.15\ K) = \mathbf{-\ (3083.890 \pm 4.430)}\ kJ\cdot mol^{-1};$$

$$S_m^o(UO_2(CO_3)_3^{4-}, aq, 298.15\ K) = \mathbf{(38.446 \pm 14.411)}\ J\cdot K\cdot mol^{-1}.$$

Devina *et al.* [1983DEV/YEF] report $\Delta_r C_{p,m}^o((9.65), 298.15\ K)$ = (380 ± 58) J·K$^{-1}$·mol$^{-1}$, a value that is reported for information only. Using literature data they find the partial molal specific heat capacity $C_{p,m}^o(UO_2(CO_3)_3^{4-}, aq)$ = – (298 ± 77) J·K$^{-1}$·mol$^{-1}$, this value is also reported for information only.

Based on a report by Rafal'skiy (in *Hydrothermal Equilibria and Mineral Formation Processes*, Atomizdat, Moscow, 1973, 273 pages, this report in Russian was not available to the present review), Devina *et al.* discuss the equilibrium constant for Reaction (9.66) at temperatures 100, 120, 140, 170 and 200 °C. The equilibrium constants were extrapolated to zero ionic strength using the Vasil'yev equation, which is similar to the corresponding SIT expression. Combining Reactions (9.65), (9.66) and (9.67) gives Reaction (9.68):

$$0.5Na_2U_2O_7(cr) + 3HCO_3^- \rightleftharpoons UO_2(CO_3)_3^{4-} + Na^+ + 1.5H_2O(l) \quad (9.66)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad (9.67)$$

$$0.5Na_2U_2O_7(cr) + 3H^+ \rightleftharpoons UO_2^{2+} + Na^+ + 1.5H_2O(l) \quad (9.68)$$

The temperature dependence of Reactions (9.65), and (9.66) is known, and from these the temperature dependent equilibrium constant for Reaction (9.68) was calculated.

The temperature dependence of Reactions (9.65), (9.66), and (9.68), from Devina *et al.*, is reported in Table 9-63.

Table 9-63: Temperature dependence of equilibrium constants for Reactions (9.65), (9.66), and (9.68) from [1983DEV/YEF].

| $t$ /°C | $\log_{10}K_s^o$ (9.66) | $\log_{10}\beta_3^o$ (9.65) | $\log_{10}K_s^o$ (9.68) |
|---|---|---|---|
| 100 | – 3.0 | 18.2 | 9.2 |
| 120 | – 3.4 | 18.8 | 8.5 |
| 140 | – 2.9 | 20.1 | 7.9 |
| 170 | – 3.8 | 20.6 | 7.0 |
| 200 | – 4.6 | 21.2 | 6.4 |

The solubility constants for Reaction (9.68) can be used to obtain the solubility constant at 298.15 K, but the long temperature extrapolation means that the constant, $\log_{10}K_s^o$ ((9.68), 298.15 K) = (13 ± 2), is not very accurate. We note however that it is of the same order of magnitude as the more accurate value reported in [2017ALT/YAL].

The most important information from Devina *et al.* is that it provides a check of the consistency of data for the carbonate and nitrate systems, and the solubility constant of $\log_{10}{}^*K_s^o$ for dissolution of $Na_2U_2O_7$(cr), reported in [2017ALT/YAL].

Götz *et al.* ([2008GOT/GEI], [2011GOT/GEI]) have investigated the temperature dependence of the equilibrium constant for the formation of $UO_2(CO_3)_3^{4-}$, Reaction (9.65), in the binary U(VI)-carbonate system. This is based on changes in the absorption spectrum of $[UO_2(CO_3)_3]^{4-}$ in the temperature range 5-70 °C, from which they report an enthalpy of reaction, $\Delta_r H_m^o(9.65) = -(36.25 \pm 4.31)$ kJ·mol$^{-1}$. This is not an independent determination of the enthalpy of reaction, because the authors have used the selected enthalpy of reaction in [1992GRE/FUG], in their analysis of the experimental data, *cf.* Appendix A. The corresponding enthalpy of reaction has not been accepted by this review. In [2011GOT/GEI], Götz *et al.* have extended their spectroscopic investigation of the U(VI)-carbonate system by using time-resolved laser fluorescence spectroscopy. This study provides information on fluorescence life-times, but no new thermodynamic data.

Reaction (9.65) is also discussed in [2003DEV/SER], which reports $\Delta_r H_m^o(298.15\ K) = -(40.6 \pm 0.5)$ kJ·mol$^{-1}$ based on the experimental data in [1983DEV/YEF], but it is not clear why the authors have changed their value.

### 9.7.1.2 Ternary M(II)-U(VI)-carbonate complexes

The complex formation in the Ca(II)-U(VI)-carbonate system was discussed in [2003GUI/FAN], but the reported equilibrium constants were not accepted. Since then new studies have appeared, [2002AMA], [2006DON/BRO], [2008DON/BRO], [2008GOT/GEI], [2013LEE/YUN], [2014END/RAO], and [2017LEE/VES] that report equilibrium constants for the Reaction (9.69). In an additional study Amayari [2002AMA], has investigated how the sorption of U(VI) on silica, phyllite and granite, in carbonate solutions is affected by the presence of $Ca^{2+}$ and $Sr^{2+}$. Nair and Merkel, [2011NAI/MER], have made a similar study using sorption on silica; these two studies provide indirect evidence on the formation of ternary complexes, but no thermodynamic data.

The equilibrium constants reported in the new studies refer to the reactions (9.69)-(9.71).

$$n\mathrm{M}^{2+} + \mathrm{UO}_2^{2+} + 3\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{M}_n[\mathrm{UO}_2(\mathrm{CO}_3)_3]^{2n-4};$$

$$n = 1, 2;\ \mathrm{M} = \mathrm{Mg, Ca, Sr, Ba};\ \log_{10}\beta^{\circ}_{n,1,3} \tag{9.69}$$

$$\mathrm{M}^{2+} + \mathrm{UO}_2(\mathrm{CO}_3)_3^{4-} \rightleftharpoons \mathrm{M}[\mathrm{UO}_2(\mathrm{CO}_3)_3]^{2-};$$

$$\mathrm{M} = \mathrm{Mg, Ca, Sr, Ba};\ \log_{10}K_1^{\circ} \tag{9.70}$$

$$2\mathrm{M}^{2+} + \mathrm{UO}_2(\mathrm{CO}_3)_3^{4-} \rightleftharpoons \mathrm{M}_2[\mathrm{UO}_2(\mathrm{CO}_3)_3](\mathrm{aq});$$

$$\mathrm{M} = \mathrm{Mg, Ca, Sr};\ \log_{10}K_2^{\circ} \tag{9.71}$$

Different experimental methods have been used to determine the equilibrium constants for Reaction (9.69): anion exchange, [2006DON/BRO], [2008DON/BRO], time-resolved laser fluorescence spectroscopy, TRLFS, [2002AMA], [2008GEI/AMA], [2017LEE/VES] and TRLFS in combination with chemical competition using EDTA, [2013LEE/YUN]. In [2014END/RAO] UV/VIS spectrophotometry at different temperatures provides information on the enthalpy of reaction; these studies are discussed in detail in Appendix A. The equilibrium constant for the formation of $Ca_2[UO_2(CO_3)_3](aq)$ by Geipel *et al.* was briefly discussed in [2003GUI/FAN] but no value was selected. The published equilibrium constants are summarised in Table 9-64.

Table 9-64: Equilibrium constants, $\log_{10}\beta^{o}_{1,1,3}$ and $\log_{10}\beta^{o}_{2,1,3}$, for reaction $n\mathrm{M}^{2+} + \mathrm{UO}_2^{2+} + 3\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{M}_n[\mathrm{UO}_2(\mathrm{CO}_3)_3]^{2n-4}$ ; $n$ = 1, 2; M = Mg, Ca, Sr, Ba, at 298.15 K and zero ionic strength. The uncertainty has been estimated by the present review based on the largest value for a given Reaction (9.69)-(9.71). The equilibrium constants accepted by this review are given in bold. The equilibrium constants are based on $\log_{10}K^{o}_{n}$ and the selected value $\log_{10}\beta^{o}_{3} = (21.84 \pm 0.04)$ for reaction $\mathrm{UO}_2^{2+} + 3\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{UO}_2(\mathrm{CO}_3)_3^{4-}$ from [2003GUI/FAN].

| | $Mg^{2+}$ | $Ca^{2+}$ | $Sr^{2+}$ | $Ba^{2+}$ | Reference |
|---|---|---|---|---|---|
| $\log_{10}\beta^{o}_{1,1,3}$ | (26.11 ± 0.04)[(a)] | (27.18 ± 0.06)[(a)] | (26.86 ± 0.04)[(a)] | (26.68 ± 0.04)[(a)] | [2006DON/BRO] |
| | (25.8 ± 0.5)[(a)] | | | | [2008DON/BRO] |
| | (26.24 ± 0.13) | | (26.07 ± 0.13) | (26.16 ± 0.32) | [2008GEI/AMA] |
| | | (27.27 ± 0.14) | | | [2013LEE/YUN] |
| | | 25.4[(c)] | | | [2001BER/GEI] |
| | (23.11 ± 0.07)[(c)] | | (25.52 ± 0.22) | (25.63 ± 0.26) | [2002AMA] |
| | (26.25 ± 0.04) | (27.00 ± 0.04) | | | [2014END/RAO] |
| | (25.8 ± 0.3) | | | | [2017LEE/VES] |
| | **(26.200 ± 0.200)** | **(27.000 ± 0.200)** | **(25.900 ± 0.200)** | **(25.600 ± 0.300)** | Selected value |
| $\log_{10}K^{o}_{1}$ (9.70) | (4.4 ± 0.2) | (5.2 ± 0.2) | (4.1 ± 0.2) | (3.8 ± 0.3) | Selected value |
| | (4.0 ± 0.3) | | | | [2017LEE/VES] |
| $\log_{10}\beta^{o}_{2,1,3}$ | | (30.70 ± 0.05)[(a)] | | (29.75 ± 0.07)[(a)] | [2006DON/BRO] |
| | | | (29.73 ± 0.47) | (29.76 ± 0.75) | [2008GEI/AMA] |
| | | (29.81 ± 0.19) | | | [2013LEE/YUN] |
| | | (30.55 ± 0.25) | | | [2001BER/GEI] |
| | | (26.8 ± 0.9)[(c)] | | | [1996BER/GEI] |
| | | (25.7 ± 0.7)[(c)] | | | [1997BER/GEI] |
| | | (30.84 ± 0.04) | | | [2014END/RAO] |
| | (27.1 ± 0.6) | | | | [2017LEE/VES] |
| | **(27.100 ± 0.600)** | **(30.800 ± 0.400)** | **(29.700 ± 0.500)** | | Selected value |
| $\log_{10}K^{o}_{2}$ (9.71) | (5.3 ± 0.6) | (9.0 ± 0.4)[(b)] | (7.9 ± 0.5)[(b)] | | Selected value |

(a) These values are reported for information only.
(b) The uncertainty is large because only small amounts of the complex is formed.
(c) Values have not been used in the calculation of the average value of the equilibrium constants.

This review notes that there are large differences between the various studies. The one by Endrizzi and Rao [2014END/RAO] is the most satisfactory from the experimental point of view, but uncertainties in Table 9-64 seem unrealistic small according to the present review. This review has not included some of the data from [2001BER/GEI], [2006DON/BRO] and [2008DON/BRO] when selecting the equilibrium constants. We have estimated the uncertainty in the selected constants as the maximum deviation from the average values for reactions in Table 9-64.

The selected thermodynamic data are listed in Table 9-65. This review has not selected an equilibrium constant for formation of $Ba_2[UO_2(CO_3)_3](aq)$, but the value proposed by [2006DON/BRO] is consistent with the ones from Ca and Sr.

The selected enthalpies of reaction, $\Delta_r H_m^o$ ( $Ca[UO_2(CO_3)_3]^{2-}$ , aq, 298.15 K) for the reaction $nM^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons M_n[UO_2(CO_3)_3]^{2n-4}$ are based on the calorimetric study by Endrizzi and Rao, [2014END/RAO], – (47 ± 6) kJ·mol$^{-1}$ and – (47 ± 7) kJ·mol$^{-1}$, respectively.

The selected entropies of reaction are $\Delta_r S_m^o$ ( $Ca[UO_2(CO_3)_3]^{2-}$ , aq, 298.15 K) = (359.272 ± 20.485) J·K$^{-1}$·mol$^{-1}$ and $\Delta_r S_m^o(Ca_2[UO_2(CO_3)_3], aq, 298.15\,K)$ = (432.024 ± 24.695) J·K$^{-1}$·mol$^{-1}$.

Using the selected equilibrium constants and enthalpies of reaction from Endrizzi and Rao, [2014END/RAO], this review selects the thermodynamic data shown in Table 9-65.

### 9.7.1.3 Solid U(VI) carbonate compounds

#### 9.7.1.3.1 Solid $UO_2(CO_3)$(cr)

A number of new experimental studies ([2003DEV/SER], [2005KUB/HEL]) of the thermodynamics of $UO_2CO_3$(cr) have been made using solubility measurements, low-temperature calorimetry and dissolution calorimetry, from which the thermodynamic quantities are reported. These data are important because they provide a consistency check on information obtained by using solubility experiments and calorimetry. The thermodynamic data for $UO_2CO_3$(cr) are used both in the analysis of equilibria in solution and for the analysis of calorimetric determinations of the enthalpies of formation of $Na_4[UO_2(CO_3)_3]$(cr) [2004KAR/CHE], $K_4[UO_2(CO_3)_3]$(cr), [2005KAR/CHE], $NaK_3[UO_2(CO_3)_3]$(cr) [2005KAR/CHE2] and minerals like andersonite, grimselite, liebigite, swartzite, bayelite, voglite and rabbitite.

Devina *et al.* [2003DEV/SER] have determined the enthalpy of formation of rutherfordine, $UO_2CO_3$(cr) using Reactions (9.72)-(9.74), where the enthalpy of reaction, $\Delta_r H_m^o$ (9.72) was determined by calorimetry at different $Na_2CO_3$ concentrations.

$$UO_2CO_3(cr) + 2CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \quad (9.72)$$

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \quad (9.73)$$

$$UO_2CO_3(cr) \rightleftharpoons UO_2^{2+} + CO_3^{2-} \quad (9.74)$$

For Reaction (9.72) this review has selected $\Delta_r H_m^o$ (9.72) = – (39.42 ± 3.0) kJ·mol$^{-1}$, see the review of [2003DEV/SER] in Appendix A. For Reaction (9.73) the current review has retained $\Delta_r H_m^o$ (9.73) = – (39.2 ± 4.1) kJ·mol$^{-1}$, selected in [1992GRE/FUG]. This result is, within the estimated uncertainty, very close to the value reported by Devina *et al.* [1983DEV/YEF], *cf.* Appendix A, $\Delta_r H_m^o$ ((9.73), 298.15 K) = – (40.63 ± 0.13) kJ·mol$^{-1}$. However, the previously selected value is based on a larger number of calorimetric studies, see the corresponding discussion in [1992GRE/FUG], and the present review has for this reason retained this, despite its larger estimated uncertainty.

Table 9-65: Selected thermodynamic data for the $M[UO_2(CO_3)_3]^{2-}$ and $M_2[UO_2(CO_3)_3](aq)$ complexes, M = Mg, Ca, Sr, Ba at 298.15 K.

| Compound | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| $Mg[UO_2(CO_3)_3]^{2-}$ | | | **– (149.551 ± 1.142)** | **– (3141.177 ± 2.740)** | | |
| $Mg_2[UO_2(CO_3)_3](aq)$ | | | **– (154.688 ± 3.425)** | **– (3601.689 ± 4.825)** | | |
| $Ca[UO_2(CO_3)_3]^{2-}$ | **– (47.000 ± 6.000)** | **(359.272 ± 20.485)**[(a)] | **– (154.117 ± 1.142)** | **– (3243.174 ± 2.613)** | **– (3634.690 ± 6.310)** | **(54.872 ± 20.944)**[(a)] |
| $Ca_2[UO_2(CO_3)_3](aq)$ | **– (47.000 ± 7.000)** | **(432.024 ± 24.695)**[(a)] | **– (175.808 ± 2.283)** | **– (3817.671 ± 3.747)** | **– (4177.690 ± 7.471)** | **(71.424 ± 25.136)**[(a)] |
| $Sr[UO_2(CO_3)_3]^{2-}$ | | | **– (147.838 ± 1.142)** | **– (3247.953 ± 2.517)** | | |
| $Sr_2[UO_2(CO_3)_3](aq)$ | | | **– (169.529 ± 2.854)** | **– (3833.508 ± 3.874)** | | |
| $Ba[UO_2(CO_3)_3]^{2-}$ | | | **– (146.126 ± 1.712)** | **– (3240.033 ± 3.744)** | | |

(a) Calculated using Gibbs-Helmholtz equation.

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From the selected values of $\Delta_r H_m^o$ (9.72) and $\Delta_r H_m^o$ (9.73), this review obtains, $\Delta_r H_m^o$ (9.74) = – (0.2 ± 5.1) kJ·mol$^{-1}$ from which we obtain, $\Delta_f H_m^o$ ($UO_2CO_3$, cr, 298.15 K) = – (1694.0 ± 5.3) kJ·mol$^{-1}$, using the selected enthalpies of formation of $UO_2^{2+}$ and $CO_3^{2-}$. This value is consistent with, but less precise than the one in [2003GUI/FAN], $\Delta_f H_m^o$ ($UO_2CO_3$, cr, 298.15 K) = – (1691.302 ± 1.798) kJ·mol$^{-1}$ that was based on the Gibbs energy of formation, $\Delta_f G_m^o$ ($UO_2CO_3$, cr, 298.15 K) = – (1564.701 ± 1.794) kJ·mol$^{-1}$, calculated from solubility data and the entropy, $S_m^o$ ($UO_2CO_3$, cr, 298.15) = (144.20 ± 0.30), from Gurevich *et al.* [1987GUR/SER]. The thermodynamic data selected in [2003GUI/FAN] for $UO_2CO_3$(cr), (Table 9-66), are retained by the present review.

Kubatko *et al.* [2005KUB/HEL] have determined the enthalpy of formation of $UO_2CO_3$(cr), using a different thermodynamic cycle and report $\Delta_f H_m^o$ ($UO_2CO_3$, cr, 298.15 K) = – (1716.4 ± 4.2) kJ·mol$^{-1}$. As discussed in the Appendix A entry, this value is not consistent with available solubility data and has therefore not been accepted by the present review.

Equilibria in the $UO_3$-$CO_2$(g)-$H_2O$(l) system have been investigated by Sergeyeva *et al.* [1972SER/NIK], who studied Reaction (9.75) over the temperature range 298-473 K.

$$UO_2CO_3(cr) + H_2O(l) \rightleftharpoons UO_2(OH)_2(cr, \alpha) + CO_2(g) \qquad (9.75)$$

From the temperature dependence of the equilibrium constant they report, $\Delta_r H_m$ (9.75) = (55.65 ± 7.5) kJ·mol$^{-1}$. Using this value and the selected enthalpies of formation of $UO_2CO_3$(cr), $H_2O$(l) and $CO_2$(g) this review finds, $\Delta_f H_m^o$ ($UO_2(OH)_2$, cr, 298.15 K) = – (1528.0 ± 7.7) kJ·mol$^{-1}$, which is consistent with the enthalpies of formation of the three α, β and γ hydroxide phases, $\Delta_f H_m^o$ ($UO_2(OH)_2$, cr, α, 298.15 K) = – (1536.4 ± 1.9) kJ·mol$^{-1}$, $\Delta_f H_m^o$ ($UO_2(OH)_2$, cr, β, 298.15 K) = – (1533.8 ± 1.3) kJ·mol$^{-1}$ and $\Delta_f H_m^o(UO_2(OH)_2, cr, \gamma, 298.15\ K)$ = – (1531.4 ± 1.3) kJ·mol$^{-1}$, selected in [2003GUI/FAN]. This confirms that the enthalpies of formation of schoepite, $UO_2(OH)_2$(cr), and rutherfordine, $UO_2CO_3$(cr) are consistent.

The solubility product of rutherfordine has been determined by several investigators and are reviewed by Devina *et al.* [2003DEV/SER]; from these data they have selected the solubility product, $\log_{10} K_s^o$ = – (14.37 ± 0.10) for Reaction (9.74) using a different extrapolation method than SIT. This value is in good agreement with the one selected in [1992GRE/FUG], $\log_{10} K_s^o$ = – (14.49 ± 0.04), but not with the value selected in [2003GUI/FAN], $\log_{10} K_s^o$ = – (14.76 ± 0.02). Guillaumont *et al.* argue that the difference might be a result of differences in crystallinity, and the present review accepts this suggestion and retains the selected solubility product, $\log_{10} K_s^o$ = – (14.76 ± 0.02) in [2003GUI/FAN].

Devina *et al.* [2003DEV/SER] note that there is a discrepancy between the enthalpy of formation of $UO_2CO_3$(cr) obtained from solubility data and the entropy $S^o_m$ ($UO_2CO_3$, cr, 298.15 K) selected in [1992GRE/FUG], and the value obtained by calorimetry. They speculate that one reason for the discrepancy might be related to the CODATA value for the enthalpy of formation and entropy for $UO_2^{2+}$. To explore this idea they present a detailed discussion of the thermodynamics of Reaction (9.76) that can be used as a consistency check, because the thermodynamics of the two phases does not depend on the enthalpy of formation and the entropy of $UO_2^{2+}$.

$$UO_2CO_3(\text{cr, rutherfordine}) + H_2O(l) \rightleftharpoons UO_2(OH)_2(\text{cr, } \alpha) + CO_2(g) \quad (9.76)$$

The comparison uses solubility data for the two phases, the enthalpy of formation of $UO_2(OH)_2$(cr, α) and the third law to calculate enthalpy of formation of $UO_2CO_3$(cr, rutherfordine), where the enthalpy of formation of $UO_2(OH)_2$(cr, α) is based on the data from Gurevich *et al.* [1997GUR/SER]. The resulting enthalpy of reaction, $\Delta_f H^o_m$ ($UO_2CO_3$, cr, 298.15 K) = – (1690.8 ± 1.7) kJ·mol$^{-1}$ is marginally different from the one obtained by calorimetry. This review has made the same calculation, but using the selected Gibbs energy of reaction for Reaction (9.76) from [2003GUI/FAN] leading to $\Delta_f H^o_m$ ($UO_2CO_3$, cr, 298.15 K) = – (1693.0 ± 3.2) kJ·mol$^{-1}$. We conclude that there is no compelling evidence for problems with the CODATA values.

In their analysis, Devina *et al.* ([2003DEV/SER]) also report the solubility constant, $\log_{10} {}^*K^o_s$ = (5.9 ± 0.1) for Reaction (9.77), which is based on the data from Sandino and Bruno [1992SAN/BRU].

$$UO_2(OH)_2 \cdot H_2O(\text{cr, schoepite}) + 2H^+ \rightleftharpoons UO_2^{2+} + 3H_2O(l) \quad (9.77)$$

$$UO_2(OH)_2(\text{cr, } \alpha) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O(l) \quad (9.78)$$

Devina *et al.* [2003DEV/SER] used their data to calculate the phase stability at different temperatures. At partial pressures of $CO_2$(g) $\log_{10} P_{CO_2} \geq -1.3$ and temperatures below 333 K rutherfordine is the stable phase and at higher temperature and $\log_{10} P_{CO_2} < -1.3$, the stable phase is $UO_2(OH)_2$(cr, α).

Table 9-66: Overview of Gibbs energies, enthalpies, entropies of formation and molar entropies at 298.15 K for different Uranyl(VI) carbonate phases. More details are given in the following tables for the different compounds. Selected values are marked in bold.

| Species | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f S_m^o$ /J·K$^{-1}$· mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$· mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$· mol$^{-1}$ | Reference |
|---|---|---|---|---|---|---|
| $UO_2CO_3$(cr) | – (1691.302 ± 1.798) | – (1564.701 ± 1.8) | | (144.200 ± 0.300)[(b)] | (120.100 ± 0.100) | [2003GUI/FAN] |
| | – (1694.0 ± 5.3)[(a)] | | | | | [2003DEV/SER] |
| | – (1716.4 ± 4.2) | | | | | [2005KUB/HEL] |
| | **– (1691.302 ± 1.798)[(a)]** | **– (1564.701 ± 1.794)[(b)]** | **– (424.620 ± 0.374)** | **(144.200 ± 0.300)** | **(120.100 ± 0.100)** | This review |
| $Li_4[UO_2(CO_3)_3]\cdot 1.5H_2O$(cr) | – (4558.5 ± 8.5) | | | | | [2003CHE/KNY5] |
| | **– (4550.800 ± 3.300)[(c)]** | | | | | |
| $Na_4[UO_2(CO_3)_3]$(cr) | – (4009.5 ± 8.0 ) | | | | | [2003CHE/KNY5], |
| | | – (3727.0 ± 8.5) | – (949.0 ± 3.0) | (451.3 ± 3.0) | (420.1 ± 2.4) | [2004KAR/CHE] |
| | **– (4003.100 ± 2.400)[(c)]** | **– (3719.960 ± 2.575)[(b)]** | **– (949.656 ± 3.126)** | **(451.300 ± 3.000)** | **(420.100 ± 2.400)** | This review |
| $K_4[UO_2(CO_3)_3]$(cr) | – (4030.0 ± 8.5) | | | | | [2003CHE/KNY5], |
| | | – (3730.0 ± 9.0) | – (1006.1 ± 2.1) | (447.8 ± 3.0) | (362.6 ± 1.8) | [2005KAR/CHE] |
| | **– (4021.100 ± 4.800)[(c)]** | **– (3720.960 ± 4.890)[(b)]** | **– (1006.676 ± 3.126)** | **(447.800 ± 3.000)** | **(362.600 ± 1.800)** | This review |
| $(NH_4)_4[UO_2(CO_3)_3]$(cr) | – (3560.5 ± 8.5) | | | | | [2003CHE/KNY5] |
| | **– (3555.1 ± 4.6)[(c)]** | | | | | |
| $NaK_3[UO_2(CO_3)_3]$(cr) | – (4001.0 ± 8.5) | | | | | [2003CHE/KNY5], |
| | | – (3716.0 ± 9.0 ) | – (955.5 ± 2.1) | (485.0 ± 2.1) | (389.0 ± 2.0) | [2005KAR/CHE2] |
| | **– (3992.800 ± 3.800)[(c)]** | **– (3707.740 ± 3.857)[(b)]** | **– (956.096 ± 2.223)** | **(485.000 ± 2.100)** | **(389.000 ± 2.000)** | This review |

(Continued on next page)



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Table 9-66 (continued)

| Species | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f S_m^o$ /J·K$^{-1}$· mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$· mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$· mol$^{-1}$ | Reference |
|---|---|---|---|---|---|---|
| $NaK_3[UO_2(CO_3)_3]\cdot H_2O$(cr) Grimselite | – (4431.6 ± 15.3) | | | | | [2005KUB/HEL] |
| $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr) | – (9110 ± 9) | | | | | [2009CHE/KNY] |
| | **– (9173.200 ± 4.200)**[c] | | | | | |
| | – (9192 ± 20) | – (7924 ± 8) | | | | [1980ALW/WIL] |
| $Mg_2[UO_2(CO_3)_3]$(cr) | – (5388 ± 10) | | | | | [2009CHE/KNY] |
| | **– (5451.300 ± 5.800)**[c] | | | | | |
| $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) | – (7029 ± 8) | | | | | [2009CHE/KNY] |
| | **– (7044.700 ± 3.700)**[c] | | | | | |
| | – (7037 ± 24) | – (6226 ± 12) | | | | [1980ALW/WIL] |
| $Ca_2[UO_2(CO_3)_3]$(cr) | – (4220 ± 9) | | | | | [2009CHE/KNY] |
| | **– (5017.400 ± 5.500)**[c] | | | | | |
| $MgCa[UO_2(CO_3)_3]\cdot 12H_2O$(cr) | (7535 ± 20) | (6607 ± 8) | | | | [1980ALW/WIL] |
| $CaNa_2[UO_2(CO_3)_3\cdot 5H_2O$(cr) | – (5593.6 ± 9.1) | | | | | [2005KUB/HEL] |
| $Sr_2[UO_2(CO_3)_3]\cdot 8H_2O$(cr) | – (6497 ± 10) | | | | | [2009CHE/KNY] |
| | **– (6508.400 ± 5.500)**[c] | | | | | |
| $Sr_2[UO_2(CO_3)_3]$(cr) | – (4904 ± 11) | | | | | [2009CHE/KNY] |
| | **– (4915.800 ± 6.800)**[c] | | | | | |
| $Ba_2[UO_2(CO_3)_3]\cdot 6H_2O$(cr) | – (5873 ± 10) | | | | | [2009CHE/KNY] |
| | **– (5882.800 ± 5.600)**[c] | | | | | |
| $Ba_2[UO_2(CO_3)_3]$(cr) | – (4636 ± 11) | | | | | [2009CHE/KNY] |
| | **– (4645.800 ± 6.900)**[c] | | | | | |

(a) Calculated internally from reaction data; (b) Calculated internally using the Gibbs-Helmholtz equation; (c) Recalculated by this review.

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#### 9.7.1.3.2 Solid $Li_4[UO_2(CO_3)_3]\cdot 1.5H_2O$(cr), $Na_4[UO_2(CO_3)_3]$(cr), $K_4[UO_2(CO_3)_3]$(cr), $NaK_3[UO_2(CO_3)_3]$(cr), $Na_4[UO_2(CO_3)_3]\cdot H_2O$(cr), $(NH_4)_4[UO_2(CO_3)_3]$(cr) and $Na_2Ca[UO_2(CO_3)_3]\cdot 5H_2O$(cr)

Karyakin *et al.* [2004KAR/CHE], [2005KAR/CHE], [2005KAR/CHE2], have used reaction calorimetry to determine the enthalpy of formation of $Na_4[UO_2(CO_3)_3]$(cr), $K_4[UO_2(CO_3)_3]$(cr) and $NaK_3[UO_2(CO_3)_3]$(cr) based on a thermodynamic cycle that provides the enthalpy of reaction for Reactions (9.79)-(9.81).

$$UO_2CO_3(cr) + 2Na_2CO_3(cr) \rightleftharpoons Na_4[UO_2(CO_3)_3](cr) \quad (9.79)$$

$$UO_2CO_3(cr) + 2K_2CO_3(cr) \rightleftharpoons K_4[UO_2(CO_3)_3](cr) \quad (9.80)$$

$$UO_2CO_3(cr) + 0.5Na_2CO_3(cr) + 1.5K_2CO_3(cr) \rightleftharpoons NaK_3[UO_2(CO_3)_3](cr) \quad (9.81)$$

The experimental data are analysed in Appendix A and the result is given in Table 9-66, in which the recalculated data are based on the selected value of the enthalpy of formation $\Delta_f H_m^o(UO_2CO_3, cr) = -(1691.302 \pm 1.798)$ kJ·mol$^{-1}$, which differs from the value used by Karyakin *et al.* $\Delta_f H_m^o(UO_2CO_3, cr) = -(1698.0 \pm 8.0)$ kJ·mol$^{-1}$. Note that these results are very similar to the ones reported earlier in [2003CHE/KNY5], who in addition reported enthalpy data for $Li_4[UO_2(CO_3)_3]\cdot 1.5H_2O$(cr) and $(NH_4)_4[UO_2(CO_3)_3]$(cr). The values of $\Delta_f H_m^o$ recalculated in this review for these compounds have been selected and are summarized in Table 9-66.

Karyakin *et al.* [2004KAR/CHE] observe two phase transitions: amorphous → crystal I → crystal II at (60.5 ± 0.5) K and (386 ± 5) K, respectively, in $Na_4[UO_2(CO_3)_3]$(s). The corresponding enthalpy and entropy changes at 60.5 K are $\Delta_{tr}H_m$ (60.5 K) = 1.5 kJ·mol$^{-1}$ and $\Delta_{tr}S_m$ (60.5 K) = 24.79 J·K$^{-1}$·mol$^{-1}$, no uncertainty estimates are reported, and at 386 K, $\Delta_{tr}H_m$ (386 K) = (50.2 ± 0.2) kJ·mol$^{-1}$ and $\Delta_{tr}S_m$ (386 K) = (130.0 ± 3.0) J·K$^{-1}$·mol$^{-1}$. Karyakin *et al.* [2004KAR/CHE] report the heat capacity at 298.15 K, $C_{p,m}^o$ ($Na_4[UO_2(CO_3)_3]$, cr) = 420.1 J·K$^{-1}$·mol$^{-1}$ and the entropy, $S_m^o$ ($Na_4[UO_2(CO_3)_3]$, cr) = (451.3 ± 3) J·K$^{-1}$·mol$^{-1}$, which are the values selected by this review.

A phase transition occurs also at (403.5 ± 0.5) K, in $K_4[UO_2(CO_3)_3]$(cr) with $\Delta_{tr}H_m^o$ = (6.9 ± 0.1) kJ·mol$^{-1}$ and $\Delta_{tr}S_m^o$ = 17.1 J·K$^{-1}$·mol$^{-1}$ [2005KAR/CHE].

There is one phase transition at (395 ± 1) K in $NaK_3[UO_2(CO_3)_3]$(cr) with $\Delta_{tr}S_m$ = 2.0 J·K$^{-1}$·mol$^{-1}$ and $\Delta_{tr}H_m$ = (0.8 ± 0.1) kJ·mol$^{-1}$ [2005KAR/CHE2].

Using the previous thermodynamic data we have calculated the enthalpy and Gibbs energy of reaction and the solubility constant for Reaction (9.82):

$$Na_4[UO_2(CO_3)_3](cr) \rightleftharpoons 4Na^+ + UO_2(CO_3)_3^{4-} \quad (9.82)$$

$\Delta_r H_m^o$ (9.82) = – (42.150 ± 5.040) kJ·mol$^{-1}$ and $\Delta_r G_m^o$ (9.82) = (11.234 ± 3.355) kJ·mol$^{-1}$ from which we obtain $\log_{10} K_s^o$ (9.82) = – (1.968 ± 0.588). This value is significantly different from the value obtained by Blake *et al.* [1956BLA/COL], $\log_{10} K_{s3}^o$ = – (5.34 ± 0.16), [1956BLA/COL], reviewed in [1992GRE/FUG], using solubility measurements, but for the reasons discussed in Appendix A, we consider the value from Karyakin *et al.*, recalculated by this review, more accurate and this has therefore been included among the selected values.

This review notes that the change in entropy between the different phases differs from the one generally observed for alkali compounds, which is an increase of about 10 J·K$^{-1}$·mol$^{-1}$, between structurally similar Na, K, Rb, and Cs phases, *cf.* reliable data for entropies of many such compounds in the handbook by Glushko *et al.* [1982GLU/GUR]. This trend is not observed between $Na_4[UO_2(CO_3)_3]$(cr) and $K_4[UO_2(CO_3)_3]$(cr). In addition the entropy of $NaK_3[UO_2(CO_3)_3]$(cr) seems unexpectedly large compared to the values of the end-member phases. Despite this comment, the present review has accepted the thermodynamic data for $Na_4[UO_2(CO_3)_3]$(cr) based on the study by Karyakin *et al.* [2004KAR/CHE].

Based on the previous data, Karyakin *et al.* have calculated the enthalpy and entropy of reaction for formation of $NaK_3[UO_2(CO_3)_3]$(cr) according to Reaction (9.83):

$$1/4Na_4[UO_2(CO_3)_3](cr) + 3/4K_4[UO_2(CO_3)_3](cr) \rightleftharpoons NaK_3[UO_2(CO_3)_3](cr) \qquad (9.83)$$

$\Delta_r H_m^o$ (9.83) = (24.0 ± 5.4) kJ·mol$^{-1}$; $\Delta_r G_m^o$ (9.83) = (13.0 ± 5.4) kJ·mol$^{-1}$; $\Delta_r S_m^o$ (9.83) = (37.0 ± 3.0) J·K$^{-1}$·mol$^{-1}$, which recalculated by this review results in $\Delta_r H_m^o$ (9.83) = (23.8 ± 4.8) kJ·mol$^{-1}$, $\Delta_r G_m^o$ (9.83) = (12.7 ± 4.8) kJ·mol$^{-1}$; $\Delta_r S_m^o$ (9.83) = (37.2 ± 13.1).

Kubatko *et al.* [2005KUB/HEL] have determined the enthalpy of formation of andersonite, $CaNa_2[UO_2(CO_3)_3]\cdot 5H_2O$(cr) and grimselite $NaK_3[UO_2(CO_3)_3]\cdot H_2O$(cr) using high-temperature oxide melt calorimetry and obtain the enthalpies of formation:

$$\Delta_f H_m^o(CaNa_2[UO_2(CO_3)_3]\cdot 5H_2O, \text{cr}, 298.15\ \text{K}) = -(5593.6 \pm 9.1)\ \text{kJ·mol}^{-1}$$

$$\Delta_f H_m^o(NaK_3[UO_2(CO_3)_3]\cdot H_2O, \text{cr}, 298.15\ \text{K}) = -(4431.6 \pm 15.3)\ \text{kJ·mol}^{-1}.$$

These values are based on auxiliary data of which several have not been reviewed by NEA, for this reason the data for andersonite and grimselite are not included among the selected values and they are reported for information only. The solubility product of grimselite has been determined by O´Brien and Williams [1983OBR/WIL] at ionic strengths of 0.428 to 0.439 m and this study was discussed by [2003GUI/FAN] who noted a problem in extrapolation to infinite dilution, in combination with information on the major anions present. They report the following Gibbs energy and enthalpy of formation $\Delta_f G_m^o(NaK_3UO_2(CO_3)_3\cdot H_2O, 298.15\ \text{K})$ = – (4051.3 ± 1.8) kJ·mol$^{-1}$ and $\Delta_f H_m^o(NaK_3UO_2(CO_3)_3\cdot H_2O, 298.15\ \text{K})$ = – (4359.0 ± 1.8) kJ·mol$^{-1}$, the latter determined from the temperature variation of the solubility product. These values differ significantly from the ones selected above and are considered unreliable by the present

review; the enthalpy of formation is also not consistent with the value reported by Kubatko *et al.* [2005KUB/HEL].

#### 9.7.1.3.3 Solid $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr), and $M_2[UO_2(CO_3)_3]$, M = Mg, Ca, Sr, Ba

Chernorukov *et al.* [2009CHE/KNY] have determined the enthalpy of formation of the crystalline phases $M[UO_2(CO_3)_3]\cdot nH_2O$(cr) and $M_2[UO_2(CO_3)_3]$(cr), M = Mg, Ca, Sr, Ba using dissolution calorimetry to obtain the enthalpy of reaction for Reaction (9.84):

$$UO_2CO_3(cr) + 2MCO_3(cr) + nH_2O(l,\ 13.5\ MHNO_3) \rightleftharpoons M_2[UO_2(CO_3)]\cdot nH_2O(cr) \quad (9.84)$$

The reported enthalpies of formation given in Table 9-67 are based on auxiliary data that are listed in Appendix A, all of these have not been reviewed and selected by NEA. It is not clear if Chernorukov *et al.* have corrected the enthalpy of formation of pure water to the value in 13.5 M $HNO_3$, as done in the present review.

Table 9-67: Standard enthalpies of formation, $\Delta_f H^o_m$, for the $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr) $n$ = 18, 10, 8, 6, 0 at 298.15 K as reported in [2009CHE/KNY] or recalculated by this review (see Appendix A).

| Compound | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | Recalculated by this review |
|---|---|---|
| $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr) | – (9110 ± 9) | **– (9173.2 ± 4.2)** |
| $Mg_2[UO_2(CO_3)_3]$(cr) | – (5388 ± 10) | **– (5451.3 ± 5.8)** |
| $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) | – (7029 ± 8) | **– (7044.7 ± 3.7)** |
| $Ca_2[UO_2(CO_3)_3]$(cr) | – (4220 ± 9) | **– (5017.4 ± 5.5)** |
| $Sr_2[UO_2(CO_3)_3]\cdot 8H_2O$(cr) | – (6497 ± 10) | **– (6508.4 ± 5.5)** |
| $Sr_2[UO_2(CO_3)_3]$(cr) | – (4904 ± 11) | **– (4915.8 ± 6.8)** |
| $Ba_2[UO_2(CO_3)_3]\cdot 6H_2O$(cr) | – (5873 ± 10) | **– (5882.8 ± 5.6)** |
| $Ba_2[UO_2(CO_3)_3]$(cr) | – (4636 ± 11) | **– (4645.8 ± 6.9)** |

The correction for the relative partial enthalpy of water is important as it gives the enthalpy of formation of water in 13.5 M $HNO_3$ equal to $\Delta_f H^o = \Delta_f H - n\overline{L_1}$, where $n$ is the number of water and $\overline{L_1}$ = – 1.99 kJ·mol$^{-1}$. Correction for this quantity is made in column 3 of Table 9-67.

Chernorukov *et al.* have used differential thermal analysis to study the decomposition of the $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr) and in this way determined the enthalpy of formation for the anhydrous $M_2[UO_2(CO_3)_3]$(cr) compounds using the enthalpies of dehydration for Reaction (9.85) reported in Table 9-68. The values of $\Delta_f H^o_m$ reported in [2009CHE/KNY] are recalculated in the present review as described in Appendix A. The resulting values are selected in this review and are summarized in Table 9-67.

$$M_2[UO_2(CO_3)_3]\cdot nH_2O(cr) \rightleftharpoons M_2[UO_2(CO_3)_3](cr) + nH_2O(g) \quad (9.85)$$

Table 9-68: Standard enthalpies of dehydration of $M_2[UO_2(CO_3)_3]\cdot nH_2O$ compounds, M = Mg, Ca, Sr, Ba in kJ·mol$^{-1}$.

| Compound | $\Delta_{dehydr}H_m^o$ /kJ·mol$^{-1}$ |
|---|---|
| $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr) | (631 ± 4) |
| $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) | (391 ± 4) |
| $Sr_2[UO_2(CO_3)_3]$ $8H_2O$(cr) | (342 ± 4) |
| $Ba_2[UO_2(CO_3)_3]$ $6H_2O$(cr) | (214 ± 4) |

The enthalpy of formation of $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) has been determined by Alwan and Williams [1980ALW/WIL] from the temperature dependence of the solubility as $\Delta_f H_m^o = -(7037 \pm 24)$ kJ·mol$^{-1}$, which is in good agreement with the calorimetric value. The corresponding value for $\Delta_f H_m^o$ ($Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$, cr) is equal to $-(9192 \pm 20)$ kJ·mol$^{-1}$, with a difference of 20 kJ·mol$^{-1}$ from the calorimetric value. The present review has analysed the solubility data from Alwan and Williams [1980ALW/WIL] in the following section.

#### 9.7.1.3.4 Mineral phases, $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) (liebigite); $MgCa[UO_2(CO_3)_3]\cdot 12H_2O$(cr) (swartzite); $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr) (bayleite) and $CaNa_2[UO_2(CO_3)_3]\cdot 6H_2O$(cr) (andersonite).

Alwan and Williams, [1980ALW/WIL], have reported Gibbs energies and enthalpies of formation for $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr), (liebigite); $MgCa[UO_2(CO_3)_3]\cdot 12H_2O$(cr), (swartzite); $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr), (bayleite) and $CaNa_2[UO_2(CO_3)_3]\cdot 6H_2O$(cr), (andersonite) using solubility measurement over the temperature range 273-298 K in water (no ionic medium). The authors made the corresponding corrections for the speciation in the aqueous phase, but the information is not sufficiently detailed to allow a re-evaluation of the original data. However, this review notes that the formation of ternary complexes $M_n[UO_2(CO_3)_3]^{2n-4}$ was not considered in [1980ALW/WIL] for the interpretation of solubility data. Accordingly, the reported thermodynamic parameters are incorrect and are disregarded by this review.

Mineral phases are characterised by their structure and they have in general a variable composition as exemplified by andersonite and grimselite, where the phases used by Kubatko *et al.* [2005KUB/HEL], discussed in previous section, have the composition $CaNa_2[UO_2(CO_3)_3]\cdot 5H_2O$(cr) and $NaK_3[UO_2(CO_3)_3]$(cr). In previous review [2003GUI/FAN], Guillaumont *et al.* discussed thermodynamic data for two of the carbonate minerals, schröckingerite, $Ca_3Na[UO_2(CO_3)_3]\cdot SO_4\cdot F\cdot 10H_2O$(cr) and grimselite $NaK_3[UO_2(CO_3)_3]\cdot H_2O$(cr), but these were not included among the selected values.

### 9.7.1.4 Uranium(IV) carbonate complexes

Hennig *et al.* [2010HEN/IKE] have studied the structure of the complex $[U(CO_3)_5]^{6-}$ in solution using EXAFS and in the solid state using an X-ray structure determination of

$K_6[U(CO_3)_5]\cdot 12H_2O$(cr); the agreement between bond distances in solution and solid phase is excellent as one often finds when the complex is present as a discrete unit in the solid state. The structure and composition of the complexes $[An(CO_3)_5]^{6-}$ are now well established for the An(IV) actinides. There are no thermodynamic data in this study.

## 9.7.2 Silicon compounds and complexes

### 9.7.2.1 Aqueous uranium silicates

Experiments on complex formation between metal ions and silicate are often carried out in solutions oversaturated in silicic acid with respect to solubility of amorphous silica. The formation of structurally poorly defined silicate polymers or colloids in such solutions strongly complicates the interpretation of experimental data in terms of stoichiometry and equilibrium constants of the complexes formed. Studies of polymerisation of silicic acid are usually carried out by the molybdate method, in which the silica monomer $Si(OH)_4$ quickly reacts with an aqueous molybdate reagent to form a coloured species, followed by determination of the concentration of polymers as the difference between the total and monomeric silica concentrations. In dilute solutions (ionic strengths $I < 0.1$-0.2 M) the rate of polymerisation depends primarily on the pH of solutions: at pH < 5 there is no change in the concentration of monomeric $Si(OH)_4$ within hours (at pH = 4 even within days [1960KIT]) with a 2.5 to 5-fold supersaturation with respect to amorphous silica, *i.e.* at [Si] = 0.005-0.010 M ([1960KIT], [2005PAN/KIM], [2007THA/SIN]). Even at [Si] = 0.03 M, within two hours of aging, the fraction of the monomer exceeds 90 % at pH < 4, as reported in [1999HRN/IRL]. At higher pH or at larger silicic acid concentrations, the polymerisation starts within the first minutes of aging of the solutions. Longer experiments, up to 100 days in duration, [2005PAN/KIM], show that all silicic acid above the solubility limit of amorphous silica (0.002 M in pure water at ambient temperature) will be polymerised given sufficient time. The presence of higher concentrations of electrolytes also increases the rate of polymerisation: for example, in a solution containing 0.005 M of silica and with $I = 0.20$ M ($NaClO_4$), the fraction of polymers after 60 minutes of aging is just a few per cent; however, in a similar solution with $I = 3.0$ M the fraction of polymers approaches to 40 % according to [2007THA/SIN].

Many studies of complex formation between silicate and metal ions were performed at pH < 4 and at low ionic strengths (0.1-0.2 M $NaClO_4$). For the reasons discussed above, one may neglect the formation of polymeric species of silica if measurements are completed within a few hours in freshly prepared acidic (pH < 4) solutions with a total silica concentration up to 0.010 M, or even more. However, the rate of polymerisation of silica in solution with pH > 4-5 and [Si] > 0.010 M depends strongly on time, pH and total silica concentrations, see, for example [2005PAN/KIM], making accurate speciation calculations for silicate at such experimental conditions hardly

possible. Based on these lines of evidence this review will not accept results of studies where undefined polymeric species dominate speciation of silica in solution.

Available experimental studies on the complex formation between uranyl ion and silica agree on the following reaction:

$$UO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons UO_2SiO(OH)_3^+ + H^+ \quad (9.86)$$

which was studied by various methods, see Table 9-69.

The review by Guillaumont *et al.* [2003GUI/FAN] selected as the most reliable the information from [1971POR/WEB], [1992SAT/CHO], [1998MOL/GEI] and [1999HRN/IRL], where three experimental methods gave concordant results, see Table 9-69, and recommended for Reaction (9.86) $\log_{10}{}^*K^\circ = -(1.84 \pm 0.10)$, with the uncertainty at the 1.96σ level. The following SIT interaction coefficients from [2003GUI/FAN] were used for ionic strength corrections: $\varepsilon(UO_2^{2+}, ClO_4^-)$ = $(0.46 \pm 0.03)$ kg·mol$^{-1}$ and $\varepsilon(UO_2SiO(OH)_3^+, ClO_4^-) = 0.3$ kg·mol$^{-1}$ (this is an estimated value). Nevertheless, the review by Guillaumont *et al.* [2003GUI/FAN] noted a large scatter of $\log_{10}{}^*K$ values "that should be resolved from new experiments". The review [2003GUI/FAN] gave no credit to the results of [1998JEN/CHO], where an indirect competition method was employed, and the present review agrees with this conclusion.

This review made the following changes compared to [2003GUI/FAN]: 1) We accepted the interaction coefficient $\varepsilon(Si(OH)_4, Na^+, ClO_4^-)$ = $(0.13 \pm 0.04)$ kg·mol$^{-1}$ [NEA TDB review on Ancillary Data – to be published]. No credit was given to the results of [1971POR/WEB], [1992SAT/CHO] because the silicic acid concentrations employed in these studies exceeded 0.010 M, resulting in formation of oligomers, which most likely dominated the silica speciation.

Table 9-69: Equilibrium constants of $UO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons UO_2SiO(OH)_3^+ + H^+$ as reported in the literature.

| Reference | $t$ /°C | Ionic medium /$NaClO_4$ | Method | [Si] /M, pH | $\log_{10}{}^*K$ | $\log_{10}{}^*K^\circ$ |
|---|---|---|---|---|---|---|
| [1971POR/WEB] | 25 | 0.2 M | spectrophoto. | 0.024-0.035, ~2.9-3.5 | $-(1.98 \pm 0.13)$ | |
| [1992SAT/CHO] | 25 | 0.2 M | extraction | 0.067, 3-4.5 | $-(2.01 \pm 0.09)$[(a)] | |
| [1998MOL/GEI] | 20 | 0.3 M | TRLFS | 0-0.0054, 3.9 | $-(1.74 \pm 0.30)$[(b,c)] | $-(1.48 \pm 0.30)$ |
| [1998JEN/CHO] | 25 | 0.1 M | spectrophoto. competition | 0.0017, 2.5-5.1 | $-(2.92 \pm 0.06)$ | |

(Continued on next page)

Table 9-69 (continued)

| Reference | $t$ /°C | Ionic medium /$NaClO_4$ | Method | [Si] /M, pH | $\log_{10}{}^{*}K$ | $\log_{10}{}^{*}K^{\circ}$ |
|---|---|---|---|---|---|---|
| [1999HRN/IRL] | 25 | 0.2 M | extraction | 0.01-0.067 3.3-4.5 | – (2.21 ± 0.40)(c) | – (1.96 ± 0.40) |
| [2005YUS/FED] | 23 | 0.1 M | spectrophoto. | 0.0115-0.088, 1.7-4.3 | – (2.39 ± 0.40)(d) | – (2.18 ± 0.40) |
| [2006PAT/CHO] | 25 | 0.2 M | extraction | 0-0.010, 3.60 | – (2.69 ± 0.50)(d) | – (2.43 ± 0.50) |

(a) As recalculated in [1998JEN/CHO].
(b) As recalculated in [2003GUI/FAN].
(c) The uncertainty is estimated in this review.
(d) As recalculated in Appendix A.

The authors of [1999HRN/IRL] used the liquid-liquid extraction method to study complex formation between U(VI) and silicate. They determined the fractions of monomeric and polymeric silica species in their test solutions by the molybdate method and evaluated the value of $\log_{10}{}^{*}K$ for Reaction (9.86) in terms of the actual concentrations of $Si(OH)_4$. However, this review increased the uncertainty of $\log_{10}{}^{*}K$ to ± 0.4, because of the scatter of the distribution coefficients and the fact that the difference between distribution values in the ionic medium with zero and 0.01 M of silica "is not pronounced".

There are two new experimental studies on aqueous uranium silicates. Yusov and Fedoseev [2005YUS/FED] studied complex formation between uranyl ion and aqueous silica in 0.1 M $NaClO_4$ medium by the spectrophotometric method, see a discussion in Appendix A. This review accepts the results at the three lowest silica concentrations (0.0057-0.014 M), where the silica monomer was predominant in the course of the measurements, as confirmed by the "molybdate" method. Yusov and Fedoseev report $\log_{10}{}^{*}K = -(2.39 \pm 0.40)$ and the corresponding values at infinite dilution $\log_{10}{}^{*}K^{\circ} = -(2.18 \pm 0.40)$, the uncertainties are estimated in this review.

Pathak and Choppin [2006PAT/CHO] used the solvent extraction method to study complex formation between $UO_2^{2+}$ ($[U(VI)] = 5 \times 10^{-5}$ M) and monomeric silicic acid ($[Si] = (0\text{-}10) \times 10^{-3}$ M) at $[H^+] = 10^{-(3.60 \pm 0.05)}$ and 5-45 °C in a 0.20 M $NaClO_4$ medium. Extractant solutions were prepared by dissolving bis(2-ethylhexyl) phosphoric acid (HDEHP) in *n*-heptane. The analysis of data showed that only the monosilicate complex $UO_2SiO(OH)_3^+$ was formed, the equilibrium constant of which was determined at 5-45 °C. The value of $\log_{10}\beta_1$ at 298.15 K was recalculated to refer to the equilibrium constant of Reaction (9.86), $\log_{10}{}^{*}K = -(2.69 \pm 0.50)$ in Appendix A, and extrapolated to $I = 0$ to give $\log_{10}{}^{*}K^{\circ} = -(2.43 \pm 0.50)$.

Values of $\log_{10}{}^{*}K^{\circ}$ from four studies ([1998MOL/GEI], [1999HRN/IRL], [2005YUS/FED], [2006PAT/CHO]) are accepted by this review: all these studies used low concentrations of silicic acid, ensuring that the monomer $Si(OH)_4$ dominated silica

speciation and that the stoichiometry corresponded to Reaction (9.86). It should be noted that the $\log_{10}{}^{*}K^{\circ}$ values from the studies accepted by this review do not overlap within their estimated uncertainties, a reason could be unknown systematic errors due to the experimental method used. The TRLFS method, used in [1998MOL/GEI], allowed a direct identification of species present in solutions, while the interpretation of extraction data depends on the assumed stoichiometry of the species extracted into the organic phase. Spectroscopic investigations capable to monitor the speciation of silica and U(VI) would be very helpful to resolve the large scatter in the published equilibrium constants of Reaction (9.86). This review selects for $\log_{10}{}^{*}K^{\circ}$ of Reaction (9.86) the weighted average (see Appendix C, Eqs. (C.6) and (C.7)) of four selected studies: $\log_{10}{}^{*}K^{\circ}$ = **– (1.880 ± 0.190)**, where the uncertainty is at the 1.96σ level, *i.e.*, $\Delta_r G_m^{\circ}$ = **(10.731 ± 1.084)** kJ·mol$^{-1}$. These values are in close agreement with the previous selection in [2003GUI/FAN], $\log_{10} K^{\circ}$ = – (1.84 ± 0.10).

The enthalpy change for Reaction (9.86), based on the temperature dependence of equilibrium constants in [2006PAT/CHO], is selected as $\Delta_r H_m^{\circ}$ = **(40 ± 6)** kJ·mol$^{-1}$ (where the uncertainty is increased to account for possible systematic errors). Combining this value with the enthalpy of formation, $UO_2^{2+}$, $\Delta_f H_m^{\circ}$ = – (1019.000 ± 1.500) kJ·mol$^{-1}$, from NEA TDB, and – (1461.070 ± 1.239) for $Si(OH)_4$(aq) from [NEA TDB review on Ancillary Data – to be published], this review calculates for $UO_2SiO(OH)_3^{+}$, $\Delta_f H_m^{\circ}$ = – (2440.070 ± 6.308) kJ·mol$^{-1}$.

The entropy change for Reaction (9.86) calculated from selected values of the Gibbs energy and enthalpy is $\Delta_r S_m^{\circ}$ (9.86) = **(98.169 ± 20.450)** J·K$^{-1}$·mol$^{-1}$.

The review [2003GUI/FAN] accepted the evidence of formation of an uncharged U(VI) silicate complex of unknown stoichiometry in the study by Hrnecek and Irlweck [1999HRN/IRL] using solvent extraction at pH > 4 and at high silica concentrations. For reaction $UO_2^{2+} + (\equiv SiOH)_j \rightleftharpoons [(\equiv SiOH)_{j-2}(\equiv SiO)_2 UO_2] + 2H^{+}$, the equilibrium constant $\log_{10}{}^{*}K^{\circ}$ = – (5.85 ± 0.06) was suggested as a guideline to evaluate the effect of silicate polymers on speciation. The formation of a complex between uranyl ion and polysilicate was qualitatively confirmed in [2005YUS/FED] at pH = 7-7.5 by monitoring the change of spectra with pH. Additional experimental studies are necessary to resolve the problems on uranyl complex formation in polysilicate solutions.

The current review has used the thermodynamic properties recommended in the NEA database for liquid water, the uranyl ion and chemical elements. For aqueous silica tetrahydroxide $Si(OH)_4$(aq) the following values have been selected from [NEA TDB review on Ancillary Data – to be published]: $\Delta_f G_m^{\circ}$ = – (1309.201 ± 1.017) kJ·mol$^{-1}$, $\Delta_f H_m^{\circ}$ = – (1461.070 ± 1.239) kJ·mol$^{-1}$, $S_m^{\circ}$ = (181.105 ± 2.501) J·K$^{-1}$·mol$^{-1}$.

The current review has selected the following thermodynamic values for the $UO_2SiO(OH)_3^{+}$ complex:

$$\Delta_f G_m^o = \mathbf{-\ (2251.021 \pm 2.294)\ kJ \cdot mol^{-1}}$$

$$\Delta_f H_m^o = \mathbf{-\ (2440.070 \pm 6.308)\ kJ \cdot mol^{-1}}$$

$$S_m^o = \mathbf{(181.074 \pm 20.820)\ J \cdot K^{-1} \cdot mol^{-1}}.$$

#### 9.7.2.2 Solid uranium silicates

A list of uranium mineral phases is given in Section 9.13.2. It includes several silicate minerals, where the only thermodynamic data accepted in the [2003GUI/FAN] review is for coffinite, $USiO_4$(cr). Experimental studies are in general made on synthetic samples in order to ensure phase purity and only studies of this type are accepted by the NEA reviews. The stability ranges of the various minerals depend on temperature, the concentration of silica, $Si(OH)_4$, pH and activities of cations like $Na^+$ and $Ca^{2+}$. In the following some of the important phase equilibria will be illustrated using predominance area diagrams.

##### 9.7.2.2.1 Solid U(IV) silicates

###### 9.7.2.2.1.1 Coffinite $USiO_4$

Coffinite, $USiO_4$, is found in nature in igneous and metamorphic rocks and uranium sedimentary deposits. This mineral is expected to be an important alteration product of spent nuclear fuel in contact with silica-bearing aqueous solutions under reducing conditions. In nature coffinite forms fine-grained crystals almost always associated with other minerals, often uraninite, quartz, and organic matter [2015GUO/SZE], hence, the determination of experimental data from natural samples is questionable. The synthesis of coffinite, either by reacting oxides at high temperatures or by precipitation from aqueous solutions, is faced with several difficulties, presumably because this phase is thermodynamically metastable with respect to quartz and uraninite, as discussed in the following. Grenthe *et al.* [1992GRE/FUG] summed up the available information on thermodynamic properties of coffinite based on estimation of the apparent equilibrium concentration of silica in the mineral association $USiO_4 + SiO_2 + UO_2$ from observations on geological systems and on estimation of the entropy of coffinite as a sum of corresponding values for quartz and uraninite. Since then, experimental values have been published, although, as shown below, the problem of precise determination of thermodynamic properties of coffinite is not yet resolved.

Szenknect *et al.* [2013SZE/COS] studied the solubility of intermediate compositions of the $Th_{1-x}U_xSiO_4$ solid solution system ($x$ = 0, 0.09, 0.20, 0.26, 0.35, 0.45, 0.51) in 0.1 M HCl aqueous solution at temperatures from 298 to 346 K. Experimental data were used to calculate solubility products for $ThSiO_4$, intermediate compositions, and, finally, for $USiO_4$ by assuming ideal U-Th mixing in this solid solution. The data treatment and speciation calculations were done using a chemical model based mostly on values selected in [2003GUI/FAN] and employing the Davies

equation to estimate activity coefficients. For the Reaction (9.87), the reported value was $\log_{10}{}^{*}K_s^o = -(6.1 \pm 0.2)$:

$$USiO_4(cr) + 4H^+ \rightleftharpoons U^{4+} + Si(OH)_4(aq) \qquad (9.87)$$

In a later study by [2016SZE/MES], it was pointed out that $\log_{10}{}^{*}K_s^o$ for Reaction (9.87) is very sensitive to the values of the hydrolysis constants of $U^{4+}$. The authors used the stability constants from [2001NEC/KIM], not from [2003GUI/FAN]. Adopting stability constants used in [2016SZE/MES] would make $\log_{10}{}^{*}K_s^o$ for Reaction (9.87) by almost 1 $\log_{10}$ unit larger, *i.e.*, close to – 5.1. The temperature dependence of equilibrium constants for Reaction (9.87) from data of Szenknect *et al.* [2013SZE/COS] resulted in $\Delta_r H_m^o = (53 \pm 12)$ kJ·mol$^{-1}$. As discussed in Appendix A, this value of $\Delta_r H_m^o$ appears to be grossly (by more than 100 kJ·mol$^{-1}$) in error, and in order to provide a positive value of the molar entropy, $S_m^o$, for coffinite, the enthalpy change for Reaction (9.87) must be negative, in other words, the solubility should decrease with temperature. As it is not clear, which solubility data are in error, the ones at low temperatures or at high temperatures, the current review does not select any thermodynamic data from [2013SZE/COS].

In another solubility study [2016SZE/MES], the authors succeeded in synthesising a pure single-phase sample of coffinite with grains of the size of ~ 80 nm. Dissolution experiments were performed in air and under Ar atmosphere in 0.1 M HCl at (298 ± 2) K and lasted up to several months (a steady-state concentration was reached within 30-50 days). Only experimental data obtained under Ar atmosphere were used to calculate the equilibrium constant for Reaction (9.87), $\log_{10}{}^{*}K_s^o = -(5.25 \pm 0.3)$, the uncertainty is estimated by this review and likely to be conservative, see discussion in Appendix A. As follows from the results of this study, coffinite is metastable with respect to the phase associations ($UO_2$(cr) + quartz) and ($UO_2$(cr) + amorphous silica), by ~ 19 and ~ 13 kJ·mol$^{-1}$, respectively, see Appendix A. However, the conclusion that coffinite is metastable with respect to the phase association $UO_2$(cr) + amorphous silica contradicts the direct experimental data obtained in [2016SZE/MES], as pointed out by the authors themselves. Indeed, Table 4 in their paper shows that the equilibrium concentrations of U and Si are much higher for the association $UO_2$(cr) + $SiO_2$(am) than for pure coffinite, indicating that coffinite should precipitate from this solution. It is worth mentioning that a complicating circumstance is the very small size of the uraninite crystals used in these experiments, ≈ 4 nm. However, it is unlikely that the inconsistent solubility results could be explained by the nano-size of the material [2012KAP]. If the solubility process is non-reversible, then its thermodynamic interpretation is questionable.

Guo *et al.* [2015GUO/SZE] determined the enthalpy of formation of coffinite using high-temperature oxide melt solution calorimetry. Two samples of pure $USiO_4$ were synthesised in independent laboratories. Two molten solvents (lead borate and sodium molybdate) were employed in these measurements. Consistent experimental data allowed determination of the enthalpy of formation of coffinite from oxides (uraninite and quartz),

$\Delta_{f,oxide}H_m^o$ = (25.6 ± 3.9) kJ·mol$^{-1}$. The corresponding value of the enthalpy of formation of $USiO_4$ is $\Delta_f H_m^o$ = – (1970.1 ± 4.2) kJ·mol$^{-1}$, see Appendix A.

This review notes that the enthalpy of formation of coffinite from oxides (uraninite and quartz), (25.6 ± 3.9) kJ·mol$^{-1}$, is rather close to the enthalpy of formation of its isostructural analog, thorite, from oxides (thorianite, $ThO_2$, and quartz), $\Delta_{f,oxide}H_m^o$ = (19.6 ± 2.0) kJ·mol$^{-1}$; both studies were made in the same laboratory [2005MAZ/USH]. However, the quality of the enthalpy of formation value for thorite was questioned by Konings *et al.* ([2008KON/POP]) who evaluated the entropy of this phase ( $S_m^o$ = (99.9 ± 2.6) J·K$^{-1}$·mol$^{-1}$) and showed that the combination of $\Delta_f H_m^o$ and $S_m^o$ of thorite clearly indicates that this phase is metastable with respect to the association of $ThO_2$ and quartz. However, this contradicts the well-known fact that $ThSiO_4$ can easily be synthesised from a mixture of $SiO_2$ and $ThO_2$, and also the results of phase equilibria studies at high $T$ and $P$ in this system by Schuiling *et al.* [1976SCH/VER]. These observations suggest that the enthalpy value of thorite in [2005MAZ/USH] is at least 20 kJ·mol$^{-1}$ too positive. For coffinite, on the other hand, all indirect results point to the fact that coffinite is metastable with respect to a mixture of oxides [1959FUC/HOE], [1982LIU], [2015GUO/SZE]. Still, the contradictory results from thorite preclude this review from selecting the result of Guo *et al.* [2015GUO/SZE] for the enthalpy of formation of coffinite.

Combining $\Delta_f G_m^o$ of coffinite from solubility data [2016SZE/MES] and its $\Delta_f H_m^o$ [2015GUO/SZE], the current review calculated $S_m^o$ = (141 ± 17) J·K$^{-1}$·mol$^{-1}$. This entropy value is exceptionally large compared to similar compounds, such as the tetragonal polymorph of $ThSiO_4$, thorite, which is isostructural with coffinite. For thorite $S_m^o$ = (99.9 ± 2.6) J·K$^{-1}$·mol$^{-1}$ was evaluated by Konings *et al.* [2008KON/POP] from experimental data. The $S_m^o$ value for thorite can be used for the independent estimation of the entropy of coffinite [2017KON/PLY], by adding the magnetic contribution of the $U^{4+}$ ion to the value for thorite, an approach that is well established for lanthanide and actinide compounds ([2004KON], [2014KON/BEN]). This magnetic contribution has been calculated from the crystal-field energies for $USiO_4$ determined by Mulak [1977MUL]. From these values [2017KON/PLY] derive a magnetic entropy of 9.2 J·K$^{-1}$·mol$^{-1}$ at $T$ = 298.15 K. When this value is added to the standard entropy of thorite, the value $S_m^o$ = (109 ± 4) J·K$^{-1}$·mol$^{-1}$ is obtained for the entropy of coffinite.

It is thus clear that the three independently derived thermodynamic quantities for coffinite ($\Delta_f G_m^o$, $\Delta_f H_m^o$ and $S_m^o$) are not consistent. However, when considering the extremes of the uncertainties, a consistent set can be obtained [2017KON/PLY]: $\Delta_f G_m^o$ = – 1864.6 kJ·mol$^{-1}$, $\Delta_f H_m^o$ = – 1974 kJ·mol$^{-1}$, $S_m^o$ = 113 J·K$^{-1}$·mol$^{-1}$. These values are given for information only.

In view of the inconsistency between $\Delta_f G_m^o$, $\Delta_f H_m^o$ and $S_m^o$ data (which amounts to ~ 9 kJ·mol$^{-1}$ at 298.15 K), no values of thermodynamic properties for coffinite

are selected in the current review. A need for additional solubility or enthalpy calorimetric data is emphasised.

#### 9.7.2.2.2 Solid U(VI) silicates

Clark *et al.* [1998CLA/EWI] and Chen *et al.* [1999CHE/EWI], [1999CHE/EWI2] describe a method for estimation of standard Gibbs energies of formation of U(VI) layered oxide hydrates and silicates. Because of the very few experimental thermodynamic data available for minerals, we found it relevant to include this study, despite the fact that it is based on estimations. Clark *et al.* [1998CLA/EWI] have extended a method originally suggested by Tardy and Garrels [1974TAR/GAR] for layer silicates, by using data on the structural hierarchy for a large number of uranium(VI) solid phases from Burns *et al.* [1996BUR/MIL]. The estimation method uses the standard Gibbs energies of formation of formal components of $U^{6+}$ compounds, represented by $UO_2(OH)_2$, $SiO_2$, and oxides of Na, K, Mg and Ca, for which numerical values have been evaluated mostly from data for oxides, hydroxides and silicates of U(VI) from Grenthe *et al.* [1992GRE/FUG], together with an estimated value for the standard Gibbs energy contribution of structural water equal to – 247 kJ·mol$^{-1}$. The authors have made an error propagation analysis of the estimated energies of formation and a comparison with experimental data. The uncertainty in the estimates is fairly large, ranging from 8 to 90 kJ·mol$^{-1}$, and the difference between experimental and estimated data is also large, up to 124 kJ·mol$^{-1}$. For becquerelite this discrepancy is 440 kJ·mol$^{-1}$ and the authors do not offer any explanation for this. Clark *et al.* [1998CLA/EWI] also report the Gibbs energy contribution of structural water that is useful for other uranium phases.

Chen *et al.* [1999CHE/EWI], [1999CHE/EWI2] revised their method and evaluated structural contributions for both the Gibbs energy of formation and the enthalpy of formation for 16 structural types (14 for $\Delta_f H_m^o$), in this way extending the method for additional classes of U(VI) compounds: carbonates, sulfates, phosphates, nitrates, *etc.* In all, the database containing 25 values of $\Delta_f G_m^o$ and 21 values of $\Delta_f H_m^o$ that was employed for parameterisation. The reported data show good agreement between the measured and predicted values, particularly for the Gibbs energy of formation. A test of the method, using a much larger database of thermodynamic properties of solid U(VI) compounds remains to be performed. Table 9-70 summarises the values of the Gibbs energy of formation of solid U(VI) compounds as estimated by the methods of Clark *et al.* [1998CLA/EWI] and Chen *et al.* [1999CHE/EWI].

Table 9-70: Estimated values of the Gibbs energy of formation at 298.15 K of solid U(VI) compounds by the methods of Clark *et al.* [1998CLA/EWI] and Chen *et al.* [1999CHE/EWI]. Formulas are given as they are written in the quoted studies, the values in bold are selected or retained in the current review. Thermodynamic data for minerals for which no experimental data are available are often estimated and the following table provides a comparison on how well the method discussed in [1998CLA/EWI] compares with the selected values in the present review.

| Mineral | Formula employed | Estimated $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|
| Schoepite | $[(UO_2)_8O_2(OH)_{12}]\cdot 12H_2O$(cr) | – (13590 ± 90) | [1998CLA/EWI] |
| Metaschoepite | $[(UO_2)_8O_2(OH)_{12}]\cdot 10H_2O$(cr) | – (12968 ± 79) | [1998CLA/EWI] |
| | $[(UO_2)_8O_2(OH)_{12}]\cdot 10H_2O$(cr) | – 13127.1 | [1999CHE/EWI] |
| | β-$UO_2(OH)_2$ | – 1399.0<br>**– (1398.683 ± 1.765)** | [1999CHE/EWI] |
| | $UO_3\cdot 0.9H_2O$(cr) | – 1375.2<br>**– (1374.560 ± 2.460)** | [1999CHE/EWI] |
| | $Na_2U_2O_7$(cr) | – 3008.6<br>**– (3011.454 ± 4.015)** | [1999CHE/EWI] |
| | $MgUO_4$(cr) | – 1750.2<br>**– (1750.601 ± 1.502)** | [1999CHE/EWI] |
| | $BaUO_4$(cr) | – 1887.0<br>**– (1883.805 ± 3.393** | [1999CHE/EWI] |
| | $BaU_2O_7$(cr) | – 3048.0 | [1999CHE/EWI] |
| Becquerelite | $Ca[(UO_2)_3O_2(OH)_3]_2\cdot 8H_2O$(cr) | – (10340 ± 55)<br>**– (10305.460± 13.964)** | [1998CLA/EWI] |
| | $Ca[(UO_2)_3O_2(OH)_3]_2\cdot 8H_2O$(cr) | – 10324.7<br>**– (10305.460 ± 13.964)** | [1999CHE/EWI] |
| Billietite | $Ba[(UO_2)_3O_2(OH)_3]_2\cdot 4H_2O$(cr) | – 9370.4 | [1999CHE/EWI] |
| Compreignacite | $K_2[(UO_2)_3O_2(OH)_3]_2\cdot 8H_2O$(cr) | – (10362 ± 55)<br>**– (10337.080 ± 10.956)** | [1998CLA/EWI] |
| Soddyite | $(UO_2)_2SiO_4\cdot 2H_2O$(cr) | – (3636 ± 14)<br>**– (3655.762 ± 3.931)** | [1998CLA/EWI] |
| | $(UO_2)_2SiO_4\cdot 2H_2O$(cr) | – 3652.0<br>**– (3655.762 ± 3.931)** | [1999CHE/EWI] |
| Uranophane | $Ca[(UO_2)_2(SiO_3OH)]_2\cdot 5H_2O$(cr) | – (6245 ± 31)<br>**– (6196.253 ± 4.281)** | [1998CLA/EWI] |
| | $Ca[(UO_2)_2(SiO_3OH)]_2\cdot 5H_2O$(cr) | – 6189.2<br>**– (6196.253 ± 4.281)** | [1999CHE/EWI] |
| Haiweeite | $Ca[(UO_2)_2(Si_2O_5)_3]\cdot 5H_2O$(cr) | – 9367.2 | [1999CHE/EWI] |
| Ursilite | $Ca_4[(UO_2)_4(Si_2O_5)_5]\cdot 15H_2O$(cr) | – 20377.4 | [1999CHE/EWI] |
| Boltwoodite | $K(H_3O)[(UO_2)(SiO_4)]$(cr) | – (2763 ± 8) | [1998CLA/EWI] |
| Sklodowskite | $Mg[(UO_2)(SiO_3OH)]_2\cdot 6H_2O$(cr) | – (6394 ± 38) | [1998CLA/EWI] |
| Weeksite | $(K_{0.62}Na_{0.38})_2(UO_2)_2(Si_5O_{13})\cdot 3H_2O$(cr) | – (8074 ± 16) | [1998CLA/EWI] |
| Na-Boltwoodite | $Na[(UO_2)(SiO_3OH)]\cdot H_2O$(cr) | – (2984 ± 13)<br>**– (2727.681 ± 3.226)** | [1998CLA/EWI] |
| Na-Boltwoodite | $Na[(UO_2)(SiO_3OH)]\cdot 1.5H_2O$(cr) | – 2838.9 | [1999CHE/EWI] |
| Na-Weeksite | $Na_2(UO_2)_2(Si_6O_{15})\cdot 4H_2O$(cr) | – (9144 ± 21) | [1998CLA/EWI] |
| Na-Weeksite | $Na_2(UO_2)_2(Si_5O_{13})\cdot 3H_2O$(cr) | – 8001.8 | [1999CHE/EWI] |
| | $(UO_2)_3(PO_4)_2$(cr) | – 5121.4<br>**– (5115.975 ± 5.452)** | [1999CHE/EWI] |

(Continued on next page)

Table 9-70 (continued)

| Mineral | Formula employed | Estimated $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|
| Chenikovite | $(UO_2)HPO_4 \cdot 4H_2O$(cr) | – 3063.5<br>**– (3064.749 ± 2.414)** | [1999CHE/EWI] |
| Rutherfordine | $UO_2CO_3$(cr) | – 1561.7<br>**– (1564.701 ± 1.794)** | [1999CHE/EWI] |
| | $Na_4(UO_2)(CO_3)_3$(cr) | – 3735.9<br>**– (3719.960 ± 2.575)** | [1999CHE/EWI] |
| Liebigite | $Ca_2(UO_2)(CO_3)_3 \cdot 11H_2O$(cr) | – 6446.4 | [1999CHE/EWI] |
| Fontanite | $Ca[(UO_2)_3(CO_3)_4] \cdot 3H_2O$(cr) | – 6524.7 | [1999CHE/EWI] |
| Urancalcarite | $Ca_2[(UO_2)_3(CO_3)(OH)_6] \cdot 3H_2O$(cr) | – 6036.7 | [1999CHE/EWI] |
| Sharpite | $Ca[(UO_2)_6(CO_3)_5(OH)_4] \cdot 6H_2O$(cr) | – 11607.6 | [1999CHE/EWI] |
| Swartzite | $CaMg[(UO_2)(CO_3)_3] \cdot 12H_2O$(cr) | – 6561.0 | [1999CHE/EWI] |
| Bayleyite | $Mg_2[(UO_2)(CO_3)_3] \cdot 18H_2O$(cr) | – 7881.0 | [1999CHE/EWI] |
| Andersonite | $Na_2Ca(UO_2)(CO_3)_3 \cdot 6H_2O$(cr) | – 5211.8 | [1999CHE/EWI] |
| | $UO_2(NO_3)_2 \cdot 6H_2O$(cr) | – 2585.7<br>**– (2584.213 ± 1.615)** | [1999CHE/EWI] |
| | $UO_2(NO_3)_2 \cdot 3H_2O$(cr) | – 1862.4<br>**– (1864.694 ± 1.965)** | [1999CHE/EWI] |
| | $UO_2(NO_3)_2 \cdot 2H_2O$(cr) | – 1621.3<br>**– (1620.500 ± 2.000)** | [1999CHE/EWI] |
| | $UO_2SO_4 \cdot 3.5H_2O$(cr) | – 2537.5<br>**– (2535.595 ± 1.806)** | [1999CHE/EWI] |
| | $UO_2SO_4 \cdot 3H_2O$(cr) | – 2416.9<br>**– (2416.561 ± 1.811)** | [1999CHE/EWI] |
| | $UO_2SO_4 \cdot 2.5H_2O$(cr) | – 2296.4<br>**– (2298.475 ± 1.803)** | [1999CHE/EWI] |

#### 9.7.2.2.2.1 $(UO_2)_2SiO_4 \cdot 2H_2O$(cr) (soddyite)

Soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O$(cr), has the simplest chemical composition of the uranyl silicates and is a common uranyl mineral in nature and an alteration product of spent nuclear fuel under oxidising conditions.

The solubility of soddyite was investigated in a number of studies, as discussed below.

The review [2003GUI/FAN] evaluated the equilibrium constants, $\log_{10}{}^{*}K^{o}_{s}$, for reaction:

$$(UO_2)_2SiO_4 \cdot 2H_2O(cr) + 4H^+ \rightleftharpoons 2UO_2^{2+} + Si(OH)_4(aq) + 2H_2O(l) \quad (9.88)$$

from different literature sources and suggested, for scoping calculations, the average value from Nguyen *et al.* [1992NGU/SIL] and Moll *et al.* [1996MOL/GEI] $\log_{10}{}^{*}K^{o}_{s}$ = (6.2 ± 1.0). It is worth noting that there is a wide scatter of $\log_{10}{}^{*}K^{o}_{s}$ when evaluated by different researchers using the same datasets. For example, Giammar and Hering [2002GIA/HER] recalculated $\log_{10}{}^{*}K^{o}_{s}$ for Reaction (9.88) employing the Davies equation for estimating activity coefficients and obtained from data of [1992NGU/SIL],

$\log_{10}{}^{*}K_s^o = 5.35$ (compared with 5.74 given in the original publication) from data in [1996MOL/GEI] in $N_2$ atmosphere and in air they obtained, $\log_{10}{}^{*}K_s^o = 5.39$ and 5.50, respectively (compared with 6.03 and 6.15, given in the original publication). The review [2003GUI/FAN] discussed experimental data in [1996MOL/GEI] on solubility of soddyite in 0.1 M $NaClO_4$ medium and pointed out that the authors used only two data points (at pH = 3.0) to evaluate $\log_{10}{}^{*}K_s^o$ for Reaction (9.88). The authors of [2003GUI/FAN] employed additional data points in the pH range from 3 to 9 to evaluate the average $\log_{10}{}^{*}K_s^o = (6.7 \pm 0.5)$. It is not clear how this recalculation was possible, as the silica concentrations were reported in [1996MOL/GEI] only at pH = 3.0. The value of $\log_{10}{}^{*}K_s^o = (6.7 \pm 0.5)$ is different from 6.03 and 6.15 calculated in [1996MOL/GEI] and from 5.39 and 5.50 evaluated in [2002GIA/HER].

In view of this scatter, the current review reinterpreted the original solubility data to evaluate $\log_{10}{}^{*}K_s^o$ for Reaction (9.88), see Table 9-71. The chemical model used included all hydroxo-, carbonate, and mixed hydroxo-carbonate complexes of uranyl, $UO_2SiO(OH)_3^+$, $UO_2NO_3^+$, dissociation of $CO_2/H_2CO_3$ (all values selected or retained in the current review) and $Si(OH)_4$ [NEA TDB review on Ancillary Data – to be published]. The activity coefficients were calculated with the SIT model where in most cases $I <$ (0.10-0.15) M, therefore the results are determined mainly by the electrostatic term and are not very sensitive to the numerical values of the SIT interaction coefficients.

Nguyen *et al.* [1992NGU/SIL] studied the solubility of synthetic well-crystallised soddyite at pH 3.0 (in the activity scale) under Ar atmosphere ($[U_{tot}] = 0.0193$ M, $[Si_{tot}] = 0.00512$ M) at 303 K. This review calculated for Reaction (9.88) $\log_{10}{}^{*}K_s^o = (5.43 \pm 0.42)$, the uncertainty is doubled as compared with one given in [1992NGU/SIL] to account for possible systematic errors.

Moll *et al.* [1996MOL/GEI] investigated solubility of synthetic soddyite at 298.15 K in 0.1 M $NaClO_4$ M over a pH range from 3 to 9 (the activity scale) under $N_2$ and in air (*i.e.* open to $CO_2$, $P(CO_2) = 10^{-3.50}$ atm). The full sets of data are given only for pH = 3.00 (under $N_2$: $[U_{tot}] = 0.0180$ M, $[Si_{tot}] = 0.00900$ M; in air: ($[U_{tot}] = 0.0195$ M, $[Si_{tot}] = 0.0100$ M). The evaluated values of $\log_{10}{}^{*}K_s^o$ are as follows: under $N_2$ $(5.52 \pm 0.45)$; in air $(5.63 \pm 0.53)$, the uncertainty is taken from [1996MOL/GEI] and determined mainly by the variations of equilibrium pH values; there is no reason to expect that the solubility should vary with the composition of the gas-phase.

Gorman-Lewis *et al.* [2007GOR/MAZ] carried out a detailed investigation of solubility of synthetic soddyite in dilute nitric acid solutions at room temperature, both from undersaturation and oversaturation, between pH 3.0 and 3.6 (the activity scale). Our calculations of $\log_{10}{}^{*}K_s^o$ for Reaction (9.88) from all 65 data points gave the average value $\log_{10}{}^{*}K_s^o = (6.14 \pm 0.42)$, where the error is given as $1.96\sigma_X$, $\sigma_X$ is the standard deviation associated with $\log_{10}{}^{*}K_s^o$, see Appendix C, Section C.3. This value is somewhat different from the one obtained in [2007GOR/MAZ]: $\log_{10}{}^{*}K_s^o = (6.43 + 0.20 / - 0.37)$.

There are three more sources of $\log_{10}{}^{*}K_s^o$ values for Reaction (9.88): Pérez *et*

*al.* [1997PER/CAS], Giammar and Hering [2002GIA/HER], and Alessi *et al.* [2013ALE/SZY]. These values were not selected in the current review. As was noted by Guillaumont *et al.* [2003GUI/FAN], the values of equilibrium constants of Reaction (9.88) calculated from data of Pérez *et al.* [1997PER/CAS], vary systematically with the bicarbonate concentrations. Giammar and Hering [2002GIA/HER] reported results of a study of dissolution of synthetic soddyite at (22 ± 2) °C in 0.01 M $NaNO_3$ medium at pH 6 (the activity scale) and concluded that the equilibrium with soddyite was not achieved due to the precipitation of a secondary "clarkeite-like" phase $Na(UO_2)O(OH)\cdot(H_2O)_{0\text{-}1}$(cr). Alessi *et al.* [2013ALE/SZY] studied the solubility of two samples of the synthetic soddyite, containing up to a mol fraction, $x = 0.0091$, of Np, at pH around 3.3 (the activity scale) in the nitrate medium. The equilibrium aqueous concentrations of U in this study are about 0.5-0.7 $\log_{10}$ units lower than those measured at similar pH values in the study of Gorman-Lewis *et al.* [2007GOR/MAZ], performed in the same laboratory. As there are no experimental data for the "pure" soddyite in [2013ALE/SZY], the $\log_{10}{}^{*}K_s^o$ values from this study were not accepted.

All selected values of $\log_{10}{}^{*}K_s^o$ for Reaction (9.88) are presented in Table 9-71. The weighted average value, calculated as described in Appendix C, see Eqs. (C.6) and (C.7), is selected in this review:

$$\log_{10}{}^{*}K_s^o = \mathbf{(5.750 \pm 0.260)}.$$

Table 9-71: Equilibrium constants considered for the selection of $\log_{10}{}^{*}K_s^o$ for Reaction (9.88).

| Reference | Medium | Comments | $\log_{10}{}^{*}K_s$ | $\log_{10}{}^{*}K_s^o$ |
|---|---|---|---|---|
| [1992NGU/SIL] | $I < 0.1$ M $NaClO_4$ | | (5.80 ± 0.42)[a,b] | (5.43 ± 0.42)[a,b] |
| [1996MOL/GEI] | 0.1 M $NaClO_4$ | In $N_2$ atmosphere at pH = 3.0 | (5.91 ± 0.45)[a] | (5.52 ± 0.45)[a] |
| | | In air at pH = 3.0 | (6.02 ± 0.53)[a] | (5.63 ± 0.53)[a] |
| [2007GOR/MAZ] | $I < 0.25$ M | Average from 65 data points | | (6.14 ± 0.42)[a] |

(a) Recalculated in this review.
(b) Value at 303.15 K.

The value of the Gibbs energy of formation for soddyite, calculated from $\log_{10}{}^{*}K_s^o = (5.75 \pm 0.26)$ for Reaction (9.88), using $\Delta_f G_m^o$, in kJ·mol$^{-1}$, for $UO_2^{2+}$ (– (952.551 ± 1.747)), $H_2O$(l) (– (237.140 ± 0.040)), all from [2003GUI/FAN], and for $Si(OH)_4$(aq) (– (1309.201 ± 1.017)) [NEA TDB review on Ancillary Data – to be published], is equal to $\Delta_f G_m^o = -(3655.762 \pm 3.931)$ kJ·mol$^{-1}$.

Calorimetry has been used to obtain values of $\Delta_f H_m^o$ and $S_m^o$ for soddyite. Gorman-Lewis *et al.* [2007GOR/MAZ] measured the enthalpy of formation of soddyite by drop solution calorimetry, see Appendix A. The obtained value of the enthalpy of formation from oxides is equal to $-(117.8 \pm 4.3)$ kJ·mol$^{-1}$. Using the auxiliary

thermochemical data accepted in NEA TDB, $\Delta_f H_m^o$ (in kJ·mol$^{-1}$) for $UO_3$(cr) (– (1223.80 ± 1.2), $H_2O$(l) (– (285.83 ± 0.04)), and $\Delta_f H_m^o$ = – (907.7 ± 1.1) for cristobalite, a polymorph of $SiO_2$ [NEA TDB review on Ancillary Data – to be published], this review calculated for soddyite $\Delta_f H_m^o$ = – (4044.8 ± 5.0) kJ·mol$^{-1}$.

Combining this value with $\Delta_f G_m^o$ = – (3655.8 ± 3.9) kJ·mol$^{-1}$, one obtains $\Delta_f S_m^o$ = – (1305 ± 21) J·K$^{-1}$·mol$^{-1}$ which is equal to the entropy change for the reaction of formation from elements in their standard states, see below

$$2U(cr) + Si(cr) + 2H_2(g) + 5O_2(g) \rightleftharpoons (UO_2)_2SiO_4 \cdot 2H_2O(cr) \qquad (9.89)$$

Using for elements at 298.15 K the following $S_m^o$ values (in J·K$^{-1}$·mol$^{-1}$, all from [2003GUI/FAN]): (50.20 ± 0.20) for U(cr), (18.81 ± 0.08) for Si(cr), (130.680 ± 0.003) for $H_2$(g), (205.152 ± 0.005) for $O_2$(g), this review obtains for soddyite $S_m^o$ = (101 ± 21) J·K$^{-1}$·mol$^{-1}$. We note that this value is far from the estimate of the entropy of soddyite by the Latimer [1951LAT] method, which gives a value of 332 J·K$^{-1}$·mol$^{-1}$. An approximation of the entropy of soddyite as a sum of the entropy of forsterite, $Mg_2SiO_4$ ($S_m^o$ = 94.1 J·K$^{-1}$·mol$^{-1}$ [1995ROB/HEM]), two entropies of $UO_3$(cr) ($S_m^o$ = 96.11 J·K$^{-1}$·mol$^{-1}$, [2003GUI/FAN]), two contributions of the entropy of water in solid hydrates, about 44.7 J·K$^{-1}$·mol$^{-1}$ ([1951LAT] as outlined in Appendix D), minus two entropies of MgO(cr), ($S_m^o$ = 26.95 J·K$^{-1}$·mol$^{-1}$, [2003GUI/FAN]), gives a value of 322 J·K$^{-1}$·mol$^{-1}$. These estimates differ from the available experimental value by about 200 J·K$^{-1}$·mol$^{-1}$. The uncertainty of such magnitude in the entropy value translates into the error of 60 kJ·mol$^{-1}$ in the value of either the enthalpy or (far less likely) of the Gibbs energy.

For the reaction:

$$2UO_3(cr) + SiO_2(cr, cristobalite) + 2H_2O(l) \rightleftharpoons (UO_2)_2SiO_4 \cdot 2H_2O(cr) \qquad (9.90)$$

data of [2007GOR/MAZ] give $\Delta_r H_m^o$ = – (117.8 ± 4.3) kJ·mol$^{-1}$ (which this review considers to be too negative by about 60 kJ·mol$^{-1}$), while the value from the enthalpies of solution of the reaction participants and products in 13.5 M HF in [2004CHE/KNY] results in $\Delta_r H_m^o$ = + (68.3 ± 2.6) kJ·mol$^{-1}$. This value is also considered unreliable, as it suggests that soddyite is metastable relative to the oxides, which obviously contradicts both mineralogical and laboratory observations. In addition, the use of $\Delta_r H_m^o$ for Reaction (9.90) obtained in [2004CHE/KNY] (calculated from heats of solution of reaction participants) in combination with $\Delta_f G_m^o$ calculated from the literature gives for soddyite $S_m^o$ ~ 758 J·K$^{-1}$·mol$^{-1}$, which is unrealistically large for this phase. Based on the discussion above, this review does not select any value of the enthalpy of formation of soddyite.

The experimental determination of the entropy of this phase by means of low-temperature calorimetry would be helpful to resolve the existing issues on the thermodynamic properties of soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O$(cr).

This review selects selects only the value of the Gibbs energy of formation for soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O$(cr):

$$\Delta_f G^o_m = \mathbf{-\ (3655.762 \pm 3.931)}\ \text{kJ}\cdot\text{mol}^{-1}.$$

#### 9.7.2.2.2.2 K(UO₂)(SiO₃OH)·H₂O(cr) (boltwoodite), Na(UO₂)(SiO₃OH)·H₂O(cr) (sodium boltwoodite) and their analogs

Boltwoodite, a layer-mineral with an idealised formula $K(UO_2)(SiO_3OH)\cdot nH_2O$(cr), is formed at oxidation and alteration of spent nuclear fuel or primary uranium ores under moist oxidising conditions [2011SHV/MAZ]. Its structure is composed of two-dimensional sheets containing uranyl polyhedra and silicate tetrahedra, while K and $H_2O$ occupy sites in the interlayer [1998BUR]. The flexibility of the boltwoodite structure permits the substitution of K by various monovalent cations, from Na to Cs in natural samples [1998BUR] and also variable water content. Chernorukov *et al.* [2004CHE/NIP] synthesised Li-, Na-, Rb-, Cs, and $NH_4$-analogs of boltwoodite in a laboratory study. There are conflicting results on the water content of boltwoodite: 1 molecule of water per formula unit [2011SHV/MAZ], 1.5 molecules [1998BUR] and also variable water content. For sodium boltwoodite, the water contents are reported varying from 1 [2004CHE/NIP] to 2 [1992NGU/SIL] molecules of water. The variable water content has practically no effect on the value of equilibrium constant of Reaction (9.91), measured in dilute solutions (M stands for a monovalent cation):

$$M(UO_2)(SiO_3OH)\cdot nH_2O(cr) + 3H^+ \rightleftharpoons M^+ + UO_2^{2+} + Si(OH)_4(aq) + nH_2O(l) \qquad (9.91)$$

because in dilute solutions water activities are close to one. However, numerical values from calorimetric measurements, such as heats of solution and low-temperature heat capacity measurements depend very strongly on the water content of the studied samples.

Aqueous solubility of boltwoodite and its analogs was investigated in a number of studies, see below.

Most studies were made for sodium boltwoodite $Na(UO_2)(SiO_3OH)\cdot H_2O$(cr). The review [2003GUI/FAN] analysed the solubility data of a synthetic sodium boltwoodite by Nguyen *et al.* [1992NGU/SIL] (at 303 K in water at pH = (4.50 ± 0.05) under an inert atmosphere) and evaluated the equilibrium constants, $\log_{10} {}^*K^o_s$, for Reaction (9.91) as > (5.82 ± 0.16). Due to concerns about the purity of the phase this value was not selected and is given for information only. The authors point out that solutions were oversaturated with respect to silica. In addition, Nguyen *et al.* [1992NGU/SIL] reported indications of soddyite formation at pH = 4.50 in the experiments with Na-boltwoodite. Indeed, calculations performed by this review, confirmed that their solutions were oversaturated with respect of soddyite, $(UO_2)_2SiO_4\cdot 2H_2O$(cr), with a saturation index, $\log_{10} SI \approx 1.6$ (*SI*, is defined as a ratio of the activity quotient for a reaction to the value of ${}^*K^o_s$, the activity quotient at equilibrium). Positive values of $\log_{10} SI$ show that the solution is oversaturated with respect to the solid phase in the dissolution reaction

$(UO_2)_2SiO_4 \cdot 2H_2O(cr) + 4H^+ \rightleftharpoons 2UO_2^{2+} + Si(OH)_4(aq) + 2H_2O(l)$. As the solubility study of Reaction (9.91) was performed outside of the field of stability of the phase, the current review does not accept $\log_{10}{}^{*}K_s^o$ for Reaction (9.91) measured by Nguyen *et al.* [1992NGU/SIL].

A reliable study on thermodynamic properties of sodium boltwoodite in aqueous solutions was presented by Ilton *et al.* [2006ILT/LIU]. These authors studied the solubility of synthetic Na-boltwoodite, $Na(UO_2)(SiO_3OH) \cdot 1.5H_2O(cr)$ (the measured composition ratios are as follows: U/Si = (1.011 ± 0.014) (1σ), U/Na = (1.039 ± 0.020) (1σ)), at 23 (± 2) °C in 0.05 M $NaNO_3/NaHCO_3$ medium (0-50 mM of $NaHCO_3$). Experiments were made in test solutions open to the atmosphere. Ten experimental data points, selected for calculation of the equilibrium constant of the Reaction (9.91), resulted in the average values of $\log_{10}{}^{*}K_s^o$, equal to (5.86 ± 0.24) (1σ) or (5.85 ± 0.26) (1σ), using, respectively, the Pitzer model and the Davies equation for the activity coefficients. Recalculation of these data, employing the SIT model with all equilibrium constants selected or retained in the present review, gave values in a good agreement with the evaluation in [2006ILT/LIU]: $\log_{10}{}^{*}K_s^o = (5.87 \pm 0.50)$, where the uncertainty is given as $1.96\sigma_X$, $\sigma_X$ is the standard deviation associated with $\log_{10}{}^{*}K_s^o$, see Appendix C, Section C.3. It was verified that test solutions were unsaturated with respect to soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O(cr)$.

Shvareva *et al.* [2011SHV/MAZ] studied solubility of synthetic Na-boltwoodite (of the composition $Na_{0.93}(UO_2)(H_{0.85}SiO_4)_{0.93} \cdot 1.25H_2O(cr)$) at 22 °C in 0.05 M $NaNO_3$ medium from both undersaturation and oversaturation, see Appendix A for a detailed review. For Reaction (9.91) the average value of equilibrium constant from 25 data points was evaluated to be $\log_{10}{}^{*}K_s^o = 6.07$ (– 0.16/+ 0.26). Recalculations performed in the present review resulted in a somewhat different value, $\log_{10}{}^{*}K_s^o = (5.59 \pm 0.95)$, the uncertainty is given as $1.96\sigma_X$. It was verified that all test solutions were unsaturated with respect to soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O(cr)$.

The weighted average of the two $\log_{10}{}^{*}K_s^o$ values for Reaction (9.91) (sodium phase), (5.87 ± 0.50) [2006ILT/LIU] and (5.59 ± 0.95) based on data [2011SHV/MAZ], calculated as described in Appendix C, see Eqs. (C.6) and (C.7), is selected by this review

$$\log_{10}{}^{*}K_s^o = \mathbf{(5.810 \pm 0.440)}.$$

For a stoichiometry of sodium boltwoodite of $Na(UO_2)(SiO_3OH) \cdot H_2O(cr)$, this review calculates

$$\Delta_f G_m^o\ (Na(UO_2)(SiO_3OH) \cdot H_2O, cr, 298.15\ K) = \mathbf{-\ (2727.681 \pm 3.226)}\ kJ \cdot mol^{-1}.$$

Shvareva *et al.* [2011SHV/MAZ], studied solubility of synthetic boltwoodite (of the composition $K_{0.75}(UO_2)(H_{0.80}SiO_4)_{0.86} \cdot 0.97H_2O(cr)$) at 22 °C in 0.05 M $KNO_3$ medium from both undersaturation and oversaturation, see Appendix A for a detailed review. For Reaction (9.91) the average value of equilibrium constant from 24 data points was evaluated to be $\log_{10}{}^{*}K_s^o = 4.12$(– 0.48/+ 0.30). Recalculations performed in the

current review, see Appendix A, resulted in a somewhat different value for the potassium phase, which is selected by this review:

$$\log_{10}{}^{*}K_{s}^{o} = \mathbf{(4.480 \pm 1.170)},$$

the uncertainty is given as $1.96\sigma_X$. It was verified that all test solutions were unsaturated with respect to soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O$(cr).

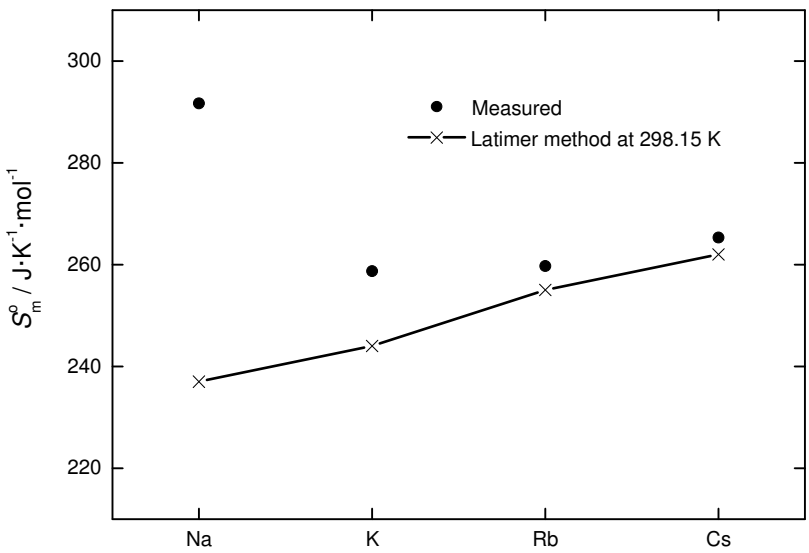
For a stoichiometry of boltwoodite of $K(UO_2)(SiO_3OH){\cdot}H_2O$(cr), and using the Gibbs energies of reactants/products of Reaction (9.91) from [2003GUI/FAN], this review calculates

$$\Delta_f G_m^o\ (K(UO_2)(SiO_3OH){\cdot}H_2O,\ cr,\ 298.15\ K) = \mathbf{-\ (2755.830 \pm 6.979)}\ kJ{\cdot}mol^{-1}.$$

There are three additional experimental studies [2004CHE/NIP], [2004CHE/NIP2], [2013NIP/CHE4], performed in the same laboratory, on the solubility of Li-, Na-, K-, Rb-, Cs-, and $NH_4$-boltwoodites in pure water, $HClO_4$ ($10^{-4}$-1.0 M) and alkali ($10^{-3}$-1.0 M) solutions. Measurements in the 2004 study were of shorter duration (~ 10 days) compared with runs in 2013 (lasting at least 50 days). The equilibrium pH values measured in 2004 and 2013 for the same initial solution may differ up to 0.8 $\log_{10}$ unit, although usually the difference is much lower. The solubility data from 2013, for various phases are rather close to the results of 2004, except for $NH_4(UO_2)(SiO_3OH){\cdot}H_2O$(cr) in pure water, where solubility data of [2013NIP/CHE4] are approximately two orders of magnitude lower compared to similar data in [2004CHE/NIP]. The authors found that phases decompose in strongly acid and alkali solutions. Recalculations, performed in the present review, see Appendix A, showed that all data from the two 2004 papers for Li-, Na-, Rb-, Cs, and $NH_4$-boltwoodites were oversaturated with respect to soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O$(cr). The same is true for data from the 2013 paper for Li-, Na-, and Cs-boltwoodites in acid solutions. Dilute solutions of $HClO_4$ in equilibrium with K-boltwoodite appear to be undersaturated with respect to soddyite; however, $\log_{10}{}^{*}K_{s}^{o}$ values for K-boltwoodite, calculated from data of [2013NIP/CHE4], are several orders of magnitude lower than the one reported in [2011SHV/MAZ]. Solutions of Rb- and $NH_4$-boltwoodite in [2013NIP/CHE4] appear to be close to equilibrium with soddyite, within a wide range of the saturation indices (± 0.7 $\log_{10}$ units). Still, in analogy with data for K-boltwoodite, these results were not accepted and the current review does not credit data from [2004CHE/NIP], [2004CHE/NIP2], [2013NIP/CHE4].

Calorimetry has been used to obtain values of $\Delta_f H_m^o$ and $S_m^o$ for boltwoodite and sodium boltwoodite. Values of $S_m^o$ at 298.15 K were determined from low-temperature heat capacity measurements for Na- [2002KAR/CHE2], K- [2002KAR/CHE], Rb- [2003KAR/CHE2], and Cs-boltwoodites [2003KAR/CHE3], all having an assumed idealised formula $M(UO_2)(SiO_3OH){\cdot}H_2O$(cr), but no chemical composition of the samples studied was reported.

Figure 9-16: Experimentally determined entropy values (black circles) and those calculated using the Latimer [1951LAT] method (crosses) at 298.15 K for Na-, K-, Rb-, and Cs-boltwoodite, see text. The line is drawn to help the eye.




Experimental results of $S^o_m$ for Na-, K-, Rb-, and Cs-boltwoodite are shown in Figure 9-16 as black circles. The observed change of $S^o_m$ between the Na- and the other alkali-compounds is very unusual for a series of isostructural alkali compounds. A typical change in entropy between a Na-compound and the analogous K, Rb, and Cs phases is an increase in entropy, $S^o_m$ (298.15 K), by about 10 J·K$^{-1}$·mol$^{-1}$ between each alkali compound. This is demonstrated by accurate entropy data for many alkali phases reported in the handbook by Glushko *et al.* [1982GLU/GUR]. The values of $S^o_m$ predicted by the Latimer [1951LAT] method (as outlined in Appendix D), shown as crosses in Figure 9-16, are in good agreement (within ± 10 J·K$^{-1}$·mol$^{-1}$) for Rb-, and Cs-boltwoodite, but not for sodium boltwoodite. The most probable explanation of this discrepancy is that the studied Na-boltwoodite phase contained not one but two molecules of water (one mole of hydrated water adds about 45 J·K$^{-1}$·mol$^{-1}$ to the entropy of a solid phase [1951LAT]). Regrettably, the exact compositions of studied samples were not reported in the cited publications. The entropy of monohydrated sodium boltwoodite is expected to be about 10 J·K$^{-1}$·mol$^{-1}$ smaller than the entropy of Rb-boltwoodite (260 ± 12) J·K$^{-1}$·mol$^{-1}$ [2003KAR/CHE2], and by about 20 J·K$^{-1}$·mol$^{-1}$ less than the entropy of Cs-boltwoodite

(265 ± 12) $J \cdot K^{-1} \cdot mol^{-1}$ [2003KAR/CHE3]. Therefore, the present review has estimated for monohydrated sodium boltwoodite

$$S_m^o(Na(UO_2)(SiO_3OH) \cdot H_2O, cr, 298.15\ K) = (248 \pm 15)\ J \cdot K^{-1} \cdot mol^{-1}.$$

For potassium boltwoodite the experimental value was selected:

$$S_m^o(K(UO_2)(SiO_3OH) \cdot H_2O, cr, 298.15\ K) = (\mathbf{259.000 \pm 12.000})\ J \cdot K^{-1} \cdot mol^{-1},$$

the uncertainty is estimated in this review. For the formation of Na- and K-boltwoodite from simple elements (M below stands for an alkali metal)

$$M(cr) + U(cr) + Si(cr) + 7/2O_2(g) + 3/2H_2(g) \rightleftharpoons M(UO_2)(SiO_3OH) \cdot H_2O(cr)$$

accepting entropies of elements from NEA TDB [2003GUI/FAN], this review calculates

$$\Delta_f S_m^o(Na(UO_2)(SiO_3OH) \cdot H_2O, cr, 298.15\ K) = -(786.362 \pm 15.003)\ J \cdot K^{-1} \cdot mol^{-1},$$

and

$$\Delta_f S_m^o(K(UO_2)(SiO_3OH) \cdot H_2O, cr, 298.15\ K) = -(788.742 \pm 12.004)\ J \cdot K^{-1} \cdot mol^{-1}.$$

From the experimental values of $\Delta_f G_m^o$ and $\Delta_f S_m^o$, we obtained the following values of the enthalpies of formation of Na- and K-boltwoodites, using the Gibbs-Helmholtz relation:

$$\Delta_f H_m^o(Na(UO_2)(SiO_3OH) \cdot H_2O, cr, 298.15\ K) = -(2962.1 \pm 5.5)\ kJ \cdot mol^{-1}.$$

and

$$\Delta_f H_m^o(K(UO_2)(SiO_3OH) \cdot H_2O, cr, 298.15\ K) = -(2991.0 \pm 7.8)\ kJ \cdot mol^{-1}.$$

These results are in poor agreement with available experimental determinations. For example, Karyakin *et al.* [2002KAR/CHE2] determined from the heats of solution in HF medium for Na-boltwoodite $\Delta_f H_m^o = -(2796.0 \pm 6.0)\ kJ \cdot mol^{-1}$, however, as discussed in Appendix A, the studied sample most likely was not a monohydrate. The same group [2002KAR/CHE] reported for K-boltwoodite $\Delta_f H_m^o = -(2958.0 \pm 4.5)\ \underline{kJ} \cdot mol^{-1}$, but, as the review in Appendix A noted, the data must be corrected for value of $\overline{L_2}$, the relative partial molar enthalpy of dilute $HNO_3$ in 18 m HF solution. This value is unknown, but its magnitude can be as large as 20 $kJ \cdot mol^{-1}$. In addition, the exact composition of the studied sample was not reported in [2002KAR/CHE], which is problematic because heats of solution strongly depend on the water content of samples.

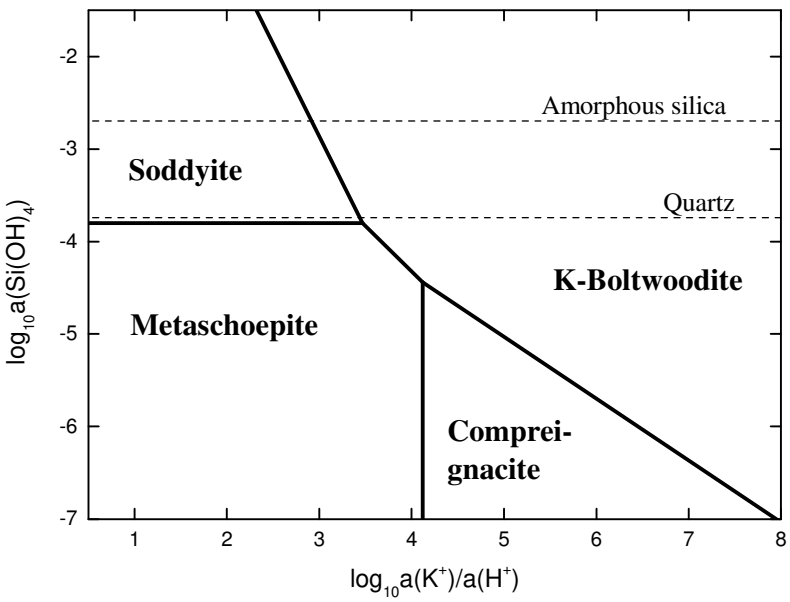
Shvareva *et al.* [2011SHV/MAZ] measured the enthalpies of formation of Na-boltwoodite with the stoichiometry $Na_{0.93}(UO_2)(H_{0.85}SiO_4)_{0.93} \cdot 1.25H_2O(cr)$, $\Delta_f H_m^o = -(2948.8 \pm 6.6)\ kJ \cdot mol^{-1}$, and of K-boltwoodite with the stoichiometry $K_{0.75}(UO_2)(H_{0.80}SiO_4)_{0.86} \cdot 0.97H_2O(cr)$, $\Delta_f H_m^o = -(2766.8 \pm 6.5)\ kJ \cdot mol^{-1}$, by drop solution calorimetry in a sodium molybdate solvent. These values were accepted by [2011SHV/MAZ] as the enthalpies of formation of Na-boltwoodite and K-boltwoodite of

the idealised stoichiometric compositions. This decision is likely to introduce a significant and hard-to-account-for error in $\Delta_f H_m^o$ values. At the same time, the authors of [2011SHV/MAZ] indicated that there is a possibility to evaluate $\Delta_f H_m^o$ of phases of the idealised stoichiometric compositions "assuming that the enthalpy of formation from oxides is the same as that measured for the slightly non-stoichiometric materials". This review calculated $\Delta_f H_m^o$ of uranyl silicates using this assumption and obtained the following values, see Appendix A: for Na-boltwoodite $\Delta_f H_m^o$ = – (2983.3 ± 6.2) kJ·mol$^{-1}$, and for K-boltwoodite $\Delta_f H_m^o$ = – (2992.3 ± 6.4) kJ·mol$^{-1}$. The large difference in the $\Delta_f H_m^o$ values demonstrates the pronounced effect of various assumptions for correcting $\Delta_f H_m^o$ for deviations in the composition of studied samples from their ideal chemical formulas.

New measurements of both $S_m^o$ and $\Delta_f H_m^o$ for boltwoodite and its analogs using samples, which have a chemical composition as close to the idealised formulas as possible, would be of value.

The figures below show the phase relations in the systems U(VI)-Si-K-$H_2O$ and U(VI)-Si-Na-$H_2O$ where the *x*- and *y*-axes denote the logarithms of activities at 298.15 K and 0.1 MPa. The diagrams are built using the Gibbs energies of solid phases and aqueous ions from the NEA data base, or selected in the current review (the data for metaschoepite, $UO_3 \cdot 2H_2O$(cr) and for compreignacite, $K_2U_6O_{19} \cdot 11H_2O$(cr), are those from [2003GUI/FAN]; for amorphous silica and quartz this review has used the selected values from [NEA TDB review on Ancillary Data – to be published]. As discussed in the text, in a number of studies the solubility of U(VI) silicates was measured outside their fields of stability, which decreases the reliability of the obtained results. The diagrams should be of help when designing new experimental studies of solubilities and phase relations of uranium silicates in aqueous solutions.

Figure 9-17: Phase equilibria among solid phases in the U(VI)-Si-K-H-O system in aqueous solutions, shown by thick lines: metaschoepite $UO_3 \cdot 2H_2O$(cr), soddyite $(UO_2)_2SiO_4 \cdot 2H_2O$(cr), K-boltwoodite $K(UO_2)(SiO_3OH) \cdot H_2O$(cr), and compreignacite $K_2U_6O_{19} \cdot 11H_2O$(cr) at 298.15 K. Dashed lines show the decadic logarithms of aqueous solubilities of amorphous silica and quartz (based on data from [NEA TDB review on Ancillary Data – to be published]).




The values of the thermodynamic functions of K-boltwoodite, $K(UO_2)(SiO_3OH) \cdot H_2O$(cr), selected in this review are:

$$\Delta_f G^o_m = \mathbf{-\ (2755.830 \pm 6.979)}\ \text{kJ} \cdot \text{mol}^{-1};$$

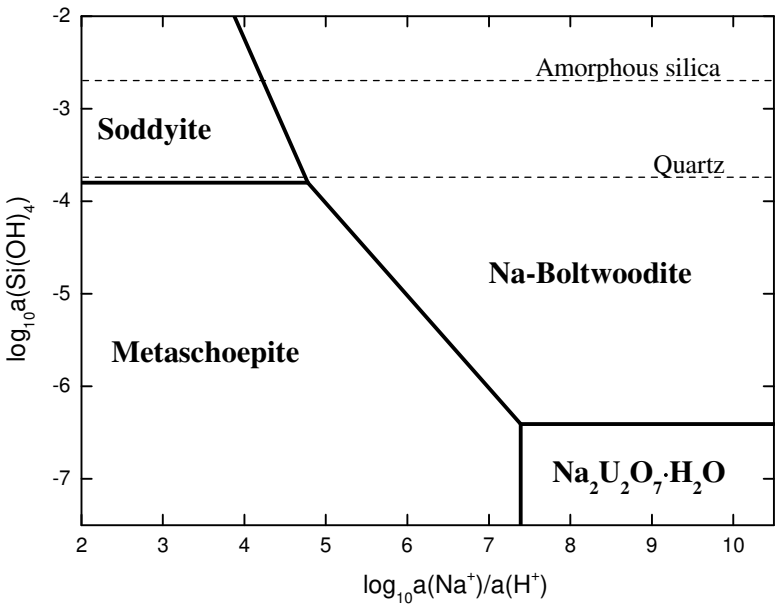
$$\Delta_f H^o_m = \mathbf{-\ (2990.993 \pm 7.843)}\ \text{kJ} \cdot \text{mol}^{-1};$$

$$S^o_m = \mathbf{(259.000 \pm 12.000)}\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

Only the Gibbs energy of formation was selected in this review for Na-boltwoodite, $Na(UO_2)(SiO_3OH) \cdot H_2O$(cr), because the $S^o_m$ value for this phase is estimated:

$$\Delta_f G^o_m = \mathbf{-\ (2727.681 \pm 3.226)}\ \text{kJ} \cdot \text{mol}^{-1}.$$

Figure 9-18: Phase equilibria among solid phases in the U(VI)-Si-Na-H-O system in aqueous solutions, shown by thick lines: metashoepite $UO_3 \cdot 2H_2O$(cr), soddyite $(UO_2)_2SiO_4 \cdot 2H_2O$(cr), Na-boltwoodite $Na(UO_2)(SiO_3OH) \cdot H_2O$(cr) and $Na_2U_2O_7 \cdot H_2O$(cr) at 298.15 K. Dashed lines show the decadic logarithms of aqueous solubilities of amorphous silica and quartz (based on data from [NEA TDB review on Ancillary Data – to be published]).




#### 9.7.2.2.3 $Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$(cr) (uranophane)

Uranophane is a U-bearing layer-mineral of the formula $Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$(cr). It belongs to the most common U(VI) minerals and forms at oxidation and alteration of spent nuclear fuel or primary uranium ores under moist oxidising conditions [2011SHV/MAZ].

The aqueous solubility of uranophane was investigated in a number of studies (see below) with the aim to evaluate $\log_{10}{}^{*}K_s^o$ for Reaction (9.92):

$$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O(cr) + 6H^+ \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 2Si(OH)_4(aq) + 5H_2O(l) \quad (9.92)$$

Nguyen *et al.* [1992NGU/SIL] studied the solubility of a synthetic uranophane at 303 K in $NaClO_4$ medium ($I < 0.1$ M) at pH = (3.50 ± 0.05) in an inert atmosphere and evaluated for Reaction (9.92), $\log_{10}{}^{*}K_s^o$ = (9.42 ± 0.48). A detailed review of this study was made in [2003GUI/FAN]. The current review reinterpreted the original solubility

data and obtained a somewhat lower value of $\log_{10}{}^{*}K_s^o = 8.91$ (as in the case of soddyite, the most likely explanation of the discrepancy in $\log_{10}{}^{*}K_s^o$ values is to assume that Nguyen *et al.* measured pH in the activity scale, but used p[$H^+$] in their data treatment). Importantly, the solution was found to be oversaturated with respect to soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O(cr)$: the calculated $\log_{10}SI = 1.13$, when using the value of $\log_{10}{}^{*}K_s^o = (5.75 \pm 0.26)$ selected in this review for reaction $(UO_2)_2SiO_4{\cdot}2H_2O(cr) + 4H^+ \rightleftharpoons 2UO_2^{2+} + Si(OH)_4(aq) + 2H_2O(l)$.

Perez *et al.* [2000PER/CAS] studied the solubility of synthetic uranophane at room temperature at a low ionic strength. For Reaction (9.92), the review [2003GUI/FAN] obtained $\log_{10}{}^{*}K_s^o = (11.7 \pm 0.6)$ and concluded that the composition of the solid phase used was uncertain as it was deficient in Ca and for this reason, the obtained equilibrium constant was not accepted. The current review recalculated $\log_{10}{}^{*}K_s^o$ values assuming that the system was open to atmospheric $CO_2$ with $P(CO_2) = 10^{-3.50}$ atm, *i.e.* the $HCO_3^-$ concentration was determined not by the initial amount of $NaHCO_3$, but by the final pH and the condition of electroneutrality of the system. The paper reported only pH and [$U_{tot}$] values, and in order to estimate the concentrations of Si and Ca, this review was forced to assume that the dissolution was congruent (as confirmed by sporadic Ca and Si analyses in the paper). It was found that at all conditions the solutions were undersaturated with respect to soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O(cr)$; in some cases (4 out of 12) they were found to be oversaturated with respect to Na-boltwoodite, $Na(UO_2)(SiO_3OH){\cdot}H_2O(cr)$, however, the calculated $\log_{10}SI$ was always less than 0.18, *i.e.* less then the uncertainty of the solubility product of sodium boltwoodite. Accepting and averaging all 12 values, this review obtained $\log_{10}{}^{*}K_s^o = (11.70 \pm 1.04)$, uncertainties are given as $1.96\sigma_X$.

Since the publication of the update [2003GUI/FAN] new studies on the solubility of uranophane in aqueous solutions have been published.

Chernorukov *et al.* [2005CHE/NIP2] studied dissolution of synthetic uranophane in water and dilute $HClO_4$ ($10^{-2}$, $10^{-3}$, and $10^{-4}$ M) solutions at 298.15 K, see Appendix A. The exact composition of the investigated sample was not reported. For Reaction (9.92) the average value of $\log_{10}{}^{*}K_s^o = (8.0 \pm 2.0)$ was reported in the paper. Recalculations in this review, performed under the assumption that the system was open to atmospheric $CO_2$ ($P(CO_2) = 10^{-3.50}$ atm), resulted in a similar value of $\log_{10}{}^{*}K_s^o = (8.7 \pm 2.4)$. There is a large scatter of the calculated $\log_{10}{}^{*}K_s^o$ values, from 7.6 to 10.0 and this review notes that in all cases the test solutions were oversaturated with respect to soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O(cr)$ and for this reason the $\log_{10}{}^{*}K_s^o$ values were not selected.

A detailed and careful study of dissolution of uranophane was presented by Prikryl [2008PRI]. The synthesised sample had a composition very close to the idealised stoichiometry: the Ca:Si:U ratio in the studied sample was equal to 0.95 (± 0.01) : 1.99 (± 0.01) : 1.99 (± 0.07) as compared with 1:2:2 for ideal uranophane.

The paper presented results of both dissolution (from undersaturation, four independent experiments) and precipitation (from supersaturation, two experiments) of uranophane in aqueous solutions at 20.5 (± 2) °C and near-neutral pH (~ 6.0) in ~ 0.01 M $CaCl_2$ and ~ $10^{-3}$ M $SiO_2$ medium, the solution did not contain "foreign" cations (for instance, alkali ions). The test solutions were open to the atmosphere during ten weeks of equilibration. The experimental data are presented graphically, but the plots are detailed enough to extract solubility values with a precision of a few per cent, except for U, which concentrations could only be read with a precision of ~ 20 %. All solutions were undersaturated with respect to soddyite. This review, see Appendix A, used the solubility data from the longest equilibration times and calculated from six data points the average $\log_{10}{}^{*}K_s^o = (11.52 \pm 0.16)$, for Reaction (9.92), the uncertainty is given as $1.96\sigma_X$. This value and the estimated uncertainty are larger than reported by Prikryl [2008PRI], (11.01 ± 0.09(1σ)). The difference appears to be due to a difference in the hydrolysis constants of uranyl(VI) in [1992GRE/FUG], used by Prikryl, and the ones selected or retained in the current review.

Shvareva *et al.* [2011SHV/MAZ] studied dissolution of synthetic uranophane, of the composition $Ca_{1.09}(UO_2)_2(H_{0.51}SiO_4)_{1.77}\cdot 5.55H_2O$(cr) as compared to the ideal formula $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$(cr), in acid solutions, with pH values ranging from 2.99 to 4.06. The dissolution was studied from both under- and supersaturation in test solutions open to the atmosphere, and similar values of equilibrium constant for Reaction (9.92) were obtained, $\log_{10}{}^{*}K_s^o = 10.82$ (– 0.62 to + 0.29). Recalculations in this review, see Appendix A, resulted in $\log_{10}{}^{*}K_s^o = (9.8 \pm 0.9)$, the uncertainties are calculated as $1.96\sigma_X$. However, no values were accepted as the test solutions were oversaturated with respect to soddyite.

This review selects for Reaction (9.92) only $\log_{10}{}^{*}K_s^o$ data obtained at conditions where uranophane was the thermodynamically stable phase: $\log_{10}{}^{*}K_s^o = (11.70 \pm 1.04)$ by Perez *et al.* [2000PER/CAS], and $\log_{10}{}^{*}K_s^o = (11.52 \pm 0.16)$ by Prikryl [2008PRI]. The weighted average value, calculated as described in Appendix C, see Eqs. (C.6) and (C.7), is:

$$\log_{10}{}^{*}K_s^o = \mathbf{(11.520 \pm 0.160)}.$$

Using the auxiliary values of $\Delta_f G_m^o$ from [2003GUI/FAN] and the NEA TDB review on Ancillary Data for $Si(OH)_4$(aq) – to be published – this review obtains:

$$\Delta_f G_m^o(Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O, \text{cr}, 298.15\ \text{K}) = \mathbf{-\ (6196.253 \pm 4.281)}\ \text{kJ}\cdot\text{mol}^{-1}.$$

Calorimetry has been used to obtain values of $\Delta_f H_m^o$ and $S_m^o$ for uranophane. Chernorukov *et al.* [2006CHE/KNY] calculated from low-temperature $C_p$ measurements the value of $S_m^o = 727.3\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for uranophane; this value appears suspect. First, the authors observed the onset of dehydration at $T > 260$ K, while the thermal instability of uranophane at such low temperatures was not observed in other experimental studies. Second, the obtained $S_m^o$ is significantly higher than several

estimates: the Latimer [1951LAT] method (as outlined in Appendix D) gives ~ 584 $J \cdot K^{-1} \cdot mol^{-1}$; while the approximation of $S^o_m$ of uranophane equals the sum of entropies of two K-boltwoodite ($S^o_m$ = 259), three moles of hydrated water ($S^o_m \approx$ 40-45 each, see [1951LAT]), one mole of $CaCl_2$(cr) ($S^o_m$ = 108.4 [1981GLU/GUR]), minus two moles of KCl(cr) ($S^o_m$ = 82.57 each [1982GLU/GUR]), gives ~ 587, all values in $J \cdot K^{-1} \cdot mol^{-1}$. It could be that the investigated sample contained additional water. Regrettably, the exact composition of the studied sample was not reported.

Chernorukov *et al.* [2006CHE/KNY] used calorimetry of dissolution in concentrated aqueous mixtures of $HNO_3$ and HF (see Appendix A) to obtain for reaction:

$$\begin{aligned} &2K(UO_2)(SiO_3OH)\cdot H_2O(cr) + Ca(NO_3)_2\cdot 4H_2O(cr) \rightleftharpoons \\ &Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O(cr) + 2KNO_3(cr) + H_2O(l) \end{aligned} \quad (9.93)$$

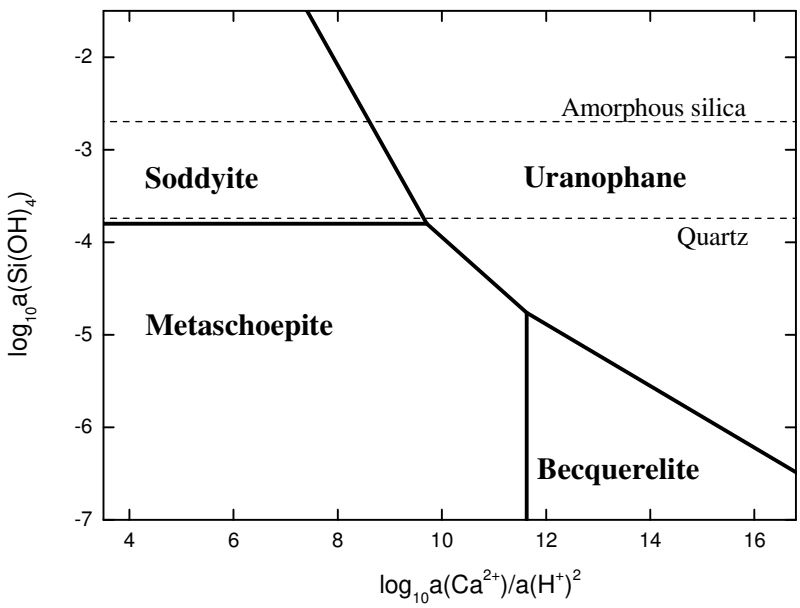
the value $\Delta_r H^o_m$ = – (6.3 ± 3.0) $kJ \cdot mol^{-1}$. Using the following values of $\Delta_f H^o_m$ (298.15 K), all in $kJ \cdot mol^{-1}$: – (2991.0 ± 7.8) for $K(UO_2)(SiO_3OH)\cdot H_2O$(cr) (evaluated in this review), – (494.0 ± 0.5) for $KNO_3$(cr) ([1982GLU/GUR]), – (285.83 ± 0.04) for $H_2O$(l) ([2003GUI/FAN]), – (2133.4 ± 1.1) for $Ca(NO_3)_2\cdot 4H_2O$(cr) ([1979GLU/MED]), this review calculates for the standard enthalpies of formation of uranophane, $\Delta_f H^o_m$ (298.15 K) = – (6848 ± 16) $kJ \cdot mol^{-1}$. Unfortunately, the exact elemental composition of the studied sample of synthetic uranophane was not reported in [2006CHE/KNY], although deviations from the exact stoichiometric composition may represent a very large and difficult-to-account-for contribution to the error in the $\Delta_f H^o_m$ value and for this reason the thermodynamic data are given for information only.

Shvareva *et al.* [2011SHV/MAZ] used drop solution calorimetry in sodium molybdate solvent (see Appendix A) to determine $\Delta_f H^o_m$ (298.15 K) = – (6799.0 ± 11.5) $kJ \cdot mol^{-1}$ for uranophane of the following composition: $Ca_{1.09}(UO_2)_2(H_{0.51}SiO_4)_{1.77}\cdot 5.55H_2O$(cr). This value was assumed equal to the enthalpy of formation of uranophane of the ideal stoichiometric composition, which is likely to introduce a significant and hard-to-account-for error. The authors of [2011SHV/MAZ] indicated that there is a possibility to evaluate $\Delta_f H^o_m$ of phases of the idealised stoichiometric compositions "assuming that the enthalpy of formation from oxides is the same as that measured for the slightly non-stoichiometric materials". This review calculated $\Delta_f H^o_m$ of uranophane using this assumption, obtaining $\Delta_f H^o_m$ = – (6935.1 ± 11.2) $kJ \cdot mol^{-1}$. The large difference between two $\Delta_f H^o_m$ results, calculated from the same value of the enthalpy of solution, illustrates a very significant effect of the phase composition on the interpretation of thermochemical data.

No $S^o_m$ and $\Delta_f H^o_m$ values of uranophane were selected in the current review. Additional calorimetric measurements using samples, which are as close in their chemical composition to the idealised formula $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$(cr) as possible, would be useful.

Figure 9-19 below shows the phase relations in the U(VI)-Si-Ca-H-O system in aqueous solutions. The diagrams are built using the Gibbs energies of solid phases and aqueous ions from the NEA data base or selected in the current review. The location of phase boundaries, especially for becquerelite, may have significant uncertainties (up to 2 $\log_{10}$ units) and new precise experimental studies would be useful.

Figure 9-19: Phase equilibria in the U(VI)-Si-Ca-H-O system in aqueous solutions among solid phases uranophane $Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O$(cr), soddyite $(UO_2)_2SiO_4{\cdot}2H_2O$(cr), metashoepite $UO_3{\cdot}2H_2O$(cr) and becquerelite $CaU_6O_{19}{\cdot}11H_2O$(cr) at 298.15 K. Dashed lines show the decadic logarithms of aqueous solubilities of amorphous silica and quartz (based on data from the NEA TDB review on Ancillary Data – to be published).




This review selects only the value of the Gibbs energy of formation for uranophane, $Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O$(cr):

$$\Delta_f G^o_m = \mathbf{-\ (6196.253 \pm 4.281)}\ \text{kJ}{\cdot}\text{mol}^{-1}.$$

#### 9.7.2.2.3.1 Other uranium (VI) silicates

There are, mostly fragmentary, solubility studies for other U(VI) silicates.

Nguyen *et al.* [1992NGU/SIL] studied solubility of a synthetic sodium weeksite, $Na_2(UO_2)_2(Si_2O_5)_3{\cdot}4H_2O$(cr), at 303 K in the $NaClO_4$ medium ($I < 0.05$ M) at

pH = 4.5 under an inert atmosphere and evaluated for the reaction:

$$Na_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O(cr) + 6H^+ + 5H_2O(l) \rightleftharpoons 2Na^+ + 2UO_2^{2+} + 6Si(OH)_4(aq) \quad (9.94)$$

$\log_{10}{}^{*}K_s^o = (1.50 \pm 0.08)$. Recalculations in the current review gave a lower value, $\log_{10}{}^{*}K_s^o = 0.94$. However, the solution was oversaturated with respect to soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O$(cr), and no solubility constant was therefore selected by the current review.

Chernorukov *et al.* [2005CHE/NIP2] studied the dissolution of synthetic $Mg[(UO_2)(SiO_3OH)]_2 \cdot 6H_2O$(cr), $Sr[(UO_2)SiO_4] \cdot H_2O$(cr), $Ba[(UO_2)SiO_4] \cdot H_2O$(cr), and $Pb[(UO_2)SiO_4] \cdot H_2O$(cr) (the mineral kasolite) in water and dilute $HClO_4$ ($10^{-2}$, $10^{-3}$, and $10^{-4}$ M) solutions at 25 °C and evaluated the solubility products for these phases. Recalculations in the current review showed that in practically all cases the solutions were oversaturated with respect to soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O$(cr).

Nipruk *et al.* [2013NIP/CHE3] investigated the solubility and phase composition of uranosilicates $M^{II}[(UO_2)(SiO_3OH)]_2 \cdot 6H_2O](cr)$ ($M^{II}$ = Mn, Co, Ni, Cu, Zn) in aqueous solutions of $HClO_4$ ($1 \times 10^{-3}$ -1 M) or NaOH ($1 \times 10^{-3}$ -1 M) at 25 °C and calculated solubility products for these phases. For reasons given in Appendix A, these results have not been accepted by the present review. The same research group investigated solubilities of REE uranosilicates of the general formula $M^{III}[(UO_2)(SiO_3OH)]_3 \cdot 10H_2O(cr)$ ($M^{III}$ = La-Lu, Y) [2013NIP/CHE2] in aqueous solutions (water, $10^{-3}$-1 M $HClO_4$, and $10^{-3}$-1 M NaOH) at 25 °C. Experimental data were used by the authors to evaluate the solubility products for these phases, see Appendix A, but for reasons given there, they have not been accepted by the present review.

## 9.8 Group 13 Boron compounds and complexes

Uranium boron compounds and complexes were not discussed in previous NEA reviews of the Chemical Thermodynamics of Uranium, [1992GRE/FUG] and [2003GUI/FAN], but they have been included in the present update both because new data are available and for their possible relevance for borosilicate based glass compositions that are considered for use in nuclear waste systems. The synthesis and structure of a large number of uranylborates have been studied by Albrecht-Schmitt and his coworkers as exemplified in [2010WAN/ALE]. The papers from this group contain important chemical information, but no thermodynamic data and are therefore not discussed in the present review.

### 9.8.1 Uranium borides

A short section on the chemistry of the uranium-boron system that includes the borides UB, $UB_2$, $UB_4$ and $UB_{12}$, but no thermodynamic data, is given in *Chemistry of the Actinide and Transactinide Elements* (eds. L. R. Mors, N. M. Edelstein and J. Fuger), Ch. 5, *Uranium,* p. 398.

### 9.8.2 Uranium borate compounds and complexes

The thermodynamics of uranyl borate and uranyl metaborate compounds have been studied by Russian groups at Nizhny Novgorod State University with N. K. Chernorukov and N. V. Karyakin as lead authors ([2002CHE/KNY], [2003CHE/KNY], [2003CHE/KNY2], [2003CHE/NIP], [2003KAR/CHE], [2004CHE/KNY], [2005CHE/NIP], [2005KAR/CHE3], [2006CHE/KNY3], [2006CHE/SMI], [2006CHE/SMI2], [2006CHE/SMI5]), [2006CHE/NIP], [2008CHE/SMI], [2011KNY/BUL], [2012KNY/KUZ]), where the latter is a review that covers most of their earlier studies. These studies include both extensive structure characterisation of the compounds using X-ray diffraction, elemental analysis, but rarely the water content, IR spectroscopy and thermal TGA and DTA analyses. The thermodynamic data are based on solubility data to obtain Gibbs energies of formation, dissolution reaction calorimetry to obtain enthalpies of formation and low temperature calorimetry to obtain molar heat capacity and molar entropy of the compounds studied. Many of these compounds form hydrates and this requires a careful analysis of their water content, data that are not always available in the publications. The analysis of the thermodynamic data requires auxiliary data that were obtained from the extensive tables by Glushko *et al. Thermodynamic Constants of Substances*, 1961-1981, issues 1-10 and Naumov *et al. Handbook of Thermodynamic Quantities*, Moscow, Atomizdat., 1971. Most of these data agree well with the NEA selected values as shown in Chapter 14. This review notes that the same experimental data are sometimes presented in different publications from the Nizhny Novgorod group and do not represent independent information. The uncertainty in the reported enthalpies and Gibbs energies of formation are often surprisingly large, in particular when compared to the errors in the enthalpies of reaction and are presumably related to uncertainties in the auxiliary data from the Glushko tables. The present review has recalculated these data using our auxiliary values, which results in smaller uncertainties. As nearly all data are made in the same laboratory, it is highly desirable to have them confirmed by new experiments. In the absence of reliable water analyses, we have based our analysis on structure information and entropy estimates using the Latimer method described in Appendix D.

The $M^{I}[UO_2BO_3]\cdot nH_2O$(cr) and $M^{II}[UO_2BO_3]_2\cdot nH_2O$(cr) compounds have layer structures where the $M^+$, $M^{2+}$ and water are located between the layers [1988GAS], [1990GAS]. Their variable water content is consistent with this structural feature. The experimental solubility studies have a duration of several days and as a result the water content of the equilibrium phase may differ from the original one. For this reason we

assume that the measured solubility refers to the "water-saturated" phase. Changes in the composition are less likely in the calorimetric experiments, because the dissolution typically takes place in a time frame of minutes, or less. Even if it is possible to test the consistency of the calorimetric data on compounds with different water content it is highly desirable to have these experiments repeated with solids that have been completely characterised by elemental and water analyses.

The Nizhny Novgorod group has used solubility measurements to determine solubility constants and Gibbs energy of reaction ([2003CHE/NIP], [2005CHE/NIP] and [2006CHE/KNY3]) and from these calculated the Gibbs energy of formation of the solid phases investigated. The Gibbs energy and enthalpy of formation of the solid, have then been used to calculate the entropy of formation using the Gibbs-Helmholtz equation, information that can be compared with the values based on determinations of the molar entropy, $S_m^o$, obtained from low-temperature calorimetry determinations of the isobaric heat capacity, $C_p(T)$.

A prerequisite for obtaining useful thermodynamic data from the solubility studies is the congruent dissolution of the solid phase, where the total concentrations of the components are corrected for the speciation, based on information on equilibrium constant and a method for calculation of activity coefficients. The equilibrium constants have been taken from the NEA reviews and the Glushko tables, while the activity coefficients have been calculated using the SIT-model. The details of these calculations are not always provided and the present review has, when possible, re-analysed the experimental data as described in the various Appendix A entries. When both solubility and calorimetric data are available it is possible to check the consistency of the thermodynamic data. In some cases, notably for the $M(UO_2BO_3)_2{\cdot}nH_2O$(cr) compounds, the data are not consistent.

#### 9.8.2.1 Alkali uranylborates, $M[UO_2BO_3]$(cr), and $M[UO_2BO_3]{\cdot}nH_2O$(cr), M = Li-Cs

Chernorukov *et al.*, [2002CHE/KNY], [2003CHE/KNY], [2003CHE/KNY2], report the synthesis of $M[UO_2BO_3]{\cdot}nH_2O$(cr), M = Li-Cs and $n$ = 0-2. In [2002CHE/KNY], they describe the preparation of $Li[UO_2(BO_3)]{\cdot}H_2O$(cr) and $Li[UO_2(BO_3)]{\cdot}0.5H_2O$(cr) from the anhydrous compound by hydrothermal heating of $Li[UO_2(BO_3)]$(cr); the compounds were characterised by X-ray powder diffraction (XRD) and IR spectroscopy and the water content by thermogravimetry. In [2003CHE/KNY], the authors describe the synthesis, crystal structures, IR spectra and thermal properties of a number of hydrated alkali uranoborates, $M[UO_2(BO_3)]{\cdot}nH_2O$(cr), $Li[UO_2(BO_3)]{\cdot}nH_2O$(cr), $n$ = 0, 2, 1.5, 1, 0.5; $Na[UO_2(BO_3)]{\cdot}nH_2O$(cr), $n$ = 1.25, 1, 0.2; $K[UO_2(BO_3)]{\cdot}nH_2O$(cr), $n$ = 1.25, 1.0, 0.2; $Rb[UO_2(BO_3)]{\cdot}nH_2O$(cr), $n$ = 1, 0.25; $Cs[UO_2(BO_3)]{\cdot}nH_2O$(cr), $n$ = 1.5, 1, 0.5, but there is no information on the elemental analyses. The alkali uranoborates are isostructural and have layer-structures built from chains of linked pentagonal $UO_5$-units that are cross-linked by $BO_3$-units.

The structures of $Na[UO_2BO_3](cr)$ and $Li[UO_2BO_3](cr)$ have been determined by single-crystal X-ray diffraction by Gasparin, [1988GAS], [1990GAS]. No elemental analyses are presented in these studies, but the structures do not indicate any presence of water. There are no thermodynamic data in these publications. In [2003CHE/KNY2] the structures, IR spectra and thermal decomposition of anhydrous $M[UO_2BO_3](cr)$ phases are reported, data that are also discussed in [2002CHE/KNY].

Seven publications from Chernorykov *et al.*, [2002KAR/CHE], [2003CHE/NIP], [2003CHE/KNY3] [2003KAR/CHE], [2003CHE/KNY2], [2005CHE/NIP] and [2005KAR/CHE3] report thermodynamic data for alkali uranyl borate compounds that are of relevance for the present review, but it is not always clear if the later publications contain new information, or if they refer to previous experimental data from the same team, *cf.* Appendix A.

In [2003CHE/NIP] and [2005CHE/NIP] the Nizhny Novgorod group has used solubility measurements to determine solubility products and Gibbs energies of formation of the compounds studied. In [2003CHE/KNY2], [2003CHE/KNY3], [2003KAR/CHE], and [2005KAR/CHE3], the authors studied the dissolution and low-temperature calorimetry to determine standard enthalpies, isobaric heat capacities (involving extrapolation from 80 to 0 K), molar entropies and Gibbs energies of formation of $M[UO_2(BO_3)](cr)$, M = Li, Na, K, Rb, Cs. The different thermodynamic cycles used to provide this information are described in the Appendix A discussions. Marochkina *et al.* [2008MAR/SMI] have re-analysed the isobaric heat capacities and molar entropies of $M[UO_2BO_3](cr)$, M = Li, Na, K, Rb, by using heat capacity measurements between 12 and 50 K. These data were then combined with the previous heat capacity measurements in [2003KAR/CHE], and [2005KAR/CHE3]. It turned out that the difference between these data and the ones based on [2008MAR/SMI] was negligible. Heat capacities and entropies for the alkali uranylborates from [2003KAR/CHE] and [2005KAR/CHE3] are reported in Table 9-75. Low-temperature heat capacity values for $Na[UO_2BO_3](cr)$ have also been reported in a recent calorimetric study by Popa *et al.* [2018POP/BEN], which also found the anomalous change in the heat capacity slope observed by [2002KAR/CHE4]. However, the standard entropy value in the former study, $S^o_m(298.15\ K) = (174.9 \pm 3.5)\ J\cdot K^{-1}\cdot mol^{-1}$, is somewhat higher than in [2002KAR/CHE4], $S^o_m(298.15\ K) = 167.2\ J\cdot K^{-1}\cdot mol^{-1}$. Contrary to expected, both molar entropy values are lower than that of $Li[UO_2BO_3](cr)$, despite the fact that these two compounds are isostructural. The Rb and Cs compounds are also iso-structural and one then expects an increase in entropy as also noted in Table 9-75. The present review has included the data by Chernorykov *et al.*, in Table 9-72 and Table 9-73 among the selected values, but we suggest that the uncertainties in the entropy and heat capacity values are higher than reported by the authors (Knyazev *et al.* report the uncertainty 2.1 $J\cdot K^{-1}\cdot mol^{-1}$ in the molar entropy, but no value for the heat capacity).

This review notes that the entropy difference between $Na[UO_2BO_3]\cdot H_2O(cr)$ and $Na[UO_2BO_3](cr)$ is 16.6 $J\cdot K^{-1}\cdot mol^{-1}$, significantly lower than an estimate based on the

Latimer method (Appendix D), 44.7 $J \cdot K^{-1} \cdot mol^{-1}$. As the two solid phases are well characterised, this review finds it unlikely that the difference is due to changes in the water content and has therefore accepted the entropy values. Table 9-75 contains all selected thermodynamic data, where the Gibbs energy of formation has been calculated from the Gibbs-Helmholtz equation.

Table 9-72: Selected standard enthalpies of formation, $\Delta_f H_m^o$ (M[$UO_2(BO_3)$], cr), for the M[$UO_2(BO_3)$](cr) compounds from [2003CHE/KNY3] at 298.15 K, recalculated (values in bold) as described in Appendix A.

| Compound | $\Delta_f H_m^o$ (M[$UO_2(BO_3)$],cr) /kJ·mol$^{-1}$ |
|---|---|
| Li[$UO_2(BO_3)$](cr) | – (2272.5 ± 4.0) |
| | **– (2272.700 ± 3.500)** |
| Na[$UO_2(BO_3)$](cr) | – (2257.5 ± 4.0) |
| | **– (2257.900 ± 3.400)** |
| K[$UO_2(BO_3)$](cr) | – (2289.5 ± 4.5) |
| | **– (2289.800 ± 3.400)** |
| Rb[$UO_2(BO_3)$](cr) | – (2287.5 ± 4.0) |
| | **– (2288.000 ± 3.300)** |
| Cs[$UO_2(BO_3)$](cr) | – (2284.0 ± 4.5) |
| | **– (2284.600 ± 3.900)** |

Chernorukov, Knyazev *et al.* [2003CHE/KNY3] and [2005KAR/CHE3] report the standard enthalpy of formation of $M[UO_2(BO_3)] \cdot nH_2O(cr)$ compounds obtained by using dissolution calorimetry and a thermodynamic cycle described in Appendix A, from which the enthalpy of reaction, $\Delta_r H_m^o$ (9.95), was obtained.

$$M[UO_2BO_3](cr) + nH_2O(l) \rightleftharpoons M[UO_2(BO_3)] \cdot nH_2O(cr) \qquad (9.95)$$

The enthalpies of formation reported by Chernorukov, Knyazev *et al.* for the hydrated compounds have been obtained using the enthalpy of formation of water $\Delta_f H_m^o$ ($H_2O$, l) = – (285.83 ± 0.04) $kJ \cdot mol^{-1}$, instead of its enthalpy in the solvent used (11.6 M HCl), which results in a significant error. The relative partial molar entropy of water, $L_1$(11.6 M HCl) = – 0.53 $kJ \cdot mol^{-1}$, and the enthalpy of formation of water, $\Delta_f H_m^o$ ($H_2O$, 11.6 M HCl) = – 286.4 $kJ \cdot mol^{-1}$, have been corrected accordingly by the present review.

The relative partial molar enthalpy of water, $L_1$, is evaluated from the concentration dependencies of enthalpies of dilution, $\varphi_L$, as:

$$\overline{L_1} = \frac{n_2}{n_1}(\varphi_L - \overline{L_2}) = \frac{m}{n_w}\left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_w} \qquad (9.96)$$

where $L_2$ is the relative partial molar enthalpy of a solute, $m$ is the molality of a solute, and $n_w$ is the number of moles of water. The enthalpies of formation of $M[UO_2(BO_3)] \cdot nH_2O(cr)$ in Table 9-73 have been included among the selected values.

Table 9-73: Standard enthalpies of formation of hydrated alkali uranoborates in kJ·mol$^{-1}$ recalculated using the enthalpies of solution of $M[UO_2BO_3]\cdot nH_2O$(cr), and the NEA selected auxiliary values for $M^+$, $UO_2^{2+}$ and $H_3BO_3$(aq). These data, corrected for the enthalpy of formation of water in 11.6 M HCl, – 286.4 kJ·mol$^{-1}$, instead of the value – 285.83 kJ·mol$^{-1}$ used by Chernorukov *et al.* are recalculated by the present review and given in bold.

| Compound | $\Delta_f H_m^\circ$ (298.15 K) /kJ·mol$^{-1}$ | Compound | $\Delta_f H_m^\circ$ (298.15 K) /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Li[UO_2BO_3]\cdot 1.5H_2O$(cr) | – (2752.0 ± 4.0)[(a)] | $K[UO_2BO_3]\cdot H_2O$(cr) | – (2609.0 ± 4.5)[(a)] |
| | **– (2753.100 ± 3.500)** | | **– (2609.800 ± 3.400)** |
| $Li[UO_2BO_3]\cdot H_2O$(cr) | – (2596.0 ± 4.0)[(a)] | $K[UO_2BO_3]\cdot 0.2H_2O$(cr) | – (2355.0 ± 4.5)[(a)] |
| | **– (2597.000 ± 3.500)** | | **– (2355.000 ± 3.400)** |
| $Li[UO_2BO_3]\cdot 0.5H_2O$(cr) | – (2435.5 ± 4.0)[(a)] | $Rb[UO_2BO_3]\cdot H_2O$(cr) | – (2602.5 ± 4.0)[(a)] |
| | **– (2436.200 ± 3.500)** | | **– (2603.500 ± 3.300)** |
| $Na[UO_2BO_3]\cdot H_2O$(cr) | – (2580.5 ± 4.0)[(a)] | $Rb[UO_2BO_3]\cdot 0.25H_2O$(cr) | – (2364.0 ± 4.0)[(a)] |
| | – (2581.600 ± 3.500)[(b)] | | **– (2365.300 ± 3.300)** |
| $Na[UO_2BO_3]\cdot 0.5H_2O$(cr) | – (2427.5 ± 4.0)[(a)] | $Cs[UO_2BO_3]\cdot H_2O$(cr) | – (2596.0 ± 4.5)[(a)] |
| | **– (2428.100 ± 3.500)** | | **– (2597.000 ± 3.900)** |
| | | $Cs[UO_2BO_3]\cdot 0.5H_2O$(cr) | – (2445.5 ± 4.5)[(a)] |
| | | | **– (2446.400 ± 3.900)** |

(a) Data reported by [2003CHE/KNY2].
(b) The selected value of $\Delta_f H_m^\circ$ has been calculated with the Gibbs-Helmholtz relation, see text.

The enthalpy contribution for each crystal water is around 320 kJ·mol$^{-1}$, as compared to the enthalpy of formation of liquid water, 285.8 kJ·mol$^{-1}$, suggesting a fairly strong bonding of water in these layer structures, as also indicated in [2002CHE/KNY].

Chernorukov *et al.* [2003CHE/NIP] and [2005CHE/NIP] have measured the solubility of $M[UO_2(BO_3)]\cdot nH_2O$(cr) compounds in 0.10 M HCl, and the experimental data seem to be the same in both studies. The present review has re-analysed these data as described in Appendix A, and included the corresponding Gibbs energies of formation in Table 9-74. The Gibbs energy of formation for $Na[UO_2BO_3]\cdot H_2O$(cr) obtained from the solubility experiments and from calorimetry are in good agreement, *cf.* Table 9-75.

At the pH used the dissolution reaction is:

$$M[UO_2BO_3]\cdot nH_2O(cr) + 2H^+ \rightleftharpoons M^+ + 0.5(UO_2)_2(OH)_2^{2+} + H_3BO_3(aq) + (n-1)H_2O(l) \quad (9.97)$$

The binuclear complex is predominant at pH ≈ 4, considering $[U]_{tot}$ = S ≈ 0.03-0.04 M (see Table A-125 in Appendix A) and $I$ ≈ 0.10 M. The error in $[UO_2^{2+}]$ using total uranium concentration is therefore large as can be seen from the mass balance $U_{tot} = [UO_2^{2+}] + 2[(UO_2)_2(OH)_2^{2+}]$.

Table 9-74: Solubility constants, $\log_{10}{}^{*}K_s^o$, Gibbs energies of reaction, $\Delta_r G_m^o$ and Gibbs energies of formation for the $M[UO_2BO_3]\cdot nH_2O(cr)$ compounds based on solubility data from [2003CHE/NIP], recalculated as described in Appendix A.

| Compound | $\log_{10}{}^{*}K_s^o$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Li[UO_2BO_3]\cdot 1.5H_2O(cr)$ | **(4.580 ± 0.200)** | **– (26.142 ± 1.142)** | **– (2528.265 ± 2.257)**[(a)] |
| $Na[UO_2BO_3]\cdot H_2O(cr)$ | **(4.470 ± 0.200)** | **– (25.515 ± 1.142)** | **– (2379.358 ± 2.256)**[(a)] |
| $K[UO_2BO_3]\cdot H_2O(cr)$ | **(3.900 ± 0.200)** | **– (22.261 ± 1.142)** | **– (2403.168 ± 2.257)**[(a)] |
| $Rb[UO_2BO_3]\cdot H_2O(cr)$ | **(3.710 ± 0.200)** | **– (21.177 ± 1.142)** | **– (2405.752 ± 2.260)**[(a)] |
| $Cs[UO_2BO_3]\cdot H_2O(cr)$ | **(3.920 ± 0.200)** | **– (22.376 ± 1.142)** | **– (2412.000 ± 2.317)**[(a)] |

(a) Experimental value from [2003CHE/KNY2] and [2005KAR/CHE3], recalculated by this review.

The values of $\Delta_f H_m^o$, $\Delta_f G_m^o$, $\Delta_f S_m^o$, $C_{p,m}^o$ and $S_m^o$, based on the information in Table 9-72, Table 9-73 and Table 9-75 have been selected; the solubility constants, $\log_{10}{}^{*}K_s^o$ and the corresponding Gibbs energies of reaction are given in Table 9-74. For $Na[UO_2BO_3]\cdot H_2O(cr)$, the agreement between the Gibbs energy of formation from calorimetric and solubility data is excellent, suggesting that there is no change in the phase composition during the solubility reaction. The selected thermodynamic data for this solid phase rely on $\log_{10}{}^{*}K_s^o$ and $S_m^o$, whereas $\Delta_f H_m^o$ has been calculated using the Gibbs-Helmholtz relation.

The difference in the entropy values between $Li[UO_2BO_3](cr, 298.15\ K)$ and $Li[UO_2BO_3]\cdot 1.5H_2O(cr, 298.15\ K)$, $Na[UO_2BO_3](cr, 298.15\ K)$ and $Na[UO_2BO_3]\cdot H_2O(cr, 298.15\ K)$, $K[UO_2BO_3](cr, 298.15\ K)$ and $K[UO_2BO_3]\cdot H_2O(cr, 298.15\ K)$ are not consistent with the estimate based on the Latimer method. On the other hand the difference between the monohydrate and the anhydrous compound for Rb and Cs are (30 ± 13) and (52.5 ± 15) J·K$^{-1}$·mol$^{-1}$, respectively, which are both consistent with this estimate. We note that the agreement between the Gibbs energy of formation of $Na[UO_2BO_3]\cdot H_2O(cr, 298.15\ K)$, from calorimetry and solubility data is very good, the same is true if we use the molar entropies of the $Rb/Cs[UO_2BO_3]\cdot H_2O(cr)$ obtained by adding 44.7 J·K$^{-1}$·mol$^{-1}$ to the entropies for the anhydrous compounds, *cf.* the values in italics in Table 9-75.

Table 9-75: Values of $\Delta_f H_m^o$, $\Delta_f G_m^o$, $\Delta_f S_m^o$, $C_{p,m}^o$ and $S_m^o$ from calorimetric and solubility data; selected values are reported in bold. The values in italics have been obtained by adding 44.7 $J \cdot K^{-1} \cdot mol^{-1}$ to the entropy for the anhydrous Rb and Cs compounds; they demonstrate the consistency of the solubility and calorimetric data.

| Compound | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ /K$^{-1}$·mol$^{-1}$ | $\Delta_f S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| Li[$UO_2BO_3$](cr) | **– (2272.700 ± 3.500)** | **(176.300 ± 1.000)** | **(178.700 ± 3.000)** | **– (419.400 ± 3.014)** | **– (2147.656 ± 3.614)**[(b)] |
| Li[$UO_2BO_3$]·1.5$H_2O$(cr) | **– (2753.100 ± 3.500)** | | **(193.887 ± 13.971)**[(b)] | **– (754.097 ± 13.968)**[(b)] | **– (2528.265 ± 2.257)**[(a)] |
| Li[$UO_2BO_3$]·$H_2O$(cr) | **– (2597.000 ± 3.500)** | | | | |
| Li[$UO_2BO_3$]·0.5$H_2O$(cr) | **– (2436.200 ± 3.500)** | | | | |
| Na[$UO_2BO_3$](cr) | **– (2257.900 ± 3.400)** | **(145.800 ± 1.000)** | **(167.200 ± 3.000)** | **– (453.080 ± 3.014)** | **– (2122.814 ± 3.517)** |
| Na[$UO_2BO_3$]·$H_2O$(cr) | – (2581.600 ± 3.500) | **(159.000 ± 1.000)** | **(183.800 ± 3.000)** | **– (669.736 ± 3.014)** | **– (2379.358 ± 2.256)**[(a)] |
| | **– (2579.039 ± 2.428)**[(b)] | | | | – (2381.918 ± 3.614)[(b)] |
| Na[$UO_2BO_3$]·0.5$H_2O$(cr) | **– (2428.100 ± 3.500)** | | | | |
| K[$UO_2BO_3$](cr) | **– (2289.800 ± 3.400)** | **(157.600 ± 1.000)** | **(187.200 ± 3.000)** | **– (446.460 ± 3.014)** | **– (2156.688 ± 3.517)**[(b)] |
| K[$UO_2BO_3$]·$H_2O$(cr) | **– (2609.800 ± 3.400)** | | **(173.871 ± 13.691)**[(b)] | **– (693.045 ± 13.688)**[(b)] | **– (2403.168 ± 2.257)**[(a)] |
| K[$UO_2BO_3$]·0.2$H_2O$(cr) | **– (2355.000 ± 3.400)** | | | | |
| Rb[$UO_2BO_3$](cr) | **– (2288.000 ± 3.300)** | **(148.800 ± 1.000)** | **(185.500 ± 3.000)** | **– (460.260 ± 3.023)** | **– (2150.773 ± 3.421)**[(b)] |
| Rb[$UO_2BO_3$]·$H_2O$(cr) | **– (2603.500 ± 3.300)** | | **(215.764 ± 13.420)**[(b)] | **– (663.252 ± 13.415)**[(b)] | **– (2405.752 ± 2.260)**[(a)] |
| | | | *230.2* | *– 642.9* | *– 2411.8* |
| Rb[$UO_2BO_3$]·0.25$H_2O$(cr) | **– (2365.300 ± 3.300)** | | | | |
| Cs[$UO_2BO_3$](cr) | **– (2284.600 ± 3.900)** | **(179.800 ± 1.000)** | **(214.500 ± 3.000)** | **– (439.710 ± 3.034)** | **– (2153.500 ± 4.004)**[(b)] |
| Cs[$UO_2BO_3$]·$H_2O$(cr) | **– (2597.000 ± 3.900)** | | **(266.971 ± 15.222)**[(b)] | **– (620.495 ± 15.215)**[(b)] | **– (2412.000 ± 2.317)**[(a)] |
| | | | *259.2* | *– 622.4* | *2411.4* |
| Cs[$UO_2BO_3$]·0.5$H_2O$(cr) | **– (2446.400 ± 3.900)** | | | | |

(a) Data from solubility experiments; the entropy data have been calculated using the Gibbs-Helmholtz relation.
(b) Calculated using the Gibbs-Helmholtz relation.



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### 9.8.2.2 Alkaline-earth uranylborates, $M[UO_2BO_3]_2{\cdot}nH_2O$(cr), M = Mg-Ba

The thermodynamics of the M(II)-uranyl(VI) borate systems, M = Mg-Ba, have been studied by Chernorukov *et al.* as reported in [2003CHE/KNY4], [2005CHE/NIP], [2006CHE/SMI], [2006CHE/SMI2], [2006CHE/SMI5], [2007CHE/SMI], [2008CHE/SMI] and [2008MAR/SMI]. In [2003CHE/KNY4], the authors report the standard enthalpy of formation of the uranyl(VI) borate compounds, $M[UO_2(BO_3)]_2{\cdot}nH_2O$(cr), M = Mg, Ca, Sr, Ba and $n$ = 0-7, obtained by using dissolution calorimetry, the same data are repeated in their following publications. The thermodynamic data have been recalculated by this review as described in the Appendix A entries, using auxiliary data from Chapter 14. The enthalpies of formation obtained by Chernorukov *et al.* for the hydrated compounds have been obtained by using the enthalpy of formation of pure water $\Delta_f H^o_m$ ($H_2O$, l) = – (285.83 ± 0.04) kJ·mol$^{-1}$, instead of its enthalpy in the solvent used in the dissolution experiments. This review has corrected for the contribution of the relative partial molar entropy of water, $L_1$(11.6 M HCl) = – 0.53 kJ·mol$^{-1}$, yielding $\Delta_f H^o_m$ ($H_2O$, 11.6 M HCl) = – 286.4 kJ·mol$^{-1}$. The enthalpies of formation for the $M[UO_2BO_3]_2{\cdot}nH_2O$(cr), M = Mg, Ca, Sr, Ba, compounds obtained by calorimetry are listed in Table 9-76, where the selected values are given in bold. The large change in the enthalpy of formation of the Mg-compounds is a result of the revised enthalpy of formation of $MgCO_3$(cr).

Table 9-76: Standard enthalpies of formation of $M[UO_2(BO_3)]_2$(cr) and $M[UO_2(BO_3)]_2{\cdot}nH_2O$(cr) in kJ·mol$^{-1}$ from Chernorukov *et al.* [2003CHE/KNY4], [2006CHE/SMI], [2006CHE/SMI2] and [2008CHE/SMI] at 298.15 K. Those values in bold are selected in this review.

| Compound | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | Compound | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2(BO_3)]_2$(cr) | – (4347.5 ± 8.0) | $Mg[UO_2(BO_3)]_2{\cdot}7H_2O$(cr) | – (6525.0 ± 8.0) |
| | **– (4363.800 ± 4.000)**[(a)] | | – (6545.1 ± 8.4)[(a)] |
| | | $Mg[UO_2(BO_3)]_2{\cdot}4H_2O$(cr) | – (5563.5 ± 8.0) |
| | | | – (5582.1 ± 7.3)[(a)] |
| | | $Mg[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | – (4658.0 ± 8.0) |
| | | | – (4673.2 ± 5.9)[(a)] |
| $Ca[UO_2(BO_3)]_2$(cr) | – (4491.0 ± 8.0) | $Ca[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | – (4813.0 ± 8.0) |
| | | | – (4814.3 ± 5.2)[(a)] |
| | **– (4491.300 ± 3.500)**[(a)] | $Ca[UO_2(BO_3)]_2{\cdot}0.66H_2O$(cr) | – (4658.0 ± 8.0) |
| | | | – (4701.8 ± 6.3)[(a)] |
| α-$Sr[UO_2(BO_3)]_2$ | – (4512.5 ± 8.0) | $Sr[UO_2(BO_3)]_2{\cdot}2H_2O$(cr) | – (5047.0 ± 9.0) |
| | **– (4512.900 ± 4.300)**[(a)] | | – (5122.9 ± 7.7)[(a)] |
| | | $Sr[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | – (4773.0 ± 8.0) |
| β-$Sr[UO_2(BO_3)]_2$ | – (4503.5 ± 8.0) | – | – (4824.7 ± 6.3)[(a)] |
| | **– (4503.700 ± 4.500)**[(a)] | – | |
| α-$Ba[UO_2(BO_3)]_2$ | – (4507.5 ± 8.0) | $Ba[UO_2(BO_3)]_2{\cdot}2H_2O$(cr) | – (5031.0 ± 8.0) |
| | **– (4509.000 ± 4.600)**[(a)] | | **– (5129.9 ± 8.0)**[(a)] |
| β-$Ba[UO_2(BO_3)]_2$ | – (4498.0 ± 8.0) | $Ba[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | – (4768.0 ± 8.0) |
| | **– (4499.100 ± 4.600)**[(a)] | | – (4820.1 ± 6.5)[(a)] |

(a) Recalculated by this review.

Isobaric heat capacities, $C_{p,m}$ (298.15 K), molar entropies, $S_m^o$ (298.15 K) and entropies of formation, $\Delta_f S_m^o$, for a number of $M[UO_2BO_3]_2 \cdot nH_2O$(cr), M = Mg, Ca, Sr, Ba, compounds have been measured using adiabatic calorimetry and these data are listed in Table 9-77. However, there is no information whether the data for Sr compounds refer to the α- or β-phases and we have assumed that the difference between them is insignificant.

Table 9-77: Isobaric heat capacities, $C_{p,m}$ (298.15 K), molar entropies, $S_m^o$ (298.15 K) and entropies of formation, $\Delta_f S_m^o$ for $M[UO_2BO_3]_2 \cdot nH_2O$(cr), M = Mg, Ca, Sr, Ba, compounds.

| Compound | $C_{p,m}$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $Mg[UO_2BO_3]_2$(cr) | **(242.200 ± 1.500)** | **(267.000 ± 2.100)** | – (903.0 ± 2.1) | [2007CHE/SMI] |
| | | | **– (903.630 ± 2.146)** | Recalc. by this review |
| $Mg[UO_2BO_3]_2 \cdot 4H_2O$(cr) | **(389.300 ± 1.500)** | **(410.200 ± 3.400)** | – (1693.4 ± 3.4) | [2006CHE/SMI2] |
| | | | **– (1693.454 ± 3.429)** | Recalc. by this review |
| $Ca[UO_2BO_3]_2$(cr) | **(252.900 ± 1.500)** | **(291.800 ± 2.100)** | – (887.8 ± 2.1) | [2006CHE/SMI5] |
| | | | **– (887.750 ± 2.181)** | Recalc. by this review |
| $Sr[UO_2BO_3]_2$(cr) | (262.200 ± 1.500) | (289.200 ± 2.100) | – (904.5 ± 2.1) | [2008MAR/SMI] |
| | | | – (904.460 ± 2.154) | Recalc. by this review |
| $Sr[UO_2BO_3]_2 \cdot 2H_2O$(cr) | **(316.400 ± 1.500)** | **(351.500 ± 2.300)** | – (1308.7 ± 2.1) | [2008MAR/SMI] |
| | | | **– (1308.672 ± 2.154)** | Recalc. by this review |
| α-$Ba[UO_2BO_3]_2$(cr) | **(229.700 ± 1.000)** | **(282.000 ± 1.800)** | – (917.9 ± 1.8) | [2008CHE/SMI] |
| | | | **– (918.380 ± 2.033)** | Recalc. by this review |
| $Ba[UO_2BO_3]_2 \cdot 2H_2O$(cr) | **(311.800 ± 1.500)** | **(360.700 ± 2.600)** | – (1305.3 ± 2.6) | [2008CHE/SMI] |
| | | | **– (1306.192 ± 2.766)** | Recalc. by this review |

The difference in entropy per crystal water between $M[UO_2BO_3]_2 \cdot nH_2O$(cr) and $M[UO_2BO_3]_2$(cr) is 35.8, 31.2 and 39.4 J·K$^{-1}$·mol$^{-1}$, for the Mg-, Sr-, and Ba-compounds respectively, as compared to an estimated value of 44.7 J·K$^{-1}$·mol$^{-1}$ based on the Latimer approach in Appendix D. This discrepancy among these isostructural compounds may be a result of differences in the water content from the composition given, but the present review has accepted the thermodynamic quantities. The Gibbs energies of formation from solubility data listed in Table 9-78, differ significantly from the ones obtained from calorimetry, and presumably refer to "water-saturated" phases of unknown composition and are are given for information only.

#### 9.8.2.2.1 Experimental solubility studies of $M[UO_2BO_3]_2 \cdot nH_2O$(cr) compounds

Chernorukov *et al.* [2005CHE/NIP] have used solubility measurements to determine the Gibbs energy of formation of $Mg[UO_2BO_3]_2 \cdot 4H_2O$(cr), $Ca[UO_2BO_3]_2 \cdot H_2O$(cr), $Sr[UO_2BO_3]_2 \cdot 2H_2O$(cr) and $Ba[UO_2BO_3]_2 \cdot 2H_2O$(cr). The corresponding Gibbs energies of formation are listed in Table 9-78, together with the values recalculated in this review and data from calorimetry. The Gibbs energy of formation for $Mg[UO_2BO_3]_2 \cdot 4H_2O$(cr) and $Ba[UO_2BO_3]_2 \cdot 2H_2O$(cr) calculated from calorimetric data differ significantly between the two available studies, and the agreement with the values from solubility data is poor as shown in Table 9-78.

Table 9-78: Gibbs energy of formation for $M[UO_2BO_3]_2{\cdot}nH_2O$(cr) compounds at 298.15 K calculated from calorimetric data in Table 9-76 and Table 9-77, and recalculated from solubility experiments (in italics).

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ from calorimetry | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ from solubility data | Reference |
|---|---|---|---|
| $Mg[UO_2BO_3]_2{\cdot}4H_2O$(cr) | | – (5180 ± 14) | [2005CHE/NIP] |
| | – (5059 ± 11) | | [2006CHE/SMI2] |
| | – (5077.197 ± 7.371) | *– (5164.236 ± 4.989)* | Recalc. |
| $Ca[UO_2BO_3]_2{\cdot}H_2O$(cr) | | – (4555 ± 10) | [2005CHE/NIP] |
| | | *– (4548.649 ± 4.920)* | Recalc. |
| $Sr[UO_2BO_3]_2{\cdot}2H_2O$(cr) | | – (4822 ± 11) | [2005CHE/NIP] |
| | – (4732.719 ± 7.727) | *– (4806.779 ± 4.870)* | Recalc. |
| $Ba[UO_2BO_3]_2{\cdot}2H_2O$(cr) | | – (4782 ± 9) | [2005CHE/NIP] |
| | – (4642.0 ± 8.5) | | [2008CHE/SMI] |
| | **– (4740.459 ± 8.042)** | *– (4793.093 ± 5.456)* | Recalc. |

The solubility of $M[UO_2BO_3]_2{\cdot}nH_2O$(cr) phases with M = Mg, Ca, Sr and Ba has been studied in [2005CHE/NIP]. The reported solubility data have been reinterpreted in this review considering Reaction (9.98). For this reaction, the solubility is $S = [M^{2+}]$ and we then have $\log_{10}{}^{*}K_s = 4\log_{10}S + \log_{10}4 - 4\log_{10}[H^+]$. The resulting solubility constants and Gibbs energies of reaction are given in Table 9-80.

$$M[UO_2(BO_3)]_2{\cdot}nH_2O(cr) + 4H^+ \rightleftharpoons M^{2+} + (UO_2)_2(OH)_2^{2+} + 2H_3BO_3(Cl^-\ soln) + (n-2)H_2O(l) \qquad (9.98)$$

The analysis of the water content has only been made for the Ba-compound in [2008CHE/SMI] and corresponds to two water of crystallisation. We are, however, not confident about the water composition in the compounds used in [2005CHE/NIP] and have for this reason not accepted the Gibbs energy of formation, and the solubility constants and Gibbs energy of reaction in Table 9-79, which refer to "water-saturated" phases and are given for information only. We note that the Gibbs energies of formation of these compounds calculated from solubility data are very different from the ones calculated from calorimetric data.

Table 9-79: Solubility constant, ${}^{*}K_s^o$ (9.98) and Gibbs energy of reaction, $\Delta_r G_m^o$ (9.98) for the dissolution of $M[UO_2(BO_3)]_2{\cdot}nH_2O$(cr), where $n$ = 4 for Mg, 1 for Ca and 2 for Sr and Ba; the values from [2005CHE/NIP] have been recalculated by this review as shown in Appendix A.

| Compound | $\log_{10}{}^{*}K_s$ (9.98) | $\Delta_r G_m^o$ (9.98) |
|---|---|---|
| $Mg[UO_2(BO_3)]_2{\cdot}4H_2O$(cr) | (8.98 ± 0.50) | – (51.258 ± 2.854) |
| $Ca[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | (9.26 ± 0.50) | – (52.856 ± 2.854) |
| $Sr[UO_2(BO_3)]_2{\cdot}2H_2O$(cr) | (7.52 ± 0.50) | – (42.924 ± 2.854) |
| $Ba[UO_2(BO_3)]_2{\cdot}2H_2O$(cr) | (8.83 ± 0.50) | – (50.402 ± 2.854) |

Table 9-80: Selected thermodynamic data for $M[UO_2BO_3]_2 \cdot nH_2O$(cr) (in bold) at 2098.15 K, M = Mg, Ca, Sr, Ba.

| Compound | $\Delta_f H_m^\circ$ /kJ·mol$^{-1}$ | $C_{p,m}^\circ$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G_m^\circ$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Mg[UO_2BO_3]_2$(cr) | **– (4363.800 ± 4.000)** | **(242.200 ± 1.500)** | **(267.000 ± 2.100)** | **– (903.630 ± 2.146)** | **– (4094.383 ± 4.052)** |
| $Ca[UO_2BO_3]_2$(cr) | **– (4491.300 ± 3.500)** | **(252.900 ± 1.500)** | **(291.800 ± 2.100)** | **– (887.750 ± 2.181)** | **– (4226.617 ± 3.560)** |
| $Sr[UO_2BO_3]_2$(α, cr) | **– (4512.900 ± 4.300)** | (262.200 ± 1.500) | (289.200 ± 2.100) | – (904.460 ± 2.154) | – (4243.235 ± 4.349) |
| $Sr[UO_2BO_3]_2$(β, cr) | **– (4503.700 ± 4.500)** | (262.200 ± 1.500) | (289.200 ± 2.100) | – (904.460 ± 2.154) | – (4234.035 ± 4.550) |
| $Ba[UO_2BO_3]_2$(α, cr) | **– (4509.000 ± 4.600)** | **(229.700 ± 1.000)** | **(282.000 ± 1.800)** | **– (918.380 ± 2.033)** | **– (4235.185 ± 4.640)** |
| $Ba[UO_2BO_3]_2$(β, cr) | **– (4499.100 ± 4.600)** | (229.700 ± 1.000) | (282.000 ± 1.800) | – (918.380 ± 2.033) | – (4225.285 ± 4.640) |
| $Mg[UO_2BO_3]_2 \cdot 4H_2O$(cr) | – (5582.100 ± 7.300) | **(389.300 ± 1.500)** | **(410.200 ± 3.400)** | **– (1693.454 ± 3.429)** | – (5077.197 ± 7.371)<br>– (5164.236 ± 4.989)[a] |
| $Ca[UO_2BO_3]_2 \cdot H_2O$(cr) | – | – | – | – | – (4548.649 ± 4.920)[a] |
| $Sr[UO_2BO_3]_2 \cdot 2H_2O$(cr) | – (5122.900 ± 7.700) | **(316.400 ± 1.500)** | **(351.500 ± 2.300)** | **– (1308.672 ± 2.154)** | – (4732.719 ± 7.727)<br>– (4806.779 ± 4.870)[a] |
| $Ba[UO_2BO_3]_2 \cdot 2H_2O$(cr) | **– (5129.900 ± 8.000)** | **(311.800 ± 1.500)** | **(360.700 ± 2.600)** | **– (1306.192 ± 2.766)** | **– (4740.459 ± 8.042)**<br>– (4793.093 ± 5.456)[a] |

(a) Data from solubility experiments are given for information only.



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The selected $\Delta_f H_m^o$, $\Delta_f G_m^o$, $\Delta_f S_m^o$, $C_{p,m}^o$ and $S_m^o$ for the $M[UO_2BO_3]_2 \cdot nH_2O$(cr) compounds, M = Mg, Ca, Sr and Ba are listed in Table 9-80.

#### 9.8.2.2.2 Heterogeneous equilibria in the system $M[UO_2BO_3]_2 \cdot nH_2O$(cr), M = Mn, Co, Ni, Zn

Chernorukov *et al.* [2006CHE/KNY3] have investigated the solubility of $M[UO_2(BO_3)]_2 \cdot nH_2O$(cr) phases, M = Mn, Co, Ni, Zn, in hydrochloric acid (0.1, 0.01, $10^{-3}$ and $10^{-4}$ M), water and $5\times10^{-3}$ M $H_3BO_3$ in order to determine the solubility constant for Reactions (9.99) and (9.100).

$$M[UO_2(BO_3)]_2 \cdot nH_2O(cr) + 6H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2H_3BO_3(aq) + nH_2O(l) \quad (9.99)$$

$$M[UO_2(BO_3)]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2BO_3^{3-} + nH_2O(l) \quad (9.100)$$

A pre-requisite for reliable information is that the dissolution is congruent, but the analytical data presented in [2006CHE/KNY3], Table 1, shows that this only takes place at pH > 6.4. Chernorukov *et al.* have used the solubility and literature information on the speciation in the equilibrium solutions to calculate the solubility product for Reaction (9.100) and the solubility constant, $\log_{10}{}^* K_s^o$ (9.99), but there is no information on the equilibrium constants used to calculate the speciation of M(II), U(VI) and borate in the equilibrated test solutions, where in particular the hydrolysis of M(II) is important and where experimental data are scarce or non-existing. To our knowledge there is no information on dissociation constants resulting in formation of $BO_3^{3-}$. The reported solubility products and Gibbs energy of formation have not been accepted by the present review.

#### 9.8.2.2.3 Thermodynamic data for uranyl metaborate, $UO_2(BO_2)_2$(cr)

Chernorukov *et al.*, [2004CHE/KNY], [2006CHE/SMI4] report thermodynamic data for uranyl metaborate obtained by using dissolution and low temperature calorimetry. As the same data are used in both studies they do not represent separate experiments. Chernorukov *et al.* report $\Delta_f H^o_m$ ($UO_2(BO_2)_2$, cr) = – (2542.5 ± 3.5) kJ·mol$^{-1}$, and recalculation by the present review results in a slightly different value, as listed below. Chernorukov *et al.* report $C^o_{p,m}$ ($UO_2(BO_2)_2$, cr) = 159.9 J·K$^{-1}$·mol$^{-1}$ and $S^o_m$ ($UO_2(BO_2)_2$, cr) = (174.2 ± 2.1) J·K$^{-1}$·mol$^{-1}$, respectively, both have been included among the selected values. From the latter and the entropy of the elements we have obtained $\Delta_f S^o_m$ ($UO_2(BO_2)_2$, cr) = – (503.256 ± 2.116) J·K$^{-1}$·mol$^{-1}$ and $\Delta_f G^o_m$ ($UO_2(BO_2)_2$, cr) = – (2391.354 ± 3.458) kJ·mol$^{-1}$, which have been included among the selected values.

$$\Delta_f H^o_m (UO_2(BO_2)_2, cr) = \mathbf{-\ (2541.400 \pm 3.400)}\ kJ\cdot mol^{-1},$$

$$C^o_{p,m} (UO_2(BO_2)_2, cr, 298.15\ K) = \mathbf{(159.900 \pm 1.000)}\ J\cdot K^{-1}\cdot mol^{-1},$$

$$S^o_m (UO_2(BO_2)_2, cr, 298.15\ K) = \mathbf{(174.200 \pm 2.100)}\ J\cdot K^{-1}\cdot mol^{-1},$$

$$\Delta_f S^o_m (UO_2(BO_2)_2, cr, 298.15\ K) = \mathbf{-\ (503.256 \pm 2.116)}\ J\cdot K^{-1}\cdot mol^{-1},$$

$$\Delta_f G^o_m (UO_2(BO_2)_2, cr) = \mathbf{-\ (2391.354 \pm 3.458)}\ kJ\cdot mol^{-1}.$$

Chernorukov *et al.* report the following data of interest for the synthesis of uranyl borate phases:

$$UO_3(cr,\gamma) + B_2O_3(cr) \rightleftharpoons UO_2(BO_2)_2(cr) \quad (9.101)$$

$$UO_2(BO_2)_2(cr) \rightleftharpoons 1/3U_3O_8(cr) + B_2O_3(cr) + 1/6O_2 \quad (9.102)$$

$\Delta_r H^o_m$ (9.101) = – (46.0 ± 4.0) kJ·mol$^{-1}$; $\Delta_r G^o_m$ (9.101) = – (52.0 ± 4.5) kJ·mol$^{-1}$;
$\Delta_r S^o_m$ (9.101) = (21.6 ± 2.2) J·K$^{-1}$·mol$^{-1}$

$\Delta_r H^o_m$ (9.102) = (81.5 ± 4.0) kJ·mol$^{-1}$; $\Delta_r G^o_m$ (9.102) = (75.5 ± 4.5) kJ·mol$^{-1}$;
$\Delta_r S^o_m$ (9.102) = – (8.1 ± 2.2) J·K$^{-1}$·mol$^{-1}$.

Phase equilibria are important in systems that use glasses for fixation of radioactive waste and enthalpies and Gibbs energy of reaction for Reactions (9.103)-(9.104) have been reported by Chernorukov *et al.* using known thermodynamic data. These values are given for information only.

$$1/2UO_2(BO_2)_2(cr) + 1/2M_2UO_4(cr) \rightleftharpoons M[UO_2(BO_3)](cr) \quad (9.103)$$

(M = Li – Cs)

$$1/2UO_2(BO_2)_2(cr) + 1/2MUO_4(cr) \rightleftharpoons 1/2M[UO_2(BO_3)]_2(cr) \quad (9.104)$$

(M = Mg – Ba)

$$1/3UO_2(BO_2)_2(cr) + 1/3M_2U_2O_7(cr) + 1/3MBO_2(cr) \rightleftharpoons M[UO_2(BO_3)](cr) \quad (9.105)$$

(M = Li – Cs)

$$1/3UO_2(BO_2)_2(cr) + 1/3MU_2O_7(cr) + 1/3M_{0.5}BO_2(cr) \rightleftharpoons 1/2M[UO_2(BO_3)]_2(cr) \quad (9.106)$$

(M = Mg – Ba)

Table 9-81: Thermodynamic functions for Reactions (9.103)-(9.104) and (9.105)-(9.106) in kJ·mol$^{-1}$ at 298.15 K; these data are given for information.

| | $\Delta_r H_m^o$ (9.103)/(9.104) /kJ·mol$^{-1}$ | $\Delta_r G_m^o$ (9.103)/(9.104) /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ (9.105) /kJ·mol$^{-1}$ | $\Delta_r G_m^o$ (9.105) /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| Li | – (18.0 ± 5.0) | – (24.5 ± 6.0) | – (13.0 ± 5.0) | – |
| Na | – (40.0 ± 5.0) | – (38.5 ± 6.0) | – (19.0 ± 5.0) | – (17.0 ± 6.0) |
| K | – (60.0 ± 5.0) | – | – (31.0 ± 5.0) | – |
| Rb | – (57.0 ± 5.5) | – (52.5 ± 6.0) | – (38.0 ± 5.5) | – |
| Cs | – (50.5 ± 5.5) | – (55.5 ± 6.0) | – (47.0 ± 5.5) | – (51.5 ± 7.0) |
| Mg | (26.0 ± 7.0) | – | – | – |
| Ca | (26.5 ± 7.0) | (30.5 ± 8.0) | – | – |
| Sr | (7.5 ± 7.0) | – | – | – |
| Ba | (16.0 ± 7.0) | – | – | – |

Note: Some of our uncertainty estimates in the selected molar entropies from low-temperature calorimetry may differ slightly from those reported by the authors.

To conclude: it is highly desirable to have new experimental data from calorimetry and solubility experiments, based on accurate elemental and water analyses in order to assess the conclusions drawn in the present review on the thermodynamics of uranyl borate systems.

## 9.9 Vanadium compounds

In previous NEA reviews, [1992GRE/FUG] and [2003GUI/FAN], there were no thermodynamic data on vanadium uranium compounds and complexes, only a list of minerals in Section 9.12.3 of [2003GUI/FAN]. Since then a number of publications have appeared dealing with the thermodynamics of uranylpyrovanadate, $(UO_2)_2(V_2O_7)(cr)$, uranovanadic acid, $H[UO_2VO_4]\cdot 2H_2O(cr)$, uranylvanadates, $M^k[UO_2VO_4]_k\cdot nH_2O(cr)$, where M is alkali, alkaline-earth or d-transition element, studies that are discussed in the following. These studies comprise determination of enthalpies of formation, $\Delta_f H_m^o$, based on dissolution calorimetry, where the thermodynamic cycles used are described in Appendix A, low-temperature calorimetry determination of isobaric heat capacities, $C_{p,m}^o$, standard entropies, $S_m^o(298.15\,K)$ and entropies of formation, $\Delta_f S_m^o$ and calculation of the Gibbs energy of formation based on these. In addition, Gibbs energies of reaction, $\Delta_r G_m^o$, have also been determined based on solubility studies. Thermodynamic data based on both calorimetry and solubility experiments allow a check on their consistency, a fact that has been used by the present review when validating experimental data. Calorimetric data are very sensitive to variations in the stoichiometry

of the samples, in particular to their water content and accurate analytical data are therefore necessary. Unfortunately this information is not always reported in the publications that we have evaluated. The $M[UO_2VO_4]\cdot nH_2O$(cr) and $M[UO_2VO_4]_2\cdot nH_2O$(cr) compounds have layer structures ([2010BUR/REY] and [2012SUL/SOM]) that result in a variable water content, a necessary information to obtain reliable thermodynamic data. The consistency between calorimetric and solubility data is generally not satisfactory. Dissolution calorimetry were performed in HF, HCl or $HNO_3$ solutions and it is then necessary to take the relative partial molar enthalpy, $L_1$ into account, which has not been done in the published studies, but the present review has made this correction based on the data in [1965PAR] and selected the thermodynamic data based on calorimetry.

The solubility experiments have in general been made in acid solutions and the analysis of these data requires information of the speciation of the reaction products. As discussed in the following, most of the solubility reactions studied by the Chernorukov-Karyakin group, [1998KAR/CHE], [2001CHE/SUL], [2001CHE/SUL2], [2003CHE/SUL4], [2013NIP/CHE], have been described by Reaction (9.107), as exemplified by $M[UO_2VO_4]_2\cdot nH_2O$(cr) but in acid solutions Reaction (9.108) is the one that describes the dissolution:

$$M[UO_2VO_4]_2\cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_4^{3-} + nH_2O(l) \quad (9.107)$$

$$M[UO_2VO_4]_2\cdot nH_2O(cr) + 8H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_2^{+} + (n+4)H_2O(l) \quad (9.108)$$

When analysing measured solubilities using Reaction (9.107) it is necessary to use auxiliary data for the protonation of $VO_4^{3-}$ and estimates of the activity coefficients of all reaction products in order to calculate the solubility constant at zero ionic strength. This method is not the most accurate one, and the present review has therefore based the analysis on Reaction (9.108) where the solubility constants at the given ionic strength were calculated from the measured total concentrations of the reaction products and extrapolated to zero ionic strength using only the Debye-Hückel term of SIT because of the low ionic strength in the experiments, around 0.1 M.

Most of the thermodynamic data on uranylvanadates are based on experimental studies from the Nizhny Novgorod group of Chernorukov, Karyakin *et al.* For calculation of enthalpies, entropies and Gibbs energies of formation from the primary experimental data, the authors used auxiliary data for vanadium and vanadium compounds that were obtained from the Glushko tables, *Thermodynamic Properties of Individual Substances*, ten volumes from 1965-1982, Nauka, Moscow (in Russian), all of which have not been reviewed by NEA. The present review has recalculated the published data using NEA selected values and data from the most recent edition of the Glushko tables [1982GLU/GUR] and these are listed in Chapter 14.

The uncertainty in the published enthalpies and Gibbs energies of formation are often surprisingly large, in particular when compared to the errors in the enthalpies of

reaction and this is presumably related to uncertainties in the auxiliary data from the early editions of the Glushko tables. This review has re-evaluated these data and reports smaller uncertainties. A problem for the present review is that nearly all data were obtained in the same laboratory and it is highly desirable to have these data confirmed by new experiments.

There are several methods to test the consistency of thermodynamic data and discussions of their use are found in the Appendix A entries:

- By comparing Gibbs energies of formation from calorimetric and solubility data.
- By looking at the systematic variation in the molar entropy among iso-structural compounds such as $M[UO_2VO_4]\cdot nH_2O(cr)$ and $M[UO_2VO_4]_2\cdot nH_2O(cr)$ where M is an alkali- or an alkaline-earth-ion.
- In hydrated compounds one can estimate the entropy contribution per water using the Latimer method, described in Appendix D; this value, 44.7 $J\cdot K^{-1}\cdot mol^{-1}$, can be compared with experimental data.

### 9.9.1 Alkali metal vanadates $M[UO_2VO_4]\cdot nH_2O(cr)$

The $M[UO_2VO_4]\cdot nH_2O(cr)$ compounds have layer structures composed of "$UO_2O_5$"-units (uranyl-ions with five coordinated oxygen in the equatorial plane) and "$V_2O_8$"-units composed of two edge-sharing $VO_4$-tetrahedra ([2012SUL/SOM], [1992DIC/STU]); these structures are different from the ones of the corresponding phosphate compounds. As the anhydrous $Na[UO_2VO_4](cr)$, $K[UO_2VO_4](cr)$ and $Cs[UO_2VO_4](cr)$ are isostructural, it is reasonable to assume that this is also the case for the Rb compound, even if no structure data is available. The $M^+$ counter-ions are located between the uranyl-vanadate layers, which also can accommodate crystal water as shown in the Na and K structures, *cf.* structures of $Na[UO_2VO_4]\cdot nH_2O(cr)$ in [2012SUL/SOM].

The thermodynamics of the alkali metal uranylvanadates $M[UO_2VO_4]\cdot nH_2O(cr)$ has been studied by Karyakin, Chernorukov *et al.* ([1992KAR/CHE], [1995KAR/CHE2], [1996KAR/CHE2], [1996KAR/CHE3], [1998KAR/CHE5], [2000KAR/CHE2], [2001CHE/SUL], [2001KAR/CHE], [2003CHE/SUL4]). The enthalpies of formation for $M[UO_2VO_4](cr)$, M = Na, K, Rb, Cs have been studied by dissolution calorimetry and the selected values are given in Table 9-82. Karyakin *et al.* [1998KAR/CHE5] report low-temperature heat capacity measurements and thermodynamic data for $Na[UO_2VO_4](cr)$ and $Na[UO_2VO_4]\cdot 2H_2O(cr)$ to obtain the enthalpy of Reaction (9.109). This review considers the data from this study the most precise ones and they have therefore been selected:

$$Na[UO_2VO_4]\cdot 2H_2O(cr) \rightleftharpoons Na[UO_2VO_4](cr) + 2H_2O(l) \qquad (9.109)$$

Isobaric molar heat capacities, molar entropies and entropies of formation have been determined by adiabatic calorimetry and are listed in Table 9-82, where we also have included the Gibbs energies of formation from calorimetric data obtained using the Gibbs-

Helmholtz equation and the corresponding quantity obtained from solubility experiments. The data in Table 9-82 demonstrate that the thermodynamic data from calorimetry are not consistent with the ones from solubility experiments. As the latter are based on measurements at a single pH, we have selected those obtained by calorimetry.

The range of existence of the crystal hydrates of $Na[UO_2VO_4]\cdot xH_2O(cr)$ and the enthalpy of dehydration are reported, based on isopiestic and static vapor pressure data [2000KAR/CHE2] of the Reactions (9.110) and (9.111). The enthalpy of reaction was calculated from the temperature dependence of the equilibrium constant, $K = p(H_2O)$. The following values have been obtained:

$$Na[UO_2VO_4]\cdot 2H_2O(cr) \rightleftharpoons Na[UO_2VO_4]\cdot H_2O(cr) + H_2O(g) \quad (9.110)$$

$$\Delta_r H_m\,(9.110) = (53.2 \pm 0.4)\ kJ\cdot mol^{-1}$$

$$Na[UO_2VO_4]\cdot H_2O(cr) \rightleftharpoons Na[UO_2VO_4](cr) + H_2O(g) \quad (9.111)$$

$$\Delta_r H_m\,(9.111) = (58.1 \pm 0.8)\ kJ\cdot mol^{-1}$$

These values are used, as outlined in Appendix A review of [2000KAR/CHE2], to calculate $\Delta_f H^\circ_m$ ($Na[UO_2VO_4\cdot H_2O]$, cr) = **– (2734.1 ± 3.3)** $kJ\cdot mol^{-1}$, which is included among the selected values.

The structures of these phases have later been studied by single-crystal X-ray diffraction by Suleimanov *et al.* [2012SUL/SOM], a study that includes a detailed discussion of a structural mechanism for transformation between the different phases.

Karyakin *et al.* have used solubility data to determine solubility constants and Gibbs energies of reaction/formation ([2001CHE/SUL] and [2003CHE/SUL4], with a review in [2001KAR/CHE]). Solubility data in contact with water for $M[UO_2VO_4]\cdot nH_2O(cr)$, M = H, Na, K, Rb, Cs and Tl, Reaction (9.112), have been reported in [2001CHE/SUL]. This review has only considered the data at pH ≈ 1.4 ($p[H^+] \approx 1.1$) where the dissolution is congruent and the results of these are shown in Table 9-83; the ionic strength is approx. 0.1 M.

$$M[UO_2VO_4]\cdot nH_2O(cr) + 4H^+ \rightleftharpoons M^+ + UO_2^{2+} + VO_2^+ + (2+n)H_2O(l) \quad (9.112)$$

Table 9-82: Thermodynamic data for $Li[UO_2VO_4](cr)$, $Na[UO_2VO_4](cr)$, $Na[UO_2VO_4]\cdot H_2O(cr)$, $Na[UO_2VO_4]\cdot 2H_2O(cr)$, $K[UO_2VO_4](cr)$, $K_2[UO_2VO_4]_2\cdot 3H_2O(cr)$, $Rb[UO_2VO_4](cr)$ and $Cs[UO_2VO_4](cr)$ from [1982ZHI/SHM], [1992KAR/CHE], [1995KAR/CHE2], [1996KAR/CHE2], [1996KAR/CHE3], [1998KAR/CHE5] and [2000KAR/CHE2], recalculated by this review as detailed in Appendix A. Data obtained from solubility experiments are denoted as (a) and are given for information only except for $K_2[UO_2VO_4]_2\cdot 3H_2O(cr)$.

| Compound | $C^o_{p,m}$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $S^o_m$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S^o_m$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f H^o_m$ (298.15 K) /kJ mol$^{-1}$ | $-\Delta_f G^o_m$ (298.15 K) /kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| $Li[UO_2VO_4](cr)$ | – | – | – | **(2398.3 ± 3.5)** | – |
| $Na[UO_2VO_4](cr)$ | **(180.2 ± 1.5)** | **(209.1 ± 3.0)** | **– (536.526 ± 3.028)** | **(2430.3 ± 4.2)** | **(2270.335 ± 4.296)** |
| $Na[UO_2VO_4]\cdot H_2O(cr)$ | – | – | – | **(2734.1 ± 3.3)** | (2507.475 ± 3.623)[(a)] |
| $Na[UO_2VO_4]\cdot 2H_2O(cr)$ | **(267.7 ± 1.5)** | **(298.4 ± 3.0)** | **– (913.738 ± 3.028)** | **(3032.9 ± 5.1)** | **(2760.469 ± 5.179)**<br>(2744.615 ± 5.179)[(a)] |
| $K[UO_2VO_4](cr)$ | **(177.0 ± 1.0)** | **(216.4 ± 0.9)** | **– (542.606 ± 0.990)** | **(2446.7 ± 6.0)** | **(2284.922 ± 6.007)**<br>(2308.982 ± 3.260)[(a)] |
| $K_2[UO_2VO_4]_2\cdot 3H_2O(cr)$ | – | – | – | – | **(5316.941 ± 5.188)**[(a)] |
| $Rb[UO_2VO_4](cr)$ | **(181.9 ± 0.9)** | **(224.0 ± 0.9)** | **– (547.106 ± 1.015)** | **(2430.8 ± 1.9)** | **(2267.680 ± 1.924)**<br>(2319.214 ± 3.261)[(a)] |
| $Cs[UO_2VO_4](cr)$ | **(179.8 ± 0.9)** | **(226.7 ± 1.0)** | **– (552.856 ± 1.136)** | **(2436.4 ± 2.8)** | **(2271.566 ± 2.820)**<br>(2337.211 ± 3.301)[(a)] |

(a) From solubility data at the lowest pH values, ≈ 1.2 – 1.4 (see Appendix A).

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Table 9-83: Solubility and recalculated solubility products, $\log_{10}{}^{*}K_s^o$, for $M[UO_2VO_4](cr)$, M = K, Rb, Cs at $p[H^+] \approx 1$, using data from [2001CHE/SUL], [2003CHE/SUL4] and [1982ZHI/SHM], recalculated by this review.

| Compound | $p[H^+]$ | $\log S$ | $\log_{10}{}^{*}K_s^o$ /M$^{-1}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $K[UO_2VO_4](cr)$ | 1.19 | – 2.06 | – (1.64 ± 0.40) | (9.361 ± 2.283) |
| $K_2[UO_2VO_4]_2\cdot 3H_2O(cr)$ | 2.15 | – 3.02 | **– (1.10 ± 0.40)**[(a)] | **(6.279 ± 2.283)**[(a)] |
| $Rb[UO_2VO_4](cr)$ | 1.07 | – 2.41 | – (3.17 ± 0.40) | (18.094 ± 2.283) |
| $Cs[UO_4VO_4](cr)$ | 1.02 | – 2.96 | – (5.02 ± 0.40) | (28.654 ± 2.283) |

(a) These values correspond to the reaction:

$$K_2(UO_2)_2(VO_4)_2\cdot 3H_2O(cr) + 8H^+ \rightleftharpoons 2K^+ + 2UO_2^{2+} + 2VO_2^+ + 7H_2O(l)$$

The present review notes that the Gibbs energy of formation obtained from solubility and calorimetric data do not agree with each other (Table 9-82). As discussed before, the present review only accepts data from calorimetry, except for the case of $K_2[UO_2VO_4]_2\cdot 3H_2O(cr)$.

Solubility data for $M[UO_2VO_4]\cdot nH_2O(cr)$, M = H, Na, K, Rb, Cs compounds are also discussed in a review article, [2001KAR/CHE] and in [2001CHE/SUL] and [2003CHE/SUL4], but the solubility data seem to be the same as in [2001CHE/SUL].

Chernorukov *et al.* have also made calculations of the solubility of the alkali uranylvanadates in aqueous solutions containing chloride, sulfate and carbonate, but these provide no new thermodynamic information.

Zhil'tsova *et al.* [1982ZHI/SHM] have made a careful review of previous studies of the thermodynamics of carnotite, $K_2[UO_2VO_4]_2\cdot 3H_2O(cr)$ pointing out several flaws in the experimental methods used there. They propose that the following reaction takes place and report $\log_{10}{}^{*}K_s^o(9.113) = -9.52$.

$$K_2[UO_2VO_4]_2\cdot 3H_2O(cr) + 4H^+ \rightleftharpoons 2K^+ + 2UO_2^{2+} + 2H_2VO_4^- + 3H_2O(l) \qquad (9.113)$$

However at pH = 2.15, the predominant form of vanadium is $VO_2^+$ based on the selected protonation constants of $VO_2^+$, and the reaction taking place is accordingly:

$$K_2[UO_2VO_4]_2\cdot 3H_2O(cr) + 8H^+ \rightleftharpoons 2K^+ + 2UO_2^{2+} + 2VO_2^+ + 7H_2O(l) \qquad (9.114)$$

The recalculation of the equilibrium constant considering Reaction (9.114) results in $\log_{10}{}^{*}K_s^o$ (9.114) = **– (1.10 ± 0.40)**, where the uncertainty is determined by the pH measurements, assumed to be ± 0.05 pH units. The Gibbs energy of reaction is $\Delta_r G_m^o$ = **(6.279 ± 2.283)** kJ·mol$^{-1}$. Using the NEA selected Gibbs energies of formation, $\Delta_f G_m^o(UO_2^{2+})$, $\Delta_f G_m^o(K^+)$ and $\Delta_f G_m^o(VO_2^+)$, we obtain, $\Delta_f G_m^o(K_2(UO_2)_2(VO_4)_2\cdot 3H_2O, cr)$ = – (6.279 ± 2.283) – 2{(952.551 ± 1.747) + (590.280 ± 1.530) + (282.510 ± 0.116)} – 7(237.14 ± 0.04) = **– (5316.941 ± 5.188)** kJ·mol$^{-1}$. This review notes that our recalculated value is significantly different from the value – 5280 kJ·mol$^{-1}$ reported by Langmuir, [1978LAN]. From the discussion in the previous section and the corresponding Appendix A entries, it seems

clear that additional experimental efforts are required in order to obtain improved thermodynamic data.

### 9.9.2 Alkaline-earth uranyl vanadates $M[UO_2VO_4]_2{\cdot}nH_2O$(cr)

The only structure information available refers to the $M[UO_2VO_4]_2{\cdot}5H_2O$(cr) compounds, $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr), [2010BUR/REY] and $Ba_{0.96}Pb_{0.04}[UO_2VO_4]_2{\cdot}5H_2O$(cr), [1986MER], all of which have the same layer type of structures as in $M[UO_2VO_4]{\cdot}nH_2O$(cr), composed of $UO_2O_5$-units (uranyl-ions with five coordinated oxygen in the equatorial plane) and $V_2O_8$-units composed of two edge-sharing $VO_4$-tetrahedra, with water and the $M^{2+}$ counter-ions located between the uranylvanadate layers, which allows for variation in the water content.

The thermodynamics of alkaline-earth uranyl vanadates $M[UO_2VO_4]_2{\cdot}nH_2O$(cr) have been studied using dissolution and low-temperature calorimetry in [1999KAR/CHE2], [1999KAR/CHE3] and [2003KAR/CHE4], and experimental details are discussed in some detail in Appendix A. Preparation, analysis and phase identification are described in [1998CHE/KAR]. A general problem with these studies is that analytical data on the water content of these compounds are often not reported. The analysis of the thermodynamic cycles in [1999KAR/CHE2] requires information on the enthalpies of formation of $Mg_2V_2O_7$(cr), $Mg_3(VO_4)_2$(cr), $Ca(VO_3)_2$(cr) and $Ba_2V_2O_7$(cr). For $Mg_2V_2O_7$(cr) and $Ca(VO_3)_2$(cr) there are high quality calorimetric data, see Chapter 14, which have been accepted by the present review. Data for $Mg_3(VO_4)_2$(cr) and $Ba_2V_2O_7$(cr) are reported in [1988FOT/SLO], but without details and the thermodynamic data based on these values are therefore not accepted and reported for information only, *cf.* Table 14-3. The present review notes the same problem with information on the analytical composition of the hydrated phases as for the alkali uranyl vanadates. The reported isobaric heat capacity, $C^{\circ}_{p,\mathrm{m}}$, and molar entropy, $S^{\circ}_{\mathrm{m}}$, derived from low-temperature calorimetry are reported in Table 9-85. Errors in the water content result in a large uncertainty in the molar entropy and in order to evaluate this effect, we have used entropy estimates based on the Latimer method as outlined in Appendix D. As an example, the difference in entropy between $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr) and $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr), 147 $J{\cdot}K{\cdot}mol^{-1}$, corresponds to an entropy contribution of 49 $J{\cdot}K{\cdot}mol^{-1}$ per water, which is in good agreement with the Latimer estimate, 44.7 $J{\cdot}K{\cdot}mol^{-1}$. We can also note that the molar entropy of $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr) is slightly larger than that of $Mg[UO_2VO_4]_2{\cdot}5H_2O$(cr), as expected for these isostructural compounds. The entropy difference between $Ba[UO_2VO_4]_2{\cdot}4H_2O$(cr) and $Ba[UO_2VO_4]_2$(cr) is 199.5 $J{\cdot}K{\cdot}mol^{-1}$, which corresponds to 50 $J{\cdot}K{\cdot}mol^{-1}$ per water, also in good agreement with the Latimer estimate. For these reasons we have included the thermodynamic data based on calorimetry for the two Ca-compounds and the Ba-compounds among the selected values. There are no entropy data reported for the anhydrous Mg, Ca and Sr compounds.

Table 9-84: Enthalpies of formation at 298.15 K for $M[UO_2VO_4]_2$(cr) compounds and their crystal hydrates reported in [2003KAR/CHE4] and recalculated by this review. The values in bold have been selected by this review. The enthalpies of formation of the Mg- and Ba- phases are given for information only.

| Compound | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | Compound | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2VO_4]_2$(cr) | – (4678.800 ± 10.300) | $Mg[UO_2VO_4]_2 \cdot 5H_2O$(cr) | – (6257.200 ± 10.300) |
| $Ca[UO_2VO_4]_2$(cr) | **– (4798.700 ± 7.100)** | $Ca[UO_2VO_4]_2 \cdot 5H_2O$(cr) | **– (6327.300 ± 7.100)** |
| | | $Ca[UO_2VO_4]_2 \cdot 8H_2O$(cr) | **– (7203.700 ± 7.000)** |
| $Sr[UO_2VO_4]_2$(cr) | **– (4858.200 ± 17.800)** | $Sr[UO_2VO_4]_2 \cdot 5H_2O$(cr) | **– (6372.100 ± 16.700)** |
| $Ba[UO_2VO_4]_2$(cr) | – (4914.700 ± 14.700) | $Ba[UO_2VO_4]_2 \cdot 4H_2O$(cr) | – (6102.800 ± 14.700) |

Table 9-85: Isobaric heat capacities, entropies and entropies of formation of uranovanadates $M[UO_2VO_4]_2 \cdot nH_2O$(cr), (M = Mg, Ca, Sr, Ba) from [1999KAR/CHE3] and [2003KAR/CHE4]. These data are included among the selected values.

| Compound | $C_{p,m}^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2VO_4]_2 \cdot 5H_2O$(cr) | **(627.5 ± 3.0)** | **(631.6 ± 4.0)** | **– (1956.002 ± 4.066)** |
| $Ca[UO_2VO_4]_2 \cdot 8H_2O$(cr) | **(777.5 ± 3.0)** | **(786.6 ± 2.0)** | **– (2509.690 ± 2.164)** |
| $Ca[UO_2VO_4]_2 \cdot 5H_2O$(cr) | **(589.6 ± 3.0)** | **(639.4 ± 4.0)** | **– (1957.122 ± 4.084)** |
| $Sr[UO_2VO_4]_2 \cdot 5H_2O$(cr) | **(650.0 ± 3.0)** | **(684.8 ± 4.0)** | **– (1925.832 ± 4.070)** |
| $Ba[UO_2VO_4]_2 \cdot 4H_2O$(cr) | **(564.9 ± 3.0)** | **(631.8 ± 2.0)** | **– (1752.296 ± 2.286)** |
| $Ba[UO_2VO_4]_2$(cr) | **(365.0 ± 3.0)** | **(432.1 ± 4.0)** | **– (1018.972 ± 4.150)** |

Chernorukov *et al.* ([2001CHE/SUL2] and [2003CHE/SUL4]) have determined the solubility of the $M[UO_2VO_4]_2 \cdot nH_2O$(cr) compounds at different pH values and from these data the solubility product, $\log_{10} K^o$, for Reaction (9.115) and their Gibbs energy of formation. As discussed in the previous section and in Appendix A, this review prefers to analyse the solubility reactions in terms of Reaction (9.116), using the solubility constant $\log_{10}{}^* K_s^o$ (9.116) to calculate the Gibbs energy of formation; these data are given in Table 9-86 and Table 9-87. Because of the low pH there is no need to take hydrolysis reactions into account.

$$M[UO_2VO_4]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_4^{3-} + nH_2O(l) \quad (9.115)$$

$$M[UO_2VO_4]_2 \cdot nH_2O(cr) + 8H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_2^+ + (n+4)H_2O(l) \quad (9.116)$$

Table 9-86: Solubility constants, $\log_{10}{}^* K_s^o$ (9.116) and Gibbs energies of reaction for $M^{II}[UO_2VO]_2 \cdot nH_2O$(cr), ($M^{II}$ = Mg, Ca, Sr, Ba) at 298.15 K. As the composition of the compounds after equilibration in water is not known, we have assumed that the reported values refer to "water-saturated" phases and they are given for information only.

| Compound | $\log_{10}{}^* K_s^o$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| $Mg[UO_2VO_4]_2 \cdot 5H_2O$(cr) | – (1.87 ± 0.40) | (10.674 ± 2.283) |
| $Ca[UO_2VO_4]_2 \cdot 8H_2O$(cr) | – (4.22 ± 0.40) | (24.088 ± 2.283) |
| $Sr[UO_2VO_4]_2 \cdot 5H_2O$(cr) | – (3.98 ± 0.40) | (22.718 ± 2.283) |
| $Ba[UO_2VO_4]_2 \cdot 5H_2O$(cr) | – (3.94 ± 0.40) | (22.490 ± 2.283) |

The solubility of a synthetic tyamyunite, $Ca[UO_2VO_4]_2\cdot(5\text{-}8)H_2O(cr)$ has been determined by Zhil'tsova *et al.* [1989ZHI/PER] that report, $\Delta_f G^o_m = -(4557.2 \pm 0.5)$ kJ·mol$^{-1}$ based on the reaction:

$$Ca[UO_2VO_4]_2(cr) \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 2VO_4^{3-} \quad (9.117)$$

For reasons detailed in the Appendix A review, we have not accepted this value.

The thermodynamic data for the $M[UO_2VO_4]_2\cdot nH_2O(cr)$, M = Mg, Ca, Sr, Ba, compounds are listed in Table 9-87; these data are all new and refer to chemically well characterised samples, with water contents in excellent agreement with the stoichiometric formulae. All data except the ones for the enthalpy of formation of Mg- and Ba-compounds (for reasons discussed in Appendix A) have been included among the selected values. This review also notes that the molar entropies of the hydrates are consistent with the Latimer estimates.

### 9.9.3 Thermodynamics of uranyl vanadates $M[UO_2VO_4]_2\cdot nH_2O(cr)$, M = Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb.

The synthesis and structure of $M[UO_2VO_4]_2\cdot nH_2O(cr)$ compounds, M = Mn, Fe, Co, Ni, Cu and Zn have been described in [1998CHE/SUL] and [1999CHE/SUL]. The compounds are properly characterised and their structures give important information on the location of the crystal water, some of which are weakly bonded. The structure of $Ni[UO_2VO_4]_2\cdot 4H_2O(cr)$ has been studied by Borene and Cesbron [1970BOR/CES] and this paper is cited in [1999CHE/SUL]. It is a layer structure composed of layers of $(UO_2VO_4)_\infty$ with crystal water located in between. The layer is composed of linked "$UO_7$" and "$V_2O_8$" units, the latter two corner sharing vanadate tetrahedra; the other $M[UO_2VO_4]_2\cdot nH_2O(cr)$ compounds, with the exception of the copper one, seem to be isostructural with the Ni-compound as judged by their X-ray powder patterns. The M(II) counter-ions are located between the layers together with water of crystallisation, some of which are coordinated to M(II) and the rest weakly bonded, similar to that in zeolites.

Table 9-87: Thermodynamic data from calorimetry and solubility experiments for the $M[UO_2VO_4]_2$(cr) and $M[UO_2VO_4]_2{\cdot}nH_2O$(cr) compounds, M = Mg, Ca, Sr, Ba at 298.15 K. All data from calorimetry, except for the enthalpy of formation of Mg- and Ba-compounds, have been accepted by this review.

| Compound | $\Delta_f H^\circ_m$ /kJ·mol$^{-1}$ | $C^\circ_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ | $S^\circ_m$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S^\circ_m$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G^\circ_m$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Mg[UO_2VO_4]_2$(cr) | – (4678.800 ± 10.300) | | | | |
| $Mg[UO_2VO_4]_2{\cdot}5H_2O$(cr) | – (6257.200 ± 10.300) | **(627.5 ± 3.0)** | **(631.6 ± 4.0)** | **– (1956.002 ± 4.066)** | – (5674.018 ± 10.371)<br>– (5685.971 ± 5.358)[a] |
| $Ca[UO_2VO_4]_2$(cr) | **– (4798.700 ± 7.100)** | | | | |
| $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr) | **– (7203.700 ± 7.000)** | **(777.5 ± 3.0)** | **(786.6 ± 2.0)** | **– (2509.690 ± 2.164)** | **– (6455.436 ± 7.030)**<br>– (6508.236 ± 5.304)[a] |
| $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr) | **– (6327.300 ± 7.100)** | **(589.6 ± 3.0)** | **(639.4 ± 4.0)** | **– (1957.122 ± 4.084)** | **– (5743.784 ± 7.204)** |
| $Sr[UO_2VO_4]_2$(cr) | **– (4858.200 ± 17.800)** | | | | |
| $Sr[UO_2VO_4]_2{\cdot}5H_2O$(cr) | **– (6372.100 ± 16.700)** | **(650.0 ± 3.0)** | **(684.8 ± 4.0)** | **– (1925.832 ± 4.070)** | **– (5797.913 ± 16.744)**<br>– (5806.504 ± 5.247)[a] |
| $Ba[UO_2VO_4]_2$(cr) | – (4914.700 ± 14.700) | **(365.0 ± 3.0)** | **(432.1 ± 4.0)** | **– (1018.972 ± 4.150)** | – (4610.893 ± 14.752) |
| $Ba[UO_2VO_4]_2{\cdot}4H_2O$(cr) | – (6102.800 ± 14.700) | **(564.9 ± 3.0)** | **(631.8 ± 2.0)** | **– (1752.296 ± 2.286)** | – (5580.353 ± 14.716) |
| $Ba[UO_2VO_4]_2{\cdot}5H_2O$(cr) | – | – | – | – | – (5800.068 ± 5.795)[a] |

(a) Data from solubility experiments.



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The enthalpies of formation of $M[UO_2VO_4]_2 \cdot nH_2O$(cr), M = Mn, Fe, Co, Ni, Cu, Zn and Pb, have been determined in [2002CHE/KAR2] and [2004SUL/CHE] using dissolution calorimetry and are reported in Table 9-88. Chernorukov *et al.* [2002CHE/KAR2] have also determined the isobaric heat capacity and the entropy for $Co[UO_2VO_4]_2 \cdot 4H_2O$(cr), using low-temperature calorimetry and report $C^{o}_{p,m}$ (298.15 K) = (655.2 ± 0.4) $J \cdot K^{-1} \cdot mol^{-1}$ and $S^{o}_{m}$ (298.15 K) = (680.7 ± 1.8) $J \cdot K^{-1} \cdot mol^{-1}$. Assuming additivity of the entropy contributions from the uranyl vanadate framework, $S^{o}_{m}([UO_2VO_4]^{2-}_{2})$, the interlayer $M^{2+}$ and water, $S^{o}_{m}(M^{2+})$ and $S^{o}_{m}(H_2O)$, the entropy of the $M[UO_2VO_4] \cdot nH_2O$(cr) compounds was calculated as follows using the cobalt compound for calibration:

$$S^{o}_{m}([UO_2VO_4]^{2-}_{2}) = S^{o}_{m}(Co[UO_2VO_4]_2 \cdot 4H_2O) - S^{o}_{m}(Co^{2+}) - 4 \times 47.8 \ J \cdot K^{-1} \cdot mol^{-1} \quad (9.118)$$

where 47.8 is the entropy contribution per water, estimated by the Latimer method. The entropy of $M[UO_4VO_4] \cdot nH_2O$(cr) is then

$$S^{o}_{m}(M[UO_2VO_4]_2 \cdot nH_2O, \text{ cr}) = S^{o}_{m}([UO_2VO_4]^{2-}_{2}) + S^{o}_{m}(M^{2+}) + n \times 47.8 \ J \cdot K^{-1} \cdot mol^{-1} \quad (9.119)$$

and these values are reported in Table 9-88. The Gibbs energy of formation has been calculated using the Gibbs-Helmholtz equation from the enthalpy of formation and the estimated molar entropy and entropy of formation. No thermodynamic properties are included in the selected data, all data are given for information only.

Chernorukov *et al.* [2002CHE/KAR2] point out that there are two different types of water in these compounds, one of "zeolitic" type that is weakly bound and the other more strongly coordinated. The difference in Gibbs energy between $Zn(UO_2VO_4)_2 \cdot 4H_2O$(cr) and $Zn(UO_2VO_4)_2 \cdot 5H_2O$(cr) is 234 $kJ \cdot mol^{-1}$; between $Cd(UO_2VO_4)_2 \cdot 4H_2O$(cr) and $Cd(UO_2VO_4)_2 \cdot 8H_2O$(cr), 931 $kJ \cdot mol^{-1}$, corresponding to 233 $kJ \cdot mol^{-1}$ for each water molecule; between $Cu(UO_2VO_4)_2 \cdot 4H_2O$(cr) and $Cu(UO_2VO_4)_2 \cdot 9H_2O$(cr), 1201 $kJ \cdot mol^{-1}$, corresponding to 240 $kJ \cdot mol^{-1}$ for each water. All these values are very close to the Gibbs energy of formation of liquid water, – 237.14 $kJ \cdot mol^{-1}$, indicating weak bonding of the crystal water.

Table 9-88: Thermodynamic data at 298.15 K for the $M^{II}[UO_2VO_4]_2 \cdot nH_2O$(cr) compounds from [2002CHE/KAR2], where the enthalpies of formation have been obtained using dissolution calorimetry and from which the Gibbs energy of formation have been obtained using the estimated entropies of formation and the Gibbs-Helmholtz equation. The Gibbs energies of formation have also been obtained from solubility data in [2001CHE/SUL2] and [2003CHE/SUL4].

| Compound | $-\Delta_f H^{o}_{m}$ /kJ·mol$^{-1}$ | $S^{o\,(a)}_{m}$ /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f S^{o\,(b)}_{m}$ /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f G^{o}_{m}$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $Mn[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5675.4 ± 12.2) | (679.4 ± 15.0) | (1674.286 ± 15.018) | (5176.212 ± 12.996) |
| $Fe[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5508.0 ± 12.3) | (679.9 ± 15.0) | (1668.861 ± 15.018) | (5010.429 ± 13.090) |
| $Co[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5506.9 ± 12.2) | (680.7 ± 10.0) | (1671.016 ± 10.027) | (5008.687 ± 12.561) (5051.776 ± 5.200)[(c)] |

(Continued on next page)

Table 9-88 (continued)

| Compound | $-\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ (a) /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f S_m^o$ (b) /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $Ni[UO_2(VO_4)]_2{\cdot}4H_2O$(cr) | (5508.3 ± 12.1) | (680.3 ± 15.0) | (1671.246 ± 15.019) | (5010.018 ± 12.902) |
| | | | | (5041.569 ± 5.243)(c) |
| $Cu[UO_2(VO_4)]_2{\cdot}4H_2O$(cr) | (5283.9 ± 12.1) | (681.1 ± 15.0) | (1673.726 ± 15.017) | (4784.879 ± 12.902) |
| $Cu[UO_2(VO_4)]_2{\cdot}9H_2O$(cr) | (6769.7 ± 12.1) | (920.1 ± 15.0) | (2601.006 ± 15.018) | (5994.210 ± 12.902) |
| | | | | (6119.824 ± 5.431)(c) |
| $Zn[UO_2(VO_4)]_2{\cdot}4H_2O$(cr) | (5565.7 ± 12.1) | (681.6 ± 15.0) | (1681.706 ± 15.017) | (5064.299 ± 12.902) |
| $Zn[UO_2(VO_4)]_2{\cdot}5H_2O$(cr) | (5855.4 ± 12.1 ) | (729.4 ± 15.0) | (1867.162 ± 15.017) | (5298.706 ± 12.902) |
| $Cd[UO_2(VO_4)]_2{\cdot}4H_2O$(cr) | (5479.4 ± 12.1) | (690.3 ± 15.0) | (1683.176 ± 15.018) | (4977.561 ± 12.902) |
| $Cd[UO_2(VO_4)]_2{\cdot}8H_2O$(cr) | (6632.7 ± 12.1) | (881.5 ± 15.0) | (2425.000 ± 15.018) | (5909.686 ± 12.902) |
| $Mn[UO_2(VO_4)]_2$(cr) | (4414.0 ± 12.3) | (488.2 ± 15.0) | (932.462 ± 15.018) | (4135.986 ± 13.090) |
| $Fe[UO_2(VO_4)_2]_2$(cr) | (4258.7 ± 12.1) | (488.7 ± 15.0) | (927.037 ± 15.018) | (3982.304 ± 12.902) |
| $Co[UO_2(VO_4)]_2$(cr) | (4258.2 ± 12.2) | (489.5 ± 15.0) | (929.192 ± 15.018) | (3981.161 ± 12.996) |
| $Ni[UO_2(VO_4)]_2$(cr) | (4655.6 ± 12.1) | (489.1 ± 15.0) | (929.422 ± 15.019) | (4378.493 ± 12.902) |
| $Cu[UO_2(VO_4)]_2$(cr) | (4035.5 ± 12.1) | (489.9 ± 15.0) | (931.902 ± 15.017) | (3757.653 ± 12.902) |
| $Zn[UO_2(VO_4)]_2$(cr) | (4318.0 ± 12.1) | (490.4 ± 15.0) | (939.882 ± 15.017) | (4037.774 ± 12.902) |
| $Cd[UO_2(VO_4)]_2$(cr) | (4254.1 ± 13.3) | (499.1 ± 15.0) | (941.352 ± 15.018) | (3973.436 ± 14.034) |

(a) The uncertainty of estimated $S_m^o$ is ± 15 J·K$^{-1}$·mol$^{-1}$.

(b) The used values of $S_m^o$ (Mn, cr) = (32.01 ± 0.13) J·K$^{-1}$·mol$^{-1}$ [1974GLU/MED] and of $S_m^o$ (Co, cr) = (30.04 ± 0.17) J·K$^{-1}$·mol$^{-1}$ [1972GLU/MED], other values are from the NEA database.

(c) Denotes data recalculated in this review from solubility experiments in [2001CHE/SUL2] and [2003CHE/SUL4].

The solubilities of $M[UO_2VO_4]_2{\cdot}nH_2O$(cr), for M = Co, $n = 4$; Ni, $n = 4$; Cu, $n = 9$; Pb, $n = 5$, have been studied by Chernorukov *et al.* ([2001CHE/SUL2], [2003CHE/SUL4]) and used to calculate the solubility product for Reaction (9.120) and the corresponding Gibbs energy of formation. The solubility data have been re-analysed by this review using Reaction (9.121) that directly describes the dissolution reaction and we have preferred our recalculated values in Table 9-89, in which our estimated uncertainties are based on the uncertainty in the solubility, *cf.* Appendix A discussion. The agreement between Gibbs energy of formation between calorimetry and solubility data is poor, and much larger than the combined very large uncertainty ranges. For this reason the thermodynamic data are reported for information only.

$$M[UO_2VO_4]_2{\cdot}nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_4^{3-} + nH_2O(l) \quad (9.120)$$

$$M[UO_2VO_4]_2{\cdot}nH_2O(cr) + 8H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_2^+ + (n+4)H_2O(l) \quad (9.121)$$

As stated in the section on alkali uranyl vanadates it is highly desirable to have additional experimental calorimetric data for the various hydrates, based on well characterised samples and performed in additional laboratories.

Table 9-89: Solubility constants, $\log_{10} {}^{*}K_s^o$, Gibbs energy of reaction and formation for $M^k[UO_2VO_4]_k \cdot nH_2O$(cr) compounds at 298.15 K, $M^k$ = Co, Ni, Cu, Pb recalculated from [2001CHE/SUL2]. Calorimetry data are from [2002CHE/KAR2], recalculated in this review. These values are reported for information only.

| Compound | $\log_{10} {}^{*}K_s^o$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ solubility | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ calorimetry |
|---|---|---|---|---|
| $Co[UO_2VO_4]_2 \cdot 4H_2O$(cr) | – (2.69 ± 0.40) | (15.354 ± 2.283) | – (5051.776 ± 5.200) | – (5008.687 ± 12.561) |
| $Ni[UO_2VO_4]_2 \cdot 4H_2O$(cr) | – (2.28 ± 0.40) | (13.014 ± 2.283) | – (5041.569 ± 5.243) | – (5010.018 ± 12.902) |
| $Cu[UO_2VO_4]_2 \cdot 9H_2O$(cr) | – (2.87 ± 0.40) | (16.382 ± 2.283) | – (6119.824 ± 5.431) | – (5994.210 ± 12.902) |
| $Pb[UO_2VO_4]_2 \cdot 5H_2O$(cr) | – (3.79 ± 0.40) | (21.633 ± 2.283) | – (5265.793 ± 5.204) | – (5226 ± 6)[(a)] |

(a) Value from [2004SUL/CHE]

## 9.9.4 Uranyl pyrovanadate, $(UO_2)_2(V_2O_7)$(cr) and uranovanadic acid, $H[UO_2VO_4] \cdot 2H_2O$(cr)

The structure of uranyl pyrovanadate, $(UO_2)_2(V_2O_7)$(cr) has been determined by single crystal X-ray diffraction by Chippindale *et al.* [1995CHI/DIC]. Karyakin *et al.* [2000KAR/CHE3] have made a calorimetric study of the thermodynamic properties of this compound and uranovanadic acid, $H[UO_2VO_4] \cdot 2H_2O$(cr), where the enthalpy of formation has been determined by dissolution calorimetry and the isobaric heat capacity and molar entropy by low temperature calorimetry between 5 and 300 K and extrapolation to $T = 0$ K using the relation $C_p(T) = 1.438 \times 10^{-3} T^3$ J·K$^{-1}$·mol$^{-1}$. This review recalculated these data using the NEA selected values and accepted values of thermodynamic functions of vanadium compounds in Chapter 14. The Gibbs energy of formation is obtained from the enthalpy and entropy of formation of the two compounds. The following thermodynamic data, all new, have been included among the selected values:

$\Delta_f H_m^o ((UO_2)_2(V_2O_7), cr, 298.15\ K) = \mathbf{-\ (3939.200 \pm 6.100)}$ kJ·mol$^{-1}$;

$\Delta_f S_m^o ((UO_2)_2(V_2O_7), cr, 298.15\ K) = \mathbf{-\ (930.076 \pm 2.221)}$ J·K$^{-1}$·mol$^{-1}$;

$\Delta_f G_m^o ((UO_2)_2(V_2O_7), cr, 298.15\ K) = \mathbf{-\ (3661.898 \pm 6.136)}$ kJ·mol$^{-1}$;

$C_{p,m}^o ((UO_2)_2(V_2O_7), cr, 298.15\ K) = \mathbf{(296.700 \pm 2.100)}$ J·K$^{-1}$·mol$^{-1}$;

$S_m^o ((UO_2)_2(V_2O_7), cr, 298.15\ K) = \mathbf{(356.000 \pm 2.100)}$ J·K$^{-1}$·mol$^{-1}$;

$\Delta_f H_m^o (H(UO_2VO_4) \cdot 2H_2O, cr, 298.15\ K) = \mathbf{-\ (2757.600 \pm 3.200)}$ kJ·mol$^{-1}$;

$\Delta_f S_m^o (H(UO_2VO_4) \cdot 2H_2O, cr, 298.15\ K) = \mathbf{-\ (930.778 \pm 2.131)}$ J·K$^{-1}$·mol$^{-1}$;

$\Delta_f G_m^o (H(UO_2VO_4) \cdot 2H_2O, cr, 298.15\ K) = \mathbf{-\ (2480.089 \pm 3.262)}$ kJ·mol$^{-1}$;

$C_{p,m}^o (H(UO_2VO_4) \cdot 2H_2O, cr, 298.15\ K) = \mathbf{(324.900 \pm 1.500)}$ J·K$^{-1}$·mol$^{-1}$;

$S_m^o (H(UO_2VO_4) \cdot 2H_2O, cr, 298.15\ K) = \mathbf{(295.400 \pm 2.100)}$ J·K$^{-1}$·mol$^{-1}$.

### 9.9.5 Uranyl orthovanadate $(UO_2)_3(VO_4)_3$(cr)

Tokumaya *et al.* [2012TOK/KIM] and Nipruk *et al.* [2013NIP/CHE] have studied the phase stability of $(UO_2)_3(VO_4)_2 \cdot 4H_2O$(cr) in aqueous solution between pH 1 and 14 by measuring the equilibrium concentrations of U and V. The data in the pH range 2.39-5.50 from [2012TOK/KIM] have been used to calculate the solubility product, $\log_{10} K_s = -(54.8 \pm 0.3)$ for Reaction (9.122), this value is given for information only.

$$(UO_2)_3(VO_4)_2 \cdot 4H_2O(cr) \rightleftharpoons 3UO_2^{2+} + 2VO_4^{3-} + 4H_2O(l) \qquad (9.122)$$

Nipruk *et al.* have made a more detailed analysis of the phase transformations taking place and report:

at pH < 2:

$$(UO_2)_3(VO_4)_2 \cdot 4H_2O(cr) + 6H^+ \rightleftharpoons V_2O_5(cr) + 3UO_2^{2+} + 7H_2O(l) \qquad (9.123)$$

at pH > 7:

$$(UO_2)_3(VO_4)_2 \cdot 4H_2O(cr) + 2NaOH + H_2O(l) \rightleftharpoons 2NaUO_2VO_4 \cdot 2H_2O(cr) + UO_3 \cdot 2H_2O(cr) \qquad (9.124)$$

at pH > 12:

$$2(UO_2)_3(VO_4)_2 \cdot 4H_2O(cr) + 18NaOH \rightleftharpoons 3Na_2U_2O_7(cr) + 4Na_3VO_4(cr) + 17H_2O(l) \qquad (9.125)$$

The data in Appendix A for both these studies demonstrates that the dissolution is not congruent and therefore the reported solubility product and the additional thermodynamic data are not accepted.

The stability of the uranyl orthovanadate at different pH was studied by Nipruk *et al.,* [2013NIP/CHE] using solubility experiments and analysis of the total concentrations of U and V. The solubility data presented do not give clear indication for congruent dissolution in the investigated pH range 0.6 to 14 and are for this reason not accepted by the present review.

### 9.9.6 Uranyl niobate and tantalates, $Na[UO_2NbO_4]$(cr) and $Rb[UO_2TaO_4]$(cr)

Standard enthalpies of formation of $Na[UO_2NbO_4]$(cr) and $Rb[UO_2TaO_4]$(cr) have been determined by dissolution calorimetry in 3 M $H_2SO_4$ and 26 M HF and reported in [1995KAR/CHE2]. The enthalpies of formation are based on auxiliary data from the Glushko Tables, Issue 10, Parts 1 and 2, Moscow 1981, in which the value for $UO_3$(s, γ) = – (1228.3 ± 3) kJ·mol$^{-1}$, is significantly different from the CODATA value selected by NEA. Using the CODATA selected value, we recalculate:

$$\Delta_f H_m^o(Na[UO_2NbO_4], cr) = -(2547.9 \pm 5.8) \text{ kJ·mol}^{-1};$$

$$\Delta_f H_m^o(Rb[UO_2TaO_4], cr) = -(2627.5 \pm 7.2) \text{ kJ·mol}^{-1}.$$

The synthesis of the compounds is well described, but there are no details on the chemical analyses. It seems clear that all phases are anhydrous. As the Gibbs energy of formation of all auxiliary data used have not been reviewed by NEA, the enthalpies of formation are given for information only.

### 9.9.7 Mineral thermodynamics

A number of different uranyl vanadate minerals belong to the becquerelite, Ca-autunite, uranophane, tuyamunite, strelkinite and carnotite structure families. Minerals of carnotite type, $K[UO_2VO_4]\cdot nH_2O$(cr), or $K_2[UO_2VO_4]_2\cdot nH_2O$(cr) are one of the most abundant minerals in vanadium-uranium ore deposits and their thermodynamics are very important. Thermodynamic data for $K_2[UO_2VO_4]_2\cdot 3H_2O$(cr), have been reported by Zhil'tsova *et al.* [1982ZHI/SHM] and $Ca[UO_2VO_4]_2$(cr) of tyuamunite type, in [1989ZHI/PER]. Based on the observed solubility products, the authors calculated the corresponding Gibbs energies of reaction and formation:

$\Delta_f G^o_m$ ($K_2[UO_2VO_4]_2\cdot 3H_2O$, cr) = – 5315 kJ·mol$^{-1}$ and $\Delta_f G^o_m$ ($Ca[UO_2VO_4]_2$, s) = – (4557.2 ± 0.5) kJ·mol$^{-1}$.

As seen in the Appendix A reviews, we have made a re-evaluation of the published data that results in $\Delta_f G^o_m$ ($K_2[UO_2VO_4]_2\cdot 3H_2O$, cr) = – (5316.941 ± 5.188) kJ·mol$^{-1}$ and $\Delta_f G^o_m$ ($Ca[UO_2VO_4]_2$, cr) = – (4537.3 ± 5.3) kJ·mol$^{-1}$. Only data for $K_2[UO_2VO_4]_2\cdot 3H_2O$(cr) are selected in this review.

Tokumaya *et al.* [2012TOK/KIM] discuss the solubility of uranium(VI) in equilibrium with different minerals, becquerelite, Ca-autunite, uranophane, tuyamunite, $Ca[UO_2VO_4]_2\cdot 8H_2O$(cr). There are two parts in this study, in the first one the authors have made a modeling study by using available thermodynamic data for soluble complexes and the different solid phases to calculate the concentration of U(VI) as a function of pH, the results indicate that the minimum solubility is obtained around pH 6-7 for all minerals and that the lowest solubility, ≈ $10^{-7}$ M, is obtained if the solubility limiting phases are becquerelite and $Ca[UO_2VO_4]_2\cdot 8H_2O$(cr). In the second part the authors have made a precipitation experiment where solid phases were formed from solutions with initial concentrations of $Ca^{2+}$, U(VI) and V(V) equal to $6 \times 10^{-5}$ M, $2 \times 10^{-5}$ M and $2 \times 10^{-5}$ M, respectively. These experiments were made by varying the pH in the range 3-9 and analysing the concentrations of Ca, U and V. The solubility varied with time at the different values of pH and it is not clear if equilibrium has been attained, or not. The U analyses of the solutions suggest that tuyamunite is the solubility determining solid phase but the vanadium analyses demonstrate that this is only the case in the pH range 3-5. These solubility data provide no new thermodynamic information.

$Na[UO_2VO_4]$(cr) and $Na[UO_2VO_4]\cdot 2H_2O$(cr) are analogues to the mineral strelkinite and the thermodynamic data in [1998KAR/CHE5] can be used also for the mineral.

# 9.10 Uranium molybdate compounds

## 9.10.1 $UO_2MoO_4$(cr)

Thermodynamic data for $UO_2MoO_4$(cr) have been reported by Suleimanov *et al.* [2010SUL/GOL] based on dissolution calorimetry in 10 M HF; low-temperature adiabatic calorimetry was used to determine the isobaric heat capacity, $C^{\circ}_{p,\mathrm{m}}$ and the molar entropy, $S^{\circ}_{\mathrm{m}}$ (298.15 K). The dissolution experiments were made in such a way that they allowed calculation of the enthalpy of Reaction (9.126):

$$K_2Mo_2O_7(\mathrm{cr}) + UO_3(\mathrm{cr}) \rightleftharpoons K_2MoO_4(\mathrm{cr}) + UO_2MoO_4(\mathrm{cr}) \qquad (9.126)$$

The enthalpies of formation $\Delta_f H^{\circ}_{\mathrm{m}}$ ($K_2Mo_2O_7$, cr) = – (2291.6 ± 1.3) kJ·mol$^{-1}$ and $\Delta_f H^{\circ}_{\mathrm{m}}$ ($K_2MoO_4$, cr) = – (1495.5 ± 0.5) kJ·mol$^{-1}$ were taken from the Glushko tables, issue 1-6, 1965-1981 and the enthalpy of formation of $UO_3$(cr) from NEA. Suleimanov *et al.* report the following values: $\Delta_f H^{\circ}_{\mathrm{m}}$ ($UO_2MoO_4$, cr, 298.15 K) = – **(1985.000 ± 8.000)** kJ·mol$^{-1}$; $C^{\circ}_{p,\mathrm{m}}(UO_2MoO_4, \mathrm{cr}, 298.15\ \mathrm{K})$ = **(162.700 ± 0.300)** J·K$^{-1}$·mol$^{-1}$, $S^{\circ}_{\mathrm{m}}$ ($UO_2MoO_4$, cr, 298.15 K) = **(192.800 ± 0.800)** J·K$^{-1}$·mol$^{-1}$. Using $S^{\circ}_{\mathrm{m}}$ (Mo, cr, 298.15 K) = (28.618 ± 0.207) J·K$^{-1}$·mol$^{-1}$ reported in the Glushko handbook, this review calculates $\Delta_f S^{\circ}_{\mathrm{m}}$ ($UO_2MoO_4$, cr, 298.15 K) = **– (501.474 ± 0.850)** J·K$^{-1}$·mol$^{-1}$ and $\Delta_f G^{\circ}_{\mathrm{m}}$ ($UO_2MoO_4$, cr, 298.15 K) = **– (1835.486 ± 8.004)** kJ·mol$^{-1}$. The enthalpy of formation is in fair agreement with the value from Dash *et al.* ([2000DAS/SIN]), $\Delta_f H^{\circ}_{\mathrm{m}}$ ($UO_2MoO_4$, cr) = – 1975.2 kJ·mol$^{-1}$. The thermodynamic data from Suleimanov *et al.* are accepted by this review.

Suleimanov *et al.* also report the melting point of $UO_2MoO_4$(cr), (1212 ± 2) K.

# 9.11 Uranium actinide complexes

## 9.11.1 Actinide-actinide interactions

Discussed in the Np chapter, Section 10.7.1

# 9.12 Uranium group 2 (alkaline-earth) compounds

## 9.12.1 General

A number of experimental studies have been reported on alkali and alkaline-earth uranium oxides since the review of [2003GUI/FAN], which are presented in more detail under the headings for the various compounds. In addition, Morss suggested a new method for estimating the enthalpies of formation of alkali and alkaline-earth ternary actinide oxides phases based on acid-base interactions [2002MOR].

In this method, the stability of the ternary oxides with respect to the binary constituent oxides is expressed by the Gibbs energy of Reaction (9.127), which is directly reflected by the value of the reaction enthalpy $\Delta_r H^\circ$ (9.127) supposing the entropy of such reaction is nearly zero:

$$AO(cr) + BO_2(cr) \rightleftharpoons ABO_3(cr) \quad (9.127)$$

Morss used the approach developed by Smith [1987SMI] based on the empirical expression (9.128), which is derived from Pauli's electronegativity scale:

$$\alpha(\text{acid}) - \alpha(\text{base}) = [-\Delta_r H^\circ(\text{reaction})]^{1/2} \quad (9.128)$$

where α is the acidity parameter, and $\Delta_r H^\circ$ the enthalpy of the above reaction. Using reactions such as (9.129) and (9.130) and the experimental enthalpies of formation reported in the literature for various alkali and alkaline-earth ternary oxides, Morss calculated a quantitative scale of oxide acidity parameters for the binary actinide oxides, *i.e.*, $ThO_2$, $PaO_2$, $UO_2$, $UO_3$, $NpO_2$, $NpO_3$, $Pu_2O_3$, $PuO_2$, $Am_2O_3$, $Cm_2O_3$, $CmO_2$, $Bk_2O_3$, $Cf_2O_3$, $CfO_2$.

$$BaO(cr) + UO_2(cr) \rightleftharpoons BaUO_3(cr) \quad (9.129)$$

$$BaO(cr) + UO_3(cr) \rightleftharpoons BaUO_4(cr) \quad (9.130)$$

The mean values derived for the uranium oxides were reported as $\alpha(UO_2) = -3.3$ and $\alpha(UO_3) = 3.7$. Based on the latter values, [2002MOR] calculated the expected enthalpies for $MUO_4$ (M = Mg, Ca, Sr, Ba), $M_3UO_6$ (M = Ca, Sr, Ba) and $M_2U_2O_7$ (M = Li, Na, K, Rb, Cs), and compared them to the values determined experimentally with solution calorimetry. The calculation is detailed in Appendix A. The overall agreement is good, which shows that such approach based on the acidities of the binary oxides can be particularly appealing to estimate the enthalpies of formation of new compositions, and to predict their stabilities. Morss pointed to the fact that the acidity parameter needs to be carefully calculated taking into account the local structural coordination geometry, however. The assessment made by Morss concerns only hexavalent uranium phases. It would be particularly interesting to assess acidity parameters for Np, Pu, Am, Ac, Cf and Cm ternary oxide phases.

## 9.12.2 Magnesium compounds

### 9.12.2.1 Magnesium uranates

#### 9.12.2.1.1 $MgUO_4$(cr)

Since the review of [1992GRE/FUG] and [2003GUI/FAN], [2016GUO/TIF] have contributed to the re-determination of the enthalpy of formation of $MgUO_4$(cr) using high temperature oxide melt solution calorimetry and a molten sodium molybdate solvent ($3Na_2O{\cdot}4MoO_3$) at 975 K. The enthalpy of formation of $MgUO_4$(cr) at 298.15 K reported by the authors, *i.e.*, $\Delta_f H_m^\circ$ ($MgUO_4$, cr, 298.15 K) = – (1859.2 ± 1.9) kJ·mol$^{-1}$, is in very

good agreement with previous measurements in the literature using solution calorimetry in a $HNO_3$ solution and $HNO_3$/HF mixtures [1977OHA/BOE], [2003GUI/FAN], *i.e.*, $\Delta_f H_m^o$ ($MgUO_4$, cr, 298.15 K) = – (1857.3 ± 1.5) kJ·mol$^{-1}$. Our re-calculation using the recommended auxiliary data yields the same result, but slightly increased uncertainties. In this review, we select the weighted average of the two measurements by [1977OHA/BOE] and [2016GUO/TIF]:

$$\Delta_f H_m^o (MgUO_4, cr, 298.15\ K) = \mathbf{-\ (1858.300 \pm 1.500)}\ kJ\cdot mol^{-1}.$$

The heat capacity and entropy data at 298.15 K for this compound, based on the low temperature heat capacity measurements of [1980WES/ZAI], [1992GRE/FUG] are retained.

$$C_{p,m}^o (MgUO_4, cr, 298.15\ K) = \mathbf{(128.100 \pm 0.300)}\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S_m^o (MgUO_4, cr, 298.15\ K) = \mathbf{(131.950 \pm 0.170)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The Gibbs energy of formation at 298.15 K has been recalculated in this review:

$$\Delta_f G_m^o (MgUO_4, cr, 298.15\ K) = \mathbf{-\ (1750.601 \pm 1.502)}\ kJ\cdot mol^{-1}.$$

## 9.12.3 Calcium compounds

### 9.12.3.1 Calcium uranates

#### 9.12.3.1.1 $CaUO_4$(cr)

Since the review of [2003GUI/FAN], the work of [2008KON/POP] has contributed to the redetermination of the heat capacity and entropy values at 298.15 K of rhombohedral $CaUO_4$ using thermal relaxation calorimetry. The latter values are significantly lower than reported by Westrum *et al.* [1980WES/ZAI]. The results of [1980WES/ZAI] are suspected to be in error as detailed in Appendix A. In this review we select the data of [2008KON/POP] with slightly increased uncertainties:

$$C_{p,m}^o (CaUO_4, cr, 298.15\ K) = \mathbf{(115.400 \pm 3.500)}\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S_m^o (CaUO_4, cr, 298.15\ K) = \mathbf{(114.700 \pm 2.300)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The enthalpy of formation determined by O'Hare, Boerio and Hoekstra [1976OHA/BOE] on a well-characterised sample of $CaUO_4$(cr) is retained in this review:

$$\Delta_f H_m^o (CaUO_4, cr, 298.15\ K) = \mathbf{-\ (2002.300 \pm 2.300)}\ kJ\cdot mol^{-1}.$$

The Gibbs energy of formation of $CaUO_4$ at 298.15 K has subsequently been recalculated in this review based on the newly determined entropy function for this compound and the recommended auxiliary data.

$$\Delta_f G_m^o (CaUO_4, cr, 298.15\ K) = \mathbf{-\ (1886.798 \pm 2.404)}\ kJ\cdot mol^{-1}.$$

## 9.12.4 Strontium compounds

### 9.12.4.1 Strontium uranates

#### 9.12.4.1.1 α-$SrUO_4$

α-$SrUO_{4-x}$(cr) shows a rhombohedral structure, in space group $R\bar{3}m$, with a wide range of oxygen stoichiometries. Takahashi *et al.* [1993TAK/FUJ] measured the standard enthalpies of formation of samples of α-$SrUO_{4-x}$(cr) for $0 < x < 0.478$ using solution calorimetry in 5.94 mol·dm$^{-3}$ HCl medium as reported in [2003GUI/FAN]. The value derived for stoichiometric α-$SrUO_4$ supports that selected in [1992GRE/FUG] and retained in [2003GUI/FAN]:

($SrUO_4$, α, 298.15 K) = **– (1989.600 ± 2.800)** kJ·mol$^{-1}$.

The heat capacity and entropy values of α-$SrUO_4$ at 298.15 K were reported in [1992GRE/FUG], [2003GUI/FAN] based on the low temperature heat capacity measurements of Westrum, Zainel and Jakes [1980WES/ZAI]. However, the latter measurements refer to the orthorhombic form of $SrUO_4$, *i.e.,* to the β phase, and not to α. There is a confusion in the literature with respect to the assignment of the α and β polymorphs, as illustrated by the work of [2005YAG/OBB], assigning the α form to the orthorhombic structure. The heat capacity and entropy of the stoichiometric rhombohedral modification are not known.

#### 9.12.4.1.2 β–$SrUO_4$

β-$SrUO_4$ shows an orthorhombic structure, in space group *Pbcm*. Since the review of [2003GUI/FAN], the work of [2008KON/POP] has contributed to the re-determination of the heat capacity and standard entropy values at 298.15 K of β-$SrUO_4$ (indicated as α-$SrUO_4$ by [2008KON/POP]) using thermal-relaxation calorimetry as detailed in Appendix A. The heat capacity and entropy values adopted in the reviews of [1992GRE/FUG], [2003GUI/FAN] were based on the measurements of Westrum *et al.* [1980WES/ZAI], who reported thermodynamic functions for the series $MgUO_4$, $CaUO_4$, β-$SrUO_4$, and $BaUO_4$ using adiabatic calorimetry. Their results for $BaUO_4$ were in strong disagreement with those of [1980OHA/FLO] and [2007POP/COL], which stimulated [2008KON/POP] to re-measure the low temperature heat capacity of $CaUO_4$ and β-$SrUO_4$. In this review, the results of [2008KON/POP] are selected, and those of [1980WES/ZAI] are discarded:

$C^{\circ}_{p,\mathrm{m}}$ ($SrUO_4$, β, 298.15 K) = **(119.700 ± 3.600)** J·K$^{-1}$·mol$^{-1}$

$S^{\circ}_{\mathrm{m}}$ ($SrUO_4$, β, 298.15 K) = **(147.200 ± 2.900)** J·K$^{-1}$·mol$^{-1}$.

The entropy value of β-$SrUO_4$ measured by [2008KON/POP] is in good agreement with the trend followed by the alkali and alkaline-earth uranates $Na_2UO_4$, $Cs_2UO_4$ [1992GRE/FUG], $BaUO_4$ [2007POP/COL], and $MgUO_4$ [1980WES/ZAI].

Combining the selected entropy value together with the enthalpy of formation recommended by [2003GUI/FAN], the Gibbs energy of formation of β-$SrUO_4$ has been calculated in this review at 298.15 K as:

$$\Delta_f G_m^o(SrUO_4, \beta, 298.15\ K) = \mathbf{-\ (1878.381 \pm 5.469)}\ kJ \cdot mol^{-1}.$$

#### 9.12.4.1.3 $Sr_3UO_6$(cr)

[2010CHE/KNY] recently re-measured the enthalpy of formation of $Sr_3UO_6$(cr) at 298.15 K using solution calorimetry in 1 $mol \cdot dm^{-3}$ HCl(aq) medium. The value found in the study of [2010CHE/KNY], *i.e.*, $\Delta_f H_m^o$ ($Sr_3UO_6$, cr, 298.15 K) = – (2995.0 ± 6.0) $kJ \cdot mol^{-1}$, is in strong disagreement with that reported by [1999COR/BOO], [1967COR/LOO], [1983MOR/WIL2] and with the value recommended by [2003GUI/FAN], *i.e.*, $\Delta_f H_m^o$ ($Sr_3UO_6$, cr, 298.15 K) = – (3263.5 ± 3.0) $kJ \cdot mol^{-1}$. A similar discrepancy was also noted for the enthalpies of formation of $Ba_2SrUO_6$, $Ba_2CaUO_6$, $Ba_2MgUO_6$, and $Ba_3UO_6$ determined by the same group [2006KNY/CHE], [2006CHE/SMI3] using a similar method. We suspect the heat of solution of SrO(cr) used in the thermochemical cycle to be in error due to carbonate and/or hydroxide impurities. Moreover, [2010CHE/KNY] gave only little information on their experimental results, and did not report the quantities of material dissolved, so that one cannot judge if all solutions had a similar final concentration. Because of the lack of information and apparent discrepancies this review discards the results of [2010CHE/KNY] and retains that recalculated by [2003GUI/FAN] based on the results of [1967COR/LOO], [1983MOR/WIL2]:

$$\Delta_f H_m^o(Sr_3UO_6, cr, 298.15\ K) = \mathbf{-\ (3263.500 \pm 3.000)}\ kJ \cdot mol^{-1}.$$

### 9.12.4.2 Other strontium uranates

#### 9.12.4.2.1 $SrUMo_4O_{16}$(cr)

[2013KES/DAS] investigated the Sr-Mo-U-O quaternary phase diagram at 1023 K in air and suggested stable phase boundaries based on the XRD analyses of 22 phases mixtures of various compositions (see Appendix A). In addition, [2013KES/DAS] reported for the first time the thermal expansion coefficients, melting temperature (1043 K) and heat capacity coefficients in the temperature range 310-759 K of the quaternary phase $SrUMo_4O_{16}$(cr) which shows a monoclinic symmetry with cell parameters $a$ = 11.474(5) Å, $b$ = 6.772(2) Å, $c$ = 8.480(2) Å, and β = 90.93 ° [1988MAR2]. Using Differential Scanning Calorimetry in the step mode, [2013KES/DAS] reported the following heat capacity function for the temperature range 310-759 K:

$$C_{p,m}^o(SrUMo_4O_{16}, cr, 298.15\ K) = 405.709 + 0.00263\,T/K - 17.532 \times 10^6\,(T/K)^{-2}\ J \cdot K^{-1} \cdot mol^{-1}.$$

The heat capacity values were found to be less than those calculated from the Neumann Kopp rule. This review points to the need to repeat the measurement on a well-characterised material to confirm the results of [2013KES/DAS].

#### 9.12.4.2.2 $Sr_3In_2UO_9$(cr)

[2009CHE/KNY2] measured for the first time the low temperature heat capacity of $Sr_3In_2UO_9$(cr) in the temperature range 80-350 K using adiabatic vacuum calorimetry. The heat capacity value obtained at 298.15 K by interpolation is a new value and selected in this review, but the uncertainty is slightly increased:

$$C^{\circ}_{p,\mathrm{m}}(Sr_3In_2UO_9, \mathrm{cr}, 298.15\ \mathrm{K}) = \mathbf{(321.300 \pm 1.900)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Using the method of Kelley-Parks [1929KEL/PAR] to estimate the heat capacity values below 80 K, the authors derived the following standard entropy at 298.15 K:

$$S^{\circ}_{\mathrm{m}}(Sr_3In_2UO_9, \mathrm{cr}, 298.15\ \mathrm{K}) = \mathbf{(384.6 \pm 11.5)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The present review assigns a rather large uncertainty to the latter result (3 %) and points to the need to collect experimental data below 80 K to confirm the derived standard entropy value.

## 9.12.5 Barium compounds

### 9.12.5.1 Barium uranates

A number of enthalpy increment and heat capacity measurements have been reported for the barium uranates [2001MAT/YAM], [2007POP/COL], [2010DAS/SIN]. Experimental details are given in Appendix A. For convenience, the derived heat capacity data are summarised and compared here (see Table 9-90). In this review, the experimental results have been combined with the recommended heat capacity values at 298.15 K, and the enthalpy increments have been recalculated imposing the necessary constraint $H_{\mathrm{m}}(T) - H^{\circ}_{\mathrm{m}}(298.15\,\mathrm{K}) = 0$ at 298.15 K. The derived heat capacity equations are summarised in the Appendix A reviews and shown in Figure 9-20.

Table 9-90: Derived heat capacity equations for the barium uranates.

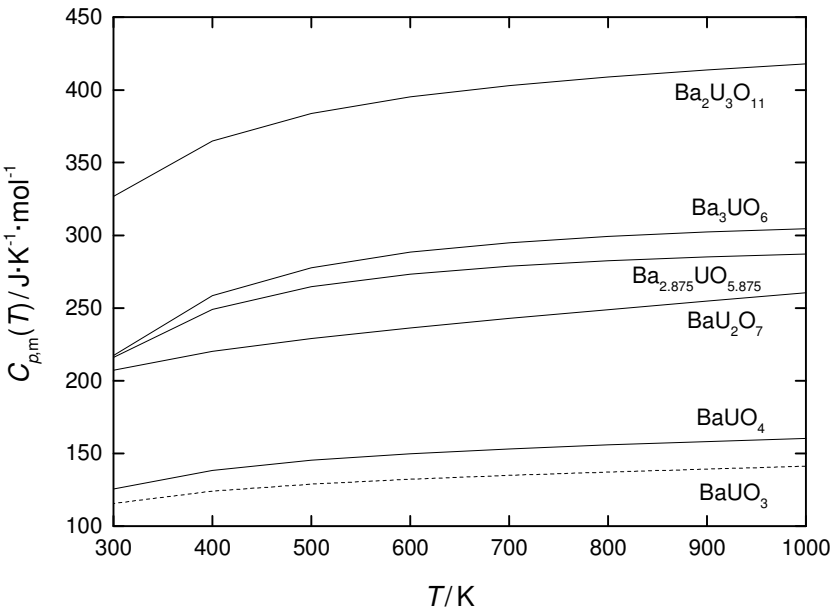
| Phase | $T$ range /K | Heat capacity coefficients $C_{p,\mathrm{m}} = \mathrm{a} + \mathrm{b}T + \mathrm{e}T^{-2}$ /J·K$^{-1}$·mol$^{-1}$ | | | $C^{\circ}_{p,\mathrm{m}}(298.15\,\mathrm{K})$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|---|
| | | a | b | e | | |
| $BaUO_3$(cr) | 373-873 | 126.6 | $1.61 \times 10^{-2}$ | $-1.42 \times 10^{6}$ | (115.4) | [2001MAT/YAM] |
| $BaUO_4$(cr) | 484.2-1566.4 | 146.43 | $1.6270 \times 10^{-2}$ | $-2.30987 \times 10^{6}$ | (125.3 ± 2.5) | [1988SAH/BAB], [1960LEO/REZ] |
| $BaU_2O_7$(cr) | 298.9-1000 | 208.95 | $5.3020 \times 10^{-2}$ | $-1.58738 \times 10^{6}$ | (206.9 ± 17.0) | [2010DAS/SIN] |
| $Ba_2U_3O_{11}$(cr) | 323.4-999.9 | 401.27 | $2.3890 \times 10^{-2}$ | $-7.34208 \times 10^{6}$ | (325.8 ± 9.8) | [2010DAS/SIN] |

(Continued on next page)

Table 9-90 (continued)

| Phase | $T$ range /K | Heat capacity coefficients $C_{p,m} = a + bT + eT^{-2}$ /J·K$^{-1}$·mol$^{-1}$ | | | $C^{o}_{p,m}$(298.15 K) /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|---|
| $Ba_{2.875}UO_{5.875}$(cr) | 306.1-1010.6 | 288.76 | $5.1100 \times 10^{-3}$ | $-6.68314 \times 10^{6}$ | (215.1 ± 6.5) | [2010DAS/SIN] |
| $Ba_3UO_6$(cr) | 302-1011.6 | 309.94 | $3.0700 \times 10^{-3}$ | $-8.40557 \times 10^{6}$ | (216.3 ± 6.5) | [2010DAS/SIN] |

Figure 9-20: Heat capacity *versus* temperature for some barium uranates.




#### 9.12.5.1.1 $BaUO_3$(cr)

Previous work has stressed the difficulty of obtaining non-oxidised stoichiometric $BaUO_3$ [2003GUI/FAN], [1975BRA/KEM], [1982BAR/JAC], [1984WIL/MOR]. The lowest oxygen content Hinatsu [1993HIN], [1993HIN2] could reach by reduction of $BaUO_4$ under a flow of hydrogen was $BaUO_{3.023}$ according to the Ce(IV)-Fe(II) back-titration method. Willams, Morss and Choi [1984WIL/MOR] measured the enthalpies of formation of $BaUO_{3.06}$(cr) and $BaUO_{3.20}$(cr) using solution calorimetry, and derived for the stoichiometric composition:

$$\Delta_f H^{o}_{m}(BaUO_3, cr, 298.15\ K) = \mathbf{-\ (1690.000 \pm 10.000)}\ kJ\cdot mol^{-1},$$

which was adopted in the previous reviews [1992GRE/FUG], [2003GUI/FAN]. In the absence of new measurements, the latter value is retained here.

[2001MAT/YAM] measured for the first time the heat capacity of "$BaUO_3$" from 373 to 873 K using Differential Scanning Calorimetry. The lattice parameter reported by them suggests an oxygen content greater than stoichiometric $BaUO_3$, however, as detailed in Appendix A. The heat capacity value obtained at 298.15 K by extrapolation of their data is $C^{o}_{p,m}$ ($BaUO_{3+x}$, cr, 298.15 K) = 115.4 $J \cdot K^{-1} \cdot mol^{-1}$, in good agreement with Neumann-Kopp's rule using the recommended auxiliary data for $UO_2$(cr) and BaO(cr). Given the uncertainty on the exact composition of the synthesised compound, the latter data cannot be selected as reference for stoichiometric $BaUO_3$(cr).

#### 9.12.5.1.2 $BaUO_4$(cr)

Low temperature heat capacity measurements by [2007POP/COL] from 1.9 to 292.6 K have allowed to solve the discrepancy raised by [1992GRE/FUG] regarding the heat capacity and entropy values reported in the literature for $BaUO_4$ at 298.15 K, as detailed in Appendix A. The results of [2007POP/COL] were found in very good agreement with those of [1980OHA/FLO], which were obtained using adiabatic calorimetry on a well-characterised sample, and selected by [1992GRE/FUG], [2003GUI/FAN]. The results of [1980WES/ZAI] have therefore been definitively discarded, and this review retains the data recommended by [1992GRE/FUG], [2003GUI/FAN]:

$$C^{o}_{p,m}(BaUO_4, cr, 298.15\ K) = \mathbf{(125.300 \pm 2.500)}\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S^{o}_{m}(BaUO_4, cr, 298.15\ K) = \mathbf{(154.000 \pm 2.500)}\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_f H^{o}_{m}(BaUO_4, cr, 298.15\ K) = \mathbf{-\ (1993.800 \pm 3.300)}\ kJ \cdot mol^{-1}$$

$$\Delta_f G^{o}_{m}(BaUO_4, cr, 298.15\ K) = \mathbf{-\ (1883.805 \pm 3.393)}\ kJ \cdot mol^{-1}.$$

The enthalpy increment measurements of Saha *et al.* [1988SAH/BAB] and Leonidov *et al.* [1960LEO/REZ] covering the temperature range 484.2-1566.4 K recommended in [1992GRE/FUG] and [2003GUI/FAN] are also retained by this review.

#### 9.12.5.1.3 $Ba_3UO_6$(cr)

[2010DAS/SIN] measured for the first time the low temperature heat capacity of $Ba_3UO_6$(cr) in the temperature range 127.1-303.3 K using Differential Scanning Calorimetry. The heat capacity value obtained at 298.15 K by interpolation is selected in this review:

$$C^{o}_{p,m}(Ba_3UO_6, cr, 298.15\ K) = \mathbf{(216.300 \pm 6.500)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

Based on the experimental results of [2010DAS/SIN], the entropy value at 298.15 K has been recalculated in this review as detailed in Appendix A:

$$S^{o}_{m}(Ba_3UO_6, cr, 298.15\ K) = \mathbf{(288.600 \pm 5.000)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

[1983MOR/WIL2] and [2006KNY/CHE] have determined the enthalpy of formation of $Ba_3UO_6$(cr) at 298.15 K using solution calorimetry in 1 mol·dm$^{-3}$ HCl(aq). Both sets of authors have obtained very different results, both for the dissolution enthalpy of $Ba_3UO_6$(cr) in 1 mol·dm$^{-3}$ HCl(aq), and the derived enthalpies of formation, namely – (3210.4 ± 8.0) kJ·mol$^{-1}$ and – (3043.2 ± 10.5) kJ·mol$^{-1}$, respectively. The data obtained by [2006KNY/CHE] are discarded, however. We suspect the heat of solution of BaO(cr) used in the thermochemical cycle to be in error due to carbonate and/or hydroxide impurities. Further details are given in Appendix A. Moreover, [2006KNY/CHE] gave only little information on their experimental results, and did not report the quantities of material dissolved, so that one cannot judge if all solutions had a similar final concentration. Because of the lack of information and apparent discrepancies the latter data are not selected. The recalculated value by [1992GRE/FUG] based on the results of [1983MOR/WIL2] is therefore retained:

$$\Delta_f H^o_m (Ba_3UO_6, cr, 298.15\ K) = \mathbf{-\ (3210.400 \pm 8.000)}\ kJ\cdot mol^{-1}.$$

The Gibbs energy of formation calculated from the selected enthalpy of formation and standard entropy is:

$$\Delta_f G^o_m (Ba_3UO_6, cr, 298.15\ K) = \mathbf{-\ (3042.149 \pm 8.173)}\ kJ\cdot mol^{-1}.$$

#### 9.12.5.1.4 $BaU_2O_7$(cr) and $Ba_2U_2O_7$(cr)

Cordfunke and Ouweltjes [1988COR/OUW] obtained the enthalpies of formation of $BaU_2O_7$(cr) and $Ba_2U_2O_7$(cr) using solution calorimetry in ($HCl + 0.0419FeCl_3 + 70.66H_2O$) medium. Using the selected auxiliary data, [1992GRE/FUG], [2003GUI/FAN] recalculated the following values, which are retained by this review:

$$\Delta_f H^o_m (BaU_2O_7, cr, 298.15\ K) = \mathbf{-\ (3237.200 \pm 5.000)}\ kJ\cdot mol^{-1}$$

$$\Delta_f H^o_m (Ba_2U_2O_7, cr, 298.15\ K) = \mathbf{-\ (3740.000 \pm 6.300)}\ kJ\cdot mol^{-1}.$$

[2004BAN/DAS] determined the Gibbs energy of formation of $BaU_2O_7$ in the temperature range (1001-1206 K) using a calcia stabilised zirconia (CSZ) solid state electrochemical cell. From the latter data and the recommended entropy and heat capacity functions for this compound, the enthalpy of formation was recalculated in this review by second and third law analyses (see Appendix A) as $\Delta_f H^o_m (BaU_2O_7, cr, 298.15\ K)$ = – (3212.3 ± 6.0) kJ·mol$^{-1}$ and – (3240.7 ± 1.4) kJ·mol$^{-1}$, respectively. The agreement between those two values is rather poor. Moreover, the third law analysis shows a slight drift with temperature. The value recommended by [1992GRE/FUG], [2003GUI/FAN] based on the solution calorimetry studies of Cordfunke and Ouweltjes [1988COR/OUW], is considered more reliable than the latter results and retained.

[2010DAS/SIN] measured for the first time the low temperature heat capacity of $BaU_2O_7$ in the temperature range 126.9-303.4 K using Differential Scanning Calorimetry. The heat capacity value obtained at 298.15 K by interpolation is much lower

than expected from Neumann-Kopp's rule, however, as detailed in Appendix A. We do not select the data of [2010DAS/SIN] in this review and prefer to suggest the following approximation based on the additive rule. These data are given for information only.

$$C^{o}_{p,m}(BaU_2O_7, cr, 298.15\ K) = (206.9 \pm 17.0)\ J\cdot K^{-1}\cdot mol^{-1}.$$

In our previous review [1992GRE/FUG], the standard entropy of $BaU_2O_7$ was derived from the estimation by Cordfunke and Ijdo [1988COR/IJD] based on phase diagram calculations, *i.e.*, $S^{o}_{m}(BaU_2O_7, cr, 298.15\ K) = (260.0 \pm 15.0)\ J\cdot K^{-1}\cdot mol^{-1}$. The latter data as well as the calculated Gibbs energy at 298.15 K, $\Delta_f G^{o}_{m}(BaU_2O_7, cr, 298.15\ K) = -(3052.093 \pm 6.714)\ kJ\cdot mol^{-1}$, are retained for scoping calculations only in this review, and complementary experimental measurements of the low temperature heat capacity of $BaU_2O_7$ are recommended.

No experimental data for the entropy or heat capacity of $Ba_2U_2O_7$(cr) are available. The data previously adopted (standard entropy and Gibbs energy) by [1992GRE/FUG] were derived from the estimation by Cordfunke and Ijdo [1988COR/IJD] based on phase diagram calculations: $S^{o}_{m}(Ba_2U_2O_7, cr, 298.15\ K) = (296.0 \pm 15.0)\ J\cdot K^{-1}\cdot mol^{-1}$, $\Delta_f G^{o}_{m}(Ba_2U_2O_7, cr, 298.15\ K) = -(3547.015 \pm 7.743)\ kJ\cdot mol^{-1}$. The latter data are reported for scoping calculations only in this review.

#### 9.12.5.1.5 $Ba_{2.875}UO_{5.875}$(cr)

[2010DAS/SIN] measured for the first time the low temperature heat capacity of $Ba_{2.875}UO_{5.875}$ in the temperature range 127-303.5 K using Differential Scanning Calorimetry. This compound has a slightly different structure compared to $Ba_3UO_6$. The heat capacity value obtained at 298.15 K by interpolation is selected in this review:

$$C^{o}_{p,m}(Ba_{2.875}UO_{5.875}, cr, 298.15\ K) = \mathbf{(215.100 \pm 6.500)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The Gibbs energy of formation of $Ba_{2.875}UO_{5.875}$ has been determined in the temperature range 1030-1220 K using a manometric technique, by measuring the equilibrium $CO_2$(g) pressure over the ternary phase field $Ba_{2.875}UO_{5.875}$(cr)-$Ba_3UO_6$(cr)-$BaCO_3$(cr) [2011DAS/SIN]. The standard enthalpy of formation and entropy at 298.15 K of $Ba_{2.875}UO_{5.875}$ have been subsequently derived by second and third law treatment of the data. The latter values have been recalculated in this review using the recommended auxiliary data as detailed in Appendix A. On the basis of the latter analyses, the following thermodynamic functions are selected:

$$\Delta_f H^{o}_{m}(Ba_{2.875}UO_{5.875}, cr, 298.15\ K) = \mathbf{-(3118.700 \pm 8.000)}\ kJ\cdot mol^{-1}$$

$$S^{o}_{m}(Ba_{2.875}UO_{5.875}, cr, 298.15\ K) = \mathbf{(297.700 \pm 5.000)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The derived entropy value is in poor accordance with the one determined from the Differential Scanning Calorimetry measurements of [2010DAS/SIN], *i.e.*, $S^{o}_{m}(Ba_{2.875}UO_{5.875}, cr, 298.15\ K) = (283.6 \pm 5.0)\ J\cdot K^{-1}\cdot mol^{-1}$. The latter calculation requires an approximation for the heat capacity values in the temperature range 0-127 K,

however. Moreover, the second and third law results of [2011DAS/SIN] are in poor agreement when using this function. This review therefore points to the need to repeat the low temperature heat capacity measurements of $Ba_{2.875}UO_{5.875}$.

The Gibbs energy of formation calculated from the selected enthalpy of formation and standard entropy is:

$$\Delta_f G^o_m (Ba_{2.875}UO_{5.875}, cr, 298.15\ K) = \mathbf{-\ (2959.312 \pm 8.170)}\ kJ \cdot mol^{-1}.$$

#### 9.12.5.1.6 $Ba_2U_3O_{11}$(cr)

[2010DAS/SIN] measured for the first time the low temperature heat capacity of $Ba_2U_3O_{11}$ in the temperature range 126.8-303.5 K using Differential Scanning Calorimetry. The heat capacity value obtained at 298.15 K by interpolation is selected in this review:

$$C^o_{p,m} (Ba_2U_3O_{11}, cr, 298.15\ K) = \mathbf{(325.800 \pm 9.800)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

Based on the experimental results of [2010DAS/SIN], the entropy value at 298.15 K has been recalculated in the present review as detailed in Appendix A:

$$S^o_m (Ba_2U_3O_{11}, cr, 298.15\ K) = \mathbf{(421.900 \pm 10.000)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

[2004BAN/DAS] determined the Gibbs energy of formation of $Ba_2U_3O_{11}$ in the temperature range (1009-1178.5 K) using a calcia stabilised zirconia (CSZ) solid state electrochemical cell. From the latter data and the recommended entropy and heat capacity functions for this compound, the enthalpy of formation was recalculated in this review (see Appendix A) as:

$$\Delta_f H^o_m (Ba_2U_3O_{11}, cr, 298.15\ K) = \mathbf{-\ (5210.500 \pm 6.000)}\ kJ \cdot mol^{-1}.$$

Combining the latter data together with the selected entropy, the Gibbs energy of formation is derived at 298.15 K as:

$$\Delta_f G^o_m (Ba_2U_3O_{11}, cr, 298.15\ K) = \mathbf{-\ (4917.754 \pm 6.721)}\ kJ \cdot mol^{-1}.$$

### 9.12.5.2 Barium alkaline-earth compounds

#### 9.12.5.2.1 $Ba_2MgUO_6$(cr)

[1982MOR/FUG] and [2006KNY/CHE] determined the enthalpy of formation of $Ba_2MgUO_6$(cr) using solution calorimetry in 1 $mol \cdot dm^{-3}$ HCl(aq) medium. Both sets of authors obtained very different results, namely $-(3245.9 \pm 6.5)\ kJ \cdot mol^{-1}$ and $-(3082.9 \pm 7.8)\ kJ \cdot mol^{-1}$, respectively. Because of the lack of information and apparent discrepancies the data of [2006KNY/CHE] are discarded, however, as detailed in Appendix A. The value recalculated by [1992GRE/FUG] based on the results of [1982MOR/FUG] is retained in this review:

$$\Delta_f H^o_m (Ba_2MgUO_6, cr, 298.15\ K) = \mathbf{-\ (3245.900 \pm 6.500)}\ kJ \cdot mol^{-1}.$$

#### 9.12.5.2.2 $Ba_2CaUO_6$(cr)

[2008FU/AU] solved for the first time the structure of $Ba_2CaUO_6$ using combined X-ray and neutron powder diffraction. It was found monoclinic, in space group *P2₁/n*, isostructural with $Sr_2CaUO_6$ and $Ba_2SrUO_6$ [1987GRO/IJD]. Previous studies by Kemmler-Sack and Seeman [1975KEM/SAC] had assigned it an orthorhombic symmetry, while Gens *et al.* had described it with a slightly distorted cubic perovskite structure [1985GEN/FUG].

[1985GEN/FUG] and [2006KNY/CHE] determined the enthalpy of formation of $Ba_2CaUO_6$(cr) using solution calorimetry in 1 mol·dm$^{-3}$ HCl(aq) medium. Both sets of authors obtained very different results, namely – (3295.8 ± 5.9) kJ·mol$^{-1}$ and – (3031.8 ± 7.9) kJ·mol$^{-1}$, respectively. Because of the lack of information and apparent discrepancies the data of [2006KNY/CHE] are discarded, however, as detailed in Appendix A. The value recalculated by [1992GRE/FUG] based on the results of [1985GEN/FUG] is retained in this review:

$$\Delta_f H^\circ_m (Ba_2CaUO_6, \text{cr}, 298.15\ \text{K}) = \mathbf{-\ (3295.800 \pm 5.900)}\ \text{kJ·mol}^{-1}.$$

#### 9.12.5.2.3 $Ba_2SrUO_6$(cr)

The structure of α-$Ba_2SrUO_6$ was shown to be a monoclinic perovskite in space group *P2₁/n* at room temperature based on neutron diffraction studies [1987GRO/IJD] and synchrotron X-ray powder diffraction data [2013REY/KEN]. [2013REY/KEN] also found that the compound shows a first order phase transition around 900 K to a rhombohedral phase in space group *R-3*, and a continuous transition to a cubic phase in space group *Fm-3m* above 1200 K. The latter results are in good agreement with those of [2006KNY/CHE], who suggested the occurrence of a reversible phase transition at 896 K based on high temperature X-ray diffraction data.

The enthalpy of formation of $Ba_2SrUO_6$ was first measured by [1985GEN/FUG] in 1 mol·dm$^{-3}$ HCl(aq) medium, and derived as $\Delta_f H^\circ_m$ ($Ba_2SrUO_6$, cr, 298.15 K) = – (3257.3 ± 5.7) kJ·mol$^{-1}$ [1992GRE/FUG], [2003GUI/FAN]. [2006CHE/SMI3] measured again the enthalpy of solution of $Ba_2SrUO_6$ in the same medium, but derived a very different result, *i.e.* – (2940.0 ± 8.5) kJ·mol$^{-1}$. We suspect the heat of solution of BaO(cr) and SrO(cr) used in their thermochemical cycle to be in error due to carbonate and/or hydroxide impurities. Further details are given in Appendix A. Moreover, [2006KNY/CHE] gave only little information on their experimental results, and did not report the quantities of material dissolved, so that one cannot judge if all solutions had a similar final concentration. Because of the lack of information and apparent discrepancies the data of [2006KNY/CHE] are discarded. This review retains the previously selected value:

$$\Delta_f H^\circ_m (Ba_2SrUO_6, \text{cr}, 298.15\ \text{K}) = \mathbf{-\ (3257.300 \pm 5.700)}\ \text{kJ·mol}^{-1}.$$

[2006CHE/SMI3] measured the low temperature heat capacity of $Ba_2SrUO_6$ in the temperature range 8-331 K using adiabatic vacuum calorimetry. The heat capacity and entropy values derived at 298.15 K from this measurement are accepted, but the associated uncertainties slightly increased:

$$C^{o}_{p,m}(Ba_2SrUO_6, cr, 298.15\ K) = \mathbf{(223.700 \pm 1.300)}\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}(Ba_2SrUO_6, cr, 298.15\ K) = \mathbf{(287.400 \pm 2.000)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

Using the aforementioned functions and the recommended auxiliary data, the Gibbs energy of formation is calculated in this review as:

$$\Delta_f G^{o}_{m}(Ba_2SrUO_6, cr, 298.15\ K) = \mathbf{-\ (3090.695 \pm 5.754)}\ kJ\cdot mol^{-1}.$$

### 9.12.5.3 Other barium uranates

#### 9.12.5.3.1 $Ba_3Sc_2UO_9$(cr)

[2007CHE/KNY] measured the low temperature heat capacity of $Ba_3Sc_2UO_9$(cr) in the temperature range 80-350 K using adiabatic vacuum calorimetry. The heat capacity value obtained at 298.15 K by interpolation is selected in this review, but the uncertainty slightly increased:

$$C^{o}_{p,m}(Ba_3Sc_2UO_9, cr, 298.15\ K) = \mathbf{(313.500 \pm 1.900)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

Using the method of Kelley-Parks [1929KEL/PAR] to estimate the heat capacity values below 80 K, the authors derived the following standard entropy at 298.15 K:

$$S^{o}_{m}(Ba_3Sc_2UO_9, cr, 298.15\ K) = \mathbf{(383.100 \pm 11.500)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The present review assigns a rather large uncertainty to the latter result (3 %) and points to the need to collect experimental data below 80 K to confirm the derived standard entropy value.

#### 9.12.5.3.2 $Ba_3Y_2UO_9$(cr)

[2007CHE/KNY] measured the low temperature heat capacity of $Ba_3Y_2UO_9$(cr) in the temperature range 80-350 K using adiabatic vacuum calorimetry. The heat capacity value obtained at 298.15 K by interpolation is selected in this review, but the uncertainty slightly increased:

$$C^{o}_{p,m}(Ba_3Y_2UO_9, cr, 298.15\ K) = \mathbf{(330.600 \pm 2.000)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

Using the method of Kelley-Parks [1929KEL/PAR] to estimate the heat capacity values below 80 K, the authors derived the following standard entropy at 298.15 K:

$$S^{o}_{m}(Ba_3Y_2UO_9, cr, 298.15\ K) = \mathbf{(416.400 \pm 12.500)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The present review assigns a rather large uncertainty to the latter result (3 %) and points to the need to collect experimental data below 80 K to confirm the derived standard entropy value.

#### 9.12.5.3.3 $Ba_3In_2UO_9$(cr)

[2009CHE/KNY2] measured the low temperature heat capacity of $Ba_3In_2UO_9$(cr) in the temperature range 80-350 K using adiabatic vacuum calorimetry. The heat capacity value obtained at 298.15 K by interpolation is selected in this review, but the uncertainty slightly increased:

$$C^{o}_{p,m}(Ba_3In_2UO_9, cr, 298.15\ K) = \mathbf{(329.100 \pm 2.000)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

Using the method of Kelley-Parks [1929KEL/PAR] to estimate the heat capacity values below 80 K, the authors derived the following standard entropy at 298.15 K:

$$S^{o}_{m}(Ba_3In_2UO_9, cr, 298.15\ K) = \mathbf{(417.900 \pm 12.500)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The present review assigns a rather large uncertainty to the latter result (3 %) and points to the need to collect experimental data below 80 K to confirm the derived standard entropy value.

#### 9.12.5.3.4 $Ba_2Sm_{2/3}UO_6$(cr)

[2006CHE/KNY2] measured the low temperature heat capacity of $Ba_2Sm_{2/3}UO_6$(cr) in the temperature range 80-300 K using adiabatic vacuum calorimetry. The heat capacity value obtained at 298.15 K by interpolation is:

$$C^{o}_{p,m}(Ba_2Sm_{2/3}UO_6, cr, 298.15\ K) = \mathbf{(186.400 \pm 5.600)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

Using the method of Kelley-Parks [1929KEL/PAR] to estimate the heat capacity values below 80 K, the authors derived the following standard entropy at 298.15 K:

$$S^{o}_{m}(Ba_2Sm_{2/3}UO_6, cr, 298.15\ K) = \mathbf{(244.100 \pm 7.300)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The present review assigns a rather large uncertainty to the latter results (3 %) as the purity of the material is unknown. The sample was analysed by X-ray diffraction but the authors did not report any structural information. This review points to the need to collect experimental data below 80 K to confirm the derived standard entropy value, and more generally to the need to repeat the measurement over the full temperature range (0-300 K) on a well-characterised material.

The same authors measured the enthalpy of formation in 1 $mol\cdot dm^{-3}$ HCl(aq) medium by solution calorimetry, but the derived data are not selected in this review in view of the discrepancies found for the dissolution enthalpies of BaO(cr) and $Sm_2O_3$(cr) (see Appendix A) [2006CHE/SMI3], [2006KNY/CHE].

# 9.13 Uranium group 1 (alkali) compounds

## 9.13.1 Lithium compounds

### 9.13.1.1 Lithium uranates

Since the review of [2003GUI/FAN], the work of [2009RAK/JAT] has contributed to the determination of the heat capacity data of several lithium uranate compounds ($Li_2UO_4$, $Li_{22}U_{18}O_{65}$, $Li_2U_{1.75}O_{6.25}$, $Li_2U_2O_7$, $Li_2U_3O_{10}$, and $Li_2U_6O_{19}$) between 300 and 860 K using Differential Scanning Calorimetry (Table 9-91). The values obtained at 298.15 K by extrapolation of the fitted equations deviate rather significantly from Neumann Kopp's rule applied to $Li_2O$(cr) [1998CHA] and $UO_3$(cr) [2003GUI/FAN] (from 1.8 to 9.3% with systematically higher values, see Appendix A). The authors also did not list their experimental points, but only reported their least-squares fitted heat capacity equations. This review does not select the equations at this time, and points to the need to repeat the measurements to confirm those results. Moreover, [2009RAK/JAT] have estimated several entropy values at 298.15 K based on Latimer's method [1974MIL], [1998SPE], but these data have not been considered in this review, which selects only experimentally determined functions.

Table 9-91: Heat capacity equations for the lithium uranates derived using Differential Scanning Calorimetry [2009RAK/JAT].

| Phase | $T$ range /K | Heat capacity coefficients $C^{o}_{p,m}$ (298.15 K) = a + b$T$ + e$T^{-2}$ /J·K$^{-1}$·mol$^{-1}$ | | | $C^{o}_{p,m}$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| | | a | b | e | |
| $Li_4UO_5$(cr) | 300-860 | 189.769 | $8.9905 \times 10^{-2}$ | – 804998.9 | 207.520 ± 4.150 |
| $Li_2UO_4$(cr) | 300-860 | 206.825 | $-1.5795 \times 10^{-2}$ | – 4821395.5 | 147.880 ± 2.960 |
| $Li_{22}U_{18}O_{65}$(cr) | 300-860 | 2735.305 | $2.7386 \times 10^{-1}$ | – 53106768.3 | 2219.54 ± 44.390 |
| $Li_2U_{1.75}O_{6.25}$(cr) | 300-860 | 227.183 | $6.3651 \times 10^{-2}$ | – 2843098.5 | 214.180 ± 4.280 |
| $Li_2U_2O_7$(cr) | 300-860 | 298.921 | $-1.2039 \times 10^{-2}$ | – 6574942.6 | 221.370 ± 4.430 |
| $Li_2U_3O_{10}$(cr) | 300-860 | 332.453 | $1.7759 \times 10^{-2}$ | – 2717165.9 | 307.180 ± 6.140 |
| $Li_2U_6O_{19}$(cr) | 300-860 | 545.813 | $1.3968 \times 10^{-1}$ | – 1344453.9 | 572.334 ± 11.450 |

## 9.13.2 Sodium compounds

### 9.13.2.1 Sodium monouranates (VI)

#### 9.13.2.1.1 $Na_4UO_5$(cr)

The enthalpy of formation of $Na_4UO_5$(cr) selected by [2003GUI/FAN] based on the study by Cordfunke and Loopstra [1971COR/LOO] and Tso *et al.* [1985TSO/BRO] and

recalculation to account for small changes made to the auxiliary data used in the reaction schemes, is retained in this review.

$$\Delta_f H^o_m (Na_4UO_5, cr, 298.15\ K) = \mathbf{-\ (2457.000 \pm 2.200)}\ kJ \cdot mol^{-1}.$$

The entropy and heat capacity of $Na_4UO_5$ have been measured by [2015SMI/GRI] using thermal-relaxation calorimetry in the temperature range 1.9 to 288.7 K as detailed in Appendix A. The values determined in their work have been selected in this review:

$$C^o_{p,m} (Na_4UO_5, cr, 298.15\ K) = \mathbf{(220.600 \pm 6.700)}\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S^o_m (Na_4UO_5, cr, 298.15\ K) = \mathbf{(247.500 \pm 6.200)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

The Gibbs energy of formation calculated from the selected enthalpy of formation and entropy is:

$$\Delta_f G^o_m (Na_4UO_5, cr, 298.15\ K) = \mathbf{-\ (2301.729 \pm 2.884)}\ kJ \cdot mol^{-1}.$$

### 9.13.2.2 Sodium monouranates (V)

#### 9.13.2.2.1 $NaUO_3$(cr)

The enthalpy of formation of $NaUO_3$ selected by [1992GRE/FUG], [2003GUI/FAN] is based on the solution calorimetry studies by Cordfunke and Loopstra [1971COR/LOO] and Cordfunke and Ouweltjes [1981COR/OUW]. In the absence of any new measurement, the present review retains the selected value, and its associated uncertainty [2003GUI/FAN]:

$$\Delta_f H^o_m (NaUO_3, cr, 298.15\ K) = \mathbf{-\ (1494.900 \pm 10.000)}\ kJ \cdot mol^{-1}.$$

The heat capacity and entropy values adopted by [1992GRE/FUG], [2003GUI/FAN] were derived from the work of Lyon *et al.* [1977LYO/OSB], who used adiabatic calorimetry, *i.e.*, $C^o_{p,m} (NaUO_3, cr, 298.15\ K) = (108.87 \pm 0.40)\ J \cdot K^{-1} \cdot mol^{-1}$ and $S^o_m (NaUO_3, cr, 298.15\ K) = (132.84 \pm 0.40)\ J \cdot K^{-1} \cdot mol^{-1}$. Recent Knudsen effusion mass spectrometry measurements performed in the ternary phase field $NaUO_3$-$Na_2U_2O_7$-$UO_2$ [2015SMI/COL] have questioned the aforementioned entropy value, however, with the possibility of a slight overestimation, as detailed in Appendix A. When using $S^o_m (NaUO_3, cr, 298.15\ K) = (126.4)\ J \cdot K^{-1} \cdot mol^{-1}$, the authors obtained a better agreement between second and third law analyses of their data. The data of Lyon *et al.* [1977LYO/OSB] were re-assessed, but no error could be identified in their data treatment. Their sample might have contained some small impurity such as $Na_2U_2O_7$, $Na_2O$, or Na, which would have been difficult to identify. In view of this discrepancy, we have increased the uncertainty on the selected values in [2003GUI/FAN] significantly:

$$C^o_{p,m} (NaUO_3, cr, 298.15\ K) = \mathbf{(108.900 \pm 7.000)}\ J \cdot K^{-1} \cdot mol^{-1},$$

$$S^o_m (NaUO_3, cr, 298.15\ K) = \mathbf{(132.800 \pm 7.000)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

The uncertainty on the Gibbs energy of formation was subsequently recalculated, but the change from the one in [2003GUI/FAN] is small and the values selected there are retained:

$$\Delta_f G_m^o (NaUO_3, cr, 298.15\ K) = \mathbf{-\ (1412.483 \pm 10.216)}\ kJ \cdot mol^{-1}.$$

#### 9.13.2.2.2 $Na_3UO_4$(cr)

In their recent structural studies, [2015SMI/RAI] have solved the crystal structure of α-$Na_3UO_4$ (monoclinic in space group *P2/c*). The authors also have clarified this compounds' polymorphism: $Na_3UO_4$ shows a low temperature cubic metastable phase (of the NaCl type), and a high temperature cubic β phase (in space group $Fd\overline{3}m$). [2015SMI/RAI] have also shown that α-$Na_3UO_4$ could accommodate excess sodium on the uranium site, with subsequent charge compensation of the uranium cation, corresponding to the α-$Na_3(U_x, Na_{1-x})O_4$ mixed valence state composition ($0 < x < 0.18$). This work has shown that very reducing conditions were necessary to synthesise stoichiometric $Na_3UO_4$. [2015SMI] have thus questioned the chemical composition of the trisodium uranate sample prepared by O'Hare *et al.*, which has been used to determine its enthalpy of formation [1972OHA/SHI], heat capacity, entropy and Gibbs energy at 298.15 K [1972OSB/FLO], as well as heat capacity at high temperatures [1972FRE/CHA]. The prepared sample might have corresponded to the mixed valence state composition $Na_{3.014}U_{0.986}O_4$ instead of stoichiometric $Na_3UO_4$ [2015SMI]. [2015SMI] have subsequently calculated thermodynamic functions for the corrected composition as detailed in Appendix A. The effect of the correction is minor, however. The assignment of the sample's exact stoichiometry is moreover not straightforward. In the absence of any further evidence for the need to correct the data, the thermodynamic functions selected by [2003GUI/FAN] have been retained:

$$\Delta_f H_m^o (Na_3UO_4, \alpha, 298.15\ K) = \mathbf{-\ (2024.000 \pm 8.000)}\ kJ \cdot mol^{-1}$$

$$C_{p,m}^o (Na_3UO_4, \alpha, 298.15\ K) = \mathbf{(173.000 \pm 0.400)}\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m^o (Na_3UO_4, \alpha, 298.15\ K) = \mathbf{(198.200 \pm 0.400)}\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_f G_m^o (Na_3UO_4, \alpha, 298.15\ K) = \mathbf{-\ (1899.909 \pm 8.003)}\ kJ \cdot mol^{-1}.$$

### 9.13.2.3 Other sodium uranates: $Na_2UMo_2O_{10}$(cr), $Na_2U_2Mo_2O_{13}$(cr), $Na_2U_2Mo_3O_{16}$(cr), $Na_2UMo_4O_{16}$(cr), $Na_2U_2Mo_4O_{19}$(cr)

Although no thermodynamic data are reported, [2002KES/AGA] give interesting information on the phase relationships in the Na-U-Mo-O quaternary system. They reported a sketch of the stable phase boundaries based on the XRD analyses of 17 phases mixtures of various compositions. In addition, [2002KES/AGA] reported the existence of five stable quaternary phases of orthorhombic symmetry, namely of $Na_2UMo_2O_{10}$, $Na_2U_2Mo_2O_{13}$, $Na_2U_2Mo_3O_{16}$, $Na_2UMo_4O_{16}$, $Na_2U_2Mo_4O_{19}$, which they indexed using X-ray diffraction. The $Na_4U_3Mo_2O_{17}$, $Na_2U_3Mo_9O_{37}$, $Na_2U_3Mo_4O_{22}$ compounds reported by

Dion and Noel [1977DIO/NOE], [1981DIO/NOE], [1982DIO/NOE] were found to correspond to phase mixtures instead of pure compounds. [2002KES/AGA] finally reported several reversible phase transitions for $Na_2UMo_2O_{10}$, $Na_2U_2Mo_2O_{13}$, $Na_2U_2Mo_3O_{16}$, $Na_2UMo_4O_{16}$, $Na_2U_2Mo_4O_{19}$ and measured their melting temperatures using thermogravimetry (TG) and differential thermal analysis. Further details are given in Appendix A. No thermodynamic data have been selected and the section is for information only.

#### 9.13.2.4 Sodium polyuranates

##### 9.13.2.4.1 $Na_2U_2O_7$(cr)

The studies of [2015IJD/AKE] and [2015SMI/COL] have allowed to clarify the polymorphism of $Na_2U_2O_7$. α-$Na_2U_2O_7$ monoclinic, in space group $P2_1/a$, presents two reversible phase transitions: one between 623 and 748 K (α-β), and one between 1223 and 1323 K (β-γ), respectively. β-$Na_2U_2O_7$ is monoclinic, in space group $C2/m$ [2015IJD/AKE], and γ-$Na_2U_2O_7$ is rhombohedral, in space group $R\bar{3}m$ [2015SMI/COL].

Knudsen effusion mass spectrometry measurements by [2015SMI/COL] have allowed deriving the enthalpy of formation of α-$Na_2U_2O_7$ as – (3208.4 ± 5.5) kJ·mol$^{-1}$, in very good agreement with the value selected by [2003GUI/FAN]. This review therefore retains the data recommended by [2003GUI/FAN]:

$$\Delta_f H^o_m (Na_2U_2O_7, \alpha, 298.15\ K) = \mathbf{-\ (3203.800 \pm 4.000)}\ kJ\cdot mol^{-1}$$

$$C^o_{p,m} (Na_2U_2O_7, \alpha, 298.15\ K) = \mathbf{(227.300 \pm 1.000)}\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^o_m (Na_2U_2O_7, \alpha, 298.15\ K) = \mathbf{(275.900 \pm 1.000)}\ J\cdot K^{-1}\cdot mol^{-1}$$

$$\Delta_f G^o_m (Na_2U_2O_7, \alpha, 298.15\ K) = \mathbf{-\ (3011.454 \pm 4.015)}\ kJ\cdot mol^{-1}.$$

### 9.13.3 Potassium compounds

#### 9.13.3.1 Potassium uranates

There are no new thermodynamic data for these compounds and this review retains the values selected by [1992GRE/FUG], [2003GUI/FAN].

#### 9.13.3.2 $K_8Sr_2U_6O_{24}$(cr)

[2011KES/AGA] investigated the K-Sr-U-O quaternary phase diagram at 1123 K in air and reported a sketch of the stable phase boundaries based on the XRD analyses of 19 phases mixtures of various compositions (see Appendix A). In addition, the authors reported a single quaternary phase in this system, namely $K_8Sr_2U_6O_{24}$(cr), isotructural with $Na_8Sr_2U_6O_{24}$ [2008KES/KAN] and $Rb_8Sr_2U_6O_{24}$ [2002KES/AGA], with cubic symmetry and cell parameter $a$ = 8.650(3) Å. In addition, [2011KES/AGA] estimated the enthalpies of formation and Gibbs energies of formation of $A_2Sr_2U_4O_{15}$ and $A_8Sr_2U_6O_{24}$

(A = Na, K, Rb, Cs) at 298.15 K using the method of Chen *et al.* [1999CHE/EWI]. However, we have not pursued this approach since the estimated functions have appreciable uncertainties.

## 9.13.4 Rubidium compounds

### 9.13.4.1 Rubidium uranates

There are no new thermodynamic data for these compounds and the present review retains the values selected by [1992GRE/FUG], [2003GUI/FAN]. [2005YAG/OBB] reported the synthesis of single crystals of $Rb_2U_2O_7$ and $Rb_8U_9O_{31}$ and differential thermal analysis (DTA), density, conductivity, and infrared spectroscopy measurements on polycrystalline materials. The authors showed that $Rb_2U_2O_7$ and $Rb_8U_9O_{31}$ crystallise with monoclinic and orthorhombic symmetries, respectively. In addition, no phase transitions or melting points were observed by DTA, and the X-ray diffraction data collected after the experiment showed that both phases were stable until 1573 K. Further details are given in Appendix A.

### 9.13.4.2 $Rb_2U(SO_4)_3$(cr)

There are no new thermodynamic data for these compounds and the present review retains the values selected by [1992GRE/FUG], [2003GUI/FAN].

### 9.13.4.3 $Rb_2Sr_2U_4O_{15}$(cr) and $Rb_8Sr_2U_6O_{24}$(cr)

Although no thermodynamic data are reported, [2002KES/AGA] give interesting information on the the Rb-Sr-U-O quaternary phase diagram, which they investigated at 1173 K in air. They suggested stable phase boundaries based on the XRD analyses of 22 phase mixtures of various compositions. In addition, they reported for the first time the existence of the quaternary phases $Rb_2Sr_2U_4O_{15}$ (isostructural with $Cs_2Sr_2U_4O_{15}$ [2006KES/AGA]) which shows monoclinic symmetry (Z = 2) with cell parameters $a$ = 7.875(4) Å, $b$ = 13.199(4) Å, $c$ = 6.667(5) Å, and β = 104.93(8) °; and $Rb_8Sr_2U_6O_{24}$ which shows cubic symmetry in space group *Im3m* with cell parameter $a$ = 8.743(1) Å. Further details are given in Appendix A.

## 9.13.5 Caesium compounds

### 9.13.5.1 Caesium uranates

There are no new thermodynamic data for these compounds and the present review retains the values selected by [1992GRE/FUG], [2003GUI/FAN].

Van den Berghe and co-workers prepared high grade purity samples of $Cs_2UO_4$, $Cs_2U_2O_7$, $Cs_4U_5O_{17}$ and $Cs_2U_4O_{12}$ and refined their crystal structures based on X-ray and neutron diffraction data [2002BER/VER]. The structure of $Cs_2U_4O_{12}$ was solved for the first time using ab-initio refinement [2002BER/LAV]. $Cs_2UO_4$ crystallises in the

tetragonal system; $Cs_2U_2O_7$ in the monoclinic system; $Cs_4U_5O_{17}$ in the orthorhombic system; $Cs_2U_4O_{12}$ has trigonal symmetry. The authors moreover investigated the uranium valence states and local environments using X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS). They confirmed the hexavalence of uranium in $Cs_2UO_4$, $Cs_2U_2O_7$, and $Cs_4U_5O_{17}$, and reported an uranyl-type configuration in all three compounds. $Cs_2U_4O_{12}$ was shown to be a mixed $U^{5+}/U^{6+}$ valence state compound with a much more symmetric environment.

#### 9.13.5.2 $Cs_2Sr_2U_4O_{15}$(cr)

[2006KES/AGA] investigated the Cs-Sr-U-O quaternary phase diagram at 1173 K in air and suggested stable phase boundaries based on the XRD analyses of 20 phases mixtures of various compositions (see Appendix A). They reported for the first time the existence of the quaternary phase $Cs_2Sr_2U_4O_{15}$ (isostructural with $Rb_2Sr_2U_4O_{15}$ [2002KES/AGA]). However, no thermodynamic data for this phase are reported.

## 9.14 Uranium compounds with elements from other groups

### 9.14.1 Thallium compounds

#### 9.14.1.1 Thallium uranates

[2005VOL/MAY] have reported the preparation and structural characterisation of the thallium uranates $Tl_4UO_5$, $Tl_2UO_4$, $Tl_2U_2O_7$, and $Tl_2U_3O_{10}$ by IR, Raman spectroscopy, electronic and X-ray absorption spectroscopy at the U-$L_{III}$ edge. In addition, the authors studied the thermal stability of the compounds by thermogravimetry. $Tl_2U_3O_{10}$ was found the most stable compound, followed by $Tl_2U_2O_7$, $Tl_2UO_4$ and $Tl_4UO_5$. No new thermodynamic data have been reported for these phases.

### 9.14.2 Zinc compounds

No new thermodynamic data have been reported for zinc compounds.

### 9.14.3 Chromium compounds

#### 9.14.3.1 $CrUO_4$(cr)

[2016GUO/TIF] have reported the measurement of the enthalpy of formation of a well-characterised sample of $CrUO_4$(cr) using high temperature solution calorimetry in a molten sodium molybdate solvent ($3Na_2O{\cdot}4MoO_3$) at 1075 K. $CrUO_4$ has an orthorhombic structure [1961SMI/CLI], [1965BAC/BER]. [2016GUO/TIF] confirmed by combined XANES and XPS measurements and DFT calculations the trivalent state of Cr and pentavalent state of U in this compound.

We have found an error in the thermochemical cycle used by the authors as detailed in Appendix A. Correcting for this error and using the recommended auxiliary data, we have re-calculated:

$$\Delta_f H_m^o (CrUO_4, cr, 298.15\ K) = \mathbf{-\ (1753.600 \pm 4.800)}\ kJ \cdot mol^{-1}.$$

which is selected in this review.

## 9.14.4 Iron compounds

### 9.14.4.1 $FeUO_4$(cr)

[2016GUO/TIF] have reported the measurement of the enthalpy of formation of a well-characterised sample of $FeUO_4$(cr) using high temperature solution calorimetry in a molten lead borate solution ($2PbO \cdot B_2O_3$) at 1075 K. $FeUO_4$ has an orthorhombic structure [1961SMI/CLI], [1965BAC/BER]. [2016GUO/TIF] confirmed by combined XANES, XPS, and $^{57}Fe$ Mössbauer spectroscopy measurements and DFT calculations the trivalent state of Fe and pentavalent state of U in this compound.

We agree with the calculation of the enthalpy of formation by [2016GUO/TIF], which is in good agreement with previous measurements reported in the literature, namely $\Delta_f H_m^o (FeUO_4, cr, 298.15\ K) = -(1588.7 \pm 1.2)\ kJ \cdot mol^{-1}$ obtained using $2PbO \cdot B_2O_3$ solvent at 988 K in air for a $FeUO_4$ sample containing $U_3O_8$ as impurity phase [2000LAB/ROG]. Based on the data of [2016GUO/TIF] and using the recommended auxiliary data, we have re-calculated:

$$\Delta_f H_m^o (FeUO_4, cr, 298.15\ K) = \mathbf{-\ (1599.700 \pm 3.100)}\ kJ \cdot mol^{-1}$$

which is selected in this review.

## 9.14.5 Titanium compounds

### 9.14.5.1 $U_{0.952}Ti_2O_6$(cr)

[2005DON/STE] have reported the measurement of the low temperature heat capacity of brannerite $UTi_2O_6$ and cerium brannerite $CeTi_2O_6$ using adiabatic calorimetry in the temperature range 10-400 K. $UTi_2O_6$ has a monoclinic symmetry [1982SZY/SCO]. The brannerite sample was prepared by solid state synthesis from $UO_2$ and $TiO_2$ starting materials, and the composition determined by XRD was $U_{0.952}Ti_{2.04806}O_6$ with 0.31 wt % $UO_2$ impurity. After correction for the heat capacity contribution of the uranium dioxide impurity based on the data of Westrum and Huntzicker [1971HUN/WES], the authors derived the following heat capacity and standard entropy values, which are selected, the uncertainties being estimated by this review:

$$C_{p,m}^o (U_{0.952}Ti_{2.04806}O_6, cr, 298.15\ K) = \mathbf{(179.460 \pm 3.400)}\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m^o (U_{0.952}Ti_{2.04806}O_6, cr, 298.15\ K) = \mathbf{(175.560 \pm 3.500)}\ J \cdot K^{-1} \cdot mol^{-1}.$$

Using the auxiliary data recommended in this review, we have recalculated the standard entropy of formation as $\Delta_f S^o_m$ ($U_{0.952}Ti_{2.04806}O_6$, cr, 298.15 K) = **– (550.600 ± 3.500)** $J \cdot K^{-1} \cdot mol^{-1}$.

### 9.14.6 Polyoxometallates

Polyoxometallates were discussed in [2003GUI/FAN] but with no selected values. There are three new studies Yusev *et al.* [2007YUS/SHI], [2007YUS/SHI2], and [2007YUS/SHI3] discussing formal redox potential of a number of actinide couples and equilibrium constants for complexes between U(VI), Np(VI) and Pu(VI) with the heteropolyanions $P_2W_{17}O_{61}^{10-}$, $SiW_{11}O_{39}^{8-}$ and $PW_{11}O_{39}^{7-}$ in acid test solutions from 2 M $H^+$ to pH 5-5.5, both with and without the presence of $Na^+$ and $K^+$ as counter-ions. They have also determined the equilibrium constants of An(III)/An(IV) and Ln(III)/Ln(IV complexes with the $P_2W_{17}O_{61}^{10-}$, hetero-polyanion. The present review notes that these data cannot be recalculated to zero ionic strength and also that the chemical information is not relevant for the behaviour of actinides in technical systems and in Nature.

## 9.15 Uranium mineral phases

### 9.15.1 Introduction

The chapter on the uranium minerals was first introduced in [1992GRE/FUG]. It consisted of a table, which included the names and formulae of minerals, and also indicated the section of the book where thermodynamic properties of a specific mineral have been discussed.

In [1995SIL/BID] the mineral part was significantly revised and expanded. The text now included short reviews of the studies on the thermodynamic properties, as a rule the solubility of minerals. It was pointed out that the quality of experimental data in these references was not sufficiently good to include them in the selection procedure. Among typical shortcomings were the lack of experimental details on the technique used and chemical analysis, as well as on the auxiliary data used, the incomplete set of complexes used in the thermodynamic treatment of solubility data, *etc*. The decision was taken to include only solid phases which are considered to be important for modeling radionuclide migration: this decision excluded solids containing alkali metals other than Na and K, intermetallic compounds and alloys, halides, nitrates, *etc.* Systems, thoroughly discussed in the main text of [1992GRE/FUG], like simple oxides, hydroxides, sulfides, sulfites, sulfates, have also been excluded from the table. Minerals, for which only stoichiometric or structural information is reported, have not been considered. The solid phases presented in the table have been rearranged into families (phosphates, arsenates, sulfates *etc.*). The revised table now included, in addition to the names and formulas of minerals,

also gives references to original experimental studies or the NEA volume where thermodynamic data for the minerals have been selected.

The discussion of studies on the solubility of uranium minerals was updated in [2003GUI/FAN], while preserving the general structure of the corresponding section in [1995SIL/BID].

## 9.15.2 Review of papers on solubility and thermochemistry of uranium minerals

Solubility and calorimetric results for many synthetic solid uranyl compounds, having analogs among minerals, have been discussed in the main text and in Appendix A of the current review. However, most studies, cited in the Table below, have not been selected, because they do not correspond to the NEA criteria for selection of thermodynamic properties; see discussions of older studies in [2003GUI/FAN]. In addition, uranyl vanadates, extensively studied recently, have not been considered in the review by Guillaumont *et al.* After the publication of the previous edition of thermodynamic properties of uranium compounds [2003GUI/FAN], many solubility and thermochemical results have been published by the group from University of Nizhny Novgorod, Russia (Chernorukov and coworkers), see [2002CHE/KAR], [2002CHE/KAR2], [2002CHE/SUL], [2002KAR/CHE4], [2002SUL/KAR], [2003CHE/SUL], [2003CHE/SUL3], [2003CHE/SUL4], [2003KAR/CHE], [2004SUL/CHE], [2005CHE/NIP2], [2006SUL/CHE], [2009CHE/KNY], [2012CHE/NIP], [2012NIP/CHE], [2013NIP/CHE], [2013NIP/CHE2], [2013NIP/CHE3]. Additional solubility studies of uranium minerals have been presented by Tokunaga *et al.* [2012TOK/KIM] for calcium uranyl vanadate (tyuyaminite) and Djogić *et al.* [2005DJO/CUC] for metastudtite ($UO_4(H_2O)_2$). Combined solubility and calorimetric studies have been performed by Kubatko *et al.* [2003HUG/HEL] for studtite ($UO_4(H_2O)_4$).

## 9.15.3 Summary of mineral information

Table 9.43 on pp. 286-292 in [2003GUI/FAN] has been updated, see Table 9-92 with the new information. As in previous editions, this table has been included to facilitate the task of geochemists searching for thermodynamic data to model uranium migration in aquatic environments. Only solid phases, which this review considers important for modeling of radionuclide migration, were retained in the table. The solid phases have been arranged into families (phosphates, sulfates, *etc.*). Note that many of the cited results have not been selected in the current review, so, it is up to the user to decide whether to use these thermodynamic data, or not. The users are advised to consult the main text to obtain information on the thermodynamic data in Table 9-92 for minerals, for which selected values are available.

Table 9-92: Minerals of uranium and related solid phases of interest for geochemical modelling. The inclusion of these formulae in the table is to be understood as information on the existence of published material. However, these data have not been critically reviewed according to the NEA criteria. Many simple oxides, hydroxides, sulfides, sulfites, sulfates, *etc*. are excluded, because they have been discussed in the main text of [1992GRE/FUG], [2003GUI/FAN] and the current review.

| ***Ternary and quaternary oxides and hydroxides*[(a)]** | | **Reference** |
|---|---|---|
| $PbU_2O_7 \cdot 2H_2O$(cr) | wölsendorfite | [1990VOC/HAV] |
| $Ni(UO_2)_3O_3(OH)_2 \cdot 2H_2O$(cr) | | [1991VOC/HAV] |
| $Mn(UO_2)_3O_3(OH)_2 \cdot 2H_2O$(cr) | | [1991VOC/HAV] |
| $MgUO_4$(cr) | | **data selected in this review** |
| $MgU_2O_6$(cr) | | [1981GOL/TRE2] |
| $MgU_2O_7$(cr) | | [1981GOL/TRE2] |
| $MgU_3O_{10}$(cr) | | **data selected** in [1992GRE/FUG] |
| $Mg(UO_2)_6O_4(OH)_4 \cdot 13H_2O$(cr) | | [1991VOC/HAV] |
| $Mg_3U_3O_{10}$(cr) | | [1983FUG] |
| $CaUO_4$(cr) | | **data selected in this review** |
| $Ca_3UO_6$(cr) | | **data selected** in [1992GRE/FUG] |
| $CaU_2O_6$(cr) | | [1981GOL/TRE], [1982MOR], [1983FUG], [1985PHI/PHI], [1986MOR], [1988PHI/HAL] |
| $CaU_2O_7$(cr) | calciouranoite, anhydr. | [1981GOL/TRE], [1982MOR], [1983FUG], [1985PHI/PHI], [1986MOR], [1988PHI/HAL] |
| $CaU_6O_{19} \cdot 11H_2O$(cr) | becquerelite | **data selected** in [2003GUI/FAN] |
| α-$SrUO_4$(cr) | | **data selected in this review** |
| β-$SrUO_4$(cr) | | **data selected in this review** |
| $SrUO_4$(cr) | | [1983KOH] |
| $Sr_2UO_5$(cr) | | **data selected** in [1992GRE/FUG] |
| $Sr_3UO_6$(cr) | | **data selected** in [2003GUI/FAN] |
| $Sr_2U_3O_{11}$(cr) | | **data selected** in [1992GRE/FUG] |
| $SrU_4O_{13}$(cr) | | **data selected** in [1992GRE/FUG] |
| $BaUO_3$(cr) | | **data selected** in [1992GRE/FUG] |
| $BaUO_4$(cr) | | **data selected in this review** |
| $Ba_3UO_6$(cr) | | **data selected in this review** |
| $BaU_2O_7$(cr) | bauranoite, anhydr. | **data selected** in [1992GRE/FUG] |
| $Ba_2U_2O_7$(cr) | | **data selected** in [1992GRE/FUG] |
| $Ba_{2.875}UO_{5.875}$(cr) | | **data selected in this review** |
| $Ba_2U_3O_{11}$(cr) | | **data selected in this review** |
| $Ba_6Dy_2(UO_6)_3$(cr) | | [1982MOR] |
| $Ba_2MgUO_6$(cr) | | **data selected** in [1992GRE/FUG] |
| $Ba_2CaUO_6$(cr) | | **data selected** in [1992GRE/FUG] |
| $Ba_2SrUO_6$(cr) | | **data selected in this review** |
| $BaU_6O_{19} \cdot 11H_2O$(cr) | billietite | [1990VOC/HAV] |
| $NaUO_3$(cr) | | **data selected in this review** |
| α-$Na_2UO_4$(cr) | | **data selected** in [2003GUI/FAN] |
| β-$Na_2UO_4$(cr) | | **data selected** in [2003GUI/FAN] |
| $Na_3UO_4$(cr) | | **data selected** in [2003GUI/FAN] |
| $Na_4UO_5$(cr) | | **data selected in this review** |
| $Na_2U_2O_7$(cr) | | **data selected** in [2003GUI/FAN] |

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Table 9-92 (continued)

| ***Ternary and quaternary oxides and hydroxides*[(a)]** | | **Reference** |
|---|---|---|
| $Na_6U_7O_{21}$(cr) | | [1978COR/OHA] |
| $Na_6U_7O_{24}$(cr) | | **data selected** in [1992GRE/FUG] |
| $Na_4O_4UO_4 \cdot 9H_2O$(cr) | | [1982WAG/EVA] |
| $Na_2U_2O_7 \cdot 1.5H_2O$(cr) | | [1965MUT],[1982WAG/EVA] |
| $KUO_3$(cr) | | **data selected** in [1992GRE/FUG] |
| $K_2UO_4$(cr) | | **data selected** in [1992GRE/FUG] |
| $K_4UO_5$(cr) | | [1981LIN/BES] |
| $K_2U_2O_7$(cr) | | **data selected** in [1992GRE/FUG] |
| $K_2U_4O_{13}$(cr) | | [1981LIN/BES] |
| $K_2U_6O_{19} \cdot 11H_2O$(cr) | compreignacite | **data selected** in [2003GUI/FAN] |
| $K_2U_7O_{22}$(cr) | | [1981LIN/BES] |
| ***Sulfates*[(b,c)]** | | **Reference** |
| $Ca_3NaUO_2(CO_3)_3FSO_4 \cdot 10H_2O$(cr) | schröckingerite | [1982HEM], [1983OBR/WIL] |
| $Zn_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O$(cr) | Zn-zippeite | [1979HAA/WIL], [1981OBR/WIL], [1982HEM][(d)] |
| $Co_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O$(cr) | Co-zippeite | [1979HAA/WIL], [1981OBR/WIL], [1982HEM][(d)] |
| $Ni_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O$(cr) | Ni-zippeite | [1979HAA/WIL], [1981OBR/WIL], [1982HEM][(d)] |
| $Mg_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O$(cr) | Mg-zippeite | [1979HAA/WIL], [1981OBR/WIL], [1982HEM][(d)] |
| $Na_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O$(cr) | Na-zippeite | [1981OBR/WIL], [1982HEM] |
| $K_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O$(cr) | zippeite | [1981OBR/WIL], [1982HEM] |
| ***Phosphates*[(c)]** | | **Reference** |
| $U_3(PO_4)_4$(cr) | | [1973MOS], [1978ALL/BEA][(e)] |
| $U(HPO_4)_2 \cdot 4H_2O$(cr) | | **data selected** in [1992GRE/FUG] |
| $U(HPO_4)_2$(cr) | | [1971MOS], [1984VIE/TAR], [1986WAN][(f)] |
| $U(HPO_4)_2H_3PO_4 \cdot 4H_2O$(cr) | | [1955SCH] |
| $UO_2HPO_4 \cdot 4H_2O$(cr) | chernikovite | **data selected in this review** |
| $UO_2HPO_4$(cr) | | **data selected in this review** |
| $(UO_2)_3(PO_4)_2$(cr) | | **data selected** in [1992GRE/FUG] |
| $(UO_2)_3(PO_4)_2$(cr)$\cdot 4H_2O$(cr) | | **data selected** in [1992GRE/FUG] |
| $NH_4(UO_2)(PO_4) \cdot 3H_2O$(cr) | uramphite | **data selected in this review** |
| $(NH_4)_2(UO_2)_2(PO_4)_2$(cr) | | [1978LAN], [1988PHI/HAL] |
| $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O$(cr) | sabugalite | [1983VOC/PEL] |
| $HAl(UO_2)_4(PO_4)_4$(cr) | sabugalite, anhydr. | [1984GEN/WEI] |
| $Al[(PO_4)(UO_2)]_2(OH) \cdot 11H_2O$(cr) | | [2002CHE/KAR] |
| $Pb_2UO_2(PO_4)_2 \cdot 2H_2O$(cr) | parsonsite | [1984NRI2] |
| $Pb_2UO_2(PO_4)_2 \cdot 0.5H_2O$(cr) | | [1991VOC/HAV2] |
| $Pb_2UO_2(PO_4)_2$(cr) | parsonsite, anhydr. | [1984GEN/WEI] |
| $Pb(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)[(c)] | | [1965MUT/HIR], [2012NIP/CHE] |
| $Pb_2(UO_2)_2(PO_4)_2 \cdot 2H_2O$(cr) | przhevalskite | [1984NRI2][(f)] |
| $Pb_2(UO_2)_2(PO_4)_2$(cr) | przhevalskite, anhydr. | [1978LAN], [1985PHI/PHI], [1988PHI/HAL] |
| $Pb_2(UO_2)_3(PO_4)_2(OH)_2$(cr) | | [1984GEN/WEI] |
| $Pb_2(UO_2)_3(PO_4)_2(OH)_4 \cdot 3H_2O$(cr) | dumontite | [1984NRI2] |
| $Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$(cr) | renardite[(g)] | [1984NRI2] |
| $Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 8H_2O$(cr) | | [1984NRI2] |
| $Cu(UO_2)_2(PO_4)_2 \cdot 12H_2O$(cr) | torbernite | [1965MUT/HIR], [1984NRI2] |

(Continued on next page)

Table 9-92 (continued)

| ***Phosphates*[c]** | | **Reference** |
|---|---|---|
| $Zn(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr) | | **data selected in this review** |
| $Zn(UO_2)_2(PO_4)_2 \cdot 8H_2O$(cr) | | **data selected in this review** |
| $Cd(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)[c] | | [2003CHE/SUL], [2003CHE/SUL3], [2012NIP/CHE] |
| $Cd(UO_2)_2(PO_4)_2$(cr) | | [2003CHE/SUL] |
| $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$(cr) | meta-torbernite | **data selected in this review** |
| $Cu(UO_2)_2(PO_4)_2$(cr) | torbernite, anhydr. | [1978LAN], [1985PHI/PHI], [1988PHI/HAL] |
| $Ni(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr) | | **data selected in this review** |
| $Ni(UO_2)_2(PO_4)_2 \cdot 8H_2O$(cr) | | **data selected in this review** |
| $Ni(UO_2)_2(PO_4)_2 \cdot 7H_2O$(cr) | | [1968PEK/VES], [1981VOC/PIR], [1984VIE/TAR] |
| $Co(UO_2)_2(PO_4)_2 \cdot 7H_2O$(cr)[c] | | [1981VOC/PIR], [1984VIE/TAR], [2000KIR/CHE], [2003CHE/SUL], [2012NIP/CHE] |
| $Co(UO_2)_2(PO_4)_2$(cr) | | [2000KIR/CHE], [2003CHE/SUL] |
| $Fe(UO_2)_2(PO_4)_2OH \cdot 6H_2O$(cr) | | [1984VOC/GRA] |
| $Fe(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)[c] | | [2000KIR/CHE], [2003CHE/SUL], [2003CHE/SUL3] |
| $Fe(UO_2)_2(PO_4)_2OH \cdot 8H_2O$(cr) | bassetite | [1965MUT/HIR], [1984VOC/GRA][h] |
| $Fe(UO_2)_2(PO_4)_2$(cr) | bassetite, anhydr. | [1978LAN], [1985PHI/PHI], [1986WAN], [1988PHI/HAL], [2000KIR/CHE], [2003CHE/SUL] |
| $Mn(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)[c] | lehnerite | [2003CHE/SUL], [2012NIP/CHE] |
| $Mn(UO_2)_2(PO_4)_2$(cr) | lehnerite, anhydr. | [2003CHE/SUL], [2003CHE/SUL3] |
| $La[(UO_2)(PO_4)]_3 \cdot 14H_2O$(cr) | | [2002KAR/CHE4] |
| $Mg(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr) | saleeite | [1965MUT/HIR], [2006SUL/CHE] |
| $Mg(UO_2)_2(PO_4)_2 \cdot 8H_2O$(cr) | meta-saleeite | **data selected in this review** |
| $Mg(UO_2)_2(PO_4)_2$(cr) | saleeite, anhydr. | [1978LAN], [1985PHI/PHI], [1986WAN], [1988PHI/HAL] |
| $CaU(PO_4)_2 \cdot 2H_2O$(cr) | ningyoite | [1965MUT], [1965MUT/HIR], [1978LAN], [1984VIE/TAR], [1988PHI/HAL] |
| $CaU(PO_4)_2$(cr) | | [1986WAN] |
| $Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr) | autunite | [1965MUT], [1965MUT/HIR], [1984VIE/TAR] |
| $Ca(UO_2)_2(PO_4)_2 \cdot 6H_2O$(cr) | meta-autunite | **data selected in this review** |
| $Ca(UO_2)_2(PO_4)_2$(cr) | autunite, anhydr. | [1978LAN], [1985PHI/PHI], [1986WAN], [1988PHI/HAL], [1996KAR/CHE] |
| $Ca(UO_2)_4(PO_4)_2(OH)_4$(cr) | | [1984GEN/WEI] |
| $Sr(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr) | | [1965MUT/HIR] |
| $Sr(UO_2)_2(PO_4)_2 \cdot 6H_2O$(cr) | | **data selected in this review** |
| $Sr(UO_2)_2(PO_4)_2$(cr) | Sr-autunite, anhydr. | [1978LAN], [1985PHI/PHI], [1986WAN], [1988PHI/HAL], [1996KAR/CHE] |
| $Ba(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr) | uranocircite | [1965MUT/HIR] |
| $Ba(UO_2)_2(PO_4)_2 \cdot 6H_2O$(cr) | uranocircite II | **data selected in this review** |
| $Ba(UO_2)_2(PO_4)_2$(cr) | uranocircite, anhydr. | [1978LAN], [1984GEN/WEI], [1985PHI/PHI], [1986WAN], [1988PHI/HAL], [1996KAR/CHE] |

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Table 9-92 (continued)

| ***Phosphates***[(c)] | | **Reference** |
|---|---|---|
| $Na(UO_2)(PO_4)\cdot 3H_2O$(cr) | Na-meta-autunite | **data selected in this review** |
| $Na(UO_2)(PO_4)$(cr) | Na-autunite, anhydr. | [1985PHI/PHI], [1986WAN], [1993KAR/CHE], [1999KAR/CHE], [2002SUL/KAR], [2000KAR/CHE] |
| $Na_2(UO_2)_2(PO_4)_2$(cr) | | [1978LAN], [1988PHI/HAL] |
| $Na_2(UO_2)_2(PO_4)_2\cdot 10H_2O$(cr) | | [1965MUT/HIR] |
| $K(UO_2)(PO_4)\cdot 3H_2O$(cr) | meta-ankoleite | **data selected in this review** |
| $K(UO_2)(PO_4)$(cr) | K-autunite, anhydr. | [1978LAN], [1982WAG/EVA], [1984VIE/TAR], [1985PHI/PHI], [1986WAN], [1988PHI/HAL], [1993KAR/CHE], [1999KAR/CHE], [2000KAR/CHE], [2002SUL/KAR] |
| $K_2(UO_2)_2(PO_4)_2\cdot 10H_2O$(cr) | | [1965MUT/HIR] |
| ***Pyrophosphates*** | | **Reference** |
| $UP_2O_7\cdot xH_2O$(cr) | | [1967MER/SKO][(i)] |
| $UP_2O_7$(cr) | | **data selected** in [1992GRE/FUG] |
| $(UO_2)_2P_2O_7$(cr) | | **data selected** in [1992GRE/FUG] |
| ***Arsenates*** | | **Reference** |
| $(UO_2)_3(AsO_4)_2\cdot 12H_2O$(cr) | troegerite | **data selected in this review** |
| $(UO_2)_3(AsO_4)_2$(cr) | troegerite, anhydr. | **data selected** in [1992GRE/FUG] |
| $UO_2HAsO_4\cdot 4H_2O$(cr) | hydrogen uranospinite | **data selected in this review** |
| $UO_2HAsO_4$(cr) | | [1984GEN/WEI] |
| $NH_4(UO_2)(AsO_4)\cdot 3H_2O$(cr) | | **data selected in this review** |
| $Pb_2UO_2(AsO_4)_2$(cr) | hallimondite | [1984GEN/WEI] |
| $Pb(UO_2)_2(AsO_4)_2\cdot 10H_2O$(cr) | | **data selected in this review** |
| $Al(AsO_4)_2(UO_2)_2(OH)\cdot 13H_2O$ | | [2002CHE/KAR] |
| $Zn(UO_2)_2(AsO_4)_2\cdot 8H_2O$(cr)[(c)] | | **data selected in this review** |
| $Zn(UO_2)_2(AsO_4)_2$(cr) | meta-lodevite, anhydr. | [1984GEN/WEI] |
| $Cd(UO_2)_2(AsO_4)_2\cdot 8H_2O$(cr)[(c)] | | **data selected in this review** |
| $Cu(UO_2)_2(AsO_4)_2\cdot 8H_2O$(cr)[(c)] | meta-zeunerite | **data selected in this review** |
| $Cu(UO_2)_2(AsO_4)_2$(cr) | meta-zeunerite, anhydr. | [1984GEN/WEI] |
| $Ni(UO_2)_2(AsO_4)_2\cdot 7H_2O$(cr)[(c)] | meta-rauchite | **data selected in this review** |
| $Co(UO_2)_2(AsO_4)_2\cdot 7H_2O$(cr)[(c)] | meta-kirchheimerite | [1984VOC/GOE], [2002CHE/SUL], [2012CHE/NIP] |
| $Co(UO_2)_2(AsO_4)_2$(cr) | kirchheimerite, anhydr. | [1984GEN/WEI] |
| $Fe(UO_2)_2(AsO_4)_2\cdot 8H_2O$(cr) | meta-kahlerite | **data selected in this review** |
| $Fe(UO_2)_2(AsO_4)_2$(cr) | kahlerite, anhydr. | [1984GEN/WEI] |
| $Mn(UO_2)_2(AsO_4)_2\cdot 8H_2O$(cr)[(c)] | | [1986VOC/GRA], [2002CHE/SUL], [2012CHE/NIP] |
| $La[(UO_2)(AsO_4)]_3\cdot 15H_2O$(cr) | | [2002KAR/CHE4] |
| $Mg(UO_2)_2(AsO_4)_2\cdot 8H_2O$(cr)[(c)] | meta-nováčekite | **data selected in this review** |
| $Mg(UO_2)_2(AsO_4)_2$(cr) | meta-nováčekite, anhydr. | [1984GEN/WEI] |
| $Ca(UO_2)_2(AsO_4)_2\cdot 8H_2O$(cr)[(c)] | meta-uranospinite | **data selected in this review** |
| $Ca(UO_2)_2(AsO_4)_2$(cr) | uranospinite, anhydr. | [1984GEN/WEI], [1991FAL/HOO] |
| $Ca(UO_2)_4(AsO_4)_2(OH)_4$(cr) | arsenuranylite, anhydr. | [1984GEN/WEI] |
| $Sr(UO_2)_2(AsO_4)_2\cdot 8H_2O$(cr)[(c)] | | **data selected in this review** |
| $Ba(UO_2)_2(AsO_4)_2\cdot 7H_2O$(cr)[(c)] | meta-heinrichite | **data selected in this review** |
| $Ba(UO_2)_2(AsO_4)_2$(cr) | heinrichite, anhydr. | [1984GEN/WEI] |
| $Na(UO_2)(AsO_4)\cdot 3H_2O$(cr) | Na-uranospinite | **data selected in this review** |
| $Na(UO_2)(AsO_4)$(cr) | Na-uranospinite, anhydr. | [1991FAL/HOO], [2000KAR/CHE], [2002ERM] |

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Table 9-92 (continued)

| *Arsenates* | | Reference |
|---|---|---|
| $K(UO_2)(AsO_4)\cdot 3H_2O$(cr) | abernathyite | **data selected in this review** |
| $K(UO_2)(AsO_4)$(cr) | abernathyite, anhydr. | [2000KAR/CHE], [2002ERM] |
| ***Carbonates*** | | **Reference** |
| $UO_2CO_3$(cr) | rutherfordine | **data selected in this review** |
| $UO_2CO_3\cdot H_2O$(cr) | | [1982HEM][(j)] |
| $UO_2(HCO_3)_2\cdot H_2O$(cr) | | [1976BOU/BON], [1978COR/OHA], [1982WAG/EVA], [1983FUG], [1986MOR] |
| $Ca_3NaUO_2(CO_3)_3FSO_4\cdot 10H_2O$(cr) | schröckingerite | [1982HEM], [1983OBR/WIL] |
| $Mg_2UO_2(CO_3)_3\cdot 18H_2O$(cr) | bayleyite | [1980ALW/WIL], [1980BEN/TEA], [1982HEM], [2009CHE/KNY] |
| $Mg_2UO_2(CO_3)_3$(cr) | | [2009CHE/KNY] |
| $CaMgUO_2(CO_3)_3\cdot 12H_2O$(cr) | swartzite | [1980ALW/WIL], [1980BEN/TEA], [1982HEM] |
| $Ca_2UO_2(CO_3)_3\cdot 10\text{-}11H_2O$(cr) | liebegite | [1980ALW/WIL], [1980BEN/TEA], [1982HEM], [1983OBR/WIL][(k)], [2009CHE/KNY] |
| $Ca_2UO_2(CO_3)_3$(cr) | | [2009CHE/KNY] |
| $Ca_2CuUO_2(CO_3)_4\cdot 6H_2O$(cr) | voglite | [1982HEM] |
| $CaNa_2UO_2(CO_3)_3\cdot 6H_2O$(cr)[(c)] | andersonite | [1980ALW/WIL], [1980BEN/TEA], [1983OBR/WIL][(k)], [2005KUB/HEL] |
| $Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4\cdot 18H_2O$(cr) | rabbittite | [1982HEM] |
| $Sr_2UO_2(CO_3)_3\cdot 8H_2O$(cr) | | [2009CHE/KNY] |
| $Sr_2UO_2(CO_3)_3$(cr) | | [2009CHE/KNY] |
| $Ba_2UO_2(CO_3)_3\cdot 6H_2O$(cr) | | [2009CHE/KNY] |
| $Ba_2UO_2(CO_3)_3$(cr) | | [2009CHE/KNY] |
| $Na_4UO_2(CO_3)_3$(cr) | cejkaite | **data selected in this review** |
| $K_4UO_2(CO_3)_3$(cr) | | **data selected in this review** |
| $K_3NaUO_2(CO_3)_3\cdot H_2O$(cr) | grimselite | [1983OBR/WIL], [2005KUB/HEL] |
| $K_3NaUO_2(CO_3)_3$(cr) | | **data selected in this review** |
| ***Silicates*** | | **Reference** |
| $USiO_4$(cr) | coffinite | [2013SZE/COS], [2015GUO/SZE], [2016SZE/MES] |
| $(UO_2)_2SiO_4\cdot 2H_2O$(cr) | soddyite | **data selected in this review** |
| $PbUO_2SiO_4\cdot H_2O$(cr) | kasolite | [1982HEM], [2005CHE/NIP2] |
| $Zn(UO_2)_2(SiO_3OH)_2\cdot 6H_2O$(cr) | | [2013NIP/CHE3] |
| $Cu(UO_2)_2(SiO_3OH)_2\cdot 6H_2O$(cr) | cupro sklodowskite | [1982HEM], [2013NIP/CHE3] |
| $Ni(UO_2)_2(SiO_3OH)_2\cdot 6H_2O$(cr) | | [2013NIP/CHE3] |
| $Co(UO_2)_2(SiO_3OH)_2\cdot 6H_2O$(cr) | | [2013NIP/CHE3] |
| $Mn(UO_2)_2(SiO_3OH)_2\cdot 6H_2O$(cr) | | [2013NIP/CHE3] |
| $M^{III}(UO_2)_3(SiO_3OH)_3 1\cdot 0H_2O$ ($M^{III}$ = La-Lu, Y) | | [2013NIP/CHE2] |
| $Mg(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$(cr)[(c)] | sklodowskite | [1982HEM][(i)], [2005CHE/NIP2] |
| $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$(cr) | uranophane | **data selected in this review** |
| $Ca(UO_2)_2(SiO_3OH)_2$(cr) | uranophane, anhydr. | [1978LAN], [1980BEN/TEA], [1986WAN], [1988LEM], [1988PHI/HAL] |
| $Ca(UO_2)_2Si_6O_{15}$(cr)$\cdot 5H_2O$(cr) | haiweeite | [1982HEM] |
| $Ba(UO_2)SiO_4\cdot H_2O$ | | [2005CHE/NIP2] |

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Table 9-92 (continued)

| *Silicates* | | Reference |
|---|---|---|
| $Sr(UO_2)SiO_4 \cdot H_2O$(cr) | | [2005CHE/NIP2] |
| $Na(UO_2)(SiO_3OH) \cdot H_2O$(cr) | Na-boltwoodite | **data selected in this review** |
| $Na_2(UO_2)_2Si_6O_{15} \cdot 4H_2O$(cr) | Na-weeksite | [1992NGU/SIL] |
| $Na_{0.7}K_{0.3}(UO_2)(SiO_3OH) \cdot H_2O$(cr) | | [1982HEM], [1992NGU/SIL] |
| $K(UO_2)(SiO_3OH) \cdot H_2O$(cr) | boltwoodite | **data selected in this review** |
| $K_2(UO_2)_2Si_6O_{15} \cdot 4H_2O$(cr) | weeksite | [1982HEM] |
| ***Vanadates*** | | **Reference** |
| $(UO_2)_3(VO_4)_2 \cdot 4H_2O$(cr) | | [2013NIP/CHE] |
| $HUO_2VO_4 \cdot 2H_2O$(cr) | vanuranylite | **data selected in this review** |
| $Pb(UO_2)_2(VO_4)_2 \cdot 5H_2O$(cr) | curienite | [1999KAR/CHE3], [2001CHE/SUL2], [2004SUL/CHE] |
| $Pb(UO_2)_2(VO_4)_2$(cr) | curienite, anhydr. | [1984GEN/WEI], [2004SUL/CHE] |
| $Al(UO_2)_2(VO_4)_2OH$(cr) | vanuralite, anhydr. | [1984GEN/WEI] |
| $Zn(UO_2)_2(VO_4)_2 \cdot 4H_2O$(cr) | | [2002CHE/KAR2] |
| $Cd(UO_2)_2(VO_4)_2 \cdot 4H_2O$(cr) | | [2002CHE/KAR2] |
| $Cu(UO_2)_2(VO_4)_2 \cdot 9H_2O$(cr) | | [2001CHE/SUL2], [2002CHE/KAR2], [2003CHE/SUL4] |
| $CuUO_2VO_4$(cr) | sengierite, anhydr. | [1984GEN/WEI] |
| $Ni(UO_2)_2(VO_4)_2 \cdot 4H_2O$(cr) | | [2001CHE/SUL2], [2002CHE/KAR2], [2003CHE/SUL4] |
| $Co(UO_2)_2(VO_4)_2 \cdot 4H_2O$(cr) | | [2001CHE/SUL2], [2002CHE/KAR2], [2003CHE/SUL4] |
| $Fe(UO_2)_2(VO_4)_2 \cdot 4H_2O$(cr) | | [2002CHE/KAR2] |
| $Mn(UO_2)_2(VO_4)_2 \cdot 4H_2O$(cr) | | [2002CHE/KAR2] |
| $Mg(UO_2)_2(VO_4)_2 \cdot 5H_2O$(cr) | | **data selected in this review** |
| $Ca(UO_2)_2(VO_4)_2 \cdot 8H_2O$(cr)[(c)] | tyuyamunite | **data selected in this review** |
| $Ca(UO_2)_2(VO_4)_2$(cr) | tyuyamunite, anhydr. | **data selected in this review** |
| $Sr(UO_2)_2(VO_4)_2 \cdot 5H_2O$(cr) | | **data selected in this review** |
| $Ba(UO_2)_2(VO_4)_2 \cdot 5H_2O$(cr)[(c)] | francevillite | [1999KAR/CHE2], [1999KAR/CHE3], [2001CHE/SUL], [2003CHE/SUL4], [2003KAR/CHE] |
| $Ba(UO_2)_2(VO_4)_2$(cr) | francevillite, anhydr. | **data selected in this review** |
| $NaUO_2VO_4 \cdot 2H_2O$(cr) | strelkinite | **data selected in this review** |
| $NaUO_2VO_4$(cr) | strelkinite, anhydr. | [1984GEN/WEI], [2001KAR/CHE], [1998KAR/CHE5] |
| $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$(cr) | carnotite | **data selected in this review** |
| $KUO_2VO_4$(cr) | | **data selected in this review** |

**(a)** Simple oxides are discussed in Section V.3.3 (pp. 131-148) of [1992GRE/FUG]. **(b)** Only binary and ternary sulfates are listed. Simple uranium sulfates are discussed in Section V.5.1.3.2 (pp.249-254) of [1992GRE/FUG]. **(c)** There is some disagreement in the literature on the number of water molecules in the formulae. **(d)** See Section 5.1.3.2.c (pp.254-255) and the Discussion of [1979HAA/WIL] in Appendix A (p.646) of [1992GRE/FUG]. **(e)** See the discussion in Section V.6.2.2.5.b (p.294) of [1992GRE/FUG]. **(f)** Nriagu ([1984NRI2]) gives four waters of hydration for this mineral (Table 1). **(g)** The stoichiometry of the mineral renardite is not clear, although it is related to dewindtite: $Pb_3(UO_2)_6(PO_4)_4O_2(OH)_2 \cdot 12H_2O$(cr) ([1991FIN/EWI]). **(h)** Muto *et al.* ([1965MUT/HIR]) give ten molecules of water of hydration for this mineral. **(i)** See the discussion of [1967MER/SKO] in Appendix A (p.603) of [1992GRE/FUG]. **(j)** Hemingway ([1982HEM]) incorrectly assigned the name of sharpite to this solid. **(k)** Discussed in Section V.7.1.2.2.b (pp.327-328) of [1992GRE/FUG]. **(l)** Hemingway ([1982HEM]) reports estimated data for a solid with six water molecules.

# Chapter 10

# Discussion of new data selection for Neptunium

## 10.1 Neptunium aqua ions

### 10.1.1 $NpO_3^+$, $Np(OH)_6^+$, $NpO_4(OH)_2^{3-}$ and redox potentials in alkaline solutions

No new experimental or theoretical studies contributing to the discussion on the predominant Np(VII) species under acidic conditions ( $NpO_3^+$ or $Np(OH)_6^+$ ) have been published since the release of the last NEA TDB update book [2003GUI/FAN]. Shilov and co-workers [2009SHI/YUS] investigated the reduction potential of the Np(VII)/Np(VI) couple under acidic conditions using the reaction with Ag(I) and Co(II). The value of $E$(Np(VII)/Np(VI)) = (2.20 ± 0.01) V determined by these authors in 1 M $HClO_4$ is 0.16 V larger than the reduction potential determined by Musikas *et al.* in a previous potentiometric study [1974MUS/COU]. Both studies confirm that under acidic conditions, Np(VII) forms well outside the stability field of water and thus is not relevant in aqueous equilibrium systems.

A conclusive evidence on the structure of the Np(VII) species predominant in strong alkaline solutions ($NpO_4(OH)_2^{3-}$) was given by Bolvin and co-workers [2001BOL/WAH] and accepted in the previous NEA TDB update [2003GUI/FAN]. Since then, new experimental and theory studies have provided additional insights on this system, all of them confirming the proposed structure. Clark and co-workers [2004CLA/PAL] investigated Np(VII) solid compounds and aqueous species using EXAFS, Raman and $^{17}O$ NMR spectroscopy. All experimental evidence collected was consistent with the predominance of the tetraoxo form $NpO_4(OH)_2^{3-}$ in the aqueous phase. These experimental results were also in line with DFT calculations conducted in [2009WRE/SCH] using a continuum model for the solvent.

Gaona *et al.* [2014GAO/FEL] investigated the solubility equilibrium between $Na_2Np(VI)_2O_7$(cr) and Np(VII)(aq) in NaCl-NaOH ($I \leq 5.0$ M, $-\log_{10}[H^+] \leq 14.8$) and NaOH ($I \leq 4.0$ M) solutions in the presence of NaClO as oxidising agent. The predominance of the species $Np(VII)O_4(OH)_2^{3-}$ in solution was confirmed by UV-vis/NIR and EXAFS. No $E_h$ measurements were conducted and thus no thermodynamic

quantities can be derived from this study. The oxidation of Np(VI) to Np(VII) in strongly alkaline conditions was studied by Shilov, Fedoseev and co-workers [2010SHI/BES] and [2012SHI/FED]. The mechanism for the oxidation of Np(VI) to Np(VII) by ozone was investigated by Shilov *et al.* [2012SHI/FED] in 0.1 and 1.0 M LiOH. The authors concluded that the main oxidation path takes place *via* reaction of Np(VI) with $O_3^-$, though a minor contribution by $O_3$ in the oxidation process was also proposed. The same research group studied the effect of high salt concentrations on the formal potential of Np(VII)/Np(VI) in strongly alkaline conditions [2010SHI/BES]. The range of ionic strengths investigated by the authors is outside the validity range of SIT, and the reported values of $E$(Np(VII)/Np(VI)) can only be taken as tentative for the reasons discussed in Appendix A. On a qualitative basis, the results by Shilov and co-workers suggest an important effect of ionic strength on the formal potential, $E$(Np(VII)/Np(VI)), in LiOH-LiCl solutions, but a significantly weaker one in NaOH-$NaClO_4$ systems (Table 10-1).

Given the known aqueous speciation of Np(VII) and Np(VI) under strongly alkaline conditions, Reaction (10.1) represents the Np(VII)/Np(VI) redox equilibrium in the potentiometric study by [1970ZIE/COH], [1972PER/KRO] in 1.0 M NaOH:

$$NpO_4(OH)_2^{3-} + 2H_2O(l) + e^- \rightleftharpoons NpO_2(OH)_4^{2-} + 2OH^- \qquad (10.1)$$

with

$$E\ ((10.1),\ 1\ M\ NaOH,\ 298.15\ K) = (0.59 \pm 0.01)\ V$$

$$\log_{10} K\ ((10.1),\ 1\ M\ NaOH,\ 298.15\ K) = (10.0 \pm 0.2).$$

The value of $\log_{10} K$ ((10.1), 1 M NaOH, 298.15 K) can be extrapolated to $I = 0$ using $\varepsilon(NpO_2(OH)_4^{2-}, Na^+) = -(0.12 \pm 0.02)$ kg·mol$^{-1}$ selected in this review and $\varepsilon(NpO_4(OH)_2^{3-}, Na^+) = -(0.25 \pm 0.20)$ kg·mol$^{-1}$ estimated by analogy with other $X^{3-}$ anions. The resulting value of $\log_{10} K^\circ$ ((10.1), 298.15 K) is not selected in this review and is given for information only.

$$\log_{10} K^\circ\ ((10.1),\ 298.15\ K) = (10.9 \pm 0.3).$$

Table 10-1: Formal potentials for Np(VII)/Np(VI) and Np(VI)/Np(V) in $x$ M MOH + $y$ M MX with M = $Na^+$, $Li^+$ and X = $Cl^-$, $ClO_4^-$ at 298.15 K.

| Reference | Method | Medium | $T$/K | $E$ (*vs.* SHE) [V] |
|---|---|---|---|---|
| Np(VII)/Np(VI) | | | | |
| [1970ZIE/COH] | potentiometry | 1.0 M NaOH | 298.15 | (0.5821 ± 0.0005) |
| [1972PER/KRO] | potentiometry | 1.0 M NaOH | 298.15 | 0.589 |
| [1977KRO/GEL][(a)] | potentiometry | 1.0 M LiOH | 298.15 | 0.604 |
| [1995PER/SHI] in [2001LEM/FUG] | Review | 1.0 M NaOH | 298.15 | 0.59 |
| [2010SHI/BES] | potentiometry / | 1.0 M LiOH + 9.7 M LiCl | 291.15-293.15 | 0.788 |
| | spectroscopy | 1.0 M NaOH + 7.7 M $NaClO_4$ | 291.15-293.15 | 0.542 |
| Np(VI)/Np(V) | | | | |
| [1973SIM/MAT] | coulometry | 1.0 M NaOH | 298.15 | 0.18 |

(Continued on next page)

Table 10-1 (continued)

| Reference | Method | Medium | $T$/K | $E$ (*vs.* SHE) [V] |
|---|---|---|---|---|
| [1974PER/ALE] | voltammetry | 1.0 M NaOH | 298.15 | 0.10-0.11 |
| [1995PER/SHI] in [2001LEM/FUG] | Review | 1.0 M NaOH | 298.15 | 0.14[(b)] |
| [2001GEL/VAN] | potentiometry | 1.00 M NaOH | 298.15 | 0.106 |
| | | 10.50 M NaOH | 298.15 | 0.056 |
| | | 1.35 M LiOH | 298.15 | 0.135 |
| | | 4.00 M LiOH | 298.15 | 0.150 |
| [2006SHI/YUS] | potentiometry | 1.0 M NaOH | 298.15 | (0.125 ± 0.005) |
| | | 1.0 M LiOH | 298.15 | (0.163 ± 0.004) |
| [2010SHI/BES] | potentiometry | 1.0 M LiOH + 10.1 M LiCl | 293.15 | 0.359 |

(a) Not reviewed in [2001LEM/FUG].
(b) Unweighted average of $E$ reported in [1973SIM/MAT] and [1974PER/ALE].

Uncertainties affecting $E$(Np(VI)/Np(V)) in strongly alkaline conditions remain in spite of the new experimental studies available [2001GEL/VAN], [2006SHI/YUS]. In 1.0 M NaOH, both publications indicate lower $E$(Np(VI)/Np(V)) values (0.106 and 0.125 V, respectively) compared to the value reported in the review work by [1995PER/SHI] (0.14 V). As discussed in Appendix A, experimental shortcomings have been identified in both publications, where the high Np concentrations used can result in oversaturation in the test solutions with respect to M(I)-Np(V)-OH(s) and M(I)-Np(VI)-OH(s) phases (with M = $Li^+$, $Na^+$ or $K^+$). The Np(V) system is especially sensitive to carbonate impurities, and the spectroscopic evidences presented in [2001GEL/VAN] point in this direction (see discussion in Appendix A). The presence of carbonate could also explain the observed increase of $E$(Np(VI)/Np(V)) with increasing [LiOH], which is in contrast to the expected monotonic decrease of the formal potential with increasing alkali concentration. Although experimental results in [2001GEL/VAN] and [2006SHI/YUS] are not considered for a quantitative evaluation of $E$(Np(VI)/Np(V)) in strongly alkaline solutions, qualitative insights can be gained from this study. The slope analysis conducted in [2006SHI/YUS] ($E$(Np(VI)/Np(V)) *vs.* $\log_{10}[OH^-]$) in systems with [MCl] + [MOH] = 1 M, suggests that 2 $OH^-$ are included in the equilibrium reaction between Np(VI) and Np(V) at 0.2 M ≤ $[OH^-]$ ≤ 1.0 M. Considering that $NpO_2(OH)_4^{2-}$ is the predominant Np(VI) species within this range of $[OH^-]$, the authors proposed Reaction (10.2) to control the redox equilibrium Np(VI)/Np(V), thus making a strong case that the Np(V) species $NpO_2(OH)_3^{2-}$ does not form below 1.0 M MOH.

$$NpO_2(OH)_4^{2-} + e^- \rightleftharpoons NpO_2(OH)_2^- + 2\ OH^- \qquad (10.2)$$

Values of $E$(Np(VI)/Np(V)) reported by Shilov *et al.* [2010SHI/BES] in concentrated LiOH + LiCl systems were obtained under conditions far beyond the applicability of SIT and are thus disregarded in this review. Similarly to the Np(VII)/Np(VI) couple, the authors observed a significant increase of $E$(Np(VI)/Np(V)) with increasing LiCl concentration (Table 10-1).

No thermodynamic quantities are selected for the redox couple Np(VI)/Np(V) in strongly alkaline conditions.

### 10.1.2 $NpO_2^{2+}$

Structural parameters of the $NpO_2^{2+}$ aquo-ion in non-complexing media (1.0 M $HClO_4$) have been investigated using EXAFS in a number of new publications [2001ANT/SOD], [2008IKE/HEN], [2012GAO/TIT]. All these publications are consistent with the coordination number five in the equatorial plane of $NpO_2^{2+}$ and the stoichiometry $NpO_2(H_2O)_5^{2+}$. The same coordination number is also supported by recent computational studies conducted by Pomogaev and co-workers [2013POM/TIW].

New experimental [2005YAM/WAT] and theoretical [2005SHA/SCH], [2006TSU/WAH] studies investigating the reduction potential of Np(VI)/Np(V) have been published. In a cyclic voltammetry study, Yamamura and co-workers [2005YAM/WAT] determined the formal potential of the Np(VI)/Np(V) couple in 1.0 M $HNO_3$ and 1.0 M HCl. *E* values reported *vs.* Ag/AgCl cannot be accurately recalculated *vs*. SHE because of missing experimental details in the publication. Estimates calculated in Appendix A of this review suggest that *E* values determined by Yamamura and co-workers in 1.0 M $HNO_3$ and 1.0 M HCl are lower than the formal potential selected in [2001LEM/FUG] for 1.0 M $HClO_4$, in line with the expected formation of chloride and nitrate complexes of Np(VI). Quantum chemical calculations have also provided reasonable estimates of the reduction potential of $NpO_2^{2+}/NpO_2^{+}$ [2005SHA/SCH], [2006TSU/WAH]. Both [2005SHA/SCH] and [2006TSU/WAH] used a continuum model to account for the solvent effect of bulk water, with the inclusion of a first hydration shell. This review does not select any thermodynamic data based on estimates provided by theory studies.

Thermodynamic quantities selected in [2001LEM/FUG] and [2003GUI/FAN] for $NpO_2^{2+}$ are retained in the present review. Note that, in spite of the low uncertainty reported for $\Delta_r G_m^o$ (10.3) from emf data, the uncertainty in $\Delta_f G_m^o(NpO_2^{2+}, aq, 298.15\ K)$ is very large. This is as a result of the low accuracy of calorimetric measurements of the enthalpy of formation, $\Delta_f H_m^o(Np^{4+}, aq, 298.15\ K)$, which is used in the thermodynamic cycle to calculate $\Delta_f G_m^o(NpO_2^{+}, aq, 298.15\ K)$. The latter value, in combination with $\Delta_r G_m^o$ (10.3) gives $\Delta_f G_m^o(NpO_2^{2+}, aq, 298.15\ K)$.

$$NpO_2^{2+} + 0.5H_2(g) \rightleftharpoons NpO_2^{+} + H^{+} \qquad (10.3)$$

with

$$E^{\circ}((10.3), 298.15\ K) = \mathbf{(1.159 \pm 0.004)}\ V$$

$$\log_{10} K^{\circ}((10.3), 298.15\ K) = \mathbf{(19.590 \pm 0.070)}$$

$$\Delta_r G_m^o((10.3), 298.15\ K) = \mathbf{-\ (111.821 \pm 0.400)}\ kJ{\cdot}mol^{-1}$$

and

$$\Delta_f G_m^o (NpO_2^{2+}, aq, 298.15\ K) = \mathbf{-\ (795.939 \pm 5.615)}\ kJ \cdot mol^{-1}.$$

### 10.1.3 $NpO_2^+$

Two new EXAFS studies support the coordination of five water molecules in the equatorial plane of the $NpO_2^+$ aquo ion in 1.0 M $HClO_4$ [2001ANT/SOD], [2008IKE/HEN]. These findings are consistent with the coordination number previously determined by EXAFS in 3.0-5.0 M LiCl [1997ALL/BUC]. A coordination number of five is also supported by a recent computational study [2013POM/TIW]. This review accepts the evidence for predominance of $NpO_2(H_2O)_5^+$ in non-complexing media.

There are no new experimental studies on the thermodynamic quantities of $NpO_2^+$, besides the voltammetry study by Yamamura and co-workers [2005YAM/WAT] reporting $E$(Np(VI)/Np(V)) and discussed in Section 10.1.2. Thermodynamic data selected in [2003GUI/FAN] for the aquo-ion $NpO_2^+$ are retained.

### 10.1.4 $Np^{4+}$

New insights on the structure of the $Np^{4+}$ aquo-ion are provided by a number of investigations involving EXAFS [2001ANT/SOD], [2008IKE/HEN], [2012GAO/TIT], semi-empirical models [2003DAV/VOK], DFT calculations [2005TSU/YAN] and *ab initio* calculations of XANES spectra [2011CHA/DIA]. The EXAFS results are not yet conclusive with regard to the coordination number of the $Np^{4+}$ in non-coordinating media, and values of (9 ± 1), (10.4 ± 1.0) and (10 ± 1) are reported in [2001ANT/SOD], [2008IKE/HEN] and [2012GAO/TIT], respectively. However, all these are consistent with a coordination number of nine, with a tri-capped trigonal prism, or square anti-prism geometry as discussed for the $U^{4+}$ aqua-ion. The semi-empirical model reported in [2003DAV/VOK] resulted in an estimated coordination number of 10.20, obtained by using a correlation between the coordination number and the crystallographic radii. DFT calculations conducted in [2005TSU/YAN] concluded that 8- and 9-coordinated structures are most favoured energetically for $Np^{4+}$. Chavoy and Díaz-Moreno [2011CHA/DIA] explored the advantages of XANES in the evaluation of the coordination environment of $An^{4+}$ aquo-ions. Published spectra for $Th^{4+}$, $U^{4+}$ and $Np^{4+}$, and *ab initio* calculations conducted by the authors indicated that a tricapped trigonal prism geometry (9-coordinated, $D_{3h}$ symmetry) of the hydration sphere provides the best description of XANES data of these aquo-ions.

Yamamura and co-workers [2005YAM/WAT] determined the formal potential of the Np(IV)/Np(III) couple in 1.0 M $HNO_3$ and 1.0 M HCl using cyclic voltammetry. As for the Np(VI)/Np(V) couple (see Section 10.1.2), $E$ values determined by these authors in 1.0 M $HNO_3$ and 1.0 M HCl are lower than the formal potential selected in [2001LEM/FUG] for 1.0 M $HClO_4$. This is consistent with the known formation of

stronger chloride and nitrate complexes for Np(IV) than for Np(III). The semi-empirical model used by David and Vokhmin [2003DAV/VOK] provides an estimate of the ion entropy ( $S_m^o$ ($Np^{4+}$, aq, calc) = – 420 $J \cdot K^{-1} \cdot mol^{-1}$) in excellent agreement with the value selected in [2001LEM/FUG] and [2003GUI/FAN] based on experimental data ( $S_m^o$ ($Np^{4+}$, aq, exp) = – (426.4 ± 12.4) $J \cdot K^{-1} \cdot mol^{-1}$). Calculated values for the standard potential of the $Np^{4+}/Np^{3+}$ couple ($E°((Np^{4+}/Np^{3+})$, calc) = 0.231 V) are in moderate agreement with the current NEA TDB selection based on potentiometric measurements ($E°((Np^{4+}/Np^{3+})$, exp) = (0.219 ± 0.010) V) [2003GUI/FAN]. This review does not select any thermodynamic quantity obtained by theoretical or semi-empirical models, and the value of $E°(Np^{4+}/Np^{3+})$ selected in [2001LEM/FUG], [2003GUI/FAN] has been retained.

### 10.1.5 $Np^{3+}$

EXAFS studies provide consistent values of the coordination number (9 ± 1) and Np-O distances (2.48-2.52 Å) in the $Np^{3+}$ aquo-ion [2001ANT/SOD], [2009BRE/BAN], [2012GAO/TIT]. David and Vokhmin [2003DAV/VOK] calculated a coordination number of 9.00 based on a semi-empirical correlation with the crystallographic radii. The DFT study by Wiebke *et al.* [2007WIE/MOR] proposed the coordination of eight to nine water molecules in the $Np^{3+}$ aquo-ion. When only the first hydration sphere of the $Np^{3+}$ aquo-ion was considered, the calculated Np-O distances were significantly larger (2.617 Å) than those obtained experimentally. The presence of a single water molecule in the second coordination sphere had a large impact on the calculated distances (2.526 Å), leading the authors to conclude that the model used and the DFT code (BP86) were probably not accurate enough for this type of calculations.

Based on the reported data, this review supports a coordination number of nine for the $Np^{3+}$ aquo-ion in non-complexing media. This is consistent with observations available for other trivalent actinides (*e.g.* $Pu^{3+}$, $Cm^{3+}$) and lanthanides of similar size (*e.g.* $Nd^{3+}$).

The cyclic voltammetry measurements conducted in [2005YAM/WAT] reporting $E$(Np(IV)/Np(III)) in 1.0 M $HNO_3$ and 1.0 M HCl are discussed in Section 10.1.4. The entropy of the $Np^{3+}$ aquo-ion estimated in [2003DAV/VOK] using a semi-empirical model ( $S_m^o$ ($Np^{3+}$, aq, calc) = – 183 $J \cdot K^{-1} \cdot mol^{-1}$) agrees within the given uncertainties with the current NEA TDB selection [2003GUI/FAN] ( $S_m^o$ ($Np^{3+}$, aq, exp) = – (193.584 ± 20.253) $J \cdot K^{-1} \cdot mol^{-1}$). A discussion on the $E°((Np^{4+}/Np^{3+})$, calc) estimated by the same authors is provided in Section 10.1.4. Thermodynamic quantities selected in [2003GUI/FAN] for the $Np^{3+}$ aquo-ion are retained.

# 10.2 Neptunium oxygen and hydrogen compounds and complexes

## 10.2.1 Aqueous neptunium hydroxide complexes

### 10.2.1.1 Neptunium(VII) hydroxide complexes

All new references available on the Np(VII) hydroxide system, [2009SHI/YUS], [2010SHI/BES], [2012SHI/FED] and [2014GAO/FEL] involve redox equilibrium with Np(VI) aqueous species or solid compounds and have been discussed in Section 10.1.1.

### 10.2.1.2 Neptunium(VI) hydroxide complexes

Only three hydrolysis species of Np(VI) ($NpO_2OH^+$, $(NpO_2)_2(OH)_2^{2+}$, $(NpO_2)_3(OH)_5^+$) were selected in the previous NEA TDB reviews, [2001LEM/FUG], [2003GUI/FAN]. The possible formation of $NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$ under alkaline conditions was discussed in [2001LEM/FUG] in connection with experimental evidence provided by potentiometric [1974PER/ALE] and solubility studies [1995MOR/PRA]. The formation of additional monomeric and polymeric hydrolysis species of Np(VI) can be predicted in analogy with those for U(VI).

A number of experimental [2009MUL/FOE], [2012GAO/TIT], [2013CLA/CON], [2013GAO/FEL], [2013GAO/WIE], semi-empirical modelling [2006MOR/SAS], [2012GAO/TIT] and theoretical [2006GAR/WIL] studies have been published and provide new insights on the hydrolysis of Np(VI). Potentiometric studies focusing on the redox couples Np(VII)/Np(VI) and Np(VI)/Np(V) under strongly alkaline conditions [2001GEL/VAN], [2006SHI/YUS], [2010SHI/BES] are discussed in Section 10.1.1, but also provide an important contribution to the evaluation of Np(VI) hydrolysis data.

#### 10.2.1.2.1 Monomeric hydroxide complexes

The spectroscopic study by Müller and co-workers [2009MUL/FOE] conducted under acidic conditions indicates an important contribution of a hydrolysis complex in aqueous solutions of Np(VI) at pH = 4. This observation does not agree with the aqueous speciation calculated with the thermodynamic data selection in [2003GUI/FAN], which predicts the predominance of $NpO_2^{2+}$ at this pH. This may indicate a problem with the currently selected value for $\log_{10}{}^{*}\beta_1^{o}$ (10.4). For the same chemical reaction, the hard-sphere model derived by Moriyama and co-workers [2006MOR/SAS] resulted in an equilibrium constant approximately 0.2 $\log_{10}$ units larger than the selection in [2003GUI/FAN]. The model in [2006MOR/SAS] is mostly based on thermodynamic data available for uranium, and thus provides similar results for other actinides (especially for monomeric species). This review notes that $\log_{10}{}^{*}\beta_1^{o}$ ((10.4), 298.15 K) is very close to the selected value for $UO_2OH^+$ and $PuO_2OH^+$. We accept that the newly reported studies

provide reliable data, but the thermodynamic selection in [2003GUI/FAN] is retained until new experimental studies are available.

$$NpO_2^{2+} + H_2O(l) \rightleftharpoons NpO_2OH^+ + H^+ \quad (10.4)$$

$$\log_{10}{}^*\beta_1^o ((10.4), 298.15\ K) = \mathbf{-\ (5.100 \pm 0.400)}.$$

Based on an empirical correlation of An hydrolysis constants with the effective charge ($Z_{eff}$) of the actinide cation, Gaona *et al.* [2012GAO/TIT] estimated $\log_{10}{}^*\beta_2^o ((10.5), 298.15\ K) = -12.2$. This value must be taken only as indicative because of the large uncertainties associated with the estimation method used. The reported $\log_{10}{}^*\beta_2^o ((10.5), 298.15\ K)$ is in excellent agreement with the equilibrium constant selected in [2003GUI/FAN] for the analogous U(VI) species, $UO_2(OH)_2(aq)$ ($\log_{10}{}^*\beta_2^o = -(12.15 \pm 0.07)$). This review does not select $\log_{10}{}^*\beta_2^o (10.5)$ estimated in [2012GAO/TIT] and the value is given for information only.

$$NpO_2^{2+} + 2H_2O(l) \rightleftharpoons NpO_2(OH)_2(aq) + 2H^+ \quad (10.5)$$

$$\log_{10}{}^*\beta_2^o ((10.5), 298.15\ K) = -12.2.$$

The possible formation of $NpO_2(OH)_3^-$ and/or $NpO_2(OH)_4^{2-}$ under strongly alkaline conditions was discussed in [2001LEM/FUG], [2003GUI/FAN], although no thermodynamic quantities were selected for these species due to the experimental shortcomings identified. Lemire and co-workers [2001LEM/FUG] provided upper limits for $\log_{10}{}^*\beta_3^o ((10.6), 298.15\ K)$ and $\log_{10}{}^*\beta_4^o ((10.7), 298.15\ K)$ based on potentiometric measurements of the Np(VI)/Np(V) formal potential in 2.5-4.0 M LiOH solutions [1977ERM/PER].

$$NpO_2^{2+} + 3H_2O(l) \rightleftharpoons NpO_2(OH)_3^- + 3H^+ \quad (10.6)$$

$$NpO_2^{2+} + 4H_2O(l) \rightleftharpoons NpO_2(OH)_4^{2-} + 4H^+ \quad (10.7)$$

with

$$\log_{10}{}^*\beta_3^o ((10.6), 298.15\ K) \leq -19$$

$$\log_{10}{}^*\beta_4^o ((10.7), 298.15\ K) \leq -33.$$

The upper limits proposed in [2001LEM/FUG] were based on the assumption that $NpO_2(OH)_2^-$ was the predominant Np(V) species in the test solutions in [1977ERM/PER], and that no Np(V) or Np(VI) solid phases were formed under these conditions. Both assumptions have been refuted in more recent studies [2001GEL/VAN], [2006SHI/YUS], and thus the values of $\log_{10}{}^*\beta_3^o ((10.6), 298.15\ K)$ and $\log_{10}{}^*\beta_4^o ((10.7), 298.15\ K)$ proposed in [2001LEM/FUG] are not accepted in the present review.

New experimental [2013CLA/CON], [2013GAO/WIE] and theoretical [2006GAR/WIL] studies provide information on the structure of anionic Np(VI) hydrolysis species formed in strongly alkaline solutions. The EXAFS studies in

[2013CLA/CON] and [2013GAO/WIE] were performed in TMA-OH solutions (2.5/3.5 M and 0.5 M, respectively) to avoid the precipitation of M-Np(VI)-OH(s) solid phases (reported for M = Na and K). Both research groups propose the predominance of $NpO_2(OH)_4^{2-}$ under the investigated conditions, although Clark *et al.* [2013CLA/CON] also suggested a minor contribution of the species $NpO_2(OH)_5^{3-}$ in 3.5 M TMA-OH based on their EXAFS and Raman observations. This is consistent with evidence available for the U(VI) system under analogous experimental conditions ([2000MOL/REI], [2010SZA/GRE]). [2013CLA/CON] and [2013GAO/WIE] reported consistent values of Np-$O_{ax}$ and Np-$O_{eq}$ distances for the species $NpO_2(OH)_4^{2-}$ ($R_{Np\text{-}Oax}$ = 1.80 Å, $R_{Np\text{-}Oeq}$ = 2.22-2.25 Å). These values are in fair agreement with distances reported for the same species using DFT methods [2001BOL/WAH], [2006GAR/WIL]. This review agrees with the main conclusions in [2013CLA/CON] and [2013GAO/WIE] concerning the aqueous speciation of Np(VI) in strongly alkaline conditions.

A number of new experimental [2013GAO/FEL] and (semi-)empirical modelling [2006MOR/SAS], [2012GAO/TIT] studies have reported thermodynamic quantities for the species $NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$. Equilibrium constants available in the literature for Reactions (10.6) and (10.7) are summarised in Table 10-2, in combination with equilibrium constants selected in [2003GUI/FAN] for the formation of the analogous U(VI) species.

Table 10-2: Equilibrium constants reported in the literature for Reactions (10.6) and (10.7). Equilibrium constants selected in [2003GUI/FAN] for the formation of the analogous U(VI) species are appended for comparison.

| Reference | Method | Medium | $T$ /K | $\log_{10}{}^{*}\beta_x$ | $\log_{10}{}^{*}\beta_x^{o}$ |
|---|---|---|---|---|---|
| $NpO_2^{2+} + 3H_2O(l) \rightleftharpoons NpO_2(OH)_3^- + 3H^+$ | | | | | |
| [1995MOR/PRA] | solubility | 0.1 M $NaClO_4$-$NaHCO_3$-NaOH | ? | – (22.39 ± 0.11) | |
| [2001LEM/FUG] | Review | | | | ≤ – 19 |
| [2003GUI/FAN] | Review | | | | – (20.25 ± 0.42)[(a)] |
| [2006MOR/SAS] | estimated | | | | – 21.67 |
| [2012GAO/TIT] | estimated | | | | – (19.6 ± 1.0) |
| [2013GAO/FEL] | solubility | 0.1-5.0 M NaCl | 295.15 | | – (21.2 ± 1.1) |
| $NpO_2^{2+} + 4H_2O(l) \rightleftharpoons NpO_2(OH)_4^{2-} + 4H^+$ | | | | | |
| [2001LEM/FUG] | Review | | | | ≤ – 33 |
| [2003GUI/FAN] | Review | | | | – (32.40 ± 0.68)[(a)] |
| [2006MOR/SAS] | estimated | | | | – 33.53 |
| [2012GAO/TIT] | estimated | | | | – (31.6 ± 1.0) |
| [2013GAO/FEL] | solubility | 0.1-5.0 M NaCl | 295.15 | | – (32.0 ± 1.1) |

(a) Value selected in [2003GUI/FAN] for the analogous U(VI) species.

Gaona and co-workers [2013GAO/FEL] studied the solubility of Np(VI) in alkaline solutions from low to high concentration of NaCl. The authors proposed that Reactions (10.8) and (10.9) controlled the solubility of Np(VI) at $-\log_{10}[H^+] \geq 9$:

$$0.5Na_2Np_2O_7 \cdot xH_2O(cr) + (1.5 - 0.5x)H_2O(l) \rightleftharpoons NpO_2(OH)_3^- + Na^+ \quad (10.8)$$

$$0.5Na_2Np_2O_7 \cdot xH_2O(cr) + (2.5 - 0.5x)H_2O(l) \rightleftharpoons NpO_2(OH)_4^{2-} + Na^+ + H^+ \quad (10.9)$$

The proposed chemical model is in line with solubility studies conducted with $Na_2U_2O_7 \cdot H_2O$(cr) in alkaline $NaClO_4$ [1998YAM/KIT] and NaCl [2017ALT/YAL] solutions. Conditional equilibrium constants determined in [2013GAO/FEL] for Reactions (10.8) and (10.9) in 0.1, 0.5, 1.0, 2.5 and 5.0 M NaCl were extrapolated to $I = 0$ using SIT, resulting in $\log_{10}{}^*K^\circ_{s,l,3}$ ((10.8), 295.15 K) = – (8.6 ± 0.1) and $\log_{10}{}^*K^\circ_{s,l,4}$ ((10.9), 295.15 K) = – (19.4 ± 0.1). SIT ion-interaction coefficients were derived accordingly as $\varepsilon(NpO_2(OH)_3^-, Na^+)$ = – (0.20 ± 0.02) kg·mol$^{-1}$ and $\varepsilon(NpO_2(OH)_4^{2-}, Na^+)$ = – (0.12 ± 0.01) kg·mol$^{-1}$. This review has recalculated the SIT plots for Reactions (10.8) and (10.9) excluding solubility data in 5.0 M NaCl (see Appendix A), which is outside the usually accepted validity range of SIT ($I_m \leq 3.5$ m). Virtually the same values of $\log_{10}{}^*K^\circ_{s,l,3}$, $\log_{10}{}^*K^\circ_{s,l,4}$ and $\varepsilon(NpO_2(OH)_3^-, Na^+)$ are obtained, whereas a slightly lower value is calculated for $\varepsilon(NpO_2(OH)_4^{2-}, Na^+)$ = – (0.16 ± 0.02) kg·mol$^{-1}$. We have accordingly increased the uncertainty of $\varepsilon(NpO_2(OH)_4^{2-}, Na^+)$ reported in [2013GAO/FEL], and select the value of $\varepsilon(NpO_2(OH)_4^{2-}, Na^+)$ = – (0.12 ± 0.04) kg·mol$^{-1}$. The combination of $\log_{10}{}^*K^\circ_{s,l,3}$ ((10.8), 295.15 K) and $\log_{10}{}^*K^\circ_{s,l,4}$ ((10.9), 295.15 K) with $\log_{10}{}^*K^\circ_{s,0}$ ($Na_2Np_2O_7 \cdot xH_2O$, cr) also determined in [2013GAO/FEL] results in:

$$\log_{10}{}^*\beta_3^\circ \text{ ((10.6), 298.15 K)} = \mathbf{-\ (21.200 \pm 1.100)}$$

$$\log_{10}{}^*\beta_4^\circ \text{ ((10.7), 298.15 K)} = \mathbf{-\ (32.000 \pm 1.100)}.$$

The large uncertainties reported in [2013GAO/FEL] for $\log_{10}{}^*\beta_3^\circ$ ((10.6), 298.15 K) and $\log_{10}{}^*\beta_4^\circ$ ((10.7), 298.15 K) are due to the large uncertainty associated with $\log_{10}{}^*K^\circ_{s,0}$ ($Na_2Np_2O_7 \cdot xH_2O$, cr) (see discussion in Section 10.9.1.5). The value of $\log_{10}{}^*\beta_3^\circ$ ((10.6), 298.15 K) reported in [2013GAO/FEL] is consistent with $\log_{10}{}^*\beta_3^\circ$ = – (20.25 ± 0.42) selected in [2003GUI/FAN] and retained in the present review for the analogous U(VI) species, $UO_2(OH)_3^-$, and also with the equilibrium constants derived for the latter in solubility studies with $Na_2U_2O_7 \cdot H_2O$(cr) ($\log_{10}{}^*\beta_3^\circ$ = – (20.86 ± 0.79) [1998YAM/KIT] and $\log_{10}{}^*\beta_3^\circ$ = – (20.7 ± 0.4) [2017ALT/YAL]). A good agreement is found between $\log_{10}{}^*\beta_4^\circ$ ((10.7), 298.15 K) reported in [2013GAO/FEL] and the equilibrium constant selected in [2003GUI/FAN] for the analogous U(VI) species, $UO_2(OH)_4^{2-}$. The latter selection was only based on the solubility study by Yamamura *et al.* [1998YAM/KIT]. The value of $\log_{10}{}^*\beta_4^\circ$ ((10.7), 298.15 K) reported in [2013GAO/FEL] is also in excellent agreement with $\log_{10}{}^*\beta_4^\circ$ = – (31.9 ± 0.2) reported for U(VI) in [2017ALT/YAL].

We note that the stepwise Reaction (10.10) resulting from the combination of Reactions (10.8) and (10.9) has a much lower uncertainty, because $\log_{10}{}^*K^\circ_{s,0}$ ($Na_2Np_2O_7 \cdot xH_2O$, cr) is not used in the calculation:

$$NpO_2(OH)_3^- + H_2O(l) \rightleftharpoons NpO_2(OH)_4^{2-} + H^+ \quad (10.10)$$

$$\log_{10}{}^*K_4^o((10.10), 298.15\ K) = -(10.80 \pm 0.14).$$

This value is somewhat different from the current thermodynamic selection for U(VI) $\log_{10}{}^*K_4^o(298.15\ K) = -(12.15 \pm 0.80)$, but is in good agreement with the stepwise reaction determined in the analogous U(VI) solubility study conducted in [2017ALT/YAL], $\log_{10}{}^*K_4^o(298.15\ K) = -(11.20 \pm 0.41)$.

This review accepts the results of the solubility study in [2013GAO/FEL] and selects $\log_{10}{}^*\beta_3^o((10.6), 298.15\ K)$, $\log_{10}{}^*\beta_4^o((10.7), 298.15\ K)$, $\varepsilon(NpO_2(OH)_3^-, Na^+)$ and $\varepsilon(NpO_2(OH)_4^{2-}, Na^+)$ reported by the authors. The large uncertainty associated to the selected equilibrium constants can be decreased by improving the accuracy of $\log_{10}{}^*K_{s,0}^o(Na_2Np_2O_7{\cdot}xH_2O, cr)$. Although agreeing within their uncertainties, the discrepancies between the equilibrium constants currently selected for $NpO_2(OH)_3^-$ and $UO_2(OH)_3^-$ are of concern. Gibbs energy of reaction for Reactions (10.6) and (10.7) and the calculated Gibbs energy of formation of $NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$ result in:

$$\Delta_r G_m^o((10.6), 298.15\ K) = \mathbf{(121.011 \pm 6.279)}\ kJ{\cdot}mol^{-1}$$

$$\Delta_r G_m^o((10.7), 298.15\ K) = \mathbf{(182.657 \pm 6.279)}\ kJ{\cdot}mol^{-1}$$

and

$$\Delta_f G_m^o(NpO_2(OH)_3^-, 298.15\ K) = \mathbf{-(1386.348 \pm 8.424)}\ kJ{\cdot}mol^{-1}$$

$$\Delta_f G_m^o(NpO_2(OH)_4^{2-}, 298.15\ K) = \mathbf{-(1561.842 \pm 8.425)}\ kJ{\cdot}mol^{-1}.$$

Different values of $\log_{10}{}^*\beta_3^o((10.6), 298.15\ K)$ and $\log_{10}{}^*\beta_4^o((10.7), 298.15\ K)$ were reported in [2006MOR/SAS] and [2012GAO/TIT] based on different (semi-) empirical models (see Table 10-2). These are in line with equilibrium constants determined in [2013GAO/FEL], but also demonstrate the limitations of (semi-)empirical models for the estimation of accurate thermodynamic quantities.

#### 10.2.1.2.2 Polymeric hydroxide complexes

There are no new experimental studies providing thermodynamic quantities for the formation of polymeric hydroxide complexes of Np(VI). Based on a hard-sphere semi-empirical model, Moriyama and co-workers [2006MOR/SAS] estimated the equilibrium constants for the formation of the polymeric species $(NpO_2)_m(OH)_n^{(2m-n)}$ with $2 \le m \le 10$ and $1 \le n \le 22$. The equilibrium constants reported in [2006MOR/SAS] are in moderate agreement with $\log_{10}{}^*\beta_{m,n}^o$ values selected in [2003GUI/FAN] for the Np(VI) polymeric species $(NpO_2)_2(OH)_2^{2+}$ and $(NpO_2)_3(OH)_5^+$ (Table 10-3).

Table 10-3: Equilibrium constants estimated in [2006MOR/SAS] for the hydrolysis reactions $m\mathrm{NpO_2^{2+}} + n\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{NpO_2})_m(\mathrm{OH})_n^{(2m-n)} + n\mathrm{H^+}$. Only polymeric species selected in [2003GUI/FAN] and in this review for either Np(VI), U(VI) or Pu(VI) are included in the table: ($m$, $n$) = (2, 1), (2, 2), (3, 4), (3, 5), (3, 7), (4, 7). Equilibrium constants selected in [2003GUI/FAN] and in this review for the same Np(VI) and analogous U(VI) and Pu(VI) species are appended for comparison.

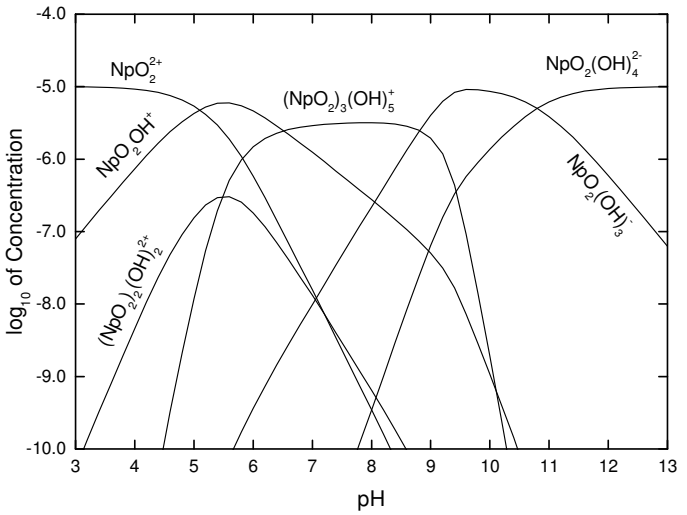
| Species | Np(VI) [2006MOR/SAS] | Np(VI) [NEA TDB] | U(VI) [NEA TDB] | Pu(VI) [NEA TDB] |
|---|---|---|---|---|
| $(\mathrm{AnO_2})_2\mathrm{OH^{3+}}$ | – 3.30 | | – (2.7 ± 1.0) | |
| $(\mathrm{AnO_2})_2(\mathrm{OH})_2^{2+}$ | – 5.87 | – (6.27 ± 0.21) | – (5.62 ± 0.08) | – (7.5 ± 1.0) |
| $(\mathrm{AnO_2})_3(\mathrm{OH})_4^{2+}$ | – 12.01 | | – (11.9 ± 0.3) | |
| $(\mathrm{AnO_2})_3(\mathrm{OH})_5^{+}$ | – 17.32 | – (17.12 ± 0.22) | – (15.55 ± 0.12) | |
| $(\mathrm{AnO_2})_3(\mathrm{OH})_7^{-}$ | – 32.17 | | – (32.2 ± 0.8) | |
| $(\mathrm{AnO_2})_4(\mathrm{OH})_7^{+}$ | – 23.52 | | – (21.9 ± 1.0) | |

This review, however, does not select any thermodynamic values obtained by theoretical or semi-empirical models. Important differences in the fraction of polymeric hydrolysis species of Np(VI) and U(VI) within pH 4 and 6 were demonstrated in [2009MUL/FOE] using ATR FT-IR. Even though the chemical analogy between U(VI) and Np(VI) is important, the choice of polymeric hydrolysis species of Np(VI) should be based on primary experimental evidence.

Table 10-4 summarises the equilibrium constants and Gibbs energy of reaction selected in [2003GUI/FAN] and updated in the present review for the formation of aqueous Np(VI) hydrolysis species at 298.15 K, according to the reaction $m\mathrm{NpO_2^{2+}} + n\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{NpO_2})_m(\mathrm{OH})_n^{(2-n)+} + n\mathrm{H^+}$. The selected equilibrium constants have been used to calculate the distribution diagram of Np(VI) hydrolysis species shown in Figure 10-1. The figure shows also the distribution diagram of U(VI) hydrolysis species calculated with the thermodynamic data updated in this book. The comparison of both figures highlights a number of points that need to be explored in order to improve the understanding and quantification of the An(VI) hydrolysis system:

- The number of monomeric and polymeric hydrolysis species of Np(VI) (as well as Pu(VI)) forming under acidic to near-neutral pH conditions is (very) limited compared to U(VI).
- The aqueous speciation of An(VI) under alkaline to hyperalkaline pH conditions is known to be dominated by $\mathrm{AnO_2(OH)_3^-}$ and $\mathrm{AnO_2(OH)_4^{2-}}$. In spite of this, important differences arise in the distribution diagrams of U(VI) and Np(VI), which mostly reflect the differences in the current thermodynamic selection for the species $\mathrm{UO_2(OH)_3^-}$ ($\log_{10}{}^{*}\beta_3^{\circ} = -(20.25 \pm 0.42)$) and $\mathrm{NpO_2(OH)_3^-}$ ($\log_{10}{}^{*}\beta_3^{\circ} = -(21.2 \pm 1.1)$). Although not plotted in a distribution diagram, a large difference is also found with the Pu(VI) system ($\log_{10}{}^{*}\beta_3^{\circ} = -(24.0 \pm 1.6)$). Further experimental studies are needed to settle the disagreement in the aqueous speciation of An(VI) under alkaline pH conditions.

Figure 10-1: Distribution diagrams of the dioxoneptunium(VI) and dioxouranium(VI) hydroxide systems at 298.15 K in the range $3 < pH < 13$. $[An(VI)]_{tot} = 1 \times 10^{-5}$ M. The precipitation of solid phases is suppressed. Calculations performed at $I = 0$. Minor differences can arise with real systems at pH = 13, where $I \approx 0.1$ M.



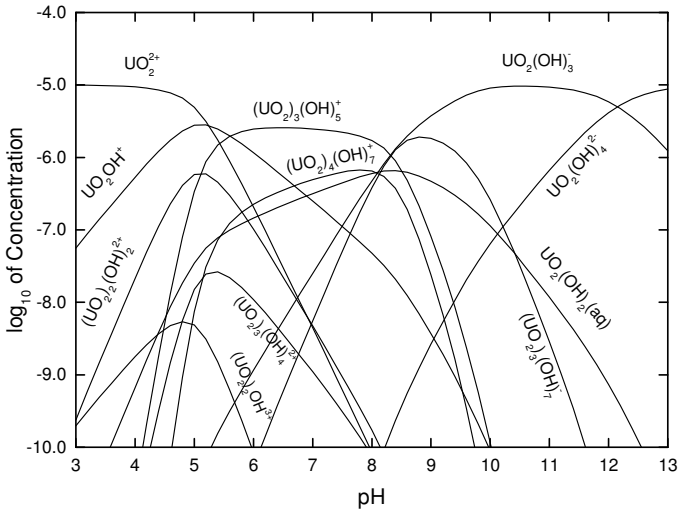



Table 10-4: Equilibrium constants ( $\log_{10}{}^{*}\beta^{\circ}_{n,m}$ ) and Gibbs energy of reaction ( $\Delta_r G^{\circ}_m$ ) at 298.15 K selected in this review and in [2003GUI/FAN] for the aqueous Np(VI) hydrolysis species according with the chemical reaction $m\mathrm{NpO_2^{2+}} + n\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{NpO_2})_m(\mathrm{OH})_n^{(2m-n)} + n\mathrm{H^+}$ .

| Species ($n$,$m$) | $\log_{10}{}^{*}\beta^{\circ}_{n,m}$ | $\Delta_r G^{\circ}_m$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|---|
| 1,1 | **– (5.100 ± 0.400)** | **(29.111 ± 2.283)** | [2003GUI/FAN] |
| 3,1 | **– (21.200 ± 1.100)** | **(121.011 ± 6.279)** | This review |
| 4,1 | **– (32.000 ± 1.100)** | **(182.657 ± 6.279)** | This review |
| 2,2 | **– (6.270 ± 0.210)** | **(35.789 ± 1.199)** | [2003GUI/FAN] |
| 5,3 | **– (17.120 ± 0.220)** | **(97.722 ± 1.256)** | [2003GUI/FAN] |

### 10.2.1.3 Neptunium(V) hydroxide complexes

The Np(V) hydrolysis system has been reviewed in detail in [2001LEM/FUG] and [2003GUI/FAN]. Thermodynamic data have been selected in [2001LEM/FUG] for fresh and aged $NpO_2OH(am)$, and the hydrolysis species $NpO_2OH(aq)$ and $NpO_2(OH)_2^-$ . Since these reviews, several experimental and theory studies on the hydrolysis of Np(V) as well as review articles on the aqueous chemistry of actinides have been reported. Shilov and co-workers provide an overview of neptunium chemistry in aqueous solutions including the hydrolysis reactions of Np(V) [2012SHI/GOG]. Fanghänel and Neck provide a review of the solubility behaviour of actinides in carbonate-free aqueous solutions and discuss the solubility behaviour of freshly precipitated and aged Np(V) hydroxide [2002FAN/NEC].

The experimental data of Np(V) hydrolysis in aqueous solution have been discussed in detail in [2001LEM/FUG] and thermodynamic data for two solution complexes have been selected:

$$\mathrm{NpO_2^+ + H_2O(l) \rightleftharpoons NpO_2OH(aq) + H^+} \quad (10.11)$$

$$\mathrm{NpO_2^+ + 2H_2O(l) \rightleftharpoons NpO_2(OH)_2^- + 2H^+} \quad (10.12)$$

with

$$\log_{10}{}^{*}\beta^{\circ}_1 \text{ ((10.11), 298.15 K)} = \mathbf{-\ (11.300 \pm 0.700)}$$

$$\log_{10}{}^{*}\beta^{\circ}_2 \text{ ((10.12), 298.15 K)} = \mathbf{-\ (23.600 \pm 0.500)}.$$

Since previous reviews, new theoretical studies that include calculations of the properties of Np(V) hydrolysis products have been published. In a recent theoretical study the reaction free energies and Gibbs free energy for the hydration reactions of $NpO_2(H_2O)_{n-1}^+$ with $n$ = 1-5 and for the hydroxy complex $NpO_2OH(H_2O)_{n-1}(aq)$ with $n$ = 1-4 have been calculated and all of them turn out to be exergonic [2012RIO/MIC]. Yusov *et al.* [2002YUS/FED] investigated experimentally the interaction of Al(III) hydrolysis products with Np(IV) and Np(V) under acidic conditions. In contrast to

Np(IV) and Np(VI), Np(V) does not coordinate with Al(III) hydroxy species below pH 5.

New experimental data on the formation of binary Np(V) hydrolysis products are reported in [2004RAO/SRI] using a tetramethylammonium chloride (TMACl) ionic medium. A combination of calorimetric, potentiometric and spectrophotometric measurements were used to measure the temperature-dependent formation of $NpO_2OH(aq)$ and $NpO_2(OH)_2^-$ according to Reactions (10.11) and (10.12), respectively. By using the absorbance features at 980 nm for $NpO_2^+$ and 991 nm for $NpO_2OH(aq)$, Rao *et al.* calculate $\log_{10}{}^*\beta_1$ ((10.11), 1.12 M TMACl) = – (9.08 ± 0.08) and $\log_{10}{}^*\beta_2$ ((10.12), 1.12 M TMACl) = – (18.85 ± 0.07) at 298.15 K, which compare well with the values obtained from the potentiometric titrations, $\log_{10}{}^*\beta_1$ ((10.11), 1.12 M TMACl) = – (9.01 ± 0.07) and $\log_{10}{}^*\beta_2$ ((10.12), 1.12 M TMACl) = – (18.95 ± 0.07). The latter values are converted to $\log_{10}{}^*\beta_1^\circ$ ((10.11), 298.15 K) = – (8.98 ± 0.09) and $\log_{10}{}^*\beta_2^\circ$ ((10.12), 298.15 K) = – (19.22 ± 0.11) at 298.15 K by using the SIT. From $\Delta_r S_m$ ((10.11), 1.12 M TMACl) and $\Delta_r S_m$ ((10.12), 1.12 M TMACl), Rao and co-workers calculate the standard molar entropies $S_m^\circ(NpO_2OH, aq)$ = – (42 ± 11) $J\cdot K^{-1}\cdot mol^{-1}$ and $S_m^\circ(NpO_2(OH)_2^-)$ = (8 ± 12) $J\cdot K^{-1}\cdot mol^{-1}$ at 298.15 K.

Table 10-5: Temperature-dependent equilibrium constants for the reactions $NpO_2^+ + nH_2O(l) \rightleftharpoons (NpO_2)_m(OH)_n^{m-n} + nH^+$ as reported in [2004RAO/SRI].

| (*n*,*m*) | *T* /K | Method | *I* (medium) | $\log_{10}{}^*\beta_{n,m}^\circ$ | $\log_{10}{}^*\beta_{n,m}^\circ$ |
|---|---|---|---|---|---|
| 1,1 | 283.15 | pot | 1.12 M TMACl | – (9.33 ± 0.08) | – (9.30 ± 0.09) |
| 1,1 | 298.15 | pot | 1.12 M TMACl | – (9.01 ± 0.07) | – (8.98 ± 0.09) |
| 1,1 | 298.15 | spect | 1.12 M TMACl | – (9.08 ± 0.08) | – (9.05 ± 0.08) |
| 1,1 | 313.15 | pot | 1.12 M TMACl | – (8.84 ± 0.10) | – (8.81 ± 0.11) |
| 1,1 | 328.15 | pot | 1.12 M TMACl | – (8.74 ± 0.11) | – (8.71 ± 0.12) |
| 1,1 | 343.15 | pot | 1.12 M TMACl | – (8.65 ± 0.21) | – (8.62 ± 0.21) |
| 1,1 | 358.15 | pot | 1.12 M TMACl | – (8.57 ± 0.12) | – (8.54 ± 0.13) |
| 1,2 | 283.15 | pot | 1.12 M TMACl | – (20.16 ± 0.11) | – (20.42 ± 0.14) |
| 1,2 | 298.15 | pot | 1.12 M TMACl | – (18.95 ± 0.07) | – (19.22 ± 0.11) |
| 1,2 | 298.15 | spect | 1.12 M TMACl | – (18.85 ± 0.07) | – (19.12 ± 0.07 |
| 1,2 | 313.15 | pot | 1.12 M TMACl | – (18.05 ± 0.06) | – (18.33 ± 0.11) |
| 1,2 | 328.15 | pot | 1.12 M TMACl | – (17.52 ± 0.05) | – (17.81 ± 0.10) |
| 1,2 | 343.15 | pot | 1.12 M TMACl | – (17.30 ± 0.12) | – (17.60 ± 0.15) |
| 1,2 | 358.15 | pot | 1.12 M TMACl | – (16.72 ± 0.04) | – (17.04 ± 0.10) |

The values reported in [2004RAO/SRI] differ significantly from those selected in [2001LEM/FUG] and [2003GUI/FAN], $\log_{10}{}^*\beta_1^\circ$ ((10.11), 298.15 K) = – (11.3 ± 0.7) and $\log_{10}{}^*\beta_2^\circ$ ((10.12), 298.15 K) = – (23.6 ± 0.5), which were mainly obtained from solubility data and spectroscopic measurements. The interpretation of the spectroscopic measurements in [2004RAO/SRI] has become the centre of discussion (for details see [2006NEC] and [2006RAO/SRI] in the Appendix); this is due to the fact that

Rao and co-workers assigned the observed absorbance at 991 nm to the first Np(V) hydroxy species, $NpO_2OH(aq)$, while numerous studies in the literature have assigned this band to the $NpO_2CO_3^-$ complex, based on its dependence on carbonate concentration. In contrast to the study in [2004RAO/SRI], complexation of Np(V) with hydroxide is reported by several research groups to occur only at pH > 10. The data in [2004RAO/SRI] imply the onset of Np(V) hydrolysis at a much lower pH and the formation constants reported by Rao *et al.* would significantly increase the Np(V) solubility at pH > 8.5 ([2006NEC]). Reinterpretation of the solubility data using $NaNpO_2(OH)_2(s)$ as the solubility controlling phase instead of $NpO_2OH(am, hyd)$ would increase the first Np(V) hydrolysis constant by about 2.5 orders of magnitude, in better agreement with the values reported in [2004RAO/SRI], but it would still require that $NpO_2OH(aq)$ is formed already at pH of about 8.5, which is in conflict with the spectroscopic observations that Np(V) hydrolysis products are not formed at pH < 10. For this reason, the reported data in [2004RAO/SRI] are not accepted by the present review.

Even though there are no new thermodynamic data on the Np(V) hydrolysis in the study of [2017PET/FEL], their combined solubility and spectroscopic study provides additional insights to this discussion. The authors performed solubility experiments from undersaturation, using $NpO_2OH(am, hyd)$ in 0.1-5.0 M NaCl-NaOH solutions, and collected UV-vis/NIR data for selected supernatant solutions within $8.9 \leq -\log_{10}[H^+] \leq 10.3$. The main observations can be summarised as follows:

- The initial amorphous phase $NpO_2OH(am, hyd)$ transforms into crystalline Na-Np(V)-OH phases at [NaCl] ≥ 1.0 M and $-\log_{10}[H^+] \geq 11.5$.
- After terminating the solubility experiments (≈ two years), all solid phases were found to have incorporated a fraction of $Na^+$ (≥ 10 %), this was also the case for those solids equilibrated in dilute NaCl with $-\log_{10}[H^+] \leq 11.5$ where no transformation into a crystalline phase is observed.
- Spectroscopic measurements confirm the predominance of $NpO_2^+$ (> 80 %, following the peak at $\lambda$ = 980-981 nm) within $8.9 \leq -\log_{10}[H^+] \leq 10.3$. The small peak arising at $\lambda$ = 991 nm with increasing pH is attributed by Petrov *et al.* to $NpO_2OH(aq)$.

Experimental observations in [2017PET/FEL] point out the limitations in deriving thermodynamic data from solubility experiments with the ill-defined $NpO_2OH(am, hyd)$ solid phase, and highlight the need of conducting accurate solid phase characterisation, especially when amorphous solid phases are involved. Spectroscopic observations reported by Petrov and co-workers disregard the earlier hydrolysis data (at $-\log_{10}[H^+] > 7$) proposed in [2004RAO/SRI] and are in line with the hydrolysis scheme selected in [2001LEM/FUG] and [2003GUI/FAN], which is retained in the present review. New experimental studies under strict exclusion of carbonate and with well-defined solid phases may contribute to settle the on-going discussion on the hydrolysis of Np(V).

Solubility experiments of Np(IV) and Pu(IV) in alkaline $CaCl_2$ solutions reported in [2010FEL/NEC] have been extended to Np(V) in [2016FEL/ROT] and [2016FEL/ALT]. In [2016FEL/ROT], the authors describe the concentrations of Np(V) in solution as function of $pH_m$ and $CaCl_2$ and the characterisation of solid phase and solution species by a number of analytical methods. These results are used in [2016FEL/ALT] to develop thermodynamic data for the Np(V) hydrolysis in $CaCl_2$ solution. The increasing Np(V) solubility at $pH_m > 10.5$ in combination with EXAFS data is interpreted by the formation of two ternary Np(V) hydroxo complexes, $Ca[NpO_2(OH)_2]^+$ and $Ca_3[NpO_2(OH)_5]^{2+}$. The fraction of binary Np(V) complexes, such as $NpO_2(OH)_2^-$, was calculated to be below 5 % and this contribution was not included in the analysis of the solubility data. From the data in 0.25 M, 1.0 M and 2.0 M $CaCl_2$ the authors derived conditional formation constants summarised in Table 10-6 according to Equations (10.13) and (10.14):

$$NpO_2^+ + Ca^{2+} + 2H_2O(l) \rightleftharpoons Ca[NpO_2(OH)_2]^+ + 2H^+ \quad (10.13)$$

$$NpO_2^+ + 3Ca^{2+} + 5H_2O(l) \rightleftharpoons Ca_3[NpO_2(OH)_5]^{2+} + 5H^+ \quad (10.14)$$

Table 10-6: Experimental conditional equilibrium constants determined in [2016FEL/ROT], [2016FEL/ALT] for the chemical Reactions (10.13) and (10.14) in 0.25, 1.0 and 2.0 M $CaCl_2$.

| $T$ /K | Method | $I$ (medium) | $\log_{10}{}^{*}\beta_{1,1,2}$ (10.13) | $\log_{10}{}^{*}\beta_{3,1,5}$ (10.14) |
|---|---|---|---|---|
| 296 ± 2 | sol | 0.25 M $CaCl_2$ | – (21.10 ± 0.25) | – (55.63 ± 0.39) |
| 296 ± 2 | sol | 1.0 M $CaCl_2$ | – (21.02 ± 0.10) | – (55.66 ± 0.18) |
| 296 ± 2 | sol | 2.0 M $CaCl_2$ | – (21.07 ± 0.12) | – (55.77 ± 0.15) |

By using the reported SIT ion interaction parameters $\varepsilon(NpO_2^+, Cl^-)$ = (0.09 ± 0.05) kg·mol$^{-1}$, $\varepsilon(Ca^{2+}, Cl^-)$ and $\varepsilon(H^+, Cl^-)$, the authors calculated the thermodynamic equilibrium constants $\log_{10}{}^{*}\beta^{o}_{1,1,2}$ ((10.13), 298.15 K) = – (20.63 ± 0.18) and $\log_{10}{}^{*}\beta^{o}_{3,1,5}$ ((10.14), 298.15 K) = – (54.81 ± 0.29), and the associated SIT ion-interaction parameters $\varepsilon(Ca[NpO_2(OH)_2]^+, Cl^-)$ = – (0.07 ± 0.08) kg·mol$^{-1}$ and $\varepsilon(Ca_3[NpO_2(OH)_5]^{2+}, Cl^-)$ = – (0.20 ± 0.11) kg·mol$^{-1}$. Based on the comprehensive solubility dataset and the detailed characterisation of the solid equilibrium phases, this review selects the following equilibrium constants with increased uncertainties:

$$\log_{10}{}^{*}\beta^{o}_{1,1,2}\text{ ((10.13), 298.15 K)} = \mathbf{-\ (20.600 \pm 0.200)}$$

$$\log_{10}{}^{*}\beta^{o}_{3,1,5}\text{ ((10.14), 298.15 K)} = \mathbf{-\ (54.800 \pm 0.300)}.$$

Gibbs energy of reaction for Reactions (10.13) and (10.14), and the calculated Gibbs energy of formation for $Ca[NpO_2(OH)_2]^+$ and $Ca_3[NpO_2(OH)_5]^{2+}$ result in:

$$\Delta_r G^o_m\text{ ((10.13), 298.15 K)} = \mathbf{(117.586 \pm 1.142)}\text{ kJ·mol}^{-1}$$

$$\Delta_r G^o_m\text{ ((10.14), 298.15 K)} = \mathbf{(312.801 \pm 1.712)}\text{ kJ·mol}^{-1}$$

and

$$\Delta_f G_m^o\ (Ca[NpO_2(OH)_2]^+,\ 298.15\ K) = \mathbf{-\ (1817.265 \pm 5.838)}\ kJ{\cdot}mol^{-1}$$

$$\Delta_f G_m^o\ (Ca_3[NpO_2(OH)_5]^{2+},\ 298.15\ K) = \mathbf{-\ (3439.082 \pm 6.676)}\ kJ{\cdot}mol^{-1}.$$

The stability constants of the ternary Ca-Np(V)-OH aqueous complexes reported in [2016FEL/ROT] and [2016FEL/ALT] can be evaluated based on the species predominant in solution. Reaction (10.15) and calculated $\log_{10}K^o$ ((10.15), 298.15 K) indicate that in the pH-range where $NpO_2(OH)_2^-$ prevails (pH above ≈ 11), the ternary complex $Ca[NpO_2(OH)_2]^+$ becomes predominant at $[Ca^{2+}] > 10^{-3}$ M. These ternary species of Np(V) are accordingly expected to play a predominant role in cementitious systems, where strongly alkaline conditions and milimolar concentrations of Ca (up to 20 mM) are given.

$$Ca^{2+} + NpO_2(OH)_2^- \rightleftharpoons Ca[NpO_2(OH)_2]^+ \qquad (10.15)$$

$$\log_{10}{}^*K^o_{1,1,2}\ ((10.15),\ 298.15\ K) = (3.0 \pm 0.5).$$

#### 10.2.1.4 Neptunium(IV) hydroxide complexes

Two new experimental studies [2004YUS/FED][1], [2008FUJ/KOH] investigating the hydrolysis of Np(IV) were published since the release of [2003GUI/FAN]. Yusov and co-workers [2004YUS/FED] studied the formation of $NpOH^{3+}$ using spectroscopic techniques, whereas Fujiwara and Kohara [2008FUJ/KOH] performed solvent extraction experiments with TTA (thenoyltrifluoroacetone) to determine the equilibrium constants for the formation of $Np(OH)_x^{4-x}$ with $x$ = 1-4. Equilibrium constants derived in these studies for Reactions (10.16) to (10.19) are summarised in Table 10-7, in combination with previous literature data reviewed in [2001LEM/FUG], [2003GUI/FAN] for the same chemical reactions:

$$Np^{4+} + H_2O(l) \rightleftharpoons NpOH^{3+} + H^+ \qquad (10.16)$$

$$Np^{4+} + 2H_2O(l) \rightleftharpoons Np(OH)_2^{2+} + 2H^+ \qquad (10.17)$$

$$Np^{4+} + 3H_2O(l) \rightleftharpoons Np(OH)_3^+ + 3H^+ \qquad (10.18)$$

$$Np^{4+} + 4H_2O(l) \rightleftharpoons Np(OH)_4(aq) + 4H^+ \qquad (10.19)$$

Spectroscopic studies result in systematically lower values of $\log_{10}{}^*\beta_1^o$ ((10.16), 298.15 K), which are often attributed to the difficulty of assigning distinct absorption bands to $Np^{4+}$ and $NpOH^{3+}$. Neck and co-workers [2001NEC/KIM2] reported approximately constant molar absorbance of Np(IV) at 723 nm up to $\log_{10}[H^+] = -2.0$, provided that [Np(IV)] remains sufficiently low to avoid colloid formation.

[1] A shorter description of the same experimental results was provided in [2003YUS/FED] and [2004YUS/FED2].

Table 10-7: Equilibrium constants reported in the literature for Reactions (10.16)-(10.19)

| Reference | Method | Medium | $T$/K | $\log_{10}{}^{*}\beta_x$ | $\log_{10}{}^{*}\beta_x^{o}$ |
|---|---|---|---|---|---|
| $Np^{4+} + H_2O(l) \rightleftharpoons NpOH^{3+} + H^+$ | | | | | |
| [1959SUL/HIN] | spectroscopy | 2.0 M $Na/HClO_4$ | 298.15 | – 2.30 | – (1.25 ± 0.40) |
| | | 2.0 M $Na/DClO_4/D_2O$ | 298.15 | – 2.49 | |
| [1970PAU] | spectroscopy | 1.0 M $Na/HClO_4$ | 298.15 | – 1.90 | |
| | | | | – 1.24[(a)] | – (0.18 ± 0.50)[(a)] |
| [1977DUP/GUI] | solvent extraction | 1.0 M $Li/HClO_4$ | 298.15 | – 0.50 | (0.56 ± 0.50) |
| [2001LEM/FUG] | review | | 298.15 | | – (0.29 ± 1.00) |
| [2003GUI/FAN] | review | | 298.15 | | (0.55 ± 0.20) |
| [2004YUS/FED2] | spectroscopy | 0.1 M $Na/HClO_4$ | (298 ± 1) | – (1.96 ± 0.04) | |
| | | 0.1 M $Na/HClO_4$ | (298 ± 1) | – (1.91 ± 0.03) | |
| | | 0.1 M $Na/HClO_4$ | (298 ± 1) | – (1.86 ± 0.07) | |
| | | 0.3 M $Na/HClO_4$ | (298 ± 1) | – (2.04 ± 0.11) | |
| | | 1.0 M $Na/HClO_4$ | (298 ± 1) | – (2.18 ± 0.10) | |
| | | 1.0 M $Na/HClO_4$ | (298 ± 1) | – (2.29 ± 0.03) | |
| | | | | | – (1.23 ± 0.06)[(b)] |
| [2008FUJ/KOH] | solvent extraction | 1.0 M $Na/HClO_4$ | (296 ± 2) | – (1.19 ± 0.25)[(c)] | – (0.09 ± 0.23) |
| $Np^{4+} + 2H_2O(l) \rightleftharpoons Np(OH)_2^{2+} + 2H^+$ | | | | | |
| [1977DUP/GUI] | solvent extraction | 1.0 M $Li/HClO_4$ | 298.15 | – 1.5 | |
| [1980SCH/GOR] | pulse radiolysis | 0.01 M $C_2H_5OH$/ 0.0005 M $NaClO_4$ | 298.15 | – 4.5 | |
| [2003GUI/FAN] | review | | 298.15 | | (0.35 ± 0.30) |
| [2008FUJ/KOH] | solvent extraction | 0.5 M $Na/HClO_4$ | (296 ± 2) | – (2.76 ± 0.31)[(c)] | |
| | | 1.0 M $Na/HClO_4$ | (296 ± 2) | – (2.57 ± 0.14)[(c)] | |
| | | | | | – (0.87 ± 0.15) |
| | | | | | – (1.47 ± 0.62)[(d)] |
| $Np^{4+} + 3H_2O(l) \rightleftharpoons Np(OH)_3^{+} + 3H^+$ | | | | | |
| [2008FUJ/KOH] | solvent extraction | 0.1 M $Na/HClO_4$ | (296 ± 2) | – (5.56 ± 0.46)[(c)] | |
| | | 0.5 M $Na/HClO_4$ | (296 ± 2) | – (6.61 ± 0.45)[(c)] | |
| | | 1.0 M $Na/HClO_4$ | (296 ± 2) | – (6.86 ± 0.44)[(c)] | |
| | | | | | – (4.30 ± 0.30) |
| | | | | | – (4.31 ± 0.45)[(d)] |
| $Np^{4+} + 4H_2O(l) \rightleftharpoons Np(OH)_4(aq) + 4H^+$ | | | | | |
| [2001LEM/FUG] | review | | 298.15 | | – (9.8 ± 1.1)[(e)] |
| [2003GUI/FAN] | review | | 298.15 | | – (8.3 ± 1.1)[(f)] |
| [2008FUJ/KOH] | solvent extraction | 0.1 M $Na/HClO_4$ | (296 ± 2) | – (10.74 ± 0.48)[(c)] | |
| | | 0.5 M $Na/HClO_4$ | (296 ± 2) | – (11.84 ± 0.52)[(c)] | |
| | | 1.0 M $Na/HClO_4$ | (296 ± 2) | – (12.24 ± 0.28)[(c)] | |
| | | | | | – (9.84 ± 0.30) |
| | | | | | – (9.63 ± 0.48)[(d)] |

(a) Recalculated in [2001LEM/FUG].
(b) Weighted mean in [2004YUS/FED2] including data from [1959SUL/HIN] and [1978FED/PER].
(c) $\log_{10}\beta$ converted to molal units in this review and recalculated to $\log_{10}{}^{*}\beta$ using $pK_{H_2O}$ at $I$ = 0.1, 0.5 and 1.0 M $NaClO_4$.
(d) Extrapolated to $I$ = 0 in this review.
(e) Calculated in [2001LEM/FUG] from solubility data.
(f) Calculated in [2003GUI/FAN] from solubility data.

The authors did also not observe any significant displacement of the characteristic Np(IV) absorption bands, and thus concluded that direct speciation based on spectroscopic data is not feasible. Yusov and co-workers [2004YUS/FED2] could not reproduce these observations, and instead reported different absorption bands for $Np^{4+}$ ($\lambda$ = 723.2 nm, $\varepsilon$ = 153 $L \cdot mol^{-1} \cdot cm^{-1}$) and $NpOH^{3+}$ ($\lambda$ = 729.5 nm, $\varepsilon$ = (57 ± 6) $L \cdot mol^{-1} \cdot cm^{-1}$). However, most of the samples investigated in [2004YUS/FED2] were oversaturated with respect to $NpO_2$(am, hyd), resulting in the presence of polymeric/colloidal Np(IV) species. For this reason and other shortcomings discussed in Appendix A, no thermodynamic data can be selected from the spectroscopic study in [2004YUS/FED2].

Solvent extraction studies result in systematically larger values of $\log_{10} {}^{*}\beta_1^{o}$ ((10.16), 298.15 K). The main criticism of this experimental approach is that the use of ultra-trace concentrations of Np makes the method sensitive to changes in the redox state due to the presence of impurities in the system. Besides this limitation, this review has identified other shortcomings in the solvent extraction study by [2008FUJ/KOH]. These affect data obtained at $-\log_{10}[H^+] > 3$, for which the authors have not provided experimental validation of the stoichiometry of the Np:TTA complex in the organic phase. Below this $-\log_{10}[H^+]$, other problems have been also identified in the data reported for $Np(OH)_2^{2+}$. Hence, the values of $\log_{10}\beta_2^{o}$ and $\varepsilon(Np(OH)_2^{2+}, ClO_4^-)$ recalculated in this review from experimental data reported by Fujiwara and Kohara differ significantly from the values reported in [2008FUJ/KOH] (see Appendix A). The value of the SIT coefficient recalculated in this review, $\varepsilon(Np(OH)_2^{2+}, ClO_4^-) = -(0.38 \pm 0.63)$ $kg \cdot mol^{-1}$ is unexpectedly large in magnitude (but very uncertain) for the interaction of a divalent cation with $ClO_4^-$.

The selection of thermodynamic data in [2003GUI/FAN] for the species $NpOH^{3+}$ and $Np(OH)_2^{2+}$ was based on the solvent extraction study by [1977DUP/GUI] at $-\log_{10}[H^+] < 3$, taking into consideration solubility data and systematic trends along the An(IV) series as discussed in [2001NEC/KIM]. Note that both [2004YUS/FED2] and [2008FUJ/KOH] fail also in providing thermodynamic quantities consistent with those selected for U(IV) and Pu(IV) in the NEA TDB reviews.

Based on the shortcomings identified in [2004YUS/FED2] and [2008FUJ/KOH], but also on the systematic trends expected for the An(IV) series, this review retains the selection in [2003GUI/FAN] for $\log_{10} {}^{*}\beta_1^{o}$ ((10.16), 298.15 K) and $\log_{10} {}^{*}\beta_2^{o}$ ((10.17), 298.15 K) as summarised in Table 10-7. However, the hydrolysis of Np(IV) is not yet a closed chapter, and new experimental work on the U(IV), Np(IV) and Pu(IV) systems would be important.

Fellhauer and co-workers [2010FEL/NEC] investigated the formation of ternary Ca-Np(IV)-OH aqueous complexes in concentrated alkaline $CaCl_2$ solutions. These complexes are characterised by a large number of OH-groups in the first coordination sphere of the actinide, whose charge is compensated by a number of $Ca^{2+}$ ions in the second coordination shell. The inner-sphere character of these complexes was confirmed

by EXAFS for Th(IV) in [2007BRE/ALT]. Based on their solubility data and the analogy with Th(IV), the authors reported the formation of the complex $Ca_4[Np(OH)_8]^{4+}$ according with the chemical Reaction (10.20):

$$4Ca^{2+} + Np^{4+} + 8H_2O(l) \rightleftharpoons Ca_4[Np(OH)_8]^{4+} + 8H^+ \quad (10.20)$$

$$\log_{10} {}^{*}\beta^{o}_{4,1,8}\,(10.20) = -\,(56.1 \pm 0.8)$$

$$\varepsilon(Ca_4[Np(OH)_8]^{4+}, Cl^-) = \varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-) = -\,(0.01 \pm 0.10)\ kg{\cdot}mol^{-1}.$$

Fellhauer and co-workers observed the formation of this species only in $[CaCl_2] \geq 2.0$ M ($I \geq 6.0$ M), that is at concentrations beyond the applicability of SIT. Consequently, this review disregards the selection of the thermodynamic data reported in [2010FEL/NEC], but the values of $\log_{10} {}^{*}\beta^{o}_{4,1,8}$ (10.20) and $\varepsilon(Ca_4[Np(OH)_8]^{4+}, Cl^-)$ are provided for information only. A more accurate description of this system is achieved with the Pitzer model also reported by the authors, but this is out of the scope of this review.

## 10.2.2 Crystalline and amorphous Np oxides and hydroxides

### 10.2.2.1 The neptunium-oxygen system phase diagram

In contrast to the extensively investigated U-O and Pu-O systems, the data available on the neptunium-oxygen system are much more limited. An outline of the Np-O diagram (Figure 10-2) was reported by Richter and Sari [1987RIC/SAR], based on ceramographic, X-ray diffraction, thermal and electron microprobe analyses on stoichiometric and hypo-stoichiometric neptunium dioxide samples. Neptunium dioxide and di-neptunium pentoxide are the only stable oxide phases in this system. The existence of neptunium sesquioxide $Np_2O_3$(cr) was recently confirmed by Seibert *et al.* [2009SEI/GOU] using X-ray and Ultra-Violet Photoelectron spectroscopy, but only as transient species in the presence of neptunium metal, with a thickness of about nine monolayers. The bulk phase is not stable, in contrast to the plutonium sesquioxide.

Since the review by [2001LEM/FUG], [2003GUI/FAN], the only new experimental phase diagram data reported for this system are from Böhler *et al.* [2012BOH/WEL], who reassessed the melting temperature of neptunium dioxide using a quasi-containerless fast laser heating technique, and found $T_{fus}(NpO_2, cr) = (3070 \pm 62)$ K. The latter value, which is about 240 K higher than in the studies by Chikalla *et al.* [1971CHI] and Richter and Sari [1987RIC/SAR], is selected in this review as detailed in Appendix A. Konings *et al.* [2014KON/BEN] suggested a slight hypo-stoichiometry at the congruent melting point given the high oxygen potential of neptunium dioxide at temperatures near the melting point.

A thermodynamic model for the Np-O system was first reported by Kinoshita *et al.* [2003KIN/SET] using the CALPHAD method. The calculated oxygen potential data for $NpO_{2-x}$ were in very good agreement with the experiment [1986BAR/SAR], but the

latter model could not reproduce correctly the data in the available experimental phase diagram (Figure 10-3). In particular, the hypo-stoichiometric homogeneity range of neptunium dioxide was found to start at about 300 K, which is much lower than found experimentally (at about 1300 K according to [1987RIC/SAR]).

Figure 10-2: Np-O phase diagram after Richter and Sari [1987RIC/SAR]. (Reprinted with permission from *J. Nucl. Mater.*, **1987**, *148* , 266. Copyright (1987) Elsevier).

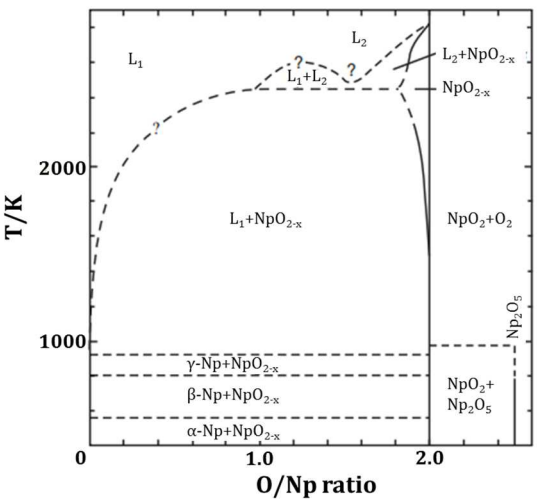
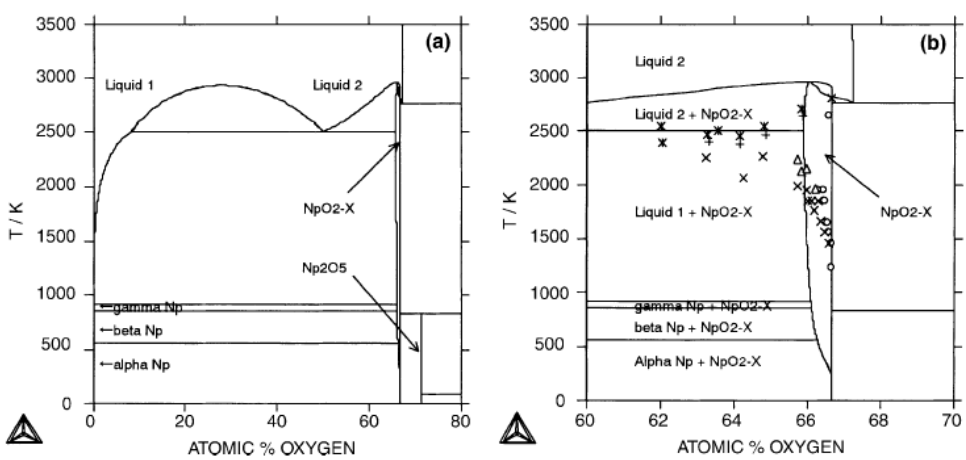
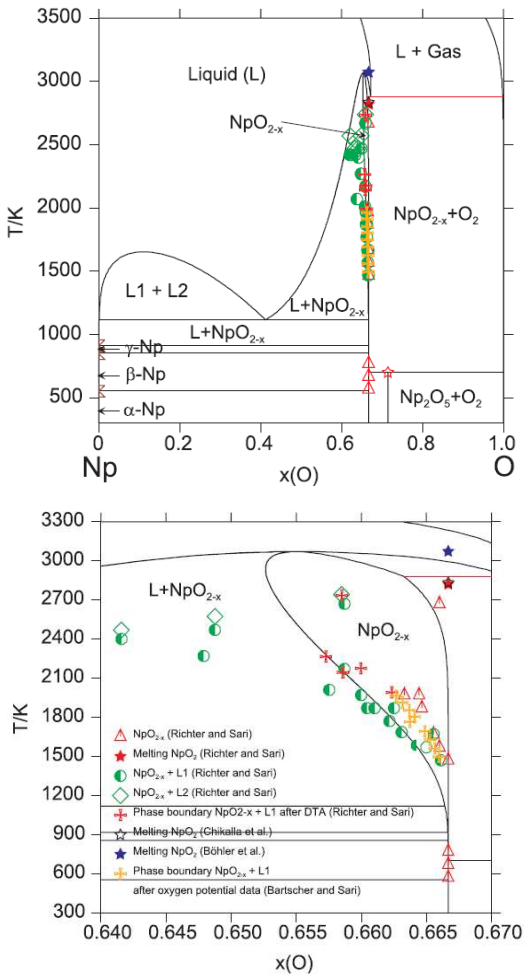



Figure 10-3: Np-O phase diagram calculated by [2003KIN/SET] and comparison with the experimental data. Figure reproduced from [2003KIN/SET]. (Reprinted with permission from *J. Chem. Thermodyn.*, **2003**, *35*, 719. Copyright (2003) Elsevier).



Smith *et al.* recently re-assessed the literature data available on the Np-O system and suggested a new thermodynamic model using the CALPHAD method [2016SMI/COL]. Their model, shown in Figure 10-4, reproduces the main features as suggested by Richter and Sari [1987RIC/SAR], in particular the boundary between the single phase region $NpO_{2-x}$ and the two-phase region {$NpO_{2-x}$(cr) + Np(l)}, and also the oxygen potential data of [1986BAR/SAR].

Figure 10-4: Np-O phase diagram calculated by [2016SMI/COL] and comparison with experimental data. Figure reproduced from [2016SMI/COL]. (Reprinted with permission from *J. Chem. Thermodyn.*, **2016**, *103*, 257. Copyright (2016) Elsevier).



The melting temperature of neptunium dioxide is calculated at $T_{fus}(NpO_2, cr) = 3069.5$ K, in good agreement with the value recommended in this review [2012BOH/WEL]. In this model, the temperature of the monotectic reaction is calculated at 1117 K, however, while Richter and Sari suggested it to be around 2450 K [1987RIC/SAR]. [2016SMI/COL] showed that the three data-sets, namely the miscibility gap, the oxygen potential data and the limit of the hypo-stoichiometric $NpO_{2-x}$(cr) domain were conflicting, as also exemplified by the results of Kinoshita *et al.* [2003KIN/SET]. The authors argued that the oxygen potential and $NpO_{2-x}$(cr) phase boundary data were most probably reliable, based on the comparison with the U-O and Pu-O systems [2016SMI/COL]. As there is no experimental evidence for the existence of a miscibility gap in the Np-O system up to date, the authors suggested that aditional investigations of the liquidus line and temperature of the monotectic reaction are highly desirable.

#### 10.2.2.2 Neptunium(VII) hydrated oxides and hydroxides

The synthesis of Np(VII) compounds by electrochemical oxidation of Np(V) or Np(VI) in acetate solutions was attempted by Fedoseev and co-workers [2012FED/BUD]. In spite of the limited solid phase characterisation, the authors claimed the formation of $NpO_3OH{\cdot}nH_2O$(s) in U(VI) and Nd(III) acetate systems. The presence of Np(V) impurities was quantified as < 10 %. A definitive proof on the formation of this solid phase is still lacking.

#### 10.2.2.3 Neptunium(VI) oxides and hydroxides

##### 10.2.2.3.1 Dioxoneptunium(VI) hydrated oxides and hydroxides

Only one Np(VI) hydrated oxide ($NpO_3{\cdot}H_2O$, cr) was selected in the previous NEA TDB reviews [2001LEM/FUG], [2003GUI/FAN]. The selection of $\log_{10}{}^{*}K^{o}_{s,0}$ ($NpO_3{\cdot}H_2O$, cr) in [2001LEM/FUG] was based on the solubility study by Kato *et al.* [1996KAT/KIM] in 0.1 M $NaClO_4$. Although acknowledging the quality of the solubility data in [1996KAT/KIM], the review by Lemire and co-workers casted some doubts on the structure of the solid phase used by Kato *et al.*, because it showed an X-ray diffraction pattern different from those reported in [1964BAG/LAI] for $NpO_3{\cdot}H_2O$(cr) and $NpO_3{\cdot}2H_2O$(cr). The work by Saito and co-workers on the Np(VI)-hydroxide system [1999SAI/WAN] was neither reviewed in [2001LEM/FUG] nor in [2003GUI/FAN], but provides insights on the structure of the solid phases under discussion. Using a combination of powder XRD, $^{237}$Np Mössbauer spectroscopy and thermogravimetric analysis, the authors determined the structure of four Np(VI) hydroxides: $NpO_2(OH)_2$(cr), $NpO_2(OH)_2{\cdot}H_2O$(cr, orth), $NpO_2(OH)_2{\cdot}H_2O$(cr, hex) and $NpO_2(OH)_2{\cdot}xH_2O{\cdot}yNH_3$(cr) (with $x + y = 1$). XRD pattern of $NpO_2(OH)_2{\cdot}H_2O$(cr, hex) showed good agreement with that of the solid used in [1996KAT/KIM].

Based on the discussion above, this review selects $NpO_2(OH)_2{\cdot}H_2O$(cr, hex) as the solid phase investigated in [1996KAT/KIM], while retaining the equilibrium constant

selected in [2001LEM/FUG] for the dissolution Reaction (10.21). Note that virtually the same equilibrium constant was selected in [2001LEM/FUG], [2003GUI/FAN] for the analogous Pu(VI) phase, $\log_{10}{}^{*}K^{\circ}_{s,0}$ ($PuO_2(OH)_2{\cdot}H_2O$, cr) = (5.5 ± 1.0). The value selected for Np(VI) is also in excellent agreement with $\log_{10}{}^{*}K^{\circ}_{s,0}$ ($UO_3{\cdot}2H_2O$, cr) = (5.35 ± 0.13) recently determined in a comprehensive solubility study by Altmaier and co-workers [2017ALT/YAL] and selected in this review (see Section 9.3.2.1.5.1, Uranium chapter).

$$NpO_2(OH)_2{\cdot}H_2O(\text{cr, hex.}) + 2H^+ \rightleftharpoons NpO_2^{2+} + 3H_2O(\text{l}) \qquad (10.21)$$

$$\log_{10}{}^{*}K^{\circ}_{s,0}\ ((10.21), 298.15\ \text{K}) = \mathbf{(5.470 \pm 0.400)}$$

$$\Delta_r G^{\circ}_m\ ((10.21), 298.15\ \text{K}) = \mathbf{-\ (31.223 \pm 2.283)}\ \text{kJ·mol}^{-1}.$$

Because of the difference in the water content in $NpO_2(OH)_2{\cdot}H_2O$(cr, hex) and $NpO_3{\cdot}H_2O$(cr), a different value of the Gibbs energy of formation is calculated from $\Delta_r G^{\circ}_m$ ((10.21), 298.15 K):

$$\Delta_f G^{\circ}_m\ (NpO_2(OH)_2{\cdot}H_2O, \text{cr, hex}, 298.15\ \text{K}) = \mathbf{-\ (1476.136 \pm 6.063)}\ \text{kJ·mol}^{-1}.$$

### 10.2.2.4 Neptunium(V) oxides and hydroxides

#### 10.2.2.4.1 Dineptunium pentoxide $Np_2O_5$(cr)

[2007FOR/BUR] reported a new method of synthesis of single crystals of $Np_2O_5$(cr) based on a low temperature, aqueous synthesis route using natural calcite crystals mixed with $NpO_2^+$ solution. The structure was shown to be monoclinic in space group *P2/c* (Z = 4) with cell parameters $a$ = 8.168(2) Å, $b$ = 6.584(1) Å, $c$ = 9.313(1) Å, $\beta$ = 116.09(1) ° [2007FOR/BUR]. Magnetic susceptibility measurements revealed a broad transition at 22(3) K resembling antiferromagnetic ordering, but the magnetic structure is probably complex [2007FOR/BUR].

Using X-ray and Ultra-Violet Photoelectron Spectroscopy, Seibert *et al.* [2009SEI/GOU] showed that the $NpO_2$(cr) surface further oxidises to form $Np_2O_5$(cr) when exposed to atomic oxygen produced by an electron cyclotron resonance plasma source. Moreover, their measurements suggested that additional oxygen could be chemisorbed on the surface of $Np_2O_5$(cr). The compound was found to decompose under ultra-high vacuum at about 473 K, while Richter and Sari [1987RIC/SAR] reported that $Np_2O_5$(cr) decomposed under oxygen atmosphere to $NpO_2$(cr) and $O_2$(g) above about 700 K.

The enthalpy of formation at 298.15 K selected in [2001LEM/FUG] and [2003GUI/FAN] is retained in this review.

$$\Delta_f H^{\circ}_m\ (Np_2O_5, \text{cr}, 298.15\ \text{K}) = \mathbf{-\ (2162.700 \pm 9.500)}\ \text{kJ·mol}^{-1}.$$

In their review of the thermodynamic properties of the actinide oxides, [2014KON/BEN] recommended the entropy value estimated by Merli and

Fuger [1994MER/FUG], *i.e.*, $S_m^o(Np_2O_5, cr, 298.15\ K) = (186 \pm 15)\ J \cdot K^{-1} \cdot mol^{-1}$, which agrees within uncertainties with the value selected in [2003GUI/FAN], *i.e.*, $S_m^o(Np_2O_5, cr, 298.15\ K) = (174.000 \pm 20.000)\ J \cdot K^{-1} \cdot mol^{-1}$.

The recent thermodynamic assessment of the Np-O system by Smith *et al.* [2016SMI/COL] has questioned the standard entropy value for $Np_2O_5$(cr). Their optimisation based on the CALPHAD method yielded $S_m^o(Np_2O_5, cr, 298.15\ K) = 242.4\ J \cdot K^{-1} \cdot mol^{-1}$. The adjustment to such high value was necessary to satisfy the decomposition temperature around 700 K for this compound.

The ill-defined functions are most probably, either the standard entropy for $Np_2O_5$(cr) (never measured experimentally), the decomposition temperature, or both, which therefore need to be re-assessed. In view of these discrepancies, no data have been selected for the standard entropy of $Np_2O_5$(cr). However, the value recently recommended by [2014KON/BEN] is considered as the best estimate and is provided here for information only.

#### 10.2.2.4.2 Dioxoneptunium(V) hydroxide

Experimental solubility data of Np(V) oxides and hydroxides were reviewed in [2001LEM/FUG] and [2003GUI/FAN] and thermodynamic solubility products were selected for fresh and aged $NpO_2OH$(am) in [2001LEM/FUG]:

$$NpO_2^+ + H_2O(l) \rightleftharpoons NpO_2OH(am, fresh) + H^+ \qquad (10.22)$$

$$\log_{10}{}^*K^o((10.22), 298.15\ K) = -(5.300 \pm 0.200)$$

and

$$NpO_2^+ + H_2O(l) \rightleftharpoons NpO_2OH(am, aged) + H^+ \qquad (10.23)$$

$$\log_{10}{}^*K^o((10.23), 298.15\ K) = -(4.700 \pm 0.500).$$

Additional studies on the solubility and enthalpy measurements of $NpO_2OH$(am) and $Np_2O_5$(cr) are discussed in [2003GUI/FAN], but the data selected in [2001LEM/FUG] were retained. Since the last review, additional studies on the Np(V) oxide and hydroxide phases have been published. The solubility of mixed-valent Np(IV/V) hydroxide solid phases is found to be very similar in simulated groundwater, $(6.5 \pm 1.5) \times 10^{-6}$ M, and in 0.1 M $NaClO_4$ $(6.1 \pm 2.4) \times 10^{-6}$ M, and orders of magnitude higher than the solubility of pure $Np(OH)_4$(am) [2006PER/KUL]. The solubility of Np(V) (as well as U(VI), Pu(IV) and Am(III)) in simulated groundwater and seawater at pH 7-9 is reported in [2002KUL/FUJ]. Solubility experiments were performed from undersaturation and, as expected, Np(V) had the highest concentrations in solution.

Petrov and co-workers [2017PET/FEL] studied the solubility of $NpO_2OH$(am) in dilute to concentrated NaCl-NaOH solutions with $8.9 \leq -\log_{10}[H^+] \leq 14.5$. Solubility data in 0.1 M NaCl are in good agreement with previous solubility studies in dilute $NaClO_4$ systems [1992NEC/KIM], whereas a significant decrease in Np(V) solubility

(0.5-2 $\log_{10}$ units) was observed in [NaCl] ≥ 1.0 M and $-\log_{10}[H^+] \geq 11.5$. Solid phase characterisation confirmed the formation of crystalline Na-Np(V)-OH phases under these conditions, but also the presence of Na (> 10 %) in the amorphous solid phases controlling the solubility of Np(V) in dilute NaCl systems under less alkaline pH conditions. Spectroscopic data reported in [2017PET/FEL] confirmed the presence of a minor fraction (< 20 %) of Np(V) hydrolysis species within $8.9 \leq -\log_{10}[H^+] \leq 10.3$, in good agreement with thermodynamic calculations using data selected in [2001LEM/FUG] and [2003GUI/FAN]. Although the presence of $Na^+$ in the solid may cast some doubts on the thermodynamic data previously derived from solubility studies with $NpO_2OH(am)$, the spectroscopic data in [2017PET/FEL] provide independent information on the reported hydrolysis constants and solubility product. Petrov *et al.* did not observe ageing of the initial $NpO_2OH(am)$, in contrast to previous observations reported in concentrated $NaClO_4$ [2001NEC/KIM] and NaCl [1996RUN/NEU] systems. The later findings were the basis for the selection in [2001LEM/FUG] of two different solid phases, $NpO_2OH$(am, fresh) and $NpO_2OH$(am, aged) with a difference of 0.6 $\log_{10}$ units in the $\log_{10}{}^{*}K^{o}_{s,0}$.

The new experimental data reported since [2003GUI/FAN] highlight the complexity of the solution chemistry of Np(V) under alkaline pH conditions, with several Na-Np(V)-OH solid phases forming at 298.15 K in addition to $NpO_2OH(am)$. Despite the important limitations identified in the solubility experiments with $NpO_2OH(am)$, the recent spectroscopic data provide sufficient support to retain the value of $\log_{10}{}^{*}K^{o}_{s,0}$ ($NpO_2OH$, am) selected in [2001LEM/FUG] and [2003GUI/FAN] for the fresh solid phase. Because of the amorphous character of this phase, no Gibbs energy of formation is selected. Although the ageing of this solid phase has been observed in some studies in concentrated Na-systems, this review does not accept the selection of $\log_{10}{}^{*}K^{o}_{s,0}$ ($NpO_2OH$, am, aged) proposed in [2001LEM/FUG].

$$NpO_2^+ + H_2O(l) \rightleftharpoons NpO_2OH(am) + H^+ \quad (10.24)$$

$$\log_{10}{}^{*}K^{o}((10.24), 298.15\ K) = \mathbf{-\ (5.300 \pm 0.200)}$$

$$\Delta_r G^{o}_{m}((10.24), 298.15\ K) = \mathbf{(30.253 \pm 1.142)}\ kJ{\cdot}mol^{-1}.$$

### 10.2.2.5 Neptunium(IV) oxides and hydroxides

#### 10.2.2.5.1 Neptunium dioxide $NpO_2$(cr)

The enthalpy of formation of neptunium dioxide $NpO_2$(cr) was determined by oxygen bomb calorimetry measurement by Huber and Holley [1968HUB/HOL], yielding:

$$\Delta_f H^{o}_{m}(NpO_2, cr, 298.15\ K) = \mathbf{-\ (1074.000 \pm 2.500)}\ kJ{\cdot}mol^{-1},$$

which is also selected in this review.

New measurements of the low temperature heat capacity of $NpO_2$(cr) have been reported by [2005MAG/SAN] in the temperature range $T$ = 0.7 to 300 K using thermal

relaxation calorimetry, which are in good agreement with the data of Westrum Jr. *et al.* [1953WES/HAT] obtained using adiabatic calorimetry in the temperature range $T$ = 10.8 to 312.7 K (Figure 10-5). However, the individual heat capacity values measured by [2005MAG/SAN] between $T$ = 0.7 to 300 K were not listed in the publication. Combining the heat capacity data of [2005MAG/SAN] below 12.4 K (private communication to the NEA reviewers) with that of [1953WES/HAT] above the latter temperature, the entropy at 298.15 K is derived as $S^{o}_{m}$ ($NpO_2$, cr, 298.15 K) = (80.2 ± 0.4) $J{\cdot}K^{-1}{\cdot}mol^{-1}$. This value is in excellent agreement with the data selected by [2003GUI/FAN], which is retained in the present review:

$$S^{o}_{m}(NpO_2, \text{cr}, 298.15\ \text{K}) = \mathbf{(80.300 \pm 0.400)}\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

[2005MAG/SAN] focused their discussion on the λ-type anomaly observed at $T_o$ = 25.7 K and its significance for an octupolar order in $NpO_2$(cr) [2002PAI/DET]. Based on the calculated magnetic entropy contribution for $NpO_2$(cr), [2005MAG/SAN] inferred that the ground state in the ordered phase was a singlet. More recent studies by Santini *et al.* [2006SAN/CAR] have concluded that the λ-anomaly at $T$ = 25.7 K was due to rank-5 triakontadipolar order.

The Gibbs energy of formation recommended in [2003GUI/FAN] is retained in this review:

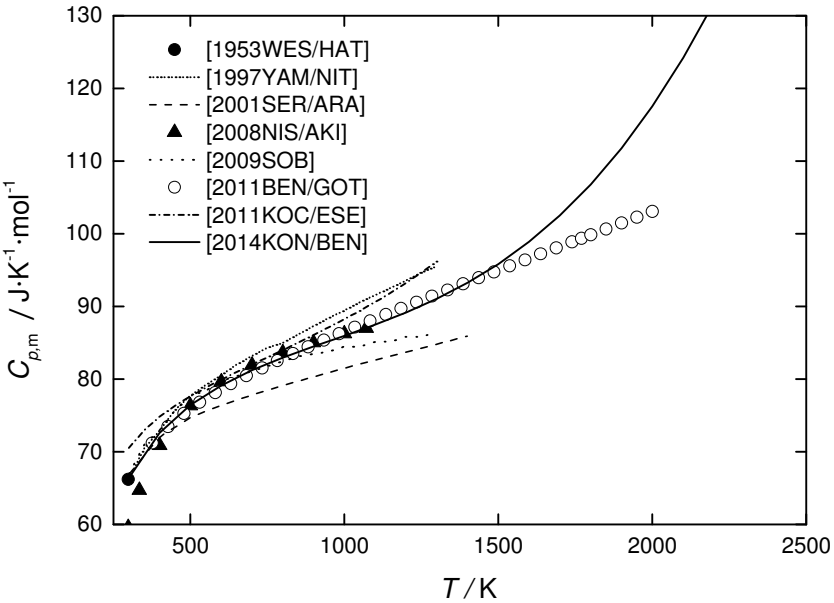
$$\Delta_f G^{o}_{m}(NpO_2, \text{cr}, 298.15\ \text{K}) = \mathbf{-\ (1021.731 \pm 2.514)}\ kJ{\cdot}mol^{-1}.$$

Numerous studies have been reported on the heat capacity of neptunium dioxide at high temperatures as detailed in the thermodynamic review by Konings *et al.* [2014KON/BEN]. Nishi *et al.* [2008NIS/AKI] and Beneš *et al.* [2011BEN/GOT] have reported enthalpy increment measurements in the temperature ranges $T$ = 334 to 1071 K and $T$ = 376 to 1770 K, respectively, by using drop calorimetry. While both measurements are in very good agreement, the sample used by [2008NIS/AKI] probably corresponded to hypo-stoichiometric $NpO_{2-x}$(cr) as detailed in Appendix A. The authors did not impose the necessary constraints on $H_m(T) - H^{o}_{m}(298.15\ \text{K}) = 0$ and $C^{o}_{p,m}$ ($NpO_2$, cr, 298.15 K) when calculating the heat capacity function by derivation of the enthalpy increment data. The derivation of Beneš *et al.* [2011BEN/GOT] is therefore preferred.

Estimates of the heat capacity data have also been reported using various methods. Serizawa *et al.* [2001SER/ARA] have used the sum of the phonon vibration $C_{ph,m}$, dilatation $C_{d,m}$ and electronic $C_{s,m}$ heat capacity contributions, derived from the Debye temperature ($\Theta_D$ = 435 K [1999SER/ARA]), linear thermal expansion and Grüneisen constant γ = 1.93 [1999SER/ARA], and crystal field energies of $NpO_2$(cr) [1991KRU/GAJ], respectively. Sobolev [2005SOB], [2009SOB] has used a simplified model of the equation of state based on a quasi-harmonic approximation for the solid lattice vibrations, and discrete spectrum for the 5f-electron excitations [2004KON]. Koç *et al.* [2011KOC/ESE] have reported an analytical method based on the series expansion

of integer and non-integer *n*-dimensional Debye functions. Those models are compared to the selected experimental data in Figure 10-5 and further discussed in Appendix A.

Figure 10-5: Heat capacity *versus* temperature for $NpO_2$(cr).




Konings and co-workers [2013KON/BEN] have estimated the contribution of oxygen Frenkel pair formation to the high temperature heat capacity of $NpO_2$(cr) by interpolation of the values of the enthalpy and entropy of oxygen Frenkel pair formation for $ThO_2$(cr), $UO_2$(cr) and $PuO_2$(cr). Although there is no experimental data available on this effect that show a significant increase in the heat capacity of $NpO_2$(cr) above about 2000 K, such behaviour is expected by analogy with the $ThO_2$(cr), $UO_2$(cr) and $PuO_2$(cr) systems [2013KON/BEN]. The analysis of [2013KON/BEN] is accepted in this review and the corresponding heat capacity equation is selected:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{NpO_2}, \mathrm{cr}, T) = 64.7712 + 43.8574\times10^{-3}T - 35.0695\times10^{-6}T^2 + 13.1917\times10^{-9}T^3 - 7.8932\times10^{5}T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Furthermore, [2014KON/BEN] have estimated the heat capacity of liquid neptunium dioxide by analogy with $UO_2$ as $C^{\circ}_{p,\mathrm{m}}(\mathrm{NpO_2}, \mathrm{l}, T)$ = **66** $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, which is accepted in this review for scoping calculations. The authors finally suggested a value for the enthalpy of fusion considering that the entropy of fusion was the same as for $UO_2$(cr)

(24 kJ·mol$^{-1}$). The reported result was not based on the revised melting point, however, and we have recalculated and selected:

$$\Delta_{fus} H^{o}_{m} (NpO_2, cr, T_{fus}) = \mathbf{(74.000 \pm 6.000)} \text{ kJ·mol}^{-1}.$$

Vapour pressure studies of neptunium dioxide have been reported by Ackermann *et al.* [1966ACK/FAI], Gotcu-Freis *et al.* [2011GOT/COL] and [2016SMI/COL] using the Knudsen effusion method to derive the enthalpy of sublimation. This review accepts the recent Knudsen effusion mass spectrometry results of [2016SMI/COL] obtained under a flow of oxygen for the reaction $NpO_2(cr) \rightleftharpoons NpO_2(g)$, as detailed in Appendix A. The average of their second and third law treatment yielded:

$$\Delta_{sub} H^{o}_{m} (NpO_2, cr, 298.15 \text{ K}) = (606.8 \pm 1.9) \text{ kJ·mol}^{-1}.$$

The latter data are about 15 kJ·mol$^{-1}$ lower than selected in the review of [2014KON/BEN] based on the results of Ackermann *et al.* [1966ACK/FAI]. From this data and the enthalpy of formation of $NpO_2(cr)$, the standard enthalpy of formation of $NpO_2(g)$ has been derived as:

$$\Delta_{f} H^{o}_{m} (NpO_2, g, 298.15 \text{ K}) = \mathbf{-\ (467.7 \pm 3.1)} \text{ kJ·mol}^{-1},$$

which is selected in this review.

#### 10.2.2.6 Neptunium(III) oxides and hydroxides

There are no new thermodynamic data on Np(III) oxides and hydroxides. Data selected in [2003GUI/FAN] are retained.

## 10.3 Neptunium group 17 (halogen) compounds and complexes

### 10.3.1 Aqueous neptunium group 17 (halogen) complexes

#### 10.3.1.1 Aqueous neptunium fluoride complexes

New studies on the fluoride complex formation of neptunium in aqueous solution are only available for Np(V). Previous studies have been reviewed in detail in [2001LEM/FUG], and the equilibrium constant for $NpO_2F(aq)$ was selected:

$$NpO_2^+ + F^- \rightleftharpoons NpO_2F(aq) \qquad (10.25)$$

$$\log_{10}\beta_1^{o} ((10.25), 298.15 \text{ K}) = (1.200 \pm 0.300).$$

Since the last review a few theoretical and experimental studies have been reported in which equilibrium constants of Np(V) fluoride complexes have been calculated from the effective charge of the actinide ions using a hard sphere model [2002MOR/FUJ]. Moriyama *et al.* calculated $\log_{10}\beta_1^{o} ((10.25), 298.15 \text{ K}) = 1.56$ and

$\log_{10}\beta_2^o$ ((10.26), 298.15 K) = 2.11 for the formation of $NpO_2F(aq)$ and $NpO_2F_2^-$, respectively. Three new experimental studies have been reported, suggesting either the formation of only $NpO_2F(aq)$ or $NpO_2F(aq)$ and $NpO_2F_2^-$, according to Reactions (10.25) and (10.26) [2006RAO/TIA], [2006XIA/FRI], [2009TIA/RAO3]:

$$NpO_2^+ + 2F^- \rightleftharpoons NpO_2F_2^- \quad (10.26)$$

Solvent extraction data in [2006XIA/FRI] and calorimetric data in [2006RAO/TIA] are interpreted by the formation of only $NpO_2F(aq)$, while both $NpO_2F(aq)$ and $NpO_2F_2^-$ are used to interpret spectrophotometric and calorimetric data reported in [2009TIA/RAO3]. The number of complexes used to analyse the experimental data depends on the fluoride concentrations in the different studies. Xia *et al.* [2006XIA/FRI] studied the Np(V) complex formation at fluoride concentrations up to $3.25 \times 10^{-2}$ M, while [2009TIA/RAO3] used fluoride concentrations up to 0.217 M in their calorimetry experiments. Tian *et al.* investigated fluoride concentrations up to 0.3 M in their spectroscopic studies and interpreted the spectral features with the formation of $NpO_2F(aq)$ and $NpO_2F_2^-$. The enthalpies of reaction reported in [2006RAO/TIA] were not experimentally determined, but calculated by interpolating data previously reported in [2006XIA/FRI].

Table 10-8: Experimental equilibrium constants for reaction $NpO_2^+ + nF^- \rightleftharpoons NpO_2F_n^{1-n}$ with $n$ = 1 and 2.

| $T$/K | Method | Medium | $\log_{10}\beta_1$ (10.25) | $\log_{10}\beta_2$ (10.26) | References |
|---|---|---|---|---|---|
| (298 ± 1) | solv. extr. | 1 M $NaClO_4$ | (1.42 ± 0.10) | | [2006XIA/FRI] |
| (308 ± 1) | solv. extr. | 1 M $NaClO_4$ | (1.63 ± 0.03) | | [2006XIA/FRI] |
| (323 ± 1) | solv. extr. | 1 M $NaClO_4$ | (1.77 ± 0.04) | | [2006XIA/FRI] |
| (333 ± 1) | solv. extr. | 1 M $NaClO_4$ | (1.80 ± 0.03) | | [2006XIA/FRI] |
| 283 | spectr | 1 M $NaClO_4$ | (1.19 ± 0.05) | (1.37 ± 0.10) | [2009TIA/RAO3] |
| 298 | spectr | 1 M $NaClO_4$ | (1.25 ± 0.05) | (1.77 ± 0.09) | [2009TIA/RAO3] |
| 313 | spectr | 1 M $NaClO_4$ | (1.36 ± 0.05) | (1.99 ± 0.10) | [2009TIA/RAO3] |
| 328 | spectr | 1 M $NaClO_4$ | (1.39 ± 0.05) | (2.04 ± 0.08) | [2009TIA/RAO3] |
| 343 | spectr | 1 M $NaClO_4$ | (1.44 ± 0.05) | (2.11 ± 0.09) | [2009TIA/RAO3] |

To extrapolate the conditional equilibrium constants at 298.15 K to $I = 0$, [2009TIA/RAO3] used $\Delta z^2 = -2$ for both Reactions (10.25) and (10.26), and $\Delta\varepsilon_{ij}(10.25) = -\varepsilon(Na^+, F^-) - \varepsilon(NpO_2^+, ClO_4^-) = -(0.02 \pm 0.02\ kg\cdot mol^{-1}) - (0.25 \pm 0.05\ kg\cdot mol^{-1}) = -(0.27 \pm 0.10)\ kg\cdot mol^{-1}$. Rao and co-workers report the equilibrium constants derived at 298.15 K, $\log_{10}\beta_1^o$ ((10.25), 298.15 K) = 1.58 [2006RAO/TIA] and (1.39 ± 0.12) [2009TIA/RAO3]. We used the conditional equilibrium constant reported by Xia and co-workers to obtain $\log_{10}\beta_1^o$ ((10.25), 298.15 K) = (1.53 ± 0.10).

The thermodynamic equilibrium constants for $NpO_2F(aq)$ reported in the literature vary, but are consistent within their large uncertainty ranges. The new equilibrium constants reported in [2006XIA/FRI], [2006RAO/TIA] and

[2009TIA/RAO3] fall within the range of previously reported values. The data in [1979RAO/GUD] and the data at 0.1 M $NaClO_4$ in [1985SAW/RIZ] are incompatible with the majority of the reported data, although the reviews [1992FUG/KHO] and [2001LEM/FUG] considered them in their selection (Table 10-9). Including the new data at 298.15 K, we obtain the unweighted average equilibrium constant $\log_{10}\beta_1^o$ ((10.25), 298.15 K) = (1.4 ± 0.3).

Table 10-9: Experimental equilibrium constants at 294.15-298.15 K for the complexation reaction $NpO_2^+ + F^- \rightleftharpoons NpO_2F(aq)$.

| Method | Medium | $\log_{10}\beta_1$ (10.25) | $\log_{10}\beta_1^o$ (10.25) | References |
|---|---|---|---|---|
| sp | 2 M $NaClO_4$ | (1.35 ± 0.30)[(a)] | (1.18 ± 0.37) | [1978RAO/PAT] |
| dis | 2 M $NaClO_4$ | (0.99 ± 0.10)[(a)] | (0.82 ± 0.24) | [1979RAO/GUD] |
| dis | 1 M $NaClO_4$ | (1.26 ± 0.30)[(a)] | (1.37 ± 0.32) | [1984CHO/RAO] |
| dis | 1 M $NaClO_4$ | (1.39 ± 0.30)[(a)] | (1.50 ± 0.32) | [1985INO/TOC] |
| ise-$F^-$ | 0.1 M $NaClO_4$ | (1.51 ± 0.50)[(a)] | (1.70 ± 0.50) | [1985SAW/RIZ] |
| ise-$F^-$ | 1 M $NaClO_4$ | (1.15 ± 0.80)[(a)] | (1.26 ± 0.81) | [1985SAW/RIZ] |
| cal | 1 M $NaClO_4$ | (1.47 ± 0.10) | 1.58 | [2006RAO/TIA] |
| solv extr | 1 M $NaClO_4$ | (1.42 ± 0.10) | (1.53 ± 0.10) | [2006XIA/FRI] |
| spectr, cal | 1 M $NaClO_4$ | (1.25 ± 0.05) | (1.39 ± 0.12) | [2009TIA/RAO3] |

(a) Uncertainties are estimated in [2001LEM/FUG].

Only two studies report the formation of the complex $NpO_2F_2^-$. Inoue *et al.* reported in [1985INO/TOC] $\log_{10}\beta_2$ ((10.26), 1.0 M $NaClO_4$) = (2.07 ± 0.50) at 298.15 K, and Tian *et al.* reported in [2009TIA/RAO3] $\log_{10}\beta_2$ ((10.26), 1.0 M $NaClO_4$) = (1.77 ± 0.09) at 298.15 K. Note that to calculate $\Delta\varepsilon_{ij}(10.26) = -(0.28 \pm 0.10)$ kg·mol$^{-1}$ in the extrapolation of $\log_{10}\beta_2$ ((10.26), 1.0 M $NaClO_4$) to $I = 0$, Rao and co-workers used $\varepsilon(Na^+, NpO_2(OH)_2^-) = -(0.01 \pm 0.07)$ kg·mol$^{-1}$ as proxy for $\varepsilon(Na^+, NpO_2F_2^-)$.

Both research groups determined the equilibrium constant, $\log_{10}\beta_2$ (10.26), together with the equilibrium constant for $NpO_2F(aq)$. Since the revised thermodynamic equilibrium constant, $\log_{10}\beta_1^o$ ((10.25), 298.15 K) = (1.38 ± 0.32), agrees well with $\log_{10}\beta_1^o$ ((10.25), 298.15 K) = (1.39 ± 0.12) reported in [2009TIA/RAO3], their value of $\log_{10}\beta_2^o$ ((10.26), 298.15 K) = (1.92 ± 0.14) at 298.15 K has been selected with an increased uncertainty. Therefore, the selected equilibrium constants are as follows:

$$\log_{10}\beta_1^o \text{ ((10.25), 298.15 K)} = \mathbf{(1.400 \pm 0.300)}$$

$$\log_{10}\beta_2^o \text{ ((10.26), 298.15 K)} = \mathbf{(1.900 \pm 0.400)}.$$

Based on the Gibbs energies of reaction for Reactions (10.25) and (10.26), the Gibbs energy of formation of $NpO_2F(aq)$ and $NpO_2F_2^-$ are:

$$\Delta_r G_m^o \text{ ((10.25), 298.15 K)} = \mathbf{-(7.991 \pm 1.712)} \text{ kJ·mol}^{-1}$$

$$\Delta_r G_m^o \text{ ((10.26), 298.15 K)} = \mathbf{-(10.845 \pm 2.283)} \text{ kJ·mol}^{-1}$$

and

$$\Delta_f G_m^o (NpO_2F, aq, 298.15\ K) = \mathbf{-\ (1197.279 \pm 5.923)}\ kJ{\cdot}mol^{-1}$$

$$\Delta_f G_m^o (NpO_2F_2^-, 298.15\ K) = \mathbf{-\ (1481.656 \pm 6.229)}\ kJ{\cdot}mol^{-1}.$$

Tian *et al.* [2009TIA/RAO3] measured the fluoride complex formation over the temperature range 283.15-343.15 K by spectroscopic means, and also the enthalpy of reaction at each temperature calorimetrically. The authors observed that reaction enthalpies for the formation of $NpO_2F(aq)$ and $NpO_2F_2^-$ increased with temperature, and calculated the heat capacities of Reactions (10.25) and (10.26) assuming constant value of $\Delta_r C_{p,m}^o$. The values of $\Delta_r H_m^o$ and $\Delta_r C_{p,m}^o$ reported are not selected in this review for the reasons given in Appendix A. Xia *et al.* [2006XIA/FRI] calculated $\Delta_r H_m^o$ ((10.25), 298.15 K) and $\Delta_r S_m^o$ ((10.25), 298.15 K) based on solvent extraction experiments between 298.15-333.15 K and assuming a constant enthalpy of reaction. This assumption is not consistent with the calorimetric results reported in [2009TIA/RAO3]. Because of the uncertainties in the temperature dependence of $\Delta_r H_m^o$, no enthalpy data is selected in this review for the Np(V)-F system.

### 10.3.1.2 Aqueous neptunium chloride complexes

The previous NEA TDB reviews [2001LEM/FUG] and [2003GUI/FAN] selected only thermodynamic quantities for chloride complexes of Np(VI) and Np(IV). New studies on the complex formation of neptunium with chloride are only available for Np(V). The chloride complexes are found to be very weak and the nature of coordination remains under discussion. Although some studies using solvent extraction or electrochemical measurements indicate complex formation of Np(V) in chloride media, spectroscopic studies do not indicate inner-sphere coordination of chloride at concentrations below 6 M $Cl^-$ [1997ALL/BUC], [2016FEL/ROT]. In the absence of inner-sphere coordination, the interaction between Np(V) and chloride at low chloride concentration can also be described by using activity coefficients and associated ion interaction coefficients. The reported equilibrium constants of aqueous Np(V) chloride complexes have been reviewed in [2001LEM/FUG]. No thermodynamic data were selected due to the absence of precise measurements and the need of large chloride concentrations to quantify the weak interactions between chloride and Np(V). The situation is different in solids where coordination of chloride is well established. As an example, a three-dimensional structure of a new Np(V) compound, $K(NpO_2)_3(H_2O)Cl_4(cr)$, is reported with bridging and terminal chloride coordinated to Np atoms [2011WAN/ALE]. Chloride ions are also coordinated in the equatorial plane of Np(V) in the mixed-valent Np(IV)/(V) compound $[Np(NpO_2)_6(H_2O)_8(OH)Cl_9]{\cdot}H_2O(cr)$ [2014CHA/FED].

Three new studies investigating the complex formation of Np(V) with chloride in aqueous systems are available in the literature [2009TOP/AUP], [2016FEL/ROT], [2016FEL/ALT]. Topin *et al.* [2009TOP/AUP] reported the equilibrium constant of $NpO_2Cl(aq)$ derived from capillary electrophoresis measurements. The electrophoretic

ion mobility data were interpreted by the formation of the 1:1 complex, $NpO_2Cl(aq)$. The authors reported conditional equilibrium constant of $\log_{10}\beta_1$ ((10.27), 1.0 M NaCl) = – (0.40 ± 0.07) and $\log_{10}\beta_1^o$ ((10.27), 298.15 K) = – (0.12 ± 0.13) for the reaction:

$$NpO_2^+ + Cl^- \rightleftharpoons NpO_2Cl(aq) \qquad (10.27)$$

The reported equilibrium constant in 1 M NaCl corresponds to 30 % of Np(V) being present as $NpO_2Cl(aq)$ complex, which is not in agreement with spectroscopic studies that have shown that much higher chloride concentrations are required to achieve inner-sphere coordination [1997ALL/BUC], [2016FEL/ROT]. Due to this inconsistency with existing spectroscopic data, the present review does not accept the reported thermodynamic equilibrium constant reported in [2009TOP/AUP].

In a combined solubility and spectroscopic (vis/NIR, EXAFS) study, Fellhauer *et al.* [2016FEL/ROT], [2016FEL/ALT] reported the formation of a Np(V)-chloride inner-sphere complex in solutions with $[CaCl_2] \geq 3.5$ M. In 4.5 M $CaCl_2$ systems, EXAFS provided evidence on the formation of ternary Ca-Np(V)-Cl complexes. Using the Pitzer approach, the authors reported $\log_{10}\beta_1^o$ ((10.27), 298.15 K) = – (1.4 ± 0.3). This complex forms in conditions well-beyond the applicability of SIT, and thus the value of $\log_{10}\beta_1^o$ ((10.27), 298.15 K) determined in [2016FEL/ROT], [2016FEL/ALT] is provided for information only.

# 10.4 Neptunium group 16 compounds and complexes

## 10.4.1 Neptunium sulfur compounds and complexes

### 10.4.1.1 Aqueous Np(VI) sulfate complexes

There are no new thermodynamic data on aqueous Np(VI) sulfate complexes. Data selected in [2003GUI/FAN] are retained.

### 10.4.1.2 Aqueous Np(V) sulfate complexes

Np(V) forms weak complexes with sulfate. The previous NEA TDB reviews [2001LEM/FUG], [2003GUI/FAN] only selected the equilibrium constant for the complex $NpO_2SO_4^-$, $\log_{10}\beta_1^o$ (10.28) = (0.440 ± 0.270). The stoichiometry at $T$ = 298.15 K was recently determined by Hennig *et al.* [2009HEN/IKE] using EXAFS spectroscopy, which also confirmed the predominance of the 1:1 complex up to a concentration of 2.0 M $(NH_4)_2SO_4$.

Four new experimental studies reporting thermodynamic data for the system Np(V)-sulfate have been published since the previous NEA TDB update [2006RAO/TIA], [2006XIA/FRI], [2009RAO/TIA], [2009TOP/AUP]. Equilibrium constants derived in these studies for Reactions (10.28) and (10.29) are summarised in Table 10-10. Experimental studies considered in [2001LEM/FUG] for the selection of thermodynamic

data for the system Np(V)-sulfate [1979RAO/GUD], [1983HAL/OLI] are also included in this table and in the corresponding discussion.

$$NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^- \quad (10.28)$$

$$NpO_2^+ + 2SO_4^{2-} \rightleftharpoons NpO_2(SO_4)_2^{3-} \quad (10.29)$$

Table 10-10: Equilibrium constants reported in the literature for Reactions (10.28) and (10.29).

| Reference | Method | Medium | $T$/K | $\log_{10}\beta_x$ | $\log_{10}\beta_x^o$ |
|---|---|---|---|---|---|
| $NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^-$ | | | | | |
| [1979RAO/GUD] | solvent extraction | 2.0 M $NaClO_4$ | 298.15 | (0.44 ± 0.09) | |
| | | | | (0.45 ± 0.10)[(a)] | |
| [1983HAL/OLI] | solvent extraction | 0.50 M $NaClO_4$ | 278.15 | – (0.43 ± 0.35) | |
| | | 1.0 M $NaClO_4$ | 278.15 | – (0.18 ± 0.09) | |
| | | 2.0 M $NaClO_4$ | 278.15 | – (0.04 ± 0.11) | |
| | | 0.50 M $NaClO_4$ | 298.15 | – (0.10 ± 0.08) | |
| | | 1.0 M $NaClO_4$ | 298.15 | (0.06 ± 0.04) | |
| | | 2.0 M $NaClO_4$ | 298.15 | (0.19 ± 0.04) | |
| | | 0.50 M $NaClO_4$ | 318.15 | (0.25 ± 0.03) | |
| | | 1.0 M $NaClO_4$ | 318.15 | (0.34 ± 0.03) | |
| | | 2.0 M $NaClO_4$ | 318.15 | (0.40 ± 0.05) | |
| [2001LEM/FUG] | review | | 298.15 | | (0.44 ± 0.27) |
| [2006XIA/FRI] | solvent extraction | 1.0 M $NaClO_4$ | (298 ± 1) | (0.49 ± 0.31) | |
| | | 1.0 M $NaClO_4$ | (313 ± 1) | (0.65 ± 0.19) | |
| | | 1.0 M $NaClO_4$ | (323 ± 1) | (0.73 ± 0.16) | |
| [2009RAO/TIA] | spectroscopy | 1.0 M $NaClO_4$ | 283.15 | (0.43 ± 0.11) | (0.92 ± 0.22) |
| | | 1.0 M $NaClO_4$ | 298.15 | (0.53 ± 0.14) | (1.03 ± 0.25) |
| | | 1.0 M $NaClO_4$ | 313.15 | (0.56 ± 0.04) | (1.09 ± 0.15) |
| | | 1.0 M $NaClO_4$ | 328.15 | (0.60 ± 0.12) | (1.15 ± 0.20) |
| | | 1.0 M $NaClO_4$ | 343.15 | (0.62 ± 0.08) | (1.21 ± 0.18) |
| [2009TOP/AUP] | CE-ICP-MS | 0.35 M $NaClO_4$ | (298 ± 1) | (0.66 ± 0.11) | |
| | | | | (0.65 ± 0.20)[(b)] | |
| | | 0.70 M $NaClO_4$ | (298 ± 1) | (0.54 ± 0.12) | |
| | | | | (0.52 ± 0.20)[(b)] | |
| | | 1.0 M $NaClO_4$ | (298 ± 1) | (0.40 ± 0.11) | |
| | | | | (0.41 ± 0.20)[(b)] | |
| | | 1.5 M $NaClO_4$ | (2985± 1) | (0.31 ± 0.11) | |
| | | | | (0.29 ± 0.20)[(b)] | |
| | | | | | (1.34 ± 0.12)[(c)] |
| | | | | | (1.32 ± 0.10)[(d)] |
| $NpO_2^+ + 2SO_4^{2-} \rightleftharpoons NpO_2(SO_4)_2^{3-}$ | | | | | |
| [2006XIA/FRI] | solvent extraction | 1.0 M $NaClO_4$ | (313 ± 1) | (1.60 ± 0.11) | |
| | | 1.0 M $NaClO_4$ | (323 ± 1) | (1.82 ± 0.07) | |

(a) Recalculated in [2001LEM/FUG].
(b) Recalculated in this review (see text).
(c) Calculated in [2009TOP/AUP] using the simplified SIT formula.
(d) Calculated in [2009TOP/AUP] using the extended SIT formula.

The formation of the complexes $NpO_2SO_4^-$ and $NpO_2(SO_4)_2^{3-}$ was reported in [2006XIA/FRI]. All other experimental observations using different techniques (solvent extraction, spectrophotometry, CE-ICP-MS, EXAFS) can be properly explained with the formation of the single complex $NpO_2SO_4^-$. This includes studies at elevated $T$ [1983HAL/OLI], [2009RAO/TIA] and at very high sulfate concentrations (2.0 M in [2009HEN/IKE]). Because of the shortcomings in [2006XIA/FRI], summarised in Appendix A, the equilibrium constants in this study were not considered in this review.

As the Np(V)-sulfate complexes are very weak it is necessary to replace a large fraction of the medium anion by sulfate in order to determine the equilibrium constants. Two different approaches were used: (i) experiments at constant ionic strength in [1979RAO/GUD], [1983HAL/OLI], [2006XIA/FRI], [2009TOP/AUP] and (ii) experiments at constant $[Na^+]$ in [2009RAO/TIA]

The substitution of a significant fraction of the original background electrolyte ($NaClO_4$) by $Na_2SO_4$ may cause important changes in the activity coefficients of the species involved, which need to be evaluated as described in the TDB guidelines for the extrapolation to zero ionic strength (Section 4 in [2013GRE/MOM]). The extrapolation of $\log_{10}\beta_1((10.28), I)$ determined in $NaClO_4$-$Na_2SO_4$ mixtures to pure $NaClO_4$ systems was only feasible with the experimental data reported in [1979RAO/GUD] and [2009TOP/AUP]. Both studies confirmed that replacement of $NaClO_4$ by $Na_2SO_4$ had only a small effect on $\log_{10}\beta_1((10.28), I)$ up to a substitution of ≈ 40 % (see Appendix A). Consequently, data reported in [1983HAL/OLI] at $I$ = 2.0 M $NaClO_4$ + $Na_2SO_4$ (45 % substitution) and [2009RAO/TIA] at $I \approx$ 1.0 M $NaClO_4$ + $Na_2SO_4$ (38 % substitution) were also taken into account for the extrapolation of $\log_{10}\beta_1(10.28)$ to $I$ = 0 without further corrections, but with increased uncertainties. The $\log_{10}\beta_1((10.28), I)$ values reported in [1983HAL/OLI] at $I$ = 0.5 M and 1.0 M $NaClO_4$ + $Na_2SO_4$ involving up 90 % substitution of the original background electrolyte have not been accepted by the present review, although they were taken into account in [2001LEM/FUG] for the extrapolation of $\log_{10}\beta_1(10.28)$ to $I$ = 0. Insufficient information is provided in the original publication to allow an estimate of how the large changes in the ionic medium composition affects the activity coefficients and $\log_{10}\beta_1((10.28), I)$. The extrapolation of $\log_{10}\beta_1((10.28), I)$ to $I$ = 0 using data reported in [1979RAO/GUD], [1983HAL/OLI] (only data at $I$ = 2.0 M $NaClO_4$ + $Na_2SO_4$), [2009RAO/TIA] and [2009TOP/AUP] is shown in Figure 10-6 and has been selected in this review:

$$\log_{10}\beta_1^\circ((10.28), 298.15\ \text{K}) = \mathbf{(1.300 \pm 0.200)}$$

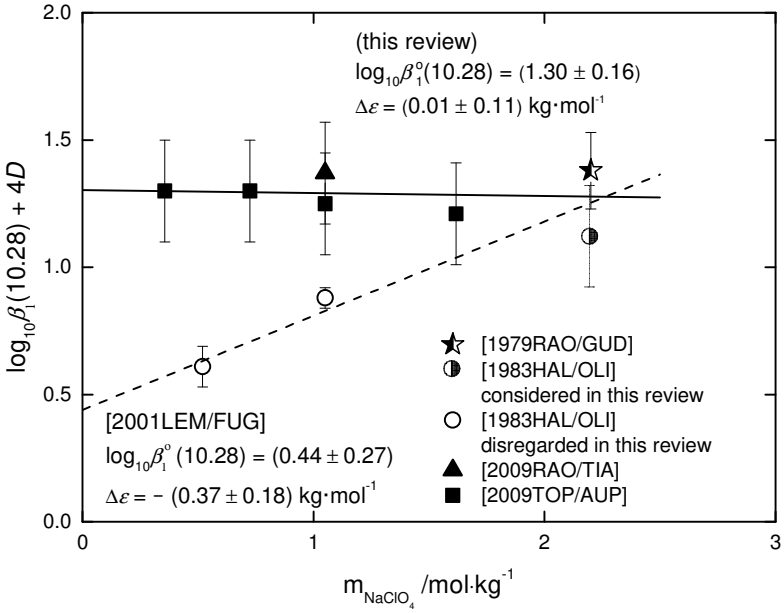
The selected Gibbs energy of reaction for Reaction (10.28) and the Gibbs energy of formation of $NpO_2SO_4^-$ are:

$$\Delta_r G_m^\circ((10.28), 298.15\ \text{K}) = \mathbf{-\ (7.420 \pm 1.142)}\ \text{kJ·mol}^{-1}$$

and

$$\Delta_f G_m^\circ(NpO_2SO_4^-, 298.15\ \text{K}) = \mathbf{-\ (1659.189 \pm 5.758)}\ \text{kJ·mol}^{-1}.$$

Figure 10-6: SIT extrapolation to $I = 0$ of $\log_{10}\beta_1$ (10.28) as reported in [2001LEM/FUG] (dashed line) and derived in this review (solid line). White symbols considered only in the linear regression in [2001LEM/FUG]. Black symbols considered only in the linear regression in this review. Black and white symbols considered in both linear regressions.




There is a large discrepancy between $\log_{10}\beta_1^{\circ}$ ((10.28), 298.15 K) = (0.440 ± 0.270) selected in [2001LEM/FUG] and the one in the present review, $\log_{10}\beta_1^{\circ}$ (10.28) = (1.300 ± 0.160). This difference is caused by the very small $\log_{10}K$ ((10.28), $I$) values reported in [1983HAL/OLI] in $I$ = 0.5 M and 1.0 M $NaClO_4$ + $Na_2SO_4$ (see Table 10-10), as compared to recent data obtained using spectrophotometry [2009RAO/TIA] and CE-ICP-MS [2009TOP/AUP]. There is a significant difference between $\Delta\varepsilon$ reported in [2001LEM/FUG] – (0.37 ± 0.18) kg·mol$^{-1}$ and the value derived in the present review (0.01 ± 0.11) kg·mol$^{-1}$. This results in very different values for the interaction coefficient $\varepsilon(NpO_2SO_4^-, Na^+)$ = – (0.31 ± 0.20) kg·mol$^{-1}$ and (0.07 ± 0.13) kg·mol$^{-1}$, respectively, when using the selected interaction coefficients from Appendix B for $\varepsilon(NpO_2^+, ClO_4^-)$ = (0.25 ± 0.05) kg·mol$^{-1}$ and $\varepsilon(SO_4^{2-}, Na^+)$ = – (0.19 ± 0.06)[1] kg·mol$^{-1}$. The value of $\varepsilon(NpO_2SO_4^-, Na^+)$ = – (0.31 ± 0.20) kg·mol$^{-1}$ appears very large in magnitude for an

[1] Ion interaction coefficient calculated as described in [1980CIA] and recommended in [2003GUI/FAN]: $\varepsilon(Na^+, SO_4^{2-}) = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$, with $\varepsilon_1$ = – (0.184 ± 0.002) kg·mol$^{-1}$ and $\varepsilon_2$ = (0.139 ± 0.006) kg·mol$^{-1}$. $\varepsilon(Na^+, SO_4^{2-})$ = – (0.19 ± 0.06) kg·mol$^{-1}$ corresponding to the average value calculated for 0.357 m ≤ $I_m$ ≤ 2.2 m.

ionic species with a charge of – 1. The present review has selected $\varepsilon(NpO_2SO_4^-, Na^+)$ = (0.07 ± 0.13) kg·mol$^{-1}$.

The selection of $\Delta_r H_m^o$ ((10.28), 298.15 K) in [2001LEM/FUG] was based on the average of $\Delta_r H_m^o$ reported in [1983HAL/OLI] for $I$ = 0.5, 1.0 M and 2.0 M $NaClO_4 + Na_2SO_4$. Following the argumentation above, this review considers only enthalpy data reported in [1983HAL/OLI] for $I$ = 2.0 M $NaClO_4 + Na_2SO_4$. The extrapolation of this enthalpy value to $I$ = 0 according with the NEA TDB guidelines is selected. The values of $\Delta_r H_m^o$ and $\Delta_r C_{p,m}^o$ reported in [2009RAO/TIA] for Reaction (10.28) are not selected in this review for the reasons given in Appendix A, although we note that $\Delta_r H_m$ ((10.28), 1.0 M Na($ClO_4$/$SO_4$), 298.15 K) reported by these authors agrees well with the reaction enthalpy selected in the present review.

$$\Delta_r H_m^o \text{ ((10.28), 298.15 K)} = \mathbf{(22.000 \pm 7.000)} \text{ kJ·mol}^{-1}$$

$$\Delta_r S_m^o \text{ ((10.28), 298.15 K)} = \mathbf{(98.675 \pm 23.789)} \text{ kJ·mol}^{-1}$$

and

$$\Delta_f H_m^o (NpO_2SO_4^-, \text{ 298.15 K}) = \mathbf{-\ (1865.521 \pm 8.402)} \text{ kJ·mol}^{-1}$$

$$S_m^o (NpO_2SO_4^-, \text{ 298.15 K}) = \mathbf{(71.271 \pm 26.090)} \text{ J·K}^{-1}\text{·mol}^{-1}.$$

#### 10.4.1.3 Aqueous Np(IV) sulfate complexes

There are no new thermodynamic data on aqueous Np(IV) sulfate complexes. Data selected in [2003GUI/FAN] are retained.

## 10.5 Neptunium group 15 compounds and complexes

### 10.5.1 Neptunium nitrogen compounds and complexes

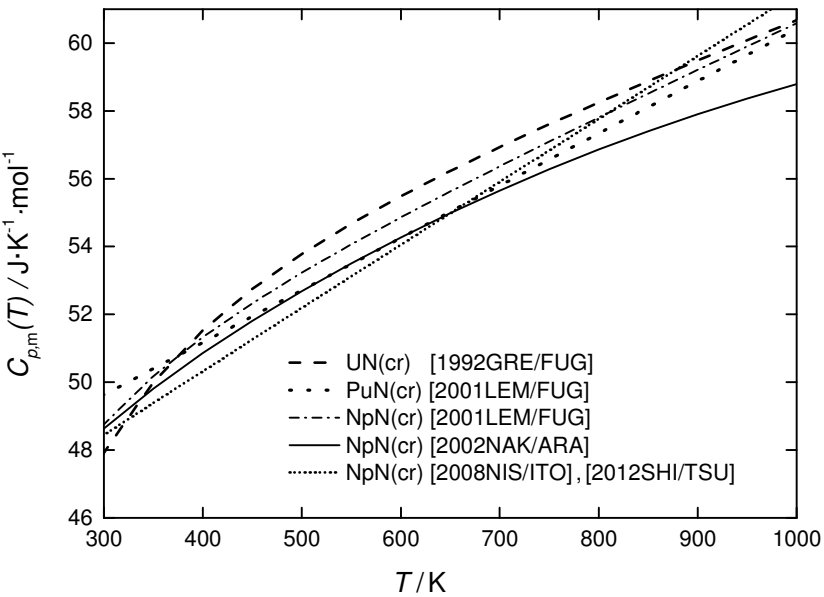
#### 10.5.1.1 NpN(cr)

Since the review of [2001LEM/FUG], [2003GUI/FAN], experimental measurements of the heat capacity [2002NAK/ARA] and enthalpy increments [2008NIS/ITO] of neptunium mononitride NpN(cr) were reported using Differential Scanning Calorimetry in the temperature range 323-1023 K [2002NAK/ARA], and drop calorimetry in the temperature range 334-1067 K [2008NIS/ITO], respectively. The heat capacity equation reported by [2002NAK/ARA], *i.e.*, $C_{p,m}^o$ (NpN, cr, $T$) = 43.4 + 2.31 × 10$^{-2}$ $T$ – 7.62 × 10$^{-6}$ $T^2$ – 9.08 × 10$^4$ $T^{-2}$ J·K$^{-1}$·mol$^{-1}$, was found to be about 3 % lower at 1000 K than the estimate by [2001LEM/FUG], and lower than calculated using the thermal functions for UN(cr) and PuN(cr), which is unexpected. The function derived in the work of [2008NIS/ITO], [2012SHI/TSU], *i.e.*, $C_{p,m}^o$ (NpN, cr, $T$) = 1.872 × 10$^{-2}$ $T$ + 42.75 J·K$^{-1}$·mol$^{-1}$ is found below that of PuN(cr) [2001LEM/FUG] up to 680 K. It yields higher values than PuN(cr) above 680 K, and higher values than UN(cr) above 885 K which is unexpected. Unfortunately the numerical details of their measurements are not reported. In this review we prefer to retain the estimation by

[2001LEM/FUG] that yields a heat capacity for NpN(cr) between that for UN(cr) and PuN(cr):

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{NpN,\ cr}.T) = 47.67 + 1.3174\times10^{-2}\,T - 2.5762\times10^{5}\,T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Figure 10-7: Heat capacity of the actinide mononitrides.




Kurosaki *et al.* [2005KUR/ADA] reported a molecular dynamics (MD) study of the thermophysical properties of the NpN(cr) in the temperature range 300-2500 K and pressure range 0.1 MPa-1.5 GPa. The calculated ($C_V + C_d$) values (heat capacity at constant volume plus a lattice dilatation term) were found to be lower than the recommended data [2001LEM/FUG], the difference being of the order of 3 J·K$^{-1}$·mol$^{-1}$ at 1000 K, which the authors attributed to the neglect of electronic contributions in [2001LEM/FUG]. Sedmidubsky *et al.* [2005SED/KON] performed *ab initio* calculations of the enthalpies of formation of the actinide mononitrides AnN(cr) (An = Ac, Th, Pa, U, Np, Pu, Am) using the full potential linearised augmented plane wave technique modified for local orbitals (APW + lo) and the GGA parametrisation scheme, as mentioned already in Section 9.6.1.2. The calculated enthalpies of formation showed a linear decrease from UN(cr) towards AmN(cr). The obtained enthalpy of formation for NpN(cr), *i.e.*, $\Delta_f H^{\circ}_{\mathrm{m}}$(NpN, cr, 298.15 K) = – 301.3 kJ·mol$^{-1}$, is in very good agreement with the recommended data [2003GUI/FAN]. The same is true for UN(cr), but large deviations are found for ThN(cr) and PuN(cr). The uncertainty of the calculated values is estimated to be around 15 kJ·mol$^{-1}$ by the present review. Benkhaled *et al.* [2012BEN/ZAO]

investigated the electronic structure, magnetic, dynamical and thermodynamic properties of NpN(cr) by *ab initio* pseudopotential and DFT methods, using the Local Density Approximation (LDA) in a plane wave basis. Further details are given in Appendix A. The calculated heat capacity increased strongly below 200 K, and more slowly above 600 K, approaching the Dulong-Petit limit (50 $J \cdot K^{-1} \cdot mol^{-1}$) around 1000 K. This is about 10 $J \cdot K^{-1} \cdot mol^{-1}$ lower at 1000 K than recommended in the present review. [2012SHI/TSU] also reported first-principles calculations of the equilibrium lattice constants, thermal expansion coefficients, bulk moduli, and specific heat at constant volume and pressure in the temperature range 0-1500 K using the project augmented wave method. The calculated heat capacity was found very close to that measured experimentally by [2008NIS/ITO]. The calculated entropy at 298.15 K (58.1 $J \cdot K^{-1} \cdot mol^{-1}$) was found 4.3 $J \cdot K^{-1} \cdot mol^{-1}$ lower than the selected value for UN(cr) [2003GUI/FAN], and 5.4 $J \cdot K^{-1} \cdot mol^{-1}$ lower than the value recommended by [2001LEM/FUG], [2003GUI/FAN], which was estimated from the data of UN(cr) and PuN(cr).

This review retains the data selected by [2001LEM/FUG], [2003GUI/FAN], which are based on estimates from the data of UN(cr) and PuN(cr):

$$\Delta_f H^o_m \text{ (NpN, cr, 298.15 K)} = \mathbf{-\ (305.000 \pm 10.\ 000)}\ kJ \cdot mol^{-1}$$

$$C^o_{p,m} \text{ (NpN, cr, 298.15 K)} = \mathbf{(48.700 \pm 0.900)}\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S^o_m \text{ (NpN, cr, 298.15 K)} = \mathbf{(63.900 \pm 1.500)}\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_f G^o_m \text{ (NpN, cr, 298.15 K)} = \mathbf{-\ (280.443 \pm 10.013)}\ kJ \cdot mol^{-1}.$$

#### 10.5.1.2 Neptunium nitrates

##### 10.5.1.2.1 Aqueous neptunium nitrates

###### 10.5.1.2.1.1 Aqueous Np(VI) nitrates

New spectroscopic studies have appeared since [2003GUI/FAN] that provide unequivocal evidence on the formation of inner-sphere complexes of Np(VI) with nitrate at high ligand concentrations ($[NO_3^-] \geq 2.0$ M). By means of EXAFS, Ikeda-Ohno *et al.* confirmed the replacement of water molecules from the first coordination sphere of Np(VI) by bidentate-coordinating nitrate ions at $[NO_3^-] \geq 5.0$ M [2008IKE/HEN]. In 14.5 M $HNO_3$, the authors observed an average of two nitrate ions coordinated to Np(VI). The same authors [2009IKE/HEN] reported larger U-N coordination numbers for the corresponding U(VI) complexes in similar $HNO_3$ solutions, indicating that the Np(VI)-$NO_3$ complexes are weaker than the U(VI) analogues.

The observations reported in [2008IKE/HEN] are consistent with the recent work by Lindqvist-Reis *et al.* [2013LIN/APO], who investigated the complex formation between nitrate and Np(VI) in $0 \leq [HNO_3] \leq 14$ M, by using a combination of spectroscopic techniques (vis/NIR, IR, Raman, EXAFS). The deconvolution of the

vis/NIR data indicated the predominance of $NpO_2NO_3^+$ and $NpO_2(NO_3)_2(aq)$ at $[NO_3^-] \approx 4$ M and $\approx 7$ M, respectively.

Kim and co-workers [2004KIM/ASA], [2005KIM/ASA] investigated the reduction of Np(VI) to Np(V) in $1.0\ M \leq [HNO_3] \leq 8.0\ M$ using a combination of electrochemical and spectro-electrochemical techniques. The decrease in the redox potential observed with increasing nitrate concentration is related to the formation of more stable nitrate complexes with Np(VI) than Np(V), but the experimental shortcomings summarised in Appendix A prevent the evaluation of the thermodynamics of this system.

#### 10.5.1.2.1.2 Aqueous Np(V) nitrates

No Np(V)-nitrate complexes were selected in [2001LEM/FUG], [2003GUI/FAN]. The available experimental studies reporting the interaction of nitrate with Np(V) [1964GAI/SYK], [1971DAN/CHI], [1979RAO/GUD], [1981PAT/RAM] were explained in [2001LEM/FUG] solely as a result of changes of activity coefficients. This finding was also in line with the lack of spectroscopic evidences on the formation of inner-sphere Np(V)-nitrate complexes below $[NO_3^-] = 4.0$ M. The comprehensive EXAFS study by Ikeda-Ohno *et al.* [2008IKE/HEN] has demonstrated the formation of inner-sphere Np(V)-nitrate complexes at $[NO_3^-] \geq 5.0$ M.

Topin *et al.* investigated the interaction of Np(V) with nitrate in 1.0 M $NaClO_4$-$NaNO_3$ mixtures using CE-ICP-MS [2010TOP/AUP]. The authors reported the formation of the outer-sphere complex $NpO_2NO_3(aq)$ according to Reaction (10.30). Because of the weak nature of the Np(V) nitrate complex, a large fraction of $NaClO_4$ was replaced by $NaNO_3$ (up to 90 %). The resulting $\log_{10}K$ ((10.30), $I$) and corresponding extrapolation to $I = 0$ using the SIT are summarised in Table 10-11, together with equilibrium constants reported in [1964GAI/SYK], [1971DAN/CHI], [1979RAO/GUD], [1981PAT/RAM] for the formation of the same aqueous species.

$$NpO_2^+ + NO_3^- \rightleftharpoons NpO_2NO_3(aq) \qquad (10.30)$$

Table 10-11: Equilibrium constants reported in the literature for Reaction (10.30).

| Reference | Method | Medium | $T$ /K | $\log_{10}\beta_1$ | $\log_{10}\beta_1^o$ |
|---|---|---|---|---|---|
| $NpO_2^+ + NO_3^- \rightleftharpoons NpO_2NO_3(aq)$ | | | | | |
| [1964GAI/SYK][a] | cation exchange | 2.0 M $HClO_4$-$HNO_3$ | 298.15 | – (0.25 ± 0.05) | |
| [1971DAN/CHI][b] | potentiometry | 4.0 M H/$NaClO_4$-H/$NaNO_3$ | (298 ± 1) | – (1.60 ± 0.02) | |
| [1979RAO/GUD][c] | solvent extraction | 2.0 M $NaClO_4$-$NaNO_3$ | (298 ± 0.1) | – (0.55 ± 0.09) | |
| [1981PAT/RAM][d] | solvent extraction | 8.5 M $NaClO_4$-$NaNO_3$ | 298.15 | – 0.52 | |

(Continued on next page)

Table 10-11 (continued)

| Reference | Method | Medium | $T$ /K | $\log_{10}\beta_1$ | $\log_{10}\beta_1^o$ |
|---|---|---|---|---|---|
| [2010TOP/AUP][e] | CE-ICP-MS | 0.95 $NaClO_4$-0.05 M $NaNO_3$ | (298 ± 1) | – (0.07 ± 0.10) | |
| | | 0.50 $NaClO_4$-0.50 M $NaNO_3$ | (298 ± 1) | – (0.15 ± 0.10) | |
| | | 0.10 $NaClO_4$-0.90 M $NaNO_3$ | (298 ± 1) | – (0.22 ± 0.10) | (0.13 ± 0.14) |

(a) $I$ = 2.0 M $HClO_4$-$HNO_3$, 0.2 M ≤ [$HNO_3$] ≤ 1.8 M.
(b) $I$ = 2.0 M $HClO_4$-$HNO_3$, [$H^+$] = 1.0 M, [$Na^+$] = 3.0 M, 0.2 M ≤ [$HNO_3$] ≤ 3.3 M.
(c) $I$ = 2.0 M $NaClO_4$-$NaNO_3$, 0.25 M ≤ [$NaNO_3$] ≤ 1.0 M.
(d) $I$ = 8.5 M $NaClO_4$-$NaNO_3$, 0 ≤ [$NaNO_3$] ≤ 1.2 M.
(e) $I$ = 1.0 M $NaClO_4$-$NaNO_3$, 0 ≤ [$NaNO_3$] ≤ 0.9 M. The authors provide nine values of $\log_{10}K$((10.30), $I$ = 1.0 M) corresponding to nine mixtures 1.0 M $NaClO_4$-$NaNO_3$. Only three $\log_{10}K$((10.30), $I$ = 1.0 M) are reproduced in Table 10-11.

The predominance of the outer-sphere complex $NpO_2NO_3$(aq) in [$NO_3^-$] = 0.9 M proposed in [2010TOP/AUP] is consistent with the lack of spectroscopic evidence on inner-sphere complex formation below [$NO_3^-$] = 4.0 M. An attempt to recalculate the available primary data in [2010TOP/AUP] by taking into account only changes in the activity coefficients was not feasible due to the shortcoming summarised in Appendix A. Note that the equilibrium constant reported by the authors at $I$ = 0, $\log_{10}\beta_1^o$ ((10.30), 298.15 K) = (0.13 ± 0.14) agrees within its uncertainty with the equilibrium constant selected in [1992GRE/FUG] for the formation of the complex $UO_2NO_3^+$, $\log_{10}\beta_1^o$ = (0.30 ± 0.15).

Based on the discussion above and considering the very large fraction of original background electrolyte substituted by $NaNO_3$ in the course of the experiment, the formation of the outer-sphere complex $NpO_2NO_3$(aq) with $\log_{10}\beta_1^o$ ((10.30), 298.15 K) reported in [2010TOP/AUP] is not selected in this review.

#### 10.5.1.2.1.3 Aqueous Np(IV) nitrates

Ikeda-Ohno *et al.* investigated the complex formation of Np(IV) with nitrate at [$NO_3^-$] = 5.0 M and 10.4 M using EXAFS [2008IKE/HEN]. For both ligand concentrations, the authors observed the formation of inner-sphere complexes with bidentate coordinating nitrate ions. The numbers of coordinated nitrate ligands determined by the authors were $N$ = 2.3 and 3.2, respectively. No evidence was found for the formation of anionic Np(IV)-$NO_3^-$ species under the experimental conditions of this study.

Several experimental and modelling studies investigating the distribution of Np(IV) between 30 % TBP in kerosene and nitric acid have been published since the last NEA TDB update [1998MAY/TAY], [2008TAY/SIN], [2009SAR/SIM], [2011SAR/SIM]. These studies provide a quantitative tool for the understanding of Np(IV) behaviour in the PUREX and UREX processes, but are not considered suitable

for deriving thermodynamic data because of the large number of fitting parameters and assumptions required (see Appendix A).

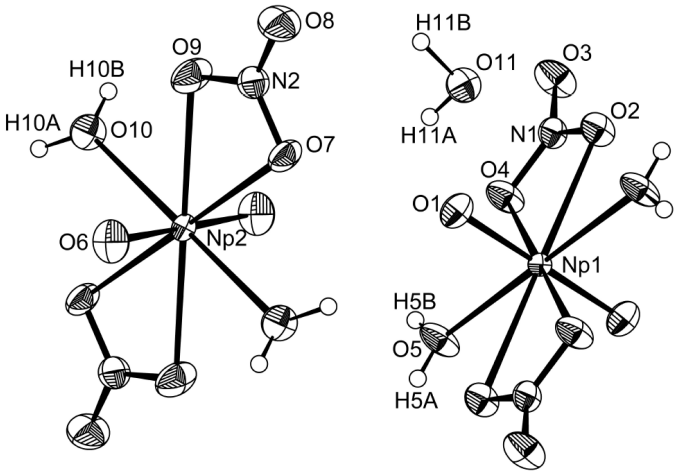
In addition to the references discussed above, there is no new thermodynamic data on aqueous Np(IV) nitrate complexes. Data selected in [2003GUI/FAN] are retained.

#### 10.5.1.2.2 Solid neptunium nitrates

##### 10.5.1.2.2.1 Solid Np(VI) nitrates

The synthesis of $NpO_2(NO_3)_2 \cdot H_2O$(cr) was described by Lindqvist-Reis *et al.* [2013LIN/APO]. The structure of this compound was characterised by single-crystal X-ray diffraction, EXAFS, Raman and IR spectroscopy. The coordination number of Np(VI) in the equatorial plane is six. Two structurally independent $[AnO_2(NO_3)_2(H_2O)_2]$ entities were reported, with nitrate ions symmetrically positioned in $C_{2v}$ symmetry, or with nitrate ions unsymmetrically positioned (Figure 10-8). No thermodynamic data were reported.

Figure 10-8: Thermal ellipsoid (70 %) plot showing the two centrosymmetric $[NpO_2(NO_3)_2(H_2O)_2]$ entities and the lattice water molecule in $[NpO_2(NO_3)_2(H_2O)_2] \cdot H_2O$(cr) as reported in [2013LIN/APO]. (Reprinted with permission from *Dalton Trans.*, **2013**, *42*, 15275. Copyright (2013) The Royal Society of Chemistry).




##### 10.5.1.2.2.2 Solid Np(V) nitrates

No thermodynamic data for solid Np(V) nitrate compounds were selected in [2001LEM/FUG] and [2003GUI/FAN], and there are no new data published between 2001 and 2016.

#### 10.5.1.2.2.3 Solid Np(IV) nitrates

No thermodynamic data for solid Np(IV) nitrate compounds were selected in [2001LEM/FUG] and [2003GUI/FAN], and there are no new data published between 2001 and 2016.

## 10.5.2 Neptunium phosphorous compounds and complexes

### 10.5.2.1 Aqueous Np(VI) phosphates

There are no new thermodynamic data on aqueous Np(VI) phosphate complexes. Data selected in [2003GUI/FAN] are retained.

### 10.5.2.2 Aqueous Np(V) phosphates

Only one aqueous Np(V)-phosphate complex ($NpO_2HPO_4^-$) was selected in [2001LEM/FUG], [2003GUI/FAN], although based on the available experimental evidence, the formation of other complexes with $H_2PO_4^-$ and $PO_4^{3-}$ ligands was suggested. Two new experimental studies reporting thermodynamic data for the system Np(V)-phosphate have been published since [2003GUI/FAN]. These studies focused on experiments in weakly acidic ($4.72 \leq -\log_{10}[H^+] \leq 5.54$) [2006XIA/FRI2] and near-neutral ($7.33 \leq -\log_{10}[H^+] \leq 7.60$) [2009XIA/FRI] solutions and report the formation of Np(V)-$H_2PO_4^-$ and Np(V)-$HPO_4^{2-}$ complexes according to Reactions (10.31)-(10.33). Equilibrium constants derived in [2006XIA/FRI2] and [2009XIA/FRI] for Reactions (10.31)-(10.33) are summarised in Table 10-12. Previous experimental studies focussing on the systems Np(V)-$H_2PO_4^-$ and Np(V)-$HPO_4^{2-}$ [1964MOS/PER], [1984REE/DAN], [1985INO/TOC2], [1996MOR/KIM] and reviewed in [2001LEM/FUG] are also included in this table and in the corresponding discussion. In spite of the proposed formation of $NpO_2PO_4^{2-}$ under alkaline conditions, no additional experimental efforts have been made since [1996MOR/KIM] to assess the stoichiometry and stability of Np(V)-$PO_4^{3-}$ species.

Table 10-12: Equilibrium constants reported in the literature for Reactions (10.31)-(10.33).

| Reference | Method | Medium | $T$ /K | $\log_{10}\beta_x$ | $\log_{10}\beta_x^\circ$ |
|---|---|---|---|---|---|
| $NpO_2^+ + H_2PO_4^- \rightleftharpoons NpO_2H_2PO_4(aq)$ | | | | | |
| [1964MOS/PER] | cation exchange | 0.2 M $NH_4ClO_4$ | (293 ± 2) | 0.8 | |
| [1985INO/TOC2] | solvent extraction | 1.0 M $NaClO_4$ | 298.15 | (1.04 ± 0.18) | |
| [2006XIA/FRI2] | solvent extraction | 1.0 M $NaClO_4$ | (298 ± 1) | (1.18 ± 0.10)<br>(1.27 ± 0.10)[(a)] | |
| | | 1.0 M $NaClO_4$ | (313 ± 1) | (1.39 ± 0.06) | |
| | | 1.0 M $NaClO_4$ | (328 ± 1) | (1.63 ± 0.03) | |

(Continued on next page)

Table 10-12 (continued)

| Reference | Method | Medium | $T$/K | $\log_{10}\beta_x$ | $\log_{10}\beta_x^\circ$ |
|---|---|---|---|---|---|
| $NpO_2^+ + HPO_4^{2-} \rightleftharpoons NpO_2HPO_4^-$ | | | | | |
| [1964MOS/PER] | cation exchange | 0.2 M $NH_4ClO_4$ | (293 ± 2) | (2.85 ± 0.15) | |
| [1984REE/DAN] | cation exchange | 0.1 M $NaClO_4$ | (283.15 ± 0.5) | (3.11 ± 0.19) | |
| | | 0.1 M $NaClO_4$ | (298.15 ± 0.5) | (2.36 ± 0.42) | |
| | | 0.1 M $NaClO_4$ | (308.15 ± 0.5) | (2.06 ± 0.39) | |
| [1985INO/TOC2] | solvent extraction | 1.0 M $NaClO_4$ | 298.15 | (2.11 ± 0.09) | |
| [1996MOR/KIM] | spectroscopy | 0.1 M $NaClO_4$ | (295 ± 2) | (2.54 ± 0.02) | |
| [2001LEM/FUG] | review | | 298.15 | | (2.95 ± 0.10) |
| [2009XIA/FRI] | solvent extraction | 1.0 M $NaClO_4$ | (298 ± 1) | (2.32 ± 0.04) | |
| | | | | (2.34 ± 0.10)[(a)] | |
| | | | (313 ± 1) | (2.08 ± 0.06) | |
| | | | | (2.16 ± 0.10)[(a)] | |
| | | | (328 ± 1) | (1.99 ± 0.13) | |
| | | | | (2.13 ± 0.15)[(a)] | |
| $NpO_2^+ + 2HPO_4^{2-} \rightleftharpoons NpO_2(HPO_4)_2^{3-}$ | | | | | |
| [1985INO/TOC2] | solvent extraction | 1.0 M $NaClO_4$ | 298.15 | (3.43 ± 0.16) | |
| [2009XIA/FRI] | solvent extraction | 1.0 M $NaClO_4$ | (298 ± 1) | (3.78 ± 0.35) | |
| | | 1.0 M $NaClO_4$ | (313 ± 1) | (4.14 ± 0.25) | |
| | | 1.0 M $NaClO_4$ | (323 ± 1) | (4.22 ± 0.24) | |

(a) Recalculated in this review (see text).

$$NpO_2^+ + H_2PO_4^- \rightleftharpoons NpO_2H_2PO_4(aq) \quad (10.31)$$

and

$$NpO_2^+ + HPO_4^{2-} \rightleftharpoons NpO_2HPO_4^- \quad (10.32)$$

$$NpO_2^+ + 2HPO_4^{2-} \rightleftharpoons NpO_2(HPO_4)_2^{3-} \quad (10.33)$$

The interpretation of Np(V) complex formation with $H_2PO_4^-$ under weakly acidic conditions is complicated by the presence of $HPO_4^{2-}$ and the formation of more stable complexes between this ligand and Np(V). This interference is strongly dependent on pH, and needs to be taken into consideration above $-\log_{10}[H^+] \approx 4.5$ [1985INO/TOC2], [2001LEM/FUG]. Solvent extraction data at $T$ = 298.15 K reported in [2006XIA/FRI2] have been reinterpreted in this review by taking into account the formation of both $NpO_2H_2PO_4$(aq) and $NpO_2HPO_4^-$ (Appendix A), resulting in $\log_{10}\beta_1$ ((10.31), $I$ = 1.0 M $NaClO_4$, 298.15 K) = (1.27 ± 0.10). Calculations assuming that only $NpO_2HPO_4^-$ is formed cannot explain the experimental extraction data. The $\log_{10}\beta_1$ ((10.31), $I$ = 1.0 M $NaClO_4$, 298.15 K) recalculated by this review from [2006XIA/FRI2] is in good agreement with the value determined in [1985INO/TOC2] under similar experimental conditions but using a different solvent extractant. This review selects the unweighted average of these two values after extrapolation to $I$ = 0. The value of $\log_{10}\beta_1$ ((10.31), $I$ = 0.2 M $NH_4ClO_4$, 298.15 K) reported in [1964MOS/PER] has been disregarded in this average because of the minor fraction of the complex $NpO_2H_2PO_4$(aq) expected under the experimental conditions used.

$$\log_{10}\beta_1^{\circ}((10.31), 298.15\ \text{K}) = \mathbf{(1.400 \pm 0.200)}.$$

The Gibbs energy of reaction for Reaction (10.31), and the Gibbs energy of formation of $NpO_2H_2PO_4(aq)$ are:

$$\Delta_r G_m^{\circ}((10.31), 298.15\ \text{K}) = \mathbf{-\ (7.991 \pm 1.142)}\ \text{kJ·mol}^{-1}$$

and

$$\Delta_f G_m^{\circ}(NpO_2H_2PO_4, aq, 298.15\ \text{K}) = \mathbf{-\ (2052.908 \pm 5.953)}\ \text{kJ·mol}^{-1}.$$

Solvent extraction data at $T = 313.15$ and 328.15 K reported in [2006XIA/FRI2] have not been considered in this review because of the shortcomings identified in the pH measurements at $T > 298.15$ K, and the resulting uncertainties in the concentrations of $HPO_4^{2-}$ and $NpO_2HPO_4^-$. No enthalpy data has been selected for Reaction (10.31).

Xia *et al.* [2009XIA/FRI] investigated the complex formation of Np(V) with $HPO_4^{2-}$ in 1.0 M $NaClO_4$ at $T = 298.15$, 313.15 and 328.15 K. Even though the authors proposed the formation of both $NpO_2HPO_4^-$ and $NpO_2(HPO_4)_2^{3-}$, the reported solvent extraction data can be explained with only the complex $NpO_2HPO_4^-$ (Appendix A). The equilibrium constant at $T = 298.15$ K recalculated in this review does not agree within the reported uncertainties in [1985INO/TOC2], even though they are made under analogous experimental conditions. Data reported at $T = 298.15$ K in 0.1 M $NaClO_4$ [1984REE/DAN], [1996MOR/KIM] and 1.0 M $NaClO_4$ [1985INO/TOC2], [2009XIA/FRI] have been extrapolated to $I = 0$ using SIT, and resulting in $\log_{10}\beta_1^{\circ}((10.32), 298.15\ \text{K}) = (2.97 \pm 0.10)$ and $-\Delta\varepsilon = (0.06 \pm 0.07)\ \text{kg·mol}^{-1}$. The calculated equilibrium constant is in excellent agreement with the selection in [2001LEM/FUG], also retained in [2003GUI/FAN]. The latter value has been retained in this review.

$$\log_{10}\beta_1^{\circ}((10.32), 298.15\ \text{K}) = \mathbf{(2.950 \pm 0.100)}$$

$$\Delta_r G_m^{\circ}((10.32), 298.15\ \text{K}) = \mathbf{-\ (16.839 \pm 0.571)}\ \text{kJ·mol}^{-1}$$

$$\Delta_f G_m^{\circ}(NpO_2H_2PO_4^-, 298.15\ \text{K}) = \mathbf{-\ (2020.589 \pm 5.870)}\ \text{kJ·mol}^{-1}.$$

The ion interaction coefficient for the anionic complex $NpO_2HPO_4^-$ has been calculated using $-\Delta\varepsilon$, $\varepsilon(NpO_2^+, ClO_4^-) = (0.25 \pm 0.05)\ \text{kg·mol}^{-1}$ [2003GUI/FAN] and $\varepsilon(HPO_4^{2-}, Na^+) = -(0.24 \pm 0.06)\ \text{kg·mol}^{-1}$.[1] The resulting value $\varepsilon(NpO_2HPO_4^-, Na^+) = -(0.05 \pm 0.11)\ \text{kg·mol}^{-1}$ is selected in this review.

Equilibrium constants reported in [2009XIA/FRI] at $T = 298.15$, 313.15 and 328.15 K and recalculated in this review have been used to determine the enthalpy of Reaction (10.32), assuming $\Delta_r C_{p,m}^{\circ} = 0$ (*i.e.*, the standard molar enthalpy of reaction does

[1] Ion interaction coefficient calculated as described in [1980CIA] and recommended in [2003GUI/FAN]: $\varepsilon(HPO_4^{2-}, Na^+) = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$, with $\varepsilon_1 = -(0.19 \pm 0.01)\ \text{kg·mol}^{-1}$ and $\varepsilon_2 = (0.11 \pm 0.03)\ \text{kg·mol}^{-1}$. $\varepsilon(HPO_4^{2-}, Na^+) = -(0.24 \pm 0.06)\ \text{kg·mol}^{-1}$ corresponding to the average value calculated for $I_m = 0.1$ and 1.05 m $NaClO_4$.

not vary within 298.15 K ≤ $T$ ≤ 328.15 K). The resulting $\Delta_r H_m^o$ ((10.32), 1 M $NaClO_4$) = – (15 ± 11) kJ·mol$^{-1}$ has been extrapolated to $I = 0$ using the NEA TDB guidelines in Appendix B and is selected in this review. However, this value should not be used beyond 328.15 K because of the uncertainty in $\Delta_r C_{p,m}^o$ .

$$\Delta_r H_m^o \text{ ((10.32), 298.15 K)} = \mathbf{-\ (11.000 \pm 11.000)}\ \text{kJ·mol}^{-1}$$

The value of $\Delta_r H_m^o$ ((10.32), 298.15 K) is used to calculate the selected enthalpy of formation. Using the selected reaction data, the entropy is calculated *via* $\Delta_r S_m^o$

$$\Delta_f H_m^o(\mathrm{NpO_2HPO_4^-}, 298.15\ \mathrm{K}) = \mathbf{-\ (2288.181 \pm 12.028)}\ \text{kJ·mol}^{-1}$$

$$S_m^o(\mathrm{NpO_2HPO_4^-}, 298.15\ \mathrm{K}) = \mathbf{-\ (59.820 \pm 38.493)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

#### 10.5.2.3 Aqueous Np(IV) phosphates

No thermodynamic data for aqueous Np(IV) phosphate complexes were selected in [2001LEM/FUG] and [2003GUI/FAN], and there are no new data published between 2001 and 2016.

#### 10.5.2.4 Aqueous Np(III) phosphates

No thermodynamic data for aqueous Np(III) phosphate complexes were selected in [2001LEM/FUG] and [2003GUI/FAN], and there are no new data published between 2001 and 2016.

## 10.6 Neptunium group 14 compounds and complexes

### 10.6.1 Neptunium carbon compounds and complexes

#### 10.6.1.1 Aqueous neptunium carbonates

##### 10.6.1.1.1 Np(VI) carbonate and mixed hydroxide-carbonate complexes

The aqueous speciation of Np(VI) in concentrated carbonate solutions (1.5 M $Na_2CO_3$, pH = 11.7) was investigated by Ikeda-Ohno *et al.* [2009IKE/TSU] using EXAFS and cyclic voltammetry. The authors confirmed the predominance of the complex $NpO_2(CO_3)_3^{4-}$ at high carbonate concentrations, as noticed in previous reviews. Np(VI)-$O_{ax}$ distances determined by the authors increase from U to Pu as expected. The model assuming a bidentate coordination of carbonate to $NpO_2^{2+}$ provides a consistent explanation of the EXAFS data for all $An^{VI}O_2(CO_3)_3^{4-}$.

The solubility study by Kato *et al.* [1998KAT/KIM] was not reviewed in [2001LEM/FUG] and [2003GUI/FAN], but provides key information for assessing the thermodynamic properties of aqueous Np(VI)-$CO_3$ complexes and the solubility product of $NpO_2CO_3$(cr). The chemical model derived by the authors included $NpO_2CO_3$(aq) and $NpO_2(CO_3)_3^{4-}$ as the predominant solution species in the aqueous phase according

to Reactions (10.34) and (10.36). The authors proposed that $NpO_2(CO_3)_2^{2-}$ (Reaction (10.35)) plays only a minor role within the carbonate concentration range used and they reported an upper limit for the corresponding equilibrium constant. Thermodynamic data reported in [1998KAT/KIM] for Reactions (10.34) and (10.35) are summarised in Table 10-13, in combination with previous literature data reviewed in [2001LEM/FUG]. The limiting complex $NpO_2(CO_3)_3^{4-}$ is discussed separately. Note that the work by Kato *et al.* provides a new path for assessing the thermodynamic properties of this species (through the solubility equilibrium $NpO_2CO_3(cr) + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{4-}$), in addition to the one in [2001LEM/FUG], which was based on the redox equilibrium $NpO_2(CO_3)_3^{5-} \rightleftharpoons NpO_2(CO_3)_3^{4-} + e^-$.

$$NpO_2^{2+} + CO_3^{2-} \rightleftharpoons NpO_2CO_3(aq) \quad (10.34)$$

$$NpO_2^{2+} + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{2-} \quad (10.35)$$

$$NpO_2^{2+} + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{4-} \quad (10.36)$$

Gelis *et al.* [2001GEL/VAN] provided qualitative indications on the formation of ternary Np(VI)-OH-$CO_3$ complexes in strongly alkaline carbonate solutions, although no thermodynamic data could be derived from this study.

Table 10-13: Equilibrium constants reported in the literature for Reactions (10.34) and (10.35).

| Reference | Method | Medium | $T$/K | $\log_{10}\beta_x$ | $\log_{10}\beta_x^o$ |
|---|---|---|---|---|---|
| $NpO_2^{2+} + CO_3^{2-} \rightleftharpoons NpO_2CO_3(aq)$ | | | | | |
| [1984MAY] | $E_h$ measurements | 1.0 M $NaClO_4$ | 298.15 | (7.9 ±1.0)<br>≤ (9.5 ± 2.1)[a] | |
| [1998VIT/CAP] | solubility | 3.0 M $NaClO_4$ | 295.15 | (8.5 ± 1.0)<br>(8.72 ± 0.52)[a] | |
| [2001LEM/FUG] | review | | 298.15 | | (9.32 ± 0.61) |
| [1998KAT/KIM] | solubility | 0.1 M $NaClO_4$ | 298.15 | (9.02 ± 0.10) | 9.85<br>(9.86 ± 0.10)[b] |
| $NpO_2^{2+} + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{2-}$ | | | | | |
| [1984MAY] | $E_h$ measurements | 1.0 M $NaClO_4$ | 298.15 | (13.5 ± 4.8)<br>≤ (14.9 ± 2.1)[a] | |
| | potentiometry | 1.0 M $NaClO_4$ | 298.15 | (16.51 ± 0.14)<br>≤ (15.4 ± 0.6)[a] | |
| [1998VIT/CAP] | solubility | 3.0 M $NaClO_4$ | 295.15 | (15.72 ± 0.51)<br>(15.77 ± 0.52)[a] | |
| [2001LEM/FUG] | review | | 298.15 | | (16.52 ± 0.73) |
| [1998KAT/KIM] | solubility | 0.1 M $NaClO_4$ | 298.15 | ≤ 14.2 | ≤ 15.0 |

(a) Recalculated in [2001LEM/FUG].
(b) Recalculated in this review (see text).

#### 10.6.1.1.2 $NpO_2CO_3(aq)$ and $NpO_2(CO_3)_2^{2-}$

The previous NEA TDB selection of thermodynamic data for the complexes

$NpO_2CO_3$(aq) and $NpO_2(CO_3)_2^{2-}$ [2001LEM/FUG] relied on a single solubility study conducted in 3.0 M $NaClO_4$ [1998VIT/CAP]. Both the original source and the NEA TDB review highlighted the limitations of this selection due to the restricted set of solubility measurements available, in addition thermodynamic equilibrium was not achieved in several of the investigated samples. Indeed, a close inspection of the thermodynamic model derived in [1998VIT/CAP] shows that only three experimental points were taken into account for the determination of $\log_{10}\beta_1$ ((10.34), $I$ = 3.0 M $NaClO_4$) and $\log_{10}\beta_2$ ((10.35), $I$ = 3.0 M $NaClO_4$). [1998KAT/KIM] provides a significantly larger dataset for the determination of the thermodynamics of $NpO_2CO_3$(aq). Hence, the authors were able to observe a $[CO_3^{2-}]$-independent behaviour of the solubility within the carbonate range $-8 \le [CO_3^{2-}] \le -6$, which corresponds to the equilibrium reaction $NpO_2CO_3(cr) \rightleftharpoons NpO_2CO_3(aq)$. The combination of the resulting conditional equilibrium constant with $\log_{10}K_{s,0}$ ($NpO_2CO_3$, cr, $I$ = 0.1 M $NaClO_4$) determined from the same dataset at lower $[CO_3^{2-}]$ results in $\log_{10}\beta_1$ ((10.34), $I$ = 0.1 M $NaClO_4$) = $\log_{10}\beta_1^o$ ((10.34), 298.15 K) = (9.86 ± 0.10). This value is in excellent agreement with the current selection for the U(VI) system, $\log_{10}\beta_1^o$ = (9.94 ± 0.03), and agrees within the uncertainties with the previous selection in [2001LEM/FUG], $\log_{10}\beta_1^o$ ((10.34), 298.15 K) = (9.32 ± 0.61). Because of the more comprehensive and accurate dataset this review selects $\log_{10}\beta_1^o$ ((10.34), 298.15 K) determined by Kato and co-workers [1998KAT/KIM].

$$\log_{10}\beta_1^o \text{ ((10.34), 298.15 K)} = \mathbf{(9.860 \pm 0.100)}$$

$$\Delta_r G_m^o \text{ ((10.34), 298.15 K)} = \mathbf{-(56.281 \pm 0.571)} \text{ kJ·mol}^{-1}$$

and

$$\Delta_f G_m^o \text{ } (NpO_2CO_3, \text{ aq, 298.15 K}) = \mathbf{-(1380.120 \pm 5.657)} \text{ kJ·mol}^{-1}.$$

The large stability assigned in [2001LEM/FUG] to $NpO_2(CO_3)_2^{2-}$ is not consistent with the experimental results in [1998KAT/KIM]. Indeed, $NpO_2CO_3$(cr) solubility data reported in 0.1 M $NaClO_4$ by the latter authors can be explained with the predominance of $NpO_2^{2+}$ at $\log_{10}[CO_3^{2-}] \le -9$, $NpO_2CO_3$(aq) between $-9 < \log_{10}[CO_3^{2-}] \le -5.5$ and $NpO_2(CO_3)_3^{4-}$ at $\log_{10}[CO_3^{2-}] > -5.5$. Based on these experimental observations, the complex $NpO_2(CO_3)_2^{2-}$ is expected to have a minor importance on the aqueous chemistry of the Np(VI)-$CO_3$ system. The upper limit proposed in [1998KAT/KIM] for $\log_{10}\beta_2^o$ ((10.35), 298.15 K) ≤ 15.0 is not selected in the present review and is reported for information only.

Thermodynamic data selected in this review can explain the $NpO_2CO_3$(cr) solubility data reported by Vitorge and Capdevila [1998VIT/CAP] in 3.0 M $NaClO_4$, because the decreased stability of $NpO_2(CO_3)_2^{2-}$ is compensated by a larger stability of $NpO_2CO_3$(aq). The selection is also consistent with $NpO_2CO_3$(cr) solubility data reported by Kato *et al.* in 0.1 M $NaClO_4$ [1998KAT/KIM].

#### 10.6.1.1.3 The Np(VI) carbonate limiting complex

The thermodynamic description of the Np(VI) carbonate limiting complex in [2001LEM/FUG] was based on the redox equilibrium (10.37):

$$NpO_2(CO_3)_3^{5-} \rightleftharpoons NpO_2(CO_3)_3^{4-} + e^- \quad (10.37)$$

Three independent experimental sources were taken into account for the assessment of this reaction, [1977SIM], [1990RIG], and [1995OFF/CAP], covering a broad range of ionic strength and carbonate concentrations (0.13 M ≤ [$Na_2CO_3$] ≤ 2.09 M). This resulted in very accurate values of $E°$ and $\Delta\varepsilon$ for the redox equilibrium (10.37). The combination of $E°$ with the standard potential for the $NpO_2^{2+}/NpO_2^+$ redox couple and the equilibrium constant of $NpO_2(CO_3)_3^{5-}$ allowed the calculation of $\log_{10}K^o$ ((10.36), 298.15 K) = (19.37 ± 0.19).

Kato *et al.* [1998KAT/KIM] explained the increase in solubility with slope of ≈ + 2 ($\log_{10}$[Np(VI)] *vs.* $\log_{10}[CO_3^{2-}]$) in 0.1 M $NaClO_4$ and $-6 \le \log_{10}[CO_3^{2-}] \le -4.5$ with the equilibrium reaction $NpO_2CO_3(cr) + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{4-}$. Within this concentration range, the authors could neglect the formation of the trinuclear species $(NpO_2)_3(CO_3)_6^{6-}$ as discussed in Appendix A. The combination of the conditional equilibrium constant with $\log_{10}K_{s,0}(NpO_2CO_3, cr, I = 0.1\ M\ NaClO_4)$ determined by the same authors results in $\log_{10}\beta_3$ ((10.36), $I$ = 0.1 M $NaClO_4$) = (20.41 ± 0.09), which can be extrapolated to $I = 0$ using the ion interaction coefficients reported in Appendix B for $NpO_2(CO_3)_3^{4-}$, $NpO_2^{2+}$ and $CO_3^{2-}$. This leads to $\log_{10}\beta_3^o$ ((10.36), 298.15 K) = (20.35 ± 0.09), which is approximately one $\log_{10}$-unit larger than the selection in [2001LEM/FUG]. This review takes both data sources into account and selects their unweighted average, $\log_{10}\beta_3^o$ ((10.36), 298.15 K) = (19.9 ± 0.5) with the uncertainty equal to the maximum deviation from the mean:

$$\log_{10}\beta_3^o\ ((10.36), 298.15\ K) = \mathbf{(19.900 \pm 0.500)}$$

$$\Delta_r G_m^o\ ((10.36), 298.15\ K) = \mathbf{-\ (113.590 \pm 2.854)}\ kJ{\cdot}mol^{-1}$$

and

$$\Delta_f G_m^o\ (NpO_2(CO_3)_3^{4-}, 298.15\ K) = \mathbf{-\ (2493.229 \pm 6.406)}\ kJ{\cdot}mol^{-1}.$$

One of the main limitations of the selected data in [2001LEM/FUG] and [2003GUI/FAN] is the large uncertainty in the ion interaction coefficient of $NpO_2(CO_3)_3^{4-}$ ($\varepsilon(NpO_2(CO_3)_3^{4-}, Na^+) = -(0.40 \pm 0.19)$ kg·mol$^{-1}$), which is a result of the large uncertainty in $\varepsilon(NpO_2(CO_3)_3^{5-}, Na^+)$. Note that $\varepsilon(NpO_2(CO_3)_3^{4-}, Na^+)$ is significantly different from the ion interaction coefficient selected for the analogous U(VI) species $\varepsilon(UO_2(CO_3)_3^{4-}, Na^+) = -(0.01 \pm 0.11)$ kg·mol$^{-1}$. Very similar values are to be expected for these species, but this review finds no compelling argument to disregard one or the other of these values. Both are retained in the present review, but we emphasise the need of further research on this topic. New experimental studies on the system Np(VI)-$CO_3$ in dilute to concentrated ionic media in addition to the redox coupling

with Np(V) would be very helpful for closing this open gap in the aquatic chemistry of Np(VI).

No new studies on the system Np(VI)-carbonate at elevated temperatures have been published since the last NEA TDB update. The value of $\Delta_r H_m^o$ ((10.36), 298.15 K) selected in [2001LEM/FUG] is retained in this review:

$$\Delta_r H_m^o \text{ ((10.36), 298.15 K)} = \mathbf{-\ (41.900 \pm 4.100)}\ \text{kJ·mol}^{-1}.$$

From this value, $\Delta_f H_m^o(\mathrm{NpO_2^{2+}}, 298.15\ \text{K}) = -\ (860.733 \pm 4.662)\ \text{kJ·mol}^{-1}$ and $\Delta_f H_m^o(\mathrm{CO_3^{2-}}, 298.15\ \text{K}) = -\ (675.230 \pm 0.250)\ \text{kJ·mol}^{-1}$

$$\Delta_f H_m^o(\mathrm{NpO_2(CO_3)_3^{4-}}, 298.15\ \text{K}) = \mathbf{-\ (2928.323 \pm 6.254)}\ \text{kJ·mol}^{-1}$$

is calculated. From $\Delta_r H_m^o$ ((10.36), 298.15 K) = – (41.9 ± 4.1) kJ·mol$^{-1}$ and $\Delta_r G_m^o$ ((10.36), 298.15 K) = – (113.590 ± 2.854) kJ·mol$^{-1}$ selected in this review, the entropy of reaction $\Delta_r S_m^o$ ((10.36), 298.15 K) = **(240.449 ± 16.755)** J·K$^{-1}$·mol$^{-1}$ is calculated using the Gibbs-Helmholtz equation, which combined with $S_m^o(\mathrm{NpO_2^{2+}}, \text{aq}, 298.15\ \text{K})$ = – (92.387 ± 10.464) J·K$^{-1}$·mol$^{-1}$ and $S_m^o(\mathrm{CO_3^{2-}}, \text{aq}, 298.15\ \text{K})$ = – (50 ± 1) J·K$^{-1}$·mol$^{-1}$ gives

$$S_m^o(\mathrm{NpO_2(CO_3)_3^{4-}}, \text{aq}, 298.15\ \text{K}) = \mathbf{-\ (1.938 \pm 19.981)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

#### 10.6.1.1.4 The trinuclear Np(VI) carbonate complex

There are no new experimental studies providing thermodynamic data for $(\mathrm{NpO_2})_3(\mathrm{CO_3})_6^{6-}$, and the selection in [2001LEM/FUG] for the equilibrium Reaction (10.38) is retained in the present review.

$$3\mathrm{NpO_2(CO_3)_3^{4-}} \rightleftharpoons (\mathrm{NpO_2})_3(\mathrm{CO_3})_6^{6-} + 3\mathrm{CO_3^{2-}} \qquad (10.38)$$

with

$$\log_{10} K^o \text{ ((10.38), 298.15 K)} = \mathbf{-\ (8.272 \pm 1.447)}$$

$$\Delta_r G_m^o \text{ ((10.38), 298.15 K)} = \mathbf{(47.215 \pm 8.260)}\ \text{kJ·mol}^{-1}.$$

Changes in the thermodynamic data selected for $\mathrm{NpO_2(CO_3)_3^{4-}}$ affect $\log_{10}\beta_{6,3}^o$ ((10.39), 298.15 K), which is accordingly recalculated:

$$3\mathrm{NpO_2^{2+}} + 6\mathrm{CO_3^{2-}} \rightleftharpoons (\mathrm{NpO_2})_3(\mathrm{CO_3})_6^{6-} \qquad (10.39)$$

with

$$\log_{10}\beta_{6,3}^o \text{ ((10.39), 298.15 K)} = \mathbf{(51.428 \pm 2.084)}$$

$$\Delta_r G_m^o \text{ ((10.39) 298.15 K)} = \mathbf{-\ (293.553 \pm 11.896)}\ \text{kJ·mol}^{-1}.$$

The value of $\Delta_f G_m^o((\mathrm{NpO_2})_3(\mathrm{CO_3})_6^{6-}, 298.15\ \text{K})$ re-calculated in order to be consistent with $\Delta_f G_m^o(\mathrm{NpO_2(CO_3)_3^{4-}}, 298.15\ \text{K}) = -\ (2493.00 \pm 6.40)\ \text{kJ·mol}^{-1}$ selected in this review gives:

$$\Delta_f G_m^o\ (\ (NpO_2)_3(CO_3)_6^{6-}\ ,\ 298.15\ K) = \mathbf{-\ (5848.772 \pm 20.951)}\ kJ{\cdot}mol^{-1}.$$

#### 10.6.1.1.5 Mixed Np(VI) hydroxide-carbonate complexes

Only one mixed Np(VI) hydroxide-carbonate complex, $(NpO_2)_2CO_3(OH)_3^-$, was selected in [2001LEM/FUG], [2003GUI/FAN] based on the potentiometric study in [1984MAY]. The equilibrium constant selected in [2001LEM/FUG] for Reaction (10.40) is retained in the present review.

$$7H^+ + 2NpO_2(CO_3)_3^{4-} \rightleftharpoons (NpO_2)_2CO_3(OH)_3^- + 5CO_2(g) + 2H_2O(l) \qquad (10.40)$$

with

$$\log_{10}{}^*K^o\ ((10.40),\ 298.15\ K) = \mathbf{(49.166 \pm 1.586)}$$

$$\Delta_r G_m^o\ ((10.40),\ 298.15\ K) = \mathbf{-\ (280.640 \pm 9.053)}\ kJ{\cdot}mol^{-1}.$$

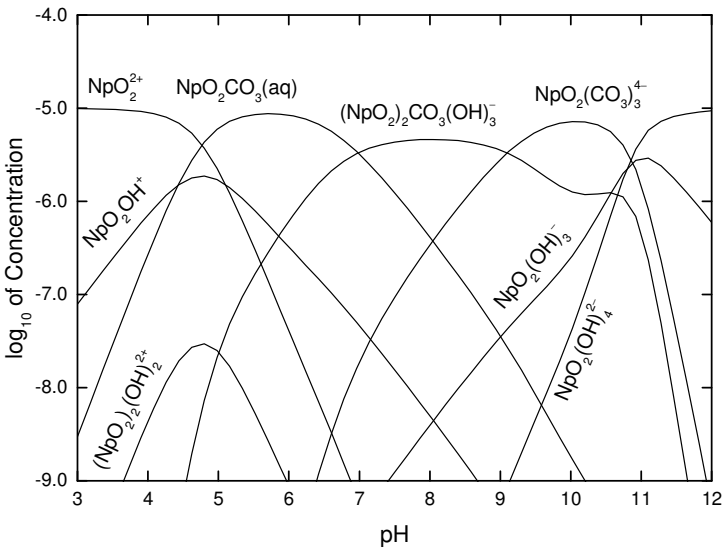
The Gibbs energy of formation of $(NpO_2)_2CO_3(OH)_3^-$ has been recalculated taking into account the new value of $\Delta_f G_m^o\ (\ NpO_2(CO_3)_3^{4-}\ ,\ 298.15\ K)$ selected in this review:

$$\Delta_f G_m^o\ (\ (NpO_2)_2CO_3(OH)_3^-\ ,\ 298.15\ K) = \mathbf{-\ (2820.953 \pm 15.702)}\ kJ{\cdot}mol^{-1}.$$

In contrast to An(IV) and An(V), no thermodynamic data is available for mixed An(VI) hydroxide-carbonate complexes that might be formed in strongly alkaline carbonate solutions with $-\log_{10}[H^+]$ above 12. Qualitative indications on the formation of such complexes of Np(VI) were provided by Gelis and co-workers using cyclic voltammetry [2001GEL/VAN]. Based on the quasi-reversible behaviour observed for the Np(VI)/Np(V) couple in strongly alkaline solutions with $1 \le [OH^-]/[\,CO_3^{2-}\,] \le 5$ and the known predominance of Np-OH-$CO_3$ complexes of Np(V) under these conditions [1997NEC/FAN], [2001LEM/FUG], the authors concluded that analogous ternary complexes might be expected to form for Np(VI). The hypothesis of ternary Np(VI)-OH-$CO_3$ complex formation is plausible for chemical reasons, even though this review finds no compelling evidence in the available voltammetry results. Further experimental efforts should be made to close this knowledge gap on the solution chemistry of An(VI).

To illustrate the updated thermodynamic selection for the dioxoneptunium(VI) hydroxide-carbonate system, we have calculated distribution diagrams in the range $3 < pH < 12$, presented in Figure 10-9 and Figure 10-10 for two different total carbonate concentrations. For comparison, the same calculations are shown for U(VI) using the thermodynamic selection in the present update. Even though there are differences in the speciation scheme for Np(VI) and U(VI) hydrolysis species, the distribution diagrams of both An(VI) hydroxide-carbonate systems are very similar, with the exception of $AnO_2(CO_3)_2^{2-}$, for which we only have selected data for U(VI).

Figure 10-9: Distribution diagram of the dioxoneptunium(VI) and dioxouranium(VI) hydroxide-carbonate systems at 298.15 K in the range $3 \leq pH \leq 12$. $[An(VI)]_{tot} = 1 \times 10^{-5}$ M; $[CO_3^{2-}]_{tot} = 2 \times 10^{-3}$ M. The precipitation of solid phases is suppressed. Calculations performed at $I = 0$.



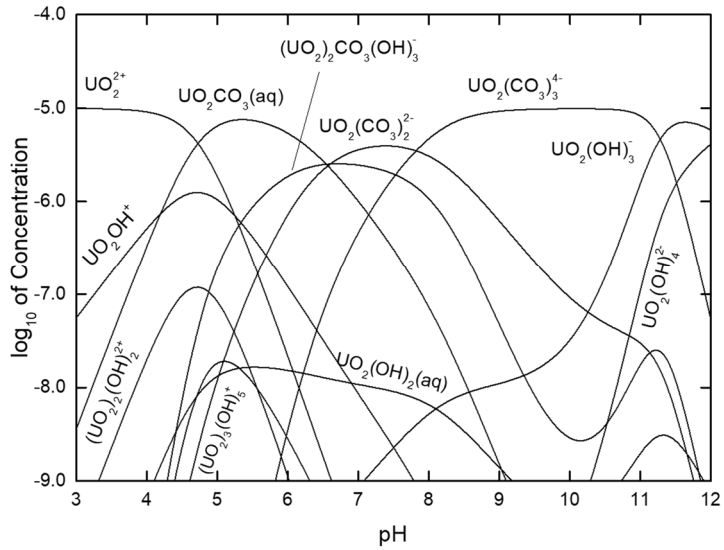
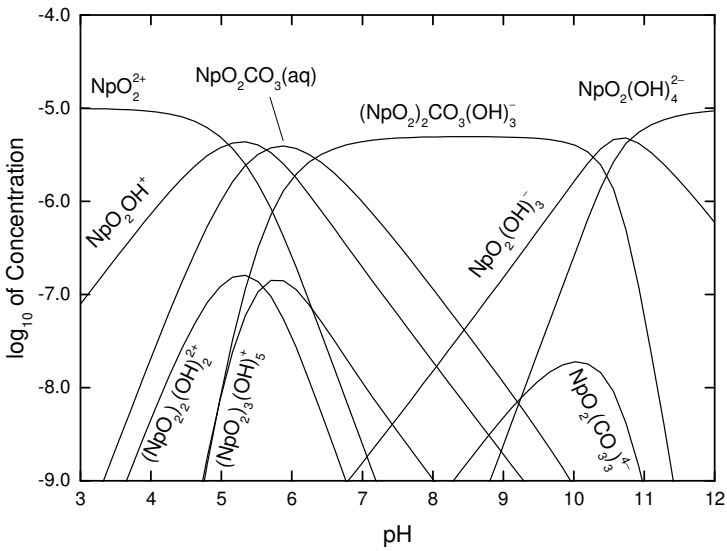
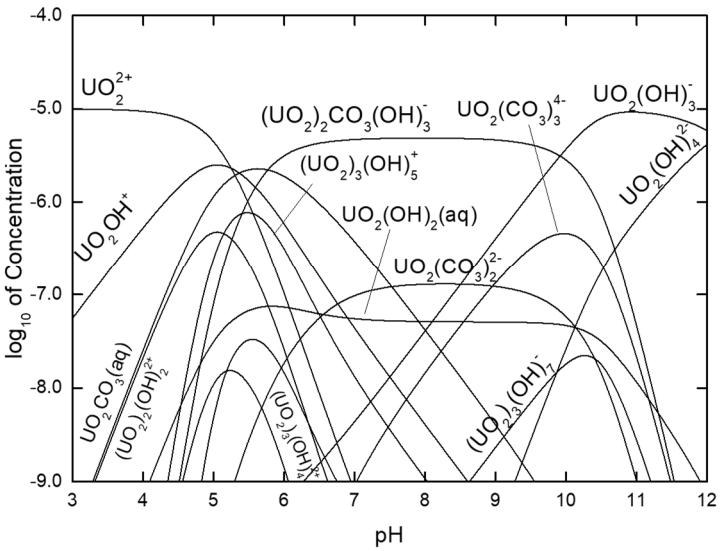



Figure 10-10: Distribution diagram of the dioxoneptunium(VI) and dioxouranium(VI) hydroxide-carbonate systems at 298.15 K in the range $3 \leq pH \leq 12$. $[An(VI)]_{tot} = 1 \times 10^{-5}$ M; $[CO_3^{2-}]_{tot} = 1.5 \times 10^{-4}$ M. The precipitation of solid phases is suppressed. Calculations performed at $I = 0$.



#### 10.6.1.1.6 Aqueous Np(V) carbonates

The binary Np(V) carbonate system has been reviewed in [2001LEM/FUG]. The formation of mixed Np(V) hydroxide-carbonate complexes and data on Np(V) solubility-controlling solid carbonate phases were discussed in [2003GUI/FAN]. Thermodynamic data have been selected for the binary Np(V) carbonate complexes, $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$, and the ternary Np(V) complex, $NpO_2(CO_3)_2OH^{4-}$:

$$NpO_2^+ + CO_3^{2-} \rightleftharpoons NpO_2CO_3^- \quad (10.41)$$

$$NpO_2CO_3^- + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{3-} \quad (10.42)$$

$$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} \quad (10.43)$$

$$NpO_2(CO_3)_3^{5-} + OH^- \rightleftharpoons NpO_2(CO_3)_2OH^{4-} + CO_3^{2-} \quad (10.44)$$

with

$$\log_{10}K_1^o((10.41), 298.15\ K) = \mathbf{(4.962 \pm 0.061)}$$

$$\log_{10}K_2^o((10.42), 298.15\ K) = \mathbf{(1.572 \pm 0.083)}$$

$$\log_{10}K_3^o((10.43), 298.15\ K) = \mathbf{-\ (1.034 \pm 0.110)}$$

$$\log_{10}K^o((10.44), 298.15\ K) = \mathbf{(3.195 \pm 1.164)}$$

Since the previous review, some new studies have been published on the structures and thermodynamics of Np(V) carbonate complexes, with a general discussion on the importance of carbonate on the solubility of Np(V).

The binary complex $NpO_2CO_3^-$ and a ternary $(NpO_2)_m(OH)_x(CO_3)_y^{m-x-2y}$ complex have been observed spectroscopically in tetramethylammonium hydroxide (TMA-OH) solutions [2012GAO/TIT]. Even though no carbonate was added to the solutions, carbonate impurities in the TMA-OH stock solution were found to be sufficiently large to result in the formation of Np(V)-carbonate complexes. At higher carbonate concentrations, EXAFS measurements in [2009IKE/TSU] confirmed the presence and structure of the limiting Np(V) carbonate complex $NpO_2(CO_3)_3^{5-}$. However, the authors did not find any evidence for a mixed complex, such as $NpO_2(CO_3)_2OH^{4-}$, in 1.5 M $Na_2CO_3$ at pH = 11.7. DFT calculations suggest that $NpO_2CO_3(H_2O)_3^-$, $NpO_2(CO_3)_2(H_2O)_2^{3-}$, and $NpO_2(CO_3)_3^{5-}$ are the energetically favoured complexes and might be formed in an aqueous system [2007BAL/CAO], [2009IKE/TSU]. Equilibrium constants of Np(V) carbonate complexes have been calculated from the effective charge of the actinide ions using a hard sphere model [2002MOR/FUJ]. Moriyama *et al.* calculated the values 4.75, 7.07 and 4.97 for the standard state equilibrium constants of $NpO_2(CO_3)_n^{1-2n}$ with $n$ = 1-3, respectively. New experimental data on the carbonate complexation of Np(V) were reported in [2009TOP/AUP2]. Topin *et al.* reported the equilibrium constants for $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ based on the different electrophoretic mobility in an applied electrical field (Table 10-14). Using the SIT parameters, the authors

calculated the equilibrium constants for the formation of $NpO_2(CO_3)_n^{1-2n}$ complexes according to the Reactions (10.45)-(10.47): $\log_{10}\beta_1^o$ ((10.45), 298.15 K) = (4.88 ± 0.12), $\log_{10}\beta_2^o$ ((10.46), 298.15 K) = (6.56 ± 0.11), and $\log_{10}\beta_3^o$ ((10.47), 298.15 K) = (5.64 ± 0.15).

$$NpO_2^+ + CO_3^{2-} \rightleftharpoons NpO_2CO_3^- \quad (10.45)$$

$$NpO_2^+ + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_2^{3-} \quad (10.46)$$

$$NpO_2^+ + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} \quad (10.47)$$

Data reported in [2009TOP/AUP2] are within the range of the selected values in [2003GUI/FAN]: $\log_{10}\beta_1^o$ ((10.45), 298.15 K) = (4.962 ± 0.061), $\log_{10}\beta_2^o$ ((10.46), 298.15 K) = (6.534 ± 0.100), and $\log_{10}\beta_3^o$ ((10.47), 298.15 K) = (5.500 ± 0.150). This review finds no compelling reason to change the values for the Np(V) carbonate aqueous complexes selected in [2001LEM/FUG] and [2003GUI/FAN].

Table 10-14: Experimental equilibrium constants for the reaction $NpO_2^+ + nCO_3^{2-} \rightleftharpoons NpO_2(CO_3)_n^{1-2n}$ with $n$ = 1-3 as reported in [2009TOP/AUP2].

| $T$ /K | Method | Medium | $\log_{10}\beta_1$ (10.45) | $\log_{10}\beta_2$ (10.46) | $\log_{10}\beta_3$ (10.47) |
|---|---|---|---|---|---|
| (298 ± 1) | electrophoresis | 0.37 M NaCl | (4.368 ± 0.10) | | |
| (298 ± 1) | electrophoresis | 0.37 M $NaClO_4$ | | (6.368 ± 0.110) | (7.764 ± 0.200) |

In [2012GAO/TIT], Gaona *et al.* corrected to $I = 0$ the conditional equilibrium constants for the mixed Np(V) hydroxide-carbonate complexes $NpO_2CO_3OH^{2-}$ ($\log_{10}K^o$ ((10.48), 3.0 M $NaClO_4$) = (7.6 ± 0.3)) and $NpO_2CO_3(OH)_2^{3-}$ ($\log_{10}K$ ((10.49), 3.0 M $NaClO_4$) = (9.56 ± 0.15)) reported in [1997NEC/FAN]. Gaona and co-workers used estimated SIT ion interaction parameters to derive $\log_{10}K^o$ ((10.48), 298.15 K) = (7.0 ± 0.3) and $\log_{10}K^o$ ((10.49), 298.15 K) = (7.66 ± 0.15).

$$NpO_2^+ + OH^- + CO_3^{2-} \rightleftharpoons NpO_2CO_3OH^{2-} \quad (10.48)$$

$$NpO_2^+ + 2OH^- + CO_3^{2-} \rightleftharpoons NpO_2CO_3(OH)_2^{3-} \quad (10.49)$$

and $\log_{10}{}^*K^o$ ((10.50), 298.15 K) = – (7.0 ± 0.3) and $\log_{10}{}^*K^o$ ((10.51), 298.15 K) = – (20.34 ± 0.15) for the equilibrium Reactions (10.50) and (10.51), respectively:

$$NpO_2^+ + H_2O(l) + CO_3^{2-} \rightleftharpoons NpO_2CO_3OH^{2-} + H^+ \quad (10.50)$$

$$NpO_2^+ + 2H_2O(l) + CO_3^{2-} \rightleftharpoons NpO_2CO_3(OH)_2^{3-} + 2H^+ \quad (10.51)$$

These data are not selected by this review and are reported for information only.

#### 10.6.1.1.7 Aqueous Np(IV) carbonates

The binary carbonate complexes of Np(IV) were discussed in [2001LEM/FUG] and the selected values are retained in the present review. New experimental [2002KIT/KOH], [2004KIT/KOH], [2009KIM/BAI2] and modelling [2010KIM/OH] studies published after [2003GUI/FAN] and focusing on the pH-range 9-13 support the formation of ternary Np(IV)-OH-$CO_3$ complexes. Due to the very low solubility of Np(IV) in this pH-range, the investigation of the aqueous speciation in the presence of carbonate is based on solubility experiments using $NpO_2$(am, hyd) as solubility-controlling phase (expressed in some publications as $Np(OH)_4$(am)). None of the newly published experimental studies determined the solubility of the Np(IV) solid phase in the absence of carbonate (neither in the acidic pH-range as $\log_{10}K^{\circ}_{s,0}$ nor under alkaline conditions as $\log_{10}K^{\circ}_{s,(1,4)}$). Because of the possible effects of the preparation method (oversaturation *vs.* undersaturation) and equilibration time on $\log_{10}K^{\circ}_{s,0}$, the discussion of these data in the present review is based on the equilibrium reactions between $NpO_2$(am, hyd) and the Np(IV)-OH-$CO_3$ aqueous complexes. Thermodynamic data reported in [2002KIT/KOH] and [2004KIT/KOH] for Reactions (10.52)-(10.54) are summarised in Table 10-15, in combination with previous literature data reviewed for these systems in [2001LEM/FUG] and [2003GUI/FAN].

$$Np(OH)_4(am) + 2HCO_3^- \rightleftharpoons Np(OH)_2(CO_3)_2^{2-} + 2H_2O(l) \quad (10.52)$$

$$Np(OH)_4(am) + CO_3^{2-} \rightleftharpoons Np(OH)_4CO_3^{2-} \quad (10.53)$$

$$Np(OH)_4(am) + 2CO_3^{2-} \rightleftharpoons Np(OH)_4(CO_3)_2^{4-} \quad (10.54)$$

The newly reported solubility data in [2002KIT/KOH], [2004KIT/KOH] support the discussion in [2003GUI/FAN] on the formation of ternary Np(IV)-OH-$CO_3$ complexes with different stoichiometries:

- Np(IV) solubility in carbonate media within $8 \leq -\log_{10}[H^+] \leq 11$ is clearly enhanced compared to carbonate-free solutions. A strong pH-dependency of the solubility is observed in this pH-region, which is ascribed in [1999RAI/HES], [2001KIT/KOH], [2002KIT/KOH], [2004KIT/KOH] to the formation of $Np(OH)_2(CO_3)_2^{2-}$. In contrast to these authors, [1993ERI/NDA] proposed the predominance of $Np(OH)_3CO_3^-$. Note that chemical and thermodynamic models selected for Th(IV) in [2008RAN/FUG] predict the predominance of the highly charged ternary complex $ThOH(CO_3)_4^{5-}$ under similar experimental conditions.

Table 10-15: Equilibrium constants reported in the literature for Reactions (10.52)- (10.54).

| Reference | Method | Medium | $T$ / K | $\log_{10} K$ | $\log_{10} K^{\circ}$ |
|---|---|---|---|---|---|
| $Np(OH)_4(am) + 2HCO_3^- \rightleftharpoons Np(OH)_2(CO_3)_2^{2-} + 2H_2O(l)$ | | | | | |
| [1990PRA/MOR] | solubility (oversaturation) | 0.1 M $Na_2S_2O_4$ | room $T$ (?) | – (0.35 ± 0.33) | |
| [1999RAI/HES] | solubility (undersaturation) | 0.01-1.04 m $KHCO_3$ | (296 ± 2) | | – 4.44 |
| [2001KIT/KOH] | solubility (oversaturation) | 0.5 M $NaClO_4$* | (295 ± 3) | – (3.30 ± 0.08) | – (3.81 ± 0.35) |
| | | 1.0 M $NaClO_4$* | (295.15 ± 3) | – (3.31 ± 0.12) | – (3.1 ± 0.4)[a] |
| [2002KIT/KOH] | solubility (oversaturation) | 0.5 M $NaClO_4$* | (295.15 ± 3) | – (2.38 ± 0.15) | – (2.78 ± 0.18) |
| | | 1.0 M $NaClO_4$* | (295.15 ± 3) | – (2.15 ± 0.16) | |
| | | 2.0 M $NaClO_4$* | (295.15 ± 3) | – (1.96 ± 0.23) | |
| [2004KIT/KOH] | solubility (oversaturation + undersaturation) | 0.5 M $NaClO_4$* | (295.15 ± 3) | – (2.4 ± 0.2) | – (3.0 ± 0.2) |
| | | 1.0 M $NaClO_4$* | (295.15 ± 3) | – (2.2 ± 0.3) | – (2.9 ± 0.2)[b] |
| | | 2.0 M $NaClO_4$* | (295.15 ± 3) | – (1.7 ± 0.2) | |
| $Np(OH)_4(am) + CO_3^{2-} \rightleftharpoons Np(OH)_4CO_3^{2-}$ | | | | | |
| [1993ERI/NDA] | solubility (undersaturation) | 0.5 M $NaClO_4$ | 293.15 | – (5.28 ± 0.26) | |
| [2001LEM/FUG] | review | | | | – (6.5 ± 0.4)[c] |
| [2004KIT/KOH] | solubility (oversaturation + undersaturation) | 0.5 M $NaClO_4$* | (295.15 ± 3) | – (6.2 ± 0.4) | – (6.2 ± 0.2) |
| | | 1.0 M $NaClO_4$* | (295.15 ± 3) | – (6.2 ± 0.4) | |
| | | 2.0 M $NaClO_4$* | (295.15 ± 3) | – (6.5 ± 0.4) | |
| | | 2.9 M $NaClO_4$* | (295.15 ± 3) | – (6.4 ± 0.2) | |
| $Np(OH)_4(am) + 2CO_3^{2-} \rightleftharpoons Np(OH)_4(CO_3)_2^{4-}$ | | | | | |
| [1990PRA/MOR] | solubility (oversaturation) | 0.1 M $Na_2S_2O_4$ | room $T$ (?) | – (1.43 ± 0.33) | |
| [2001KIT/KOH] | solubility (oversaturation) | 0.5 M $NaClO_4$* | (295.15 ± 3) | – (5.41 ± 0.26) | – (6.82 ± 1.03) |
| | | 1.0 M $NaClO_4$* | (295.15 ± 3) | – (5.43 ± 0.37) | – (6.9 ± 0.4)[a] |
| [2002KIT/KOH] | solubility (oversaturation) | 0.5 M $NaClO_4$* | (295.15 ± 3) | – (5.39 ± 0.32) | |
| | | 1.0 M $NaClO_4$* | (295.15 ± 3) | – (5.26 ± 0.40) | |
| | | 2.0 M $NaClO_4$* | (295.15 ± 3) | – (4.28 ± 0.32) | – (7.15 ± 0.41) |

* as $NaHCO_3$-$Na_2CO_3$-NaOH-$NaClO_4$ mixtures of constant ionic strength.

(a) Recalculated in [2001LEM/FUG].

(b) Recalculated in this review (see text).

(c) Re-interpretation of experimental data reported in [2001KIT/KOH]. Value not selected.



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- The pH-independent behaviour of the solubility observed in solutions with $-\log_{10}[H^+] \geq 11$ is attributed by [1993ERI/NDA], [2004KIT/KOH] to the predominance of $Np(OH)_4CO_3^{2-}$, whereas [1990PRA/MOR], [2001KIT/KOH], [2002KIT/KOH] favoured the selection of $Np(OH)_4(CO_3)_2^{4-}$. As discussed in Appendix A, the slope analysis conducted in [2004KIT/KOH] (as $\log_{10}[Np]$ *vs.* $\log_{10}[CO_3^{2-}]$) is inconclusive, and thus the stoichiometry $Np:CO_3^{2-}$ 1:1 remains speculative. Note, however, that according to the thermodynamic selection in [2008RAN/FUG], the (1,4,1) complex plays an important role in the aquatic chemistry of Th(IV) in carbonated hyperalkaline systems.

In addition to the different chemical models described in the literature for the ternary Np(IV)-OH-$CO_3$ system, there are also large discrepancies between experimental data obtained by different authors under similar experimental conditions, resulting in significant differences in the equilibrium constants, even if the same chemical model is used to describe experimental data (see Table 10-15). As discussed in [2003GUI/FAN], such discrepancies are likely related to differences in the solid phases controlling the solubility in the various studies. The lack of solubility measurements in the absence of carbonate in many of the published studies hinders a conclusive explanation of these observations in the presence of carbonate. Although not summarised in Table 10-15, this review notes that Rai and Ryan [1985RAI/RYA] observed no effect of 0.01 M carbonate solutions on the solubility of Np(IV) within $7 \leq pH \leq 14$, which is in disagreement with experimental observations reported in [1993ERI/NDA], [2001KIT/KOH], [2002KIT/KOH], [2004KIT/KOH], [2009KIM/BAI2].

Based on the discussion above, this review does not select any thermodynamic data for the ternary system Np(IV)-OH-$CO_3$. The series of publications by Kitamura and Kohara [2001KIT/KOH], [2002KIT/KOH], [2004KIT/KOH] are considered as the most comprehensive ones for this system, but the thermodynamic data and activity models derived in [2004KIT/KOH] (and recalculated in the present review) are reported for information only.

$$\log_{10} K^\circ((10.52), 298.15\ K) = -(2.9 \pm 0.2)$$

$$\log_{10} K^\circ((10.53), 298.15\ K) = -(6.2 \pm 0.2).$$

Additional experimental studies with well-characterised Np(IV) solid phases in the absence and presence of carbonate are necessary to clarify the thermodynamic inconsistencies in the Np(IV)-OH-$CO_3$ system.

### 10.6.1.2 Solid neptunium carbonates

#### 10.6.1.2.1 Solid Np(VI) carbonates

Kato *et al.* [1998KAT/KIM] performed a comprehensive solubility study with $NpO_2CO_3$(cr) in 0.1 M $NaClO_4$ under a controlled atmosphere with 80 % $CO_2$/20 % $O_2$.

Thermodynamic data determined by the authors for Reaction (10.55) are summarised in Table 10-16, together with previous studies reviewed in [2001LEM/FUG].

$$NpO_2CO_3(cr) \rightleftharpoons NpO_2^{2+} + CO_3^{2-} \quad (10.55)$$

Table 10-16. Equilibrium constants reported in the literature for Reaction (10.55).

| Reference | Method | Medium | $T$/K | $\log_{10}K_{s,0}$ | $\log_{10}K^{o}_{s,0}$ |
|---|---|---|---|---|---|
| $NpO_2CO_3(cr) \rightleftharpoons NpO_2^{2+} + CO_3^{2-}$ | | | | | |
| [1996KAT/KIM] | solubility | 0.1 M $NaClO_4$ | 298.15 | – (14.62 ± 0.12) | |
| | | | | – (14.18 ± 0.56)[a] | – (15.02 ± 0.56)[a] |
| [1998VIT/CAP] | solubility | 3.0 M $NaClO_4$ | 295.15 | – 13.98 | – (14.60 ± 0.47)[b] |
| [2001LEM/FUG] | review | | 298.15 | | – (14.60 ± 0.47) |
| [1998KAT/KIM] | solubility | 0.1 M $NaClO_4$ | 298.15 | – (14.04 ± 0.07) | – (14.87 ± 0.07) |
| | | | | | – (14.88 ± 0.07)[b] |

(a) Recalculated in [2001LEM/FUG].
(b) Recalculated in this review.

Equilibrium constants reported in the literature for Reaction (10.55) span over a relatively broad range, from $\log_{10}K^{o}_{s,0}$ ((10.55), 298.15 K) = – (14.60 ± 0.47) to $\log_{10}K^{o}_{s,0}$ ((10.55), 298.15 K) = – (15.02 ± 0.56). The existing discrepancies are possibly a result of differences in the crystallinity of the solid phases investigated, but may also reflect limitations and shortcomings in the experimental approaches.

The solubility study reported in [1996KAT/KIM] was conducted using a relatively short equilibration time (≈ two weeks). The originally reported $\log_{10}K_{s,0}$ ((10.55), 0.1 M $NaClO_4$) was corrected in [2001LEM/FUG] to account for limitations in the experimental approach, which were also identified in the investigation of $UO_2CO_3$(cr) by the same authors.

Solubility data reported in [1998VIT/CAP] provided the main basis for the selection of $\log_{10}K^{o}_{s,0}$ ((10.55), 298.15 K) in [2001LEM/FUG]. Only two experimental points collected between $-9.7 \le \log_{10}[CO_3^{2-}] \le -9.5$ were available in the original publication for the determination of $\log_{10}K$ ((10.55), 3.0 M $NaClO_4$). Furthermore, the solid phase was not characterised, but assumed to be $NpO_2CO_3$(cr) based on a previous study conducted in the same laboratory and using the same experimental approach.

The publication by Kato and co-workers [1998KAT/KIM] is the most comprehensive solubility study on $NpO_2CO_3$(cr) available to date. Experiments were conducted using long equilibration time (> one year), solid phases equilibrated at different pH values were characterised using several techniques (XRD, UV-vis/NIR photoacoustic spectroscopy, FT-IR photoacoustic spectroscopy), and a broad range of carbonate concentrations ($-12 \le \log_{10}[CO_3^{2-}] \le -9$) was used for the determination of $\log_{10}K^{o}_{s,0}$ ((10.55), 0.1 M $NaClO_4$). The extrapolation of this value to $I = 0$ using $\varepsilon(NpO_2^{2+}, ClO_4^{-}) = (0.46 \pm 0.05)$ kg·mol$^{-1}$ and $\varepsilon(CO_3^{2-}, Na^{+}) = -(0.08 \pm 0.03)$ kg·mol$^{-1}$ as reported in Appendix B results in $\log_{10}K^{o}_{s,0}$ ((10.55), 298.15 K) = – (14.88 ± 0.07),

which is virtually the same as the unweighted average of all available data; this value is selected in the present review with an associated uncertainty covering $\log_{10} K^{o}_{s,0}$ ((10.55), 298.15 K) recalculated from both [1996KAT/KIM] and [1998VIT/CAP]:

$$\log_{10} K^{o}_{s,0} \text{ ((10.55), 298.15 K)} = \mathbf{-\ (14.830 \pm 0.230)}$$

$$\Delta_r G^{o}_{m} \text{ ((10.55), 298.15 K)} = \mathbf{(84.650 \pm 1.313)}\ \text{kJ·mol}^{-1}$$

and

$$\Delta_f G^{o}_{m} (NpO_2CO_3, \text{cr, 298.15 K}) = \mathbf{-\ (1408.489 \pm 5.780)}\ \text{kJ·mol}^{-1}.$$

The value selected in this review for $\log_{10} K^{o}_{s,0}$ ((10.55), 298.15 K) agrees within the uncertainty with the previous selection in [2001LEM/FUG]. The change in the selected value is nevertheless considered necessary, given the more comprehensive and accurate solubility study by [1998KAT/KIM] and the limitations in the experimental dataset considered in [2001LEM/FUG]. Note that $\log_{10} K^{o}_{s,0}$ ((10.55), 298.15 K) selected in this review is in excellent agreement with the solubility product selected for the analogous U(VI) solid phase, $UO_2CO_3$(cr) ($\log_{10} K^{o}_{s,0} = -(14.76 \pm 0.02)$). Both phases are isostructural and are expected to have very similar lattice energies.

The formation of ternary Na-Np(VI)-$CO_3$ solid phases is also expected to take place at high [$Na^+$] and [$CO_3^{2-}$]. No thermodynamic studies targeting these ternary phases are available so far in the literature, although [1998VIT/CAP] provided an estimate of the solubility product of $Na_4NpO_2(CO_3)_3$(s) based on observations in their solubility experiments with $NpO_2CO_3$(cr).

There are no new experimental studies providing thermodynamic data for $(NH_4)_4NpO_2(CO_3)_3$(cr) and $K_4NpO_2(CO_3)_3$(cr), and the selection in [2001LEM/FUG] for the equilibrium Reactions (10.56) and (10.57) are retained in the present review.

$$(NH_4)_4 NpO_2(CO_3)_3(cr) \rightleftharpoons NpO_2(CO_3)_3^{4-} + 4NH_4^+ \qquad (10.56)$$

$$K_4 NpO_2(CO_3)_3(cr) \rightleftharpoons NpO_2(CO_3)_3^{4-} + 4K^+ \qquad (10.57)$$

with

$$\log_{10} K^{o} \text{ ((10.56), 298.15 K)} = \mathbf{-\ (7.443 \pm 0.297)}$$

$$\Delta_r G^{o}_{m} \text{ ((10.56), 298.15 K)} = \mathbf{(42.485 \pm 1.698)}\ \text{kJ·mol}^{-1}$$

and

$$\log_{10} K^{o} \text{ ((10.57), 298.15 K)} = \mathbf{-\ (7.033 \pm 0.876)}$$

$$\Delta_r G^{o}_{m} \text{ ((10.57), 298.15 K)} = \mathbf{(40.147 \pm 5.001)}\ \text{kJ·mol}^{-1}.$$

The values of $\Delta_f G^{o}_{m}$ ($(NH_4)_4NpO_2(CO_3)_3$, cr, 298.15 K) and $\Delta_f G^{o}_{m}$ ($K_4NpO_2(CO_3)_3$, cr, 298.15 K) re-calculated in order to be consistent with the selected value of $\Delta_f G^{o}_{m}$ ($NpO_2(CO_3)_3^{4-}$, 298.15 K) are:

$$\Delta_f G_m^o ((NH_4)_4NpO_2(CO_3)_3, cr) = \mathbf{-\ (2853.306 \pm 6.720)}\ kJ{\cdot}mol^{-1}$$

$$\Delta_f G_m^o (K_4NpO_2(CO_3)_3, cr) = \mathbf{-\ (3663.416 \pm 8.140)}\ kJ{\cdot}mol^{-1}.$$

From the selected values of $\log_{10}K^o$ ((10.56), 298.15 K) and $\log_{10}K^o$ ((10.57), 298.15 K), and the new value of $\log_{10}K^o$ ((10.36), 298.15 K) selected in this review (Section 10.6.1.1.1), the values $\log_{10}K_{s,0}^o$ ((10.58), 298.15 K) = – (27.343 ± 0.582) and $\log_{10}K_{s,0}^o$ ((10.59), 298.15 K) = – (26.933 ± 1.009) are calculated for the reactions:

$$(NH_4)_4NpO_2(CO_3)_3(cr) \rightleftharpoons NpO_2^{2+} + 3CO_3^{2-} + 4NH_4^+ \quad (10.58)$$

$$K_4NpO_2(CO_3)_3(cr) \rightleftharpoons NpO_2^{2+} + 3CO_3^{2-} + 4K^+ \quad (10.59)$$

#### 10.6.1.2.2 Solid Np(V) carbonates

Thermodynamic data for solid Np(V) carbonates have been discussed and selected in [2003GUI/FAN]:

$$3Na^+ + NpO_2^+ + 2CO_3^{2-} \rightleftharpoons Na_3NpO_2(CO_3)_2(cr) \quad (10.60)$$

$$Na^+ + NpO_2^+ + CO_3^{2-} + 3.5H_2O(l) \rightleftharpoons NaNpO_2CO_3 \cdot 3.5H_2O(cr) \quad (10.61)$$

$$3K^+ + NpO_2^+ + 2CO_3^{2-} \rightleftharpoons K_3NpO_2(CO_3)_2(cr) \quad (10.62)$$

$$K^+ + NpO_2^+ + CO_3^{2-} \rightleftharpoons KNpO_2CO_3(cr) \quad (10.63)$$

with

$$\log_{10}K^o ((10.60), 298.15\ K) = \mathbf{(14.220 \pm 0.500)}$$

$$\log_{10}K^o ((10.61), 298.15\ K) = \mathbf{(11.000 \pm 0.240)}$$

$$\log_{10}K^o ((10.62), 298.15\ K) = \mathbf{(15.460 \pm 0.160)}$$

$$\log_{10}K^o ((10.63), 298.15\ K) = \mathbf{(13.150 \pm 0.190).}$$

Since the previous review, there are few new studies on the solubility and thermodynamic data of solid Np(V) carbonates. Vitorge and Capdevila in [2003VIT/CAP] performed a consistency analysis of existing data and calculated the Np(V) solubility with a solubility-controlling solid phase $Na_{2x-1}NpO_2(CO_3)_x(cr)$ with $x$ = 1 and 2 and the Np(V) complexes $NpO_2(CO_3)_n^{1-2n}$ with $n$ = 0-3. The authors used the solubility products $\log_{10}K_{s,0}$ = – 10.65 for $NaNpO_2(CO_3)(cr)$ and $\log_{10}K_{s,0}$ = – 12.10 for $Na_3NpO_2(CO_3)_2(cr)$ and the constants $\log_{10}\beta_1 = 5.25$, $\log_{10}\beta_2 = 8.15$, and $\log_{10}\beta_3 = 10.64$ to model the complex formation reactions in 3 M $NaClO_4$. The thermodynamic data set used, predicted the available experimental data very well, confirming that the Np(V) carbonate system is well understood.

## 10.6.2 Neptunium silicate compounds and complexes

A number of experimental difficulties affect the study of silicate systems and their interaction with actinides. These need to be accounted for to derive correct chemical and thermodynamic models for the investigated systems:

- Formation of silicate polymers or colloids, and their interaction with metal cations. Many of the studies of actinide-silicate complexation deal with Si concentrations clearly above the solubility limit of amorphous silica, where the presence of Si polymers/colloids is expected and where the formation of actinide-silicate complexes of polymeric or colloidal nature cannot be ruled out.

- Polymerisation reactions of Si are strongly dependent on pH, the total concentration of silicate and kinetics. The equilibration time used in the experiment must be reported and carefully considered in the interpretation of the data.

- $Si(OH)_4$ is a very weak acid, and the concentration of silicate complexes with actinides under acidic conditions (pH < 4) is therefore small, especially in An(V) complexes where the equilibrium constant is smaller than for the An(VI) ones. Studies in this pH-region must therefore use very sensitive and selective techniques, in order to obtain accurate quantification of small amounts of the actinide-silicate complex.

### 10.6.2.1 Aqueous Np(VI) silicates

Two new experimental studies provide thermodynamic data for aqueous Np(VI)-silicate complexes, both in acidic [2005YUS/SHI] and alkaline [2004SHI/FED] conditions according to Reactions (10.64) and (10.65), respectively. The reported equilibrium constants are summarised in Table 10-17.

$$NpO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons NpO_2SiO(OH)_3^+ + H^+ \quad (10.64)$$

$$NpO_2^{2+} + SiO_2(OH)_2^{2-} \rightleftharpoons NpO_2SiO_2(OH)_2(aq) \quad (10.65)$$

Table 10-17: Equilibrium constants reported in the literature for the formation of $NpO_2SiO(OH)_3^+$ and $NpO_2SiO_2(OH)_2(aq)$ complexes.

| Reference | Reaction | Method | Medium | $T$/K | $\log_{10}K$ | $\log_{10}K^\circ$ |
|---|---|---|---|---|---|---|
| [2005YUS/SHI] | (10.64) | spec. | 0.1-0.2 M $NaClO_4$ | RT (?) | – (2.88 ± 0.12) | – (2.61 ± 0.12) |
| [2004SHI/FED] | (10.65) | spec. | 0.1 M $NaClO_4$ | 296.15 | 16.5 | |

The complexation of silicate with Np(VI) under acidic conditions was investigated spectroscopically in [2005YUS/SHI]. All experiments were performed in test solutions over-saturated with respect to $SiO_2$(am), and the presence of dimeric, trimeric and tetrameric Si species was experimentally confirmed in all samples. The

$\log_{10} K^{\circ}$ (10.64) reported by the authors is not selected in this review for the reasons given in Appendix A, and the value $\log_{10} K^{\circ}$ ((10.64), 0.1 M $NaClO_4$) = – 2.8 calculated from the experiments with the lowest silicate concentration ($[Si]_{tot}$ = 0.022 M) is probably the best estimate available and is given for information.

Shilov *et al.* [2004SHI/FED] studied the complexation of silicate with Np(VI) under alkaline conditions (10.13 ≤ pH ≤ 12) using the competition with $NpO_2(CO_3)_3^{4-}$, which is the predominant species in a $5 \times 10^{-3}$ M $NaHCO_3$-$Na_2CO_3$ solution. Based on the spectroscopic results obtained at different pH and $[Si]_{tot}$ conditions, the authors proposed that Reaction (10.66) is the predominant one and determined the corresponding equilibrium constant.

$$NpO_2(CO_3)_3^{4-} + SiO_2(OH)_2^{2-} \rightleftharpoons NpO_2SiO_2(OH)_2(aq) + 3CO_3^{2-} \quad (10.66)$$

$$\log_{10} K \text{ ((10.66), 0.1 M } NaClO_4) = -3.91.$$

The combination of $\log_{10} K$ ((10.66), in 0.1 M $NaClO_4$) with $\log_{10} K(NpO_2(CO_3)_3^{4-}$, in 0.1 M $NaClO_4$) reported in [1998KAT/KIM] was used to calculate $\log_{10} K$ ((10.65), in 0.1 M $NaClO_4$) as reported in Table 10-17. There are experimental shortcomings described in Appendix A, and the stoichiometry of the complex proposed in Shilov *et al.* is considered speculative by this review due to the lack of a systematic variation of carbonate concentration in the experiments. Note that aqueous complexes with other stoichiometries (*e.g.* $NpO_2CO_3SiO_2(OH)_2^{2-}$ or $NpO_2(CO_3)_2SiO_2(OH)_2^{4-}$) might also explain the reported experimental observations. No thermodynamic data are recommended from this study.

### 10.6.2.2 Aqueous Np(V) silicates

Two new experimental studies providing thermodynamic data on the Np(V)-silicate system have been published since the previous review [2003GUI/FAN], both referring to the reaction:

$$NpO_2^+ + SiO(OH)_3^- \rightleftharpoons NpO_2SiO(OH)_3(aq) \quad (10.67)$$

Equilibrium constants determined in [2005YUS/FED2] and [2007PAT/CHO] for Reaction (10.67) are summarised in Table 10-18. The reported values are very different, which reflects the experimental difficulties encountered in the study of silicate systems.

Table 10-18: Equilibrium constants reported in the literature for Reaction (10.67).

| Reference | Method | Medium | $T$/K | $\log_{10} K$ | $\log_{10} K^{\circ}$ |
|---|---|---|---|---|---|
| [2005YUS/FED2] | spectroscopy | 0.1 M $NaClO_4$ | (296 ± 2) | (2.1 ± 0.3) | |
| [2007PAT/CHO] | solvent extraction | 0.1 M $NaClO_4$ | (295 ± 2) | (6.83 ± 0.01) | (7.04 ± 0.02) |
| | | 1.0 M $NaClO_4$ | | (6.51 ± 0.02) | |

For reasons given in Appendix A, this review does not accept the data in [2007PAT/CHO]. Important shortcomings have also been identified in [2005YUS/FED2] and are summarised in Appendix A. The equilibrium constant reported by these authors for Reaction (10.67) is not selected in this review, but $\log_{10}K$ ((10.67), 0.1 M $NaClO_4$) = 2.3 determined in [2005YUS/FED2] at the lowest silicate concentration ($[Si]_{tot}$ = 0.004 M) is reported for information.

Shilov *et al.* [2004SHI/FED] evaluated the complex formation of Np(V) with silicate under alkaline conditions in the presence of an undefined concentration of carbonate. The predominance of $NpO_2CO_3^-$ was confirmed by UV-vis spectroscopy and the concentration was not affected by the presence of $8.6 \times 10^{-4}$ M $Na_2SiO_3$, suggesting that silicate complexes are much weaker than the carbonate ones.

The use of the linear free energy relationship (LFER) between silicate and hydrolysis species was proposed by Jensen [1994JEN] (see also [1998JEN/CHO]) to estimate the equilibrium constants of metal-silicate complexes. Jensen used this approach to estimate $4.4 \leq \log_{10}K$ (10.67) $\leq 5.1$, based on $\log_{10}K$ ($NpO_2OH$, aq, 0.1 M $NaClO_4$) = 4.9 as reported in [1993SMI/MAR]. The later value is significantly higher than the current selection in [2003GUI/FAN] ($\log_{10}K^\circ$ ($NpO_2OH$, aq) = (2.700 ± 0.700)). This review does not consider these estimated values reliable enough to include them in the selection of thermodynamic quantities.

### 10.6.2.3 Aqueous Np(IV) silicates

One new spectroscopic study providing thermodynamic data on the Np(IV)-silicate system has been published since [2003GUI/FAN]. The study by Yusov and co-workers was performed under acidic conditions ($0.66 \leq pH \leq 2.30$) in order to minimise hydrolysis and to avoid precipitation of Np(IV) hydrous oxides [2004YUS/FED2]. Based on their spectroscopic observations, the authors proposed the formation of the aqueous complex $NpSiO(OH)_3^{3+}$ according to Reaction (10.68). Equilibrium constants determined in [2004YUS/FED2] for this reaction are summarised in Table 10-19.

$$Np^{4+} + Si(OH)_4(aq) \rightleftharpoons NpSiO(OH)_3^{3+} + H^+ \quad (10.68)$$

Table 10-19: Equilibrium constants reported in the literature for Reaction (10.68).

| Reference | Method | Medium | $T$/K | $\log_{10}K$ | $\log_{10}K^\circ$ |
|---|---|---|---|---|---|
| [2004YUS/FED2] | spectroscopy | 0.1 M $Na/HClO_4$ | (298 ± 1) | (0.66 ± 0.04) | |
| | | 0.12-0.13 M $Na/HClO_4$ | (298 ± 1) | (0.75 ± 0.08) | |
| | | 1.0 M $Na/HClO_4$ | (298 ± 1) | (0.41 ± 0.02) | |
| | | | | | 1.4 |

Important shortcomings in the experimental approach and in the interpretation of the spectroscopic data in [2004YUS/FED2] have been identified by this review and

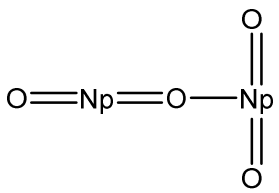
are summarised in Appendix A. As a result, these data cannot be used for selection of the thermodynamic data for the system Np(IV)-silicate.

## 10.7 Neptunium actinide complexes

### 10.7.1 Actinide-actinide interactions

No thermodynamic quantities are selected in previous NEA TDB reviews for the interaction of neptunium with other actinides. Several experimental studies [2003DEN/GRE], [2003GRE/MOI], [2003KAP/MOI], [2008SKA/ANT] and one theory publication [2005MCK/SWA] investigating cation-cation complexes of Np(V) were published since the latest NEA TDB update [2003GUI/FAN]. The EXAFS study by Den Auwer and co-workers [2003DEN/GRE] confirmed the formation of a dimeric complex in concentrated Np(V) solutions, but they were unable to provide a definitive insight on the structure of this complex. Skanthakumar *et al.* [2008SKA/ANT] proposed the T-shaped configuration in Figure 10-11 based on their high-energy X-ray scattering (HEXS) results and comparison with known solid-state structures. The same configuration was proposed by McKee and Swart using DFT calculations and a continuum model for the solvent [2005MCK/SWA]. Calculations by these authors predicted the stabilisation of $NpO_2^+ \cdot NpO_2^+$ and $NpO_2^+ \cdot UO_2^{2+}$ complexes in solution, but disregard the formation of $UO_2^{2+} \cdot UO_2^{2+}$ because of the increased electrostatic repulsion.

Figure 10-11: T-shaped configuration proposed in [2008SKA/ANT] for the $NpO_2^+ \cdot NpO_2^+$ cation-cation interaction.




Gregoire-Kappenstein and co-workers [2003GRE/MOI], [2003KAP/MOI] performed the most comprehensive quantitative study available to date on the dimerisation of Np(V) in solutions with $0.02\ M \leq [NpO_2NO_3] \leq 3.56\ M$. Using a combination of vis/NIR, Raman and water activity measurements, the authors identified that only the species $NpO_2^+$ and the dimer $NpO_2^+ \cdot NpO_2^+$ were present in solutions with $0.2\ M \leq [Np] \leq 2.0\ M$. Two additional species were identified at $[Np] \geq 2.0\ M$, suggesting the formation of additional polynuclear species. Equilibrium constants reported in [2003GRE/MOI] for the Reaction (10.69) ($-0.6 \leq \log_{10} K$ ((10.69), $I = x$ M $NpO_2NO_3$-$y$ M $HNO_3$) $\leq -0.1$) confirm the very weak interactions in the $NpO_2^+ \cdot NpO_2^+$ complex. These equilibrium constants are slightly lower than those previously reported in the

literature for Reaction (10.69) in concentrated $HClO_4$-$NaClO_4$ solutions, with $\log_{10}K$ ((10.69), $I$ = 4.25 M $NpO_2ClO_4$-$HClO_4$-$NaClO_4$) = – 0.09 [1982GUI/BEG] and $\log_{10}K$ ((10.69), $I$ = 6.0 M $NpO_2ClO_4$-$HClO_4$-$NaClO_4$) = 0.15 [1993STO/CHO]. A similar trend with increasing ionic strength was recently reported by Xian and co-workers [2012XIA/TIA] for the system $NpO_2^+ \cdot UO_2^{2+}$.

$$2NpO_2^+ \rightleftharpoons NpO_2^+ \cdot NpO_2^+ \quad (10.69)$$

Based on the correlation of $\log_{10}K$ (10.69) with the water activity and $\sigma$, the sum of concentrations of all the species in solution, Gregoire-Kappenstein *et al.* were able to explain cation-cation interaction data in $NpO_2NO_3$-$HNO_3$ and $NpO_2ClO_4$-$HClO_4$-$NaClO_4$ systems. This review does not select any thermodynamic data from [2003GRE/MOI], but the empirical correlation suggested by the authors might be used to estimate $\log_{10}K$ (10.69), provided that $a_{H_2O}$ and $\sigma$ values of the investigated system are known.

Cation-cation interactions or cation-cation bonds are also present in a large number of Np(V) solid compounds where X-ray data provide accurate information on structures and bond distances. Since the very comprehensive review by Krot and Grigoriev [2004KRO/GRI] summarising the structures of 23 Np(V) compounds involving cation-cation bonds, many new structures of Np(V) with inorganic ligands of interest for the present review have been reported in the literature: $NpO_2(IO_3)$(cr) and β-$AgNpO_2(SeO_3)$(cr) [2003ALB/ALM], $(NpO_2)_2SO_4 \cdot 6H_2O$(cr) [2006CHA/KRO], $NaK_3(NpO_2)_4(SO_4)_4(H_2O)_2$(cr) and $NaNpO_2SO_4H_2O$(cr) [2006FOR/BUR], $NaNpO_2(OH)_2$(cr) [2007ALM/SKA], $K_4(NpO_2)_3Cl_7(H_2O)_4$(cr) [2007FOR/BUR], $(NpO_2)_2(SO_4)(H_2O)_4$(cr) [2009FOR/BUR], $(NpO_2)_2(SeO_4)(H_2O)_n$(cr) ($n$ = 1, 2 and 4) [2011JIN/SKA], $K(NpO_2)_3(H_2O)Cl_4$(cr) [2011WAN/ALE], $NaNpO_2SeO_4H_2O$(cr) [2012JIN/SKA], $NpO_2Cl(H_2O)_2$(cr) [2016JIN], among many others. Cation-cation interactions have an important effect on the properties of these solid phases, often promoting low solubility accompanied by (very) slow precipitation kinetics. So far, very limited thermodynamic data have been reported for these solid phases.

# 10.8 Neptunium group 2 (alkaline-earth) compounds

## 10.8.1 Neptunium calcium compounds

### 10.8.1.1 $CaNpO_2(OH)_{2.6}Cl_{0.4} \cdot 2H_2O$(cr), $Ca_{0.5}NpO_2(OH)_2 \cdot 1.3H_2O$(cr) and $Ca_{0.5}NpO_2(OH)_2$(cr)

Three new $Ca^{2+}$-containing Np(V) hydroxide solid phases have been identified at different $-\log_{10}[H^+]$ and $CaCl_2$ concentrations. In [2016FEL/ROT], the authors describe experimental observations, including the concentrations of Np(V) as function of $-\log_{10}[H^+]$ and $CaCl_2$ and the characterisation of solid phase and solution species by a number of analytical methods. These results are used in [2016FEL/ALT] to determine

thermodynamic data for the Np(V) hydrolysis in $CaCl_2$ solutions. The Np(V) solubility data are described using different solid equilibrium phases and with the solution species $NpO_2^+$(aq) and two ternary Np(V) hydroxo complexes, $Ca[NpO_2(OH)_2]^+$ and $Ca_3[NpO_2(OH)_5]^{2+}$. The solid phase $NpO_2OH$(am, hyd) is found to be unstable in $CaCl_2$ solutions at $-\log_{10}[H^+] > 8.5$ and transforms to $CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O$(cr) in 2 M $CaCl_2$ at $-\log_{10}[H^+] = 11$. At $CaCl_2$ concentrations below 2 M and $-\log_{10}[H^+] < 10.5$, this solid converts into a reddish ternary hydrated solid phase, $Ca_{0.5}NpO_2(OH)_2\cdot 1.3H_2O$(cr). The anhydrous form, $Ca_{0.5}NpO_2(OH)_2$(cr), is found in 4.5 M $CaCl_2$ at $-\log_{10}[H^+] = 11.6$.

Although Fellhauer *et al.* characterised the solid phases, they did not provide conditional solubility products for them at the different $CaCl_2$ concentrations investigated. From the experimental data in [2016FEL/ROT] we calculated the conditional $\log_{10}{}^*K_{s,0}$ value only for $Ca_{0.5}NpO_2(OH)_2\cdot 1.3H_2O$(cr) at $-\log_{10}[H^+] \le 10.54$ and $[CaCl_2] \le 2$ M (Table 10-20). The solubility products of $CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O$(cr) and $Ca_{0.5}NpO_2(OH)_2$(cr) for $[CaCl_2] \le 2$ M are dependent on the hydrolysis constants used, because they are obtained at $-\log_{10}[H^+] > 10.5$. Under these conditions, the Np(V) hydrolysis products present in $CaCl_2$ solution, are mainly $Ca[NpO_2(OH)_2]^+$ and $Ca_3[NpO_2(OH)_5]^{2+}$. Fellhauer *et al.* calculated a set of solubility products and hydrolysis constants using solubility data from undersaturation with $Ca_{0.5}NpO_2(OH)_2\cdot 1.3H_2O$(cr) as the solid phase. The calculated hydrolysis constants for the ternary Ca-Np(V)-OH solution complexes were then used to calculate the solubility product for $CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O$(cr). The solubility product of $Ca_{0.5}NpO_2(OH)_2$(cr) was only calculated with the Pitzer formalism since the $CaCl_2$ concentration of 4.5 M is too high for the use of SIT.

The authors report the thermodynamic solubility products according to Reactions (10.70), (10.71) and (10.72):

$$CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O(cr) + 2.6H^+ \rightleftharpoons NpO_2^+ + Ca^{2+} + 4.6H_2O(l) + 0.4Cl^- \quad (10.70)$$

$$Ca_{0.5}NpO_2(OH)_2\cdot 1.3H_2O(cr) + 2H^+ \rightleftharpoons NpO_2^+ + 0.5Ca^{2+} + 3.3H_2O(l) \quad (10.71)$$

$$Ca_{0.5}NpO_2(OH)_2(cr) + 2H^+ \rightleftharpoons NpO_2^+ + 0.5Ca^{2+} + 2H_2O(l) \quad (10.72)$$

The results from the SIT calculations are $\log_{10}{}^*K^\circ_{s,0}$((10.70), 298.15 K) = (19.90 ± 0.10) and $\log_{10}{}^*K^\circ_{s,0}$((10.71), 298.15 K) = (12.30 ± 0.07). The present review selects the following solubility product reported by [2016FEL/ALT]:

$$\log_{10}{}^*K^\circ_{s,0}((10.71), 298.15\ K) = \mathbf{(12.300 \pm 0.070)}$$

$$\Delta_r G^\circ_m((10.71), 298.15\ K) = \mathbf{-(70.209 \pm 0.400)}\ kJ\cdot mol^{-1}$$

and

$$\Delta_f G^\circ_m(Ca_{0.5}NpO_2(OH)_2\cdot 1.3H_2O, cr, 298.15\ K) = \mathbf{-(1896.521 \pm 5.668)}\ kJ\cdot mol^{-1}.$$

This solid phase might control the solubility of Np(V) in alkaline solutions containing Ca such as in cementitious systems or salt brines.

Table 10-20: Experimental solubility products for the dissolution reaction $Ca_{0.5}NpO_2(OH)_2 \cdot 1.3H_2O(cr) + 2H^+ \rightleftharpoons NpO_2^+ + 0.5Ca^{2+} + 3.3H_2O(l)$ calculated from experimental data provided in [2016FEL/ROT], [2016FEL/ALT].

| $T$/K | Method | Medium | $\log_{10}{}^{*}K_{s,0}$ (10.71) |
|---|---|---|---|
| (296 ± 2) | sol | 0.252 m $CaCl_2$ | (12.09 ± 0.15) |
| (296 ± 2) | sol | 1.024 m $CaCl_2$ | (12.56 ± 0.16) |
| (296 ± 2) | sol | 2.110 m $CaCl_2$ | (13.03 ± 0.16) |

# 10.9 Neptunium group 1 (alkali) compounds

## 10.9.1 Neptunium sodium compounds

Structural studies of the sodium neptunates have been reported based on X-ray diffraction [2011SMI/RAI], [2015SMI], Mössbauer spectroscopy [2015SMI/RAI], [2015SMI/HEN], [2015SMI/HEN2] and X-ray Absorption Spectroscopy [2016SMI/MAR] data. The compounds formed in the Na-Np-O system are numerous, with the neptunium oxidation state varying between +IV and +VII. $Na_2NpO_3$(cr) is monoclinic in space group *C2/c*, $Na_3NpO_4$(cr) is orthorhombic in space group *Fmmm*, $Na_2Np_2O_7$(cr) is monoclinic in space group $P2_1$, α-$Na_2NpO_4$ is orthorhombic in space group *Pbam*, β-$Na_2NpO_4$ is orthorhombic in space group *Pbca*, $Na_4NpO_5$(cr) is tetragonal in space group *I4/m*, $Na_5NpO_6$(cr) is monoclinic in space group *C2/m*.

### 10.9.1.1 α-$Na_2NpO_4$

The enthalpy of formation of α-$Na_2NpO_4$ was first measured by Goudiakas *et al.* using solution calorimetry [1991GOU/JEM]. Using the NEA auxiliary data, [2001LEM/FUG], [2003GUI/FAN] recalculated:

$$\Delta_f H_m^o (\alpha\text{-}Na_2NpO_4, cr, 298.15\ K) = \mathbf{-\ (1763.800 \pm 5.700)}\ kJ{\cdot}mol^{-1}.$$

The Knudsen effusion mass spectrometric measurements of [2013SMI/COL] yielded a very similar result, *i.e.*, – (1761.0 ± 7.7) kJ·mol$^{-1}$, by second law analysis of the data as detailed in Appendix A. The selected value is therefore retained in the present review.

The entropy and heat capacity of α-$Na_2NpO_4$ were recently obtained by [2015SMI/GRI2] using thermal relaxation calorimetry in the temperature range 2.1 to 301 K as:

$$C_{p,m}^o (\alpha\text{-}Na_2NpO_4, cr, 298.15\ K) = \mathbf{(151.900 \pm 4.600)}\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$S_m^o (\alpha\text{-}Na_2NpO_4, cr, 298.15\ K) = \mathbf{(178.300 \pm 4.300)}\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

The present review selects these values as well as the Gibbs energy of formation obtained by combining the latter entropy value with the recommended enthalpy of formation:

$$\Delta_f G_m^o (\alpha\text{-}Na_2NpO_4, cr, 298.15\ K) = \mathbf{-\ (1648.993 \pm 5.848)}\ kJ\cdot mol^{-1}.$$

#### 10.9.1.2 β-$Na_2NpO_4$

The enthalpy of formation of β-$Na_2NpO_4$ selected by [2001LEM/FUG], [2003GUI/FAN] is based on the solution calorimetry studies of Goudiakas *et al.* [1991GOU/JEM]. The present review retains the selected value, and its associated uncertainty:

$$\Delta_f H_m^o (\beta\text{-}Na_2NpO_4, cr, 298.15\ K) = \mathbf{-\ (1748.500 \pm 6.100)}\ kJ\cdot mol^{-1}.$$

#### 10.9.1.3 β-$Na_4NpO_5$

The enthalpy of formation of β-$Na_4NpO_5$ selected by [2001LEM/FUG], [2003GUI/FAN] is based on the solution calorimetry studies of Goudiakas *et al.* [1991GOU/JEM]. The present review retains the selected value, and its associated uncertainty:

$$\Delta_f H_m^o (\beta\text{-}Na_4NpO_5, cr, 298.15\ K) = \mathbf{-\ (2315.400 \pm 5.700)}\ kJ\cdot mol^{-1}.$$

The entropy and heat capacity of β-$Na_4NpO_5$ were recently measured by [2015SMI/GRI] using thermal relaxation calorimetry in the temperature range 2.4 to 292.2 K, as detailed in Appendix A. The values determined in their work are selected in the present review:

$$C_{p,m}^o (\beta\text{-}Na_4NpO_5, cr, 298.15\ K) = \mathbf{(219.000 \pm 6.600)}\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S_m^o (\beta\text{-}Na_4NpO_5, cr, 298.15\ K) = \mathbf{(247.500 \pm 6.200)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The Gibbs energy of formation calculated using the selected data is:

$$\Delta_f G_m^o (\beta\text{-}Na_4NpO_5, cr, 298.15\ K) = \mathbf{-\ (2160.052 \pm 6.002)}\ kJ\cdot mol^{-1}.$$

#### 10.9.1.4 $Na_5NpO_6$(cr)

[2015SMI] reported measurements of the low temperature heat capacity of $Na_5NpO_6$(cr) using thermal relaxation calorimetry in the temperature range 2.0 to 283.7 K. However, the sample used was not analysed chemically and we cannot rule out the presence of remaining sodium or sodium oxide impurities. Their data, $C_{p,m}^o$ ($Na_5NpO_6$, cr, 298.15 K) = (293.0 ± 8.9) $J\cdot K^{-1}\cdot mol^{-1}$ and $S_m^o$ ($Na_5NpO_6$, cr, 298.15 K) = (334.3 ± 9.0) $J\cdot K^{-1}\cdot mol^{-1}$ are therefore not selected in the present review, but only provided for information and scoping calculations.

#### 10.9.1.5 $Na_2Np_2O_7$(cr) and $Na_2Np_2O_7\cdot xH_2O$(cr)

The enthalpy of formation of $Na_2Np_2O_7$(cr) selected in [2001LEM/FUG] and [2003GUI/FAN] is based on the solution calorimetry studies of Fuger [1985FUG] in 1.0 M HCl. The present review retains the selected value, and its associated uncertainty:

$$\Delta_f H_m^o (Na_2Np_2O_7, cr, 298.15\ K) = \mathbf{-\ (2894.000 \pm 11.000)}\ kJ\cdot mol^{-1}.$$

Gaona and co-workers [2013GAO/FEL] investigated the solubility of $Na_2Np_2O_7$(cr) in dilute to concentrated alkaline NaCl solutions. Reactions (10.73) and (10.74) were proposed to describe the solubility of Np(VI) at $-\log_{10}[H^+] > 9$. Conditional equilibrium constants determined in 0.1, 0.5, 1.0, 2.5 and 5.0 M NaCl were extrapolated to $I = 0$ using SIT.

$$0.5Na_2Np_2O_7(cr) + 1.5H_2O(l) \rightleftharpoons NpO_2(OH)_3^- + Na^+ \quad (10.73)$$

$$0.5Na_2Np_2O_7(cr) + 2.5H_2O(l) \rightleftharpoons NpO_2(OH)_4^{2-} + Na^+ + H^+ \quad (10.74)$$

with

$$\log_{10}K^\circ_{s,1,3}\ ((10.73), 298.15\ K) = -(8.6 \pm 0.1)$$

$$\log_{10}K^\circ_{s,1,4}\ ((10.74), 298.15\ K) = -(19.4 \pm 0.1).$$

Equilibrium constants in alkaline systems containing $Na^+$ were determined in [2013GAO/FEL] for Reactions (10.73) and (10.74), and are accepted in this review. For the reasons given in Appendix A, this review selects the solid phase investigated in [2013GAO/FEL] as $Na_2Np_2O_7{\cdot}xH_2O$(cr) instead of $Na_2Np_2O_7$(cr). Gaona *et al.* determined $\log_{10}K^\circ_{s,0}$ (0.5 $Na_2Np_2O_7{\cdot}xH_2O$, cr) considering the transformation of $Na_2Np_2O_7{\cdot}xH_2O$(cr) into $NpO_2(OH)_2{\cdot}H_2O$(cr) observed within $-\log_{10}[H^+] \approx 7.5$ and 8.5 in 0.1 M NaCl. The equilibrium between both solid phases is only dependent on the pH and $Na^+$ concentration, but is independent of the aqueous speciation of Np:

$$0.5Na_2Np_2O_7 \cdot xH_2O(cr) + (1.5 - 0.5x)H_2O(l) + H^+ \rightleftharpoons NpO_2(OH)_2 \cdot H_2O(cr) + Na^+ \quad (10.75)$$

with

$$\log_{10}{}^*K^\circ_{s,0}(0.5\,Na_2Np_2O_7{\cdot}xH_2O, cr) + (1.5 - 0.5x)\log_{10}a_{H_2O} + \log_{10}[H^+] + \log_{10}[\gamma_{H^+}] =$$

$$\log_{10}{}^*K^\circ_{s,0}(NpO_2(OH)_2{\cdot}H_2O, cr) + \log_{10}[Na^+] + \log_{10}\gamma_{Na^+} \quad (10.76)$$

The authors used $\log_{10}{}^*K^\circ_{s,0}$ ($NpO_2(OH)_2{\cdot}H_2O$, cr) = (5.47 ± 0.40) as reported in [2001LEM/FUG] and obtained $\log_{10}{}^*K^\circ_{s,0}$ (0.5 $Na_2Np_2O_7{\cdot}xH_2O$, cr) = (12.6 ± 1.1) according to Equation (10.76). The very large uncertainty assigned in [2013GAO/FEL] to $\log_{10}{}^*K^\circ_{s,0}$ (0.5 $Na_2Np_2O_7{\cdot}xH_2O$, cr) accounts for the uncertainty in the determination of the pH at which the solid phase transformation takes place. The equilibrium constant reported in [2013GAO/FEL] for Reaction (10.77) is selected in this review as a first estimate, although this value needs to be refined in the future by using independent experimental observations on the formation of $NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$ under alkaline conditions. Given the uncertainties affecting to $x$ in $Na_2Np_2O_7{\cdot}xH_2O$(cr), no $\Delta_f G^\circ_m$ has been selected. We note that the selected value of $\log_{10}{}^*K^\circ$ ((10.77), 298.15 K) is in good agreement with $\log_{10}{}^*K^\circ_{s,0}$ (0.5 $Na_2U_2O_7{\cdot}H_2O$, cr) = (12.2 ± 0.2) recently reported by Altmaier and co-workers [2017ALT/YAL] and selected in this review.

$$0.5\,Na_2Np_2O_7{\cdot}xH_2O(cr) + 3H^+ \rightleftharpoons Na^+ + NpO_2^{2+} + (1.5 + 0.5x)H_2O(l) \quad (10.77)$$

$$\log_{10}{}^{*}K^{\circ}((10.77), 298.15\ \text{K}) = \mathbf{(12.600 \pm 1.100)}$$

with

$$\Delta_r G_m^{\circ}((10.77), 298.15\ \text{K}) = \mathbf{-\ (71.921 \pm 6.279)}\ \text{kJ·mol}^{-1}.$$

More precise thermodynamic calculations of the Np(VI) solubility in alkaline NaCl (or $NaClO_4$) systems can be performed using $\log_{10}K^{\circ}_{s,1,3}$ ((10.73), 298.15 K) and $\log_{10}K^{\circ}_{s,1,4}$ ((10.74), 298.15 K) determined in [2013GAO/FEL].

#### 10.9.1.6 $NaNpO_2(OH)_2$(cr) and other neptunium(V) sodium compounds

[2007ALM/SKA] reported for the first time the synthesis of single crystals of $NaNpO_2(OH)_2$(cr) by the hydrothermal method, and found the corresponding structure to be orthorhombic in space group $P2_12_12_1$. No thermodynamic data have been reported for this phase.

Petrov and co-workers studied the solubility of Np(V) hydroxide in NaCl solutions and observed changes in the solid equilibrium phase [2017PET/FEL]. The authors observed that $NpO_2OH$(am, hyd) converts to different Na-Np(V)-OH(s) crystalline phases at [NaCl] ≥ 1.0 M and $-\log_{10}[H^+]$ above ≈ 11.5. This study indicates that these ternary solid phases are expected to control the solubility of Np(V) in strongly alkaline, Na-containing systems. However, reported experimental data are insufficient for the parametrisation of the system, and thus no thermodynamic quantities can be selected for these compounds yet.

# Chapter 11

# Discussion of new data selection for Plutonium

## 11.1 Plutonium aqua ions

Plutonium has been found in aqueous solutions in oxidation states III, IV, V, VI, VII, and at highly oxidising conditions also in the VIII oxidation state. The redox potentials of several of these oxidation states are close together enabling the coexistence of multiple oxidation states in solution and solid state. The formal potentials for the Pu redox couples have been discussed in [2001LEM/FUG]. Since then, several new experimental studies ([2003CHI/SOD], [2004NIK/GOG], [2004NIK/GOG2], [2005GIB/HAI], [2005NIK/GOG], [2006NEC/ALT], [2007TAN/NIK], [2007YUS/SHI4], [2007YUS/SHI2], [2007YUS/SHI3], [2009BRE/BAN], [2009SHI/BES], [2011SHI/GOG], [2012GOG/FED], [2013KIM/ASA], [2014BAN/BRE]) have been reported on the chemistry and redox potentials of Pu in its different oxidation states. In addition, a number of theoretical studies ([2003DAV/VOK], [2005HAS], [2006MOS/MAT], [2006MOS/MAT2], [2006TSU/WAH], [2007HAS], [2012RIO/MIC], [2013ODO/BYL], [2013POM/TIW]) have been published that calculate geometries, vibrational frequencies, thermodynamic properties, and the interaction of plutonium ions with water molecules. The calculated data can be compared with experimental data to corroborate proposed structures and coordination. Reported data from quantum chemical calculations are briefly discussed for information only and are not included in the data selection by this review.

### 11.1.1 Plutonium(VIII) and (VII)

The majority of reported studies on the highest oxidation states of Pu, +VIII and +VII, have been conducted in highly oxidising alkaline solutions. The formation of Pu(VIII) and Pu(VII) has been proposed by assigning the changes in the electronic absorbance spectra to the oxidation products of Pu(VI). The ozonation of Pu(VI) in NaOH solutions produces blue-black solutions with a characteristic absorbance feature at 635 nm as described in [2004NIK/GOG2]. The peak intensity is found to oscillate, which causes the extinction coefficient at 635 nm to vary between 530 to 600 $L \cdot mol^{-1} \cdot cm^{-1}$. The molar extinction coefficient for the Pu(VII) absorbance at 500-550 nm was estimated to

be ~ 100 $L \cdot mol^{-1} \cdot cm^{-1}$, and the molar extinction coefficient of Pu(VIII) is estimated as (2600 ± 400) $L \cdot mol^{-1} \cdot cm^{-1}$ in [2004NIK/GOG2] and [2007TAN/NIK]. Additional studies are necessary to exclude other reactions of Pu(VI) and Pu(VII) and to unequivocally prove the formation of Pu(VIII). The redox potentials measured and estimated in NaOH solutions are listed in Table 11-1.

Haschke ([2005HAS], [2007HAS]) proposes that the Pu(V) disproportionation and Pu(VI) self-reduction in solution takes place via the formation of hydroxo-bridged, dimeric Pu(V) and dimeric Pu(VI) species, and with Pu(VII) as a transient species. The latter species immediately reacts with water. The suggested formation of Pu(V) and Pu(VI) dimers is based on the proposed dependence of the Pu(V) disproportionation rate constant on pH and on $[Pu(V)]^2$, and the Pu(VI) self-reduction rate being proportional to [Pu(VI)]. However, there is no experimental evidence that could support this claim. Nikonov *et al.* report in several publications on the formation of both Pu(VII) and Pu(VIII) after oxidation of Pu(VI) in 0.7-3.5 M NaOH. [2004NIK/GOG] report the formation of Pu(VII) upon the oxidation of Pu(VI) in solution after the transfer of $PuO_3 \cdot H_2O$(s) from saturated NaOH to 5 M LiOH. The oxidation of Pu(VI) to Pu(VII) was identified based on the appearance of absorption features at 605 and 630 nm, which were assigned to Pu(VII). The authors estimated that at least 20 % of the total Pu content was initially oxidised to Pu(VII). The Pu(VII)/Pu(VI) redox potential measured in 2-12 M NaOH was observed to correlate with the concentration of NaOH, which could be expressed by the empirical equation:

$$E((\mathrm{Pu(VII)/Pu(VI)}) = 0.874 - 0.0355\ [\mathrm{NaOH}] \qquad (11.1)$$

The same authors also report in [2004NIK/GOG2] that the treatment of Pu(VI) with ozone produced Pu(VII) and Pu(VIII). The amount of Pu(VIII) produced is estimated by using spectroscopic techniques to about 12 % of the total Pu(VI) concentration. The fraction of Pu(VIII) in the final solution is estimated based on changes in the electronic absorption spectra and the associated molar extinction coefficient. In [2005NIK/GOG], Nikonov *et al.* discussed the reaction of Pu(VI) with ozone in NaOH solutions to form Pu(VII) and Pu(VIII). The potential for the Pu(VI/VII) redox couple, $E$(Pu(VII)/Pu(VI)), is estimated to be (0.685 ± 0.35) V *vs.* NHE based on the ability of ferrate $E$(Fe(VI)/Fe(III)) = 0.72 V in 1 M NaOH to oxidise Pu(VI) in 1.5 M NaOH and by comparison with the stability of Am(VI) and the redox potential $E$(Am(VI)/Am(V)) = 0.65 V in 1 M NaOH. The reduction potential $E$(Pu(VII)/Pu(VI)) is estimated to be lower than 0.72 V in 1.5 M NaOH. This value is in fair agreement with the 0.85 V in 1 M NaOH reported in [1995PER/SHI] and discussed in [2001LEM/FUG].

Tananaev *et al.* estimated in [2007TAN/NIK] the yield of Pu(VIII) to be about (15 ± 5) % when produced by reaction with ozone or bulk electrolysis of Pu(VI) at 1.0 V (relative to Hg/HgO) in 2 M NaOH. The reduction potential for the Pu(VIII)/Pu(VII) redox couple in 2 M NaOH was estimated to exceed 0.90 V and the

value $E$(Pu(VII)/Pu(VI)) = (0.68 ± 0.05) V *vs.* NHE in 2 M NaOH was estimated from electrochemical measurements.

Shilov *et al.* [2009SHI/BES] report the oxidation of Pu(VI) to Pu(VII) in ≥ 8 M NaOH in the presence of $Fe(CN)_6^{3-}$. The redox potential $E(Fe(CN)_6^{3-}/Fe(CN)_6^{4-})$ was estimated to be close to 0.6 V in 10.3 M NaOH and $E$(Pu(VII)/Pu(VI)) was estimated to be 0.05-0.1 V.

In a later study Gogolev *et al.* [2012GOG/FED] estimated the redox potential for the Pu(VIII)/Pu(VII) couple to be ≥ 1.15 V *vs.* NHE in 1 M NaOH.

The spectrophotometric and electrochemistry data on Pu(VIII) and Pu(VII) measured in these studies at high NaOH concentrations are generally of only qualitative nature and spectra were analysed by referring only to the total concentrations of Pu in each oxidation state without any consideration of detailed species distribution. The data reported in the studies discussed above are not considered for data selection by this review.

Table 11-1: Experimental redox potentials for Pu(VIII) and Pu(VII) in alkaline solutions.

| Redox couple | Medium | Potential | Reference |
|---|---|---|---|
| Pu(VII)/Pu(VI) | 1 M NaOH | 0.85 V | [1995PER/SHI] |
| Pu(VII)/Pu(VI) | 1 M NaOH | (0.685 ± 0.35) V | [2005NIK/GOG] |
| Pu(VIII)/Pu(VII) | 2 M NaOH | > 0.90 V | [2007TAN/NIK] |
| Pu(VII)/Pu(VI) | 2 M NaOH | (0.68 ± 0.05) V | [2007TAN/NIK] |
| Pu(VII)/Pu(VI) | 10.3 M NaOH | 0.05-0.10 V | [2009SHI/BES] |
| Pu(VIII)/Pu(VII) | 1 M NaOH | ≥ 1.15 V | [2012GOG/FED] |

## 11.1.2 $PuO_2^{2+}$

Since the last review and the data selection in [2001LEM/FUG], a number of calculations have been conducted to obtain thermodynamic data for the $PuO_2^{2+}$ ion. There are several quantum chemical studies on the structure of the $PuO_2^{2+}$ ion, its thermodynamic properties and hydration energies. There is general agreement for a hydration number of 5 for the $PuO_2^{2+}(aq)$ ion, which is consistent with experimental and theoretical studies on the $AnO_2(H_2O)_5^{2+}$ structures in aqueous solution for An = U, Np and Am as described in the corresponding chapters in this Review. The quantum chemical calculations are generally performed for Pu(VI) species in the gas phase, thus we list those results for information only.

The mechanism of the Pu(VI) reduction has been the topic of several reports. Haschke ([2005HAS], [2007HAS]) claims that the decrease in Pu(VI) concentration at pH 1.5 and 6 is caused by disproportionation via the formation of hydroxo-bridged dimeric Pu species. Shilov *et al.* [2011SHI/GOG] explain the reduction of Pu(VI) in

acidic solutions with radiolytic effects induced by the α-radiation of Pu, thus disputing Haschke's hypothesis that Pu(VI) disproportionates to form Pu(VII) and Pu(V). According to Shilov *et al.* the reduction of Pu(VI) includes the formation of a dimeric Pu(VI) complex, which rapidly decomposes to Pu(V) and $H_2O_2$.

Moskaleva *et al.* [2006MOS/MAT] calculated the enthalpy of formation of $PuO_2^{2+}(g)$ from first principles, using experimental enthalpies of formation for $PuF_4(g)$, $PuF_6(g)$ and $PuO_2(g)$. The calculated value $\Delta_f H_m^o(PuO_2^{2+}, g)$ = (1750 ± 63) kJ·mol$^{-1}$ at 0 K agrees well with the value of (1727 ± 66) kJ·mol$^{-1}$ determined from cyclotron resonance mass spectrometry experiments in [2005GIB/HAI]. Moskaleva *et al.* [2006MOS/MAT2] used this methodology to calculate the enthalpy of formation of $UO_2^{2+}(g)$, $\Delta_f H_m^o(UO_2^{2+}, g)$ = (1528 ± 42) kJ·mol$^{-1}$ at 0 K, which differs significantly from the value of 1210 kJ·mol$^{-1}$ estimated by Marcus [1975MAR]. Due to the larger uncertainties associated with the reactions involving $PuO_2(g)$ as reagent, Moskaleva *et al.* derive $\Delta_f H_m^o(PuO_2^{2+}, g)$ = (1750 ± 63) kJ·mol$^{-1}$ at 0 K by taking into account only the reactions with $PuF_4(g)$ and $PuF_6(g)$ as reagents. Based on the close agreement of the calculated values of $\Delta_f H_m^o(PuO_2^{2+}, g)$ when using $PuF_4(g)$ and $PuF_6(g)$ ($\Delta_f H_m^o(PuF_6, g, 298.15\,K)$ = – (1814.1 ± 29.3) kJ·mol$^{-1}$) as starting reagents (calculated results are within ± 17 kJ·mol$^{-1}$), the authors recommend $\Delta_f H_m^o(PuF_4, g, 298.15\,K)$ = – (1385 ± 50) kJ·mol$^{-1}$ instead of a previous value, $\Delta_f H_m^o(PuF_4, g, 298.15\,K)$ = – 1445.3 kJ·mol$^{-1}$. This value is quite different from the value recommended in [2001LEM/FUG], $\Delta_f H_m^o(PuF_4, g, 298.15\,K)$ = – (1548 ± 22) kJ·mol$^{-1}$. This review agrees with the approach Moskaleva *et al.* proposed, recognising that the close agreement of the $\Delta_f H_m^o(PuO_2^{2+}, g)$ values on the basis of $PuF_4(g)$ and $PuF_6(g)$ relies on the revision of $\Delta_f H_m^o(PuF_4, g)$.

Tsushima and co-workers [2006TSU/WAH] calculated the reduction potentials for the light actinide redox couples $AnO_2(H_2O)_5^{2+}/AnO_2(H_2O)_5^{+}$ with An = U, Np, Pu and Am from quantum chemical models ([2006TSU/WAH]). The structures were calculated in the gas-phase and the gas phase reaction energies were then combined with a continuum model for the solvent. The calculated reduction potentials and reaction enthalpy were within 35 kJ·mol$^{-1}$ and 25 kJ·mol$^{-1}$ of experimental values, respectively, which made the authors conclude that a second solvation sphere is unnecessary to describe these gas-phase calculations. Gibson and co-workers [2005GIB/HAI] investigated the gas phase reactions of $An^{2+}$ ions with oxidants and/or water to form $AnO^{2+}$, $AnOH^{2+}$, and $AnO_2^{2+}$ by using ion cyclotron resonance mass spectrometry. By combining the calculated value of $\Delta_f H_m^o(PuO_2^{+}, g)$ = (270 ± 54) kJ·mol$^{-1}$ with the ionisation energy for $PuO_2^{+}$ reported in this study, IE[$PuO_2^{+}$] = (15.1 ± 0.4) eV, Gibson *et al.* derived $\Delta_f H_m^o(PuO_2^{2+}, g)$ = (1727 ± 66) kJ·mol$^{-1}$. From this new $\Delta_f H_m^o(PuO_2^{2+}, g)$ value and $\Delta_f H_m^o(PuO_2^{2+}, aq)$ = – (822 ± 7) kJ·mol$^{-1}$, which was selected in [2003GUI/FAN], the authors calculate the hydration enthalpy of the $PuO_2^{2+}$ ion, $\Delta_{hyd} H_m^o(PuO_2^{2+})$ = – (1671 ± 67) kJ·mol$^{-1}$. As thermodynamic data for

gaseous ions are not included in the NEA reviews, no value of $\Delta_f H_m^o(PuO_2^{2+}, g)$ is included in the selected data.

Odoh and co-workers [2013ODO/BYL] evaluated the coordination of water with Pu(III), Pu(IV), Pu(V) and Pu(VI) and their hydrolysis reactions by using classical molecular dynamics with a density functional theory approach. $PuO_2(H_2O)_4^{2+}$ is calculated to be about 10.68 kJ·mol$^{-1}$ higher in energy than the $PuO_2(H_2O)_5^{2+}$ ion, which is in agreement with several DFT calculations available in the literature. However, it is well established that the difference in energy between structures with different number of coordinated water is small and differences in the calculated hydration number are dependent on the quantum chemical method used.

Quantum mechanical calculations were used in [2013POM/TIW] to develop intermolecular force-field parameters for the hexavalent actinide ions $AnO_2^{2+}(aq)$, where An = U, Np, Pu and Am, and their interactions with water. The calculations showed that in aqueous systems the coordination of 5 water molecules is preferred in $AnO_2^{2+}(aq)$, which agrees well with published experimental observations. The $AnO_2(H_2O)_5^{2+}$ coordination was used to model the Gibbs energies for hydration of the actinyl(VI) ions, that are given in Table 11-2 for information only and are not included among selected values. Although the absolute values in Table 11-2 differ, the trends are the same when using MD and DFT.

The thermodynamic data for the $PuO_2^{2+}(aq)$ ion selected in [2001LEM/FUG] are retained in this review.

Table 11-2: Calculated Gibbs free energy of hydration for the actinyl(VI) ions at 298.15 K using molecular dynamics and density function theory simulations [2013POM/TIW].

| $AnO_2^{n+}$ | $\Delta_{hyd}G_m^o$ /kJ·mol$^{-1}$ from MD | $\Delta_{hyd}G_m^o$ /kJ·mol$^{-1}$ from DFT |
|---|---|---|
| $UO_2^{2+}$ | – 1390 | – 1702 |
| $NpO_2^{2+}$ | – 1389 | – 1703 |
| $PuO_2^{2+}$ | – 1372 | – 1697 |
| $AmO_2^{2+}$ | – 1376 | – 1644 |

## 11.1.3 $PuO_2^+$

Since the last review, few experimental data and theoretical evaluations of Pu(V) chemistry in the gas phase have been reported. The quantum chemical calculations are generally performed for Pu(V) species in the gas phase, thus we list those results for information only.

Gibson and co-workers [2005GIB/HAI] investigated the gas phase reactions of $An^{2+}$ ions with oxidants and/or water to form $AnO^{2+}$, $AnOH^{2+}$, and $AnO_2^{2+}$ by using ion

cyclotron resonance mass spectrometry. The authors revised previously reported values for $AnO_2$ ionisation potentials [1985HIL/GUR] and calculated $\Delta_f H_m^o(PuO_2^+, g) = (270 \pm 54)$ kJ·mol$^{-1}$. The hydration enthalpy of the actinyl ion $PuO_2^+$, $\Delta_{hyd} H_m^o(PuO_2^+) = -(746 \pm 55)$ kJ·mol$^{-1}$, was obtained by using $\Delta_f H_m^o(PuO_2^+, g) = (270 \pm 54)$ kJ·mol$^{-1}$ and $\Delta_f H_m^o(PuO_2^+, aq) = -(915 \pm 6)$ kJ·mol$^{-1}$ reported in [1986MOR]. The latter value is within the uncertainties of $\Delta_f H_m^o(PuO_2^+, aq) = -(910.127 \pm 8.920)$ kJ·mol$^{-1}$ selected in [2003GUI/FAN]. The second ionisation energy of the $PuO_2^+$ ion is estimated from the reaction kinetics of the electron transfer from $N_2O$ to the actinyl ion to be $(15.1 \pm 0.4)$ eV, which is identical with IE[$NpO_2^+$] but differs from IE[$UO_2^+$] = $(14.6 \pm 0.4)$ eV. As thermodynamic data for gaseous ions are not included in the NEA reviews, no value of $\Delta_f H_m^o(PuO_2^+, g)$ is included among the selected thermodynamic data. Rios *et al.* [2012RIO/MIC] used DFT calculations in the gas phase and gas phase electrospray ionisation of Np(VI) and Pu(VI) to study the hydration of monopositive An(V) and An(VI) (An = $^{238}$U, $^{237}$Np, $^{242}$Pu) ions. The computed hydration energies and Gibbs free energies of hydration are exothermic with very similar $\Delta G^o$ levels calculated for $PuO_2(H_2O)_4^+$ and $PuO_2(H_2O)_5^+$. However, the change in Gibbs free energy for the formation of $PuO_2(H_2O)_5^+$ is nearly neutral and thus $PuO_2(H_2O)_4^+$ is slightly favoured energetically. This is in agreement with other theoretical studies that report a higher stability for $PuO_2(H_2O)_4^+$ over $PuO_2(H_2O)_5^+$. This result is in line with the dissociative mechanism for the interaction of water with $UO_2(H_2O)_5^+$ reported in [2004VAL/PRI]. However, this mechanism disregarded symmetry constraints on $UO_2(H_2O)_6^{2+}$. Upon the removal of these the associative mechanism for the U(VI) aquo ion was more favoured. The associative mechanism is also favoured for Np(VI). Similarly, the first hydrolysis products of Pu(VI) are found to associate three water molecules in the inner coordination sphere to form a four-coordinated complex, $PuO_2(OH)(H_2O)_3^+$. Rios and co-workers calculated the Gibbs free energy for the hydration reactions of $PuO_2(H_2O)_{n-1}^+$ with $n$ = 1-5 and for the hydration reactions of the hydroxo complex $PuO_2(OH)(H_2O)_{n-1}^+$ with $n$ = 1-4. These reactions are all found to be exothermic. Odoh and co-workers [2013ODO/BYL] evaluated the coordination of Pu(III), Pu(IV), Pu(V) and Pu(VI) with water and their hydrolysis reactions by using classical molecular dynamics with a density functional theory approach. The Pu(V) aqueous complex, $PuO_2(H_2O)_4^+$, is calculated to be 12.98 kJ·mol$^{-1}$ more stable than $PuO_2(H_2O)_5^+$. The higher stability of the tetra-aqua complex is in agreement with other reports in the literature. Quantum mechanical calculations were performed in [2013POM/TIW] to develop intermolecular force-field parameters for the penta- and hexavalent actinide ions $AnO_2^{n+}(aq)$, where $n$ = 1 or 2 and An = U, Np, Pu and Am, and their interactions with water. The calculations showed that in aqueous systems the coordination of five water molecules is preferred for $AnO_2^+(aq)$, which is in contrast to the study by Rios *et al.* [2012RIO/MIC]. The $AnO_2(H_2O)_5^+$ coordination was used to model the Gibbs energies of hydration for the actinyl ions, with the $AnO_2^+$ ions being about 900-1000 kJ·mol$^{-1}$ less exothermic compared to the $AnO_2^{2+}$ ions. The hydration Gibbs free energies calculated from MD and DFT simulations are given in Table 11-3

for information only and are not included among the selected values. Although the trends of the results agree, the different models result in significant differences in the corresponding absolute values of the Gibbs free energy of hydration.

Table 11-3: Calculated Gibbs energy of hydration for the actinyl(V) ions using molecular dynamics and density function theory simulations [2013POM/TIW].

| $AnO_2^+$ | $\Delta_{hyd}G_m^o$ /kJ·mol$^{-1}$ from MD | $\Delta_{hyd}G_m^o$ /kJ·mol$^{-1}$ from DFT |
|---|---|---|
| $UO_2^+$ | – 499 | – 716 |
| $NpO_2^+$ | – 492 | – 709 |
| $PuO_2^+$ | – 474 | – 670 |
| $AmO_2^+$ | – 417 | – 639 |

Yusov and co-workers [2007YUS/SHI4] estimated the redox potentials for the Pu(V)/(IV) redox couple in acidic and near-neutral aqueous solutions containing $K_{10}P_2W_{17}O_{61}$. From formation constants reported in [2007YUS/SHI2], [2007YUS/SHI3], Yusov *et al.* derive $E$((Pu(V)/Pu(IV)) > 1.74 in 1 M $H^+$ solution and $E$((Pu(V)/Pu(IV)) > 1.76 in 1 M $Na^+$ solution at pH ~ 5. The authors did not clearly identify the electrolyte counteranion (we assume $ClO_4^-$ is the counteranion for 1 M $H^+$ solution and $NO_3^-$ for 1 M $Na^+$ solutions at pH 5-5.5), which precludes the comparison with other data reported.

The thermodynamic data for the $PuO_2^+(aq)$ ion selected in [2001LEM/FUG] are retained in this review, including the standard redox potential for the $PuO_2^{2+}/PuO_2^+$ couple of $E°$(298.15 K) = **(0.936 ± 0.005)** V *vs.* NHE.

## 11.1.4 $Pu^{4+}$

David and Vokhmin [2003DAV/VOK] used a semi-empirical model to calculate Gibbs energies of formation and standard entropies for the $Pu^{3+}$ and $Pu^{4+}$ ions and calculated the NHE-redox potentials of the $Pu^{4+}/Pu^{3+}$ couple. The calculated $Pu^{4+}$ entropy of – 409 J·K$^{-1}$·mol$^{-1}$ is in good agreement with – (414.5 ± 10.2) J·K$^{-1}$·mol$^{-1}$ selected in [2001LEM/FUG] based on experimental data. Like the redox potentials of the $U^{4+}/U^{3+}$ and $Np^{4+}/Np^{3+}$ couples calculated by David and Vokhmin, the calculated redox potential for the $Pu^{4+}/Pu^{3+}$ couple, $E_{NHE}^o$ (calc) = 1.007 V, is reasonably close to the value selected in [2001LEM/FUG], $E_{NHE}^o$ (exp) = (1.047 ± 0.003) V, and in good agreement with $E_{NHE}^o$ (exp) = 0.988 V, corrected for the ionic strength in the experimental value 0.982 V reported in [2001LEM/FUG].

Neck *et al.* [2006NEC/ALT] amended the SIT ion-interaction parameters for tetravalent actinide ions and used the ion-interaction parameters reported in [2003GUI/FAN], $\varepsilon(Pu^{4+}, ClO_4^-)$ = (0.82 ± 0.07) kg·mol$^{-1}$, $\varepsilon(Pu^{3+}, ClO_4^-)$ = (0.49 ± 0.05) kg·mol$^{-1}$, $\varepsilon(Pu^{3+}, Cl^-) = \varepsilon(Am^{3+}, Cl^-)$ = (0.23 ± 0.02) kg·mol$^{-1}$, to obtain

$\varepsilon(Pu^{4+}, Cl^-) = (0.37 \pm 0.05)$ kg·mol$^{-1}$. The latter value appears to be consistent with the previously selected value $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)$ kg·mol$^{-1}$. Neck *et al.* calculated $\varepsilon(Pu^{4+}, Cl^-)$ by using the redox potential for the Pu(IV/III) couple, $E°(Pu^{4+}/Pu^{3+}) = (1.047 \pm 0.003)$ V, and the thermodynamic equilibrium constant, $\log_{10} K^{o}_{IV.III} = (17.69 \pm 0.04)$, determined for the one-electron transfer Reaction (11.2):

$$Pu^{4+} + e^- \rightleftharpoons Pu^{3+} \quad (11.2)$$

The ion-interaction parameter $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)$ kg·mol$^{-1}$ was selected in [2001LEM/FUG] and is close to the analogous data in the NEA TDB for U(IV), $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol$^{-1}$ and $\varepsilon(Np^{4+}, ClO_4^-) = (0.84 \pm 0.06)$ kg·mol$^{-1}$. It should be noted that Neck and co-workers derive this value by extrapolating the experimental equilibrium constant for Reaction (11.2) in 1 M HCl, $\log_{10} K_{IV,III}(11.2) = (16.40 \pm 0.01)$, reported in [1951RAB/LEM] to $I = 0$ without considering the presence of Pu(IV) chloro complexes in 1 M HCl. In fact, the conditional equilibrium constant of 0.32 for the formation of $PuCl^{3+}$ in 1 M HCl reported by Rabideau *et al.* [1951RAB/LEM] and corrected in [2001LEM/FUG] corresponds to about 30 % of the Pu(IV) being complexed with chloride. Neglecting the existing $PuCl^{3+}$ complex in 1 M HCl in equilibrium (11.2) causes some error in the calculation of $\varepsilon(Pu^{4+}, Cl^-)$. However, the value reported by Neck and co-workers agrees reasonably well with other SIT ion interaction parameters $\varepsilon(M^{n+}, Cl^-)$. The value $\varepsilon(Pu^{4+}, Cl^-) = (0.37 \pm 0.10)$ kg·mol$^{-1}$ reported in [2006NEC/ALT] (with uncertainty increased by this review) can be used in speciation models where chloride complexes have been excluded.

The electrochemical potentials for the quasi-reversible redox Reaction (11.2) between Pu(IV) to Pu(III) were measured electrochemically in 1-7 M nitric acid by Kim and co-workers [2013KIM/ASA]. The cathodic and the corresponding anodic peak in the cyclic voltammograms demonstrate a quasi-reversible redox reaction between Pu(IV) and Pu(III). The values of the standard rate constants increased, and the conditional $E$ values decreased with increasing nitric acid concentration. These trends are associated with the inner-sphere complex formation between Pu(IV) and nitrate ligands, which is supported by the observed changes in the electronic absorption spectra of Pu(IV) with increasing nitrate concentration. A number of Pu(IV) complexes $Pu(NO_3)_n^{4-n}$ ($n$ = 1-3) are proposed to exist in 1-4 M $HNO_3$, with $Pu(NO_3)_6^{3-}$ as the predominant species in the more concentrated nitric acid solutions. Thus, the electrochemical redox potentials measured in that study represent a one-electron transfer reaction between Pu(IV) and Pu(III) nitrate complexes in solution. However, this reaction is obviously not equivalent with Reaction (11.2) for the $Pu^{3+/4+}$ aquo ions since the effects caused by the complex formation of the $Pu^{3+/4+}$ aquo ions with nitrate must be considered. The impact of nitrate coordination is reflected in $\Delta E$(Pu(IV)/Pu(III)) = 0.064 V between $E$(Pu(IV)/Pu(III), 1 M $HNO_3$) = 0.918 V *vs.* NHE derived from the reported value in [2013KIM/ASA],

$E$(Pu(IV)/Pu(III), 1 M $HNO_3$) = 0.721 V *vs.* Ag/AgCl, and the formal redox potential $E^o$(Pu(IV)/Pu(III), 1 M $HClO_4$) = (0.9821 ± 0.0005) V selected in [2001LEM/FUG] for non-complexing perchloric acid solutions. The redox potential difference suggests that Pu(IV) nitrate complexes are stronger than those of Pu(III). The $\Delta E$ value should relate to the thermodynamic equilibrium constants for Pu(III) and Pu(IV) nitrate complexes according to $\Delta E^\circ = RT/nF(\ln K_n^o(\text{Pu(IV)}) - \ln K_n^o(\text{Pu(III)}))$. Using the selected equilibrium constant for Pu(IV), $\log_{10} K_1^o(\text{Pu}(NO_3)^{3+}) = (1.950 \pm 0.150)$, and, in the absence of available data on Pu(III) nitrate complexes, adopting $\log_{10} K_1^o(\text{Pu}(NO_3)^{2+}) \sim \log_{10} K_1^o(\text{Am}(NO_3)^{2+}) = (1.330 \pm 0.200)$, we derive a much smaller value of $\Delta E^\circ = 0.0367$ V. The discrepancy could be caused by a higher nitrate complexation in 1 M $HNO_3$, erroneous equilibrium constants or inconsistencies in the spectroscopic and electrochemical measurements reported in [2013KIM/ASA]. It is to note that Kim *et al.* report redox potentials of (0.705 ± 0.001) V *vs.* Ag/AgCl in 3-5 M $HNO_3$.

Odoh and co-workers [2013ODO/BYL] evaluated the coordination of Pu(III), Pu(IV), Pu(V) and Pu(VI) with water and their hydrolysis reactions by using a combination of classical molecular dynamics with a density functional theory description of the electronic structure. The energy difference of 5.86 kJ·mol$^{-1}$ between the hydrated Pu(IV) species $Pu(H_2O)_8^{4+}$ and $Pu(H_2O)_9^{4+}$ is very small, suggesting that both structures may be isoenergetic. However, based on the observations that the ninth water molecule is ejected after about 6-8 ps in the simulation and the better agreement of calculated Pu-O bond lengths with experimental data, the dominance of $Pu(H_2O)_8^{4+}$ in aqueous solution was suggested.

Chiang and co-workers [2003CHI/SOD] measured the redox potential of the Pu(IV)/(III) couple in 1 M $HClO_4$ at pH 3.5 in the presence of the polyoxotungstate anion α-2-$P_2W_{17}O_{61}^{10-}$. The formal redox potential was calculated from the Nernst equation using XANES spectro-electrochemical data and found to be $E$(Pu(IV)/Pu(III)) = – (0.17 ± 0.01) V for the electron transfer in $[\text{Pu}(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$. Yusov and co-workers [2007YUS/SHI4] calculated the redox potentials for the redox couple Pu(IV)/Pu(III) in aqueous solutions containing $K_{10}P_2W_{17}O_{61}$. Using the equilibrium constants in $[P_2W_{17}O_{61}]^{10-}$-containing solutions reported in [2007YUS/SHI2], [2007YUS/SHI3], Yusov *et al.* calculate the conditional redox potentials $E$(Pu(IV)/Pu(III)) < 0.416 V in 1 M $H^+$ solution and $E$(Pu(IV)/Pu(III)) = – 0.1 V in 1 M $Na^+$ solution at pH ~ 5. The reported redox potentials for Pu(IV)/Pu(III) is a result not only of the electron transfer in the Pu redox couple, but also of the reduction of the ligand to form a heteropoly tungsten-blue complex that contains a reduced form of the heteropolyanion. The values reported for Pu(IV)/Pu(III) in the presence of the $[P_2W_{17}O_{61}]^{10-}$ anion differ from the measured formal redox potential $E(Pu^{4+}(aq)/Pu^{3+}(aq))$ = + 0.810 V due to the complex formation of Pu(IV) and the electron transfer between Pu(IV)/Pu(III) and within the ligand.

The published data on the redox potential for the Pu(IV)/Pu(III) couple were evaluated in [2001LEM/FUG]. The value $E^o$(Pu(IV)/Pu(III), 298.15 K) =

(1.047 ± 0.003) V was selected in [2001LEM/FUG] based on the experimentally determined values of $E$(Pu(IV)/Pu(III)) = (0.982 ± 0.002) V in 1 M $HClO_4$ reported in [1951CON/MCV] and (0.9821 ± 0.0005) V reported in [1951RAB/LEM].

This review retains $E$(Pu(IV)/Pu(III), 1 M $HClO_4$) = (0.9821 ± 0.0005) V and $E$(Pu(IV)/Pu(III), 298.15 K) = (1.047 ± 0.003) V selected in [2001LEM/FUG].

Table 11-4: Electrochemical reduction potentials for the Pu(IV)/Pu(III) redox couple in nitric acid.

| $T$ /K | Method | $I$ (medium) | $E$(V *vs.* Ag/AgCl) | Reference |
|---|---|---|---|---|
| 298.15 | vlt | 1 M $HNO_3$ | 0.721 | [2013KIM/ASA] |
| 298.15 | vlt | 2 M $HNO_3$ | 0.712 | [2013KIM/ASA] |
| 298.15 | vlt | 3 M $HNO_3$ | 0.706 | [2013KIM/ASA] |
| 298.15 | vlt | 4 M $HNO_3$ | 0.705 | [2013KIM/ASA] |
| 298.15 | vlt | 5 M $HNO_3$ | 0.704 | [2013KIM/ASA] |
| 298.15 | vlt | 6 M $HNO_3$ | 0.694 | [2013KIM/ASA] |
| 298.15 | vlt | 7 M $HNO_3$ | 0.696 | [2013KIM/ASA] |

### 11.1.5 $Pu^{3+}$

Since the last review in [2001LEM/FUG] there have been no new thermodynamic data reported for the $Pu^{3+}$(aq) cation. In a qualitative study, Banik and co-workers [2014BAN/BRE] evaluate the stability of the trivalent actinide ions U(III), Np(III) and Pu(III) in the presence of several reducing agents. Hydroxylamine hydrochloride was found to be the most effective one and able to stabilise about 80 % of Pu(III) at pH up to about 5.5. In contrast, the Np(III) and U(III) aquo ions could only be stabilised at pH below 2.5 and 1.0, respectively. No thermodynamic data are provided in this study.

Brendebach and co-workers [2009BRE/BAN] conducted EXAFS measurements to determine the hydration number of Pu(III) in acidic solutions. In solutions up to pH 3, the $Pu^{3+}$(aq) cation was found to be coordinated by ten O atoms at an average distance of 2.49 Å. In contrast, at pH 1.5 $Np^{3+}$(aq) is coordinated by nine O atoms with a slightly longer distance of 2.52 Å. However, the uncertainty in the coordination numbers is large, at best ± 1. Odoh and co-workers [2013ODO/BYL] evaluated the coordination of Pu(III), Pu(IV), Pu(V) and Pu(VI) with water and their hydrolysis reactions by using classical molecular dynamics with a density functional theory approach. The Pu(III) octa-aquo ion, $Pu(H_2O)_8^{3+}$, is calculated to be about 20.5 kJ·mol$^{-1}$ more stable than $Pu(H_2O)_9^{3+}$ and is considered the dominant Pu(III) species. Taking into account the large uncertainty in the experimental hydration number in [2009BRE/BAN], (9 ± 1), the two sets are consistent.

The thermodynamic data on the $Pu^{3+}$ aqua ion selected in [2001LEM/FUG] are retained in this review.

# 11.2 Plutonium oxygen and hydrogen compounds and complexes

## 11.2.1 Aqueous plutonium hydroxide complexes

There have been a large number of studies on the hydrolysis of plutonium in its main oxidation states in aqueous systems. Hydrolysis complexes of Pu(III), (IV), (V) and (VI) have been discussed in [2001LEM/FUG] and [2003GUI/FAN] and data have been selected for a number of complexes, including both monomeric and polynuclear species. Since the last review, several experimental and theoretical studies have been reported on the hydrolysis reactions of plutonium. In a series of publications ([2003SIL], [2003SIL2], [2003SIL3], [2006SIL], [2010SIL], [2011SIL], [2011SIL2], [2011SIL3], [2012SIL], [2012SIL2]), Silver conducted purely mathematical evaluations to estimate the first hydrolysis constant of Pu(IV) [2011SIL], to quantify the disproportionation reactions of Pu ([2003SIL], [2003SIL2], [2003SIL3], [2011SIL2], [2011SIL3]), and to develop criteria to evaluate the reliability of estimated hydrolysis constants ([2006SIL], [2012SIL2]). Those discussions are of theoretical nature and do not reveal any new experimental information and data reported therein are not considered by this review.

### 11.2.1.1 Plutonium(VI) hydroxide complexes

The hydrolysis of Pu(VI) has been studied in detail and both structural information and thermodynamic data are available for the complexes $PuO_2OH^+$, $PuO_2(OH)_2(aq)$, and $(PuO_2)_2(OH)_2^{2+}$. Thermodynamic data for these complexes were selected in [2001LEM/FUG] and retained in [2003GUI/FAN]:

$$PuO_2^{2+} + H_2O(l) \rightleftharpoons PuO_2OH^+ + H^+,\ \log_{10}{}^*K^o_{1,1} = -(5.500 \pm 0.500)$$

$$PuO_2^{2+} + 2H_2O(l) \rightleftharpoons PuO_2(OH)_2(aq) + 2H^+,\ \log_{10}{}^*K^o_{1,2} = -(13.200 \pm 1.500)$$

$$2PuO_2^{2+} + 2H_2O(l) \rightleftharpoons (PuO_2)_2(OH)_2^{2+}(aq) + 2H^+,\ \log_{10}{}^*K^o_{2,2} = -(7.500 \pm 1.000).$$

A number of new studies have been published on the hydrolysis of hexavalent Pu in aqueous systems. Equilibrium constants and thermodynamic data for monomeric and polymeric Pu hydroxo complexes were derived from spectrophotometric titration data. Spectroscopic features characteristic to Pu(VI) were analysed to study the formation of Pu(VI) hydroxo complexes ([2003YUS/FED], [2006REI/NEU], [2007WAL/CHO], [2010CHO/JUN], [2011RAO/TIA]). New equilibrium constants reported since the last review are summarised in Table 11-5 and Table 11-6.

Two semi-empirical modelling studies were conducted to calculate the first hydrolysis constants of Pu aquo ions [2013ODO/BYL] and the reaction enthalpies for the reactions of Pu(VI) fluorides ($PuO_2F_2$ and $PuF_6$) and Pu(VI) oxide ($PuO_3$) with water [2003SCH/PRI]. Odoh and co-workers [2013ODO/BYL] evaluated the hydration of Pu(VI) and its hydrolysis reactions by using classical molecular dynamics with a

density functional theory approach. The authors used the energetics and optimised coordination of the hydrated Pu(VI) ion, $PuO_2(H_2O)_5^{2+}$, to calculate the Gibbs energy of reaction, 32.74 kJ·mol$^{-1}$ and a $pK_a$ of 5.70 at 300 K for the first hydrolysis reaction of Pu(VI). Schimmelpfennig *et al.* [2003SCH/PRI] calculated the reaction enthalpies for the gas phase Reactions (11.3) and (11.4) at 298.15 K to form the bishydroxo complex $PuO_2(OH)_2(g)$:

$$PuO_2F_2(g) + 2H_2O(g) \rightleftharpoons PuO_2(OH)_2(g) + 2HF(g) \quad (11.3)$$

$$PuO_3(g) + H_2O(g) \rightleftharpoons PuO_2(OH)_2(g) \quad (11.4)$$

Schimmelpfennig and co-workers report $\Delta_r H_m^o$ (11.3) = 90 kJ·mol$^{-1}$ and $\Delta_r H_m^o$ (11.4) = – 136 kJ·mol$^{-1}$, which are similar to those calculated for the analogous reactions of U, $\Delta_r H_m^o$ (U, (11.3)) = 86 kJ·mol$^{-1}$ and $\Delta_r H_m^o$ (U, (11.4)) = – 151 kJ·mol$^{-1}$, and Np, $\Delta_r H_m^o$ (Np, (11.3)) = 71 kJ·mol$^{-1}$ and $\Delta_r H_m^o$ (Np, (11.4)) = – 119 kJ·mol$^{-1}$. The data from these calculations are not considered for data selection.

Moriyama and co-workers [2006MOR/SAS] used the effective charge of solution complexes to predict Pu(VI) (as well as U(VI) and Np(VI)) hydrolysis constants for potential monomeric and polynuclear hydrolysis species. The calculated formation constants $\log_{10}\beta_{1,1}^o$ = 8.63 for $PuO_2OH^+$, $\log_{10}\beta_{1,2}^o$ = 15.43 for $PuO_2(OH)_2$(aq), and $\log_{10}\beta_{2,2}^o$ = 20.15 for $(PuO_2)_2(OH)_2^{2+}$ are consistent (within the uncertainties) with the data in [2003GUI/FAN]. It should be noted that Moriyama calculated the formation constant for a large number of polynuclear hydrolysis species with varying stoichiometric ratios of An(VI):$OH^-$ up to a ratio of 5:12. There is no experimental evidence for the majority of these complexes. [2009CAO/BAL] performed DFT calculations in the gas and aqueous phase to evaluate the structure and thermodynamic properties of An(VI) monohydroxo complexes and to predict the change in Gibbs energy for the reaction

$$AnO_2(H_2O)_5^{2+} + H_2O \rightleftharpoons AnO_2(OH)(H_2O)_4^{+} + H_3O^+ \quad (11.5)$$

The authors used – 26.377 kJ·mol$^{-1}$ for $\Delta_{solv}G(H_2O)$ and – 427.054 kJ·mol$^{-1}$ for $\Delta_{solv}G(H_3O^+)$ to calculate $\Delta_{solv}G$ = 122.966 kJ·mol$^{-1}$ for An = Np(V) and 16.203 kJ·mol$^{-1}$ for An = Pu(VI) in Reaction (11.5). The $\Delta_{gas}G$ value used for Pu(VI) was listed as – 57.527 kJ·mol$^{-1}$.

Several experimental studies have been published since the last review. Steppert and Walther [2013STE/WAL] measured the Pu(VI) species distribution in aqueous solution at pH 4.5-5.3 by using nano-electrospray ionisation mass spectrometry. Mass spectra were interpreted with the presence of $PuO_2^+$ (9.5-17.6 %), $PuO_2^{2+}$ (73.3-75.1 %), and the Pu(VI) hydrolysis products $PuO_2OH^+$(3.8-4.1 %) and $(PuO_2)_2(OH)_2^{2+}$ (4.5-7.7 %). The species distribution matches qualitatively the speciation calculated from stability constants in the NEA TDB. No thermodynamic data were derived from the mass spectrometry data.

Although Yusov *et al.* [2003YUS/FED] focused on the complex formation of Pu(VI) with silicic acid, the authors also determined spectroscopically the equilibrium constants for $PuO_2OH^+$, $PuO_2(OH)_2(aq)$ and $(PuO_2)_2(OH)_2^{2+}$, and used these data to take into account the Pu(VI) hydrolysis reactions necessary to calculate the fraction of Pu(VI) complexed by silicate. The authors determined the conditional stability constant $\log_{10}\beta^{o}_{1,1} = (7.95 \pm 0.12)$ for $PuO_2OH^+$ in 0.2 M $NaClO_4$ using a molar extinction coefficient of $\varepsilon_{841} = (138 \pm 12)$ L·mol$^{-1}$·cm$^{-1}$, and calculated the conditional stability constants for $PuO_2(OH)_2(aq)$ $(14.54 \pm 0.24)$ and $(PuO_2)_2(OH)_2^{2+}$ $(19.60 \pm 0.30)$. These constants refer to the reactions between $PuO_2^{2+}(aq)$ and $OH^-$ according to the following reactions:

$$PuO_2^{2+} + OH^- \rightleftharpoons PuO_2OH^+ \tag{11.6}$$

$$PuO_2^{2+} + 2OH^- \rightleftharpoons PuO_2(OH)_2(aq) \tag{11.7}$$

$$2PuO_2^{2+} + 2OH^- \rightleftharpoons (PuO_2)_2(OH)_2^{2+} \tag{11.8}$$

Using the ion-interaction parameters in the NEA TDB, $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)$ kg·mol$^{-1}$ and $\varepsilon(PuO_2OH^+, ClO_4^-) = \varepsilon(UO_2OH^+, ClO_4^-) = -(0.06 \pm 0.40)$ kg·mol$^{-1}$, we correct the conditional equilibrium constants to $\log_{10}\beta^{o}_{1,1} = (8.38 \pm 0.12)$, $\log_{10}\beta^{o}_{1,2} = (15.25 \pm 0.24)$, and $\log_{10}\beta^{o}_{2,2} = (20.33 \pm 1.00)$. These values agree within the uncertainties with the corresponding values in the NEA TDB, $\log_{10}\beta^{o}(PuO_2OH^+) = (8.50 \pm 0.50)$, $\log_{10}\beta^{o}(PuO_2(OH)_2, aq) = (14.80 \pm 1.50)$ and $\log_{10}\beta^{o}((PuO_2)_2(OH)_2^{2+}) = (20.50 \pm 1.00)$.

Reilly and Neu [2006REI/NEU] studied the hydrolysis reactions of Pu(VI) by spectro-potentiometric titrations and interpreted the experimental data according to equilibrium (11.9):

$$nPuO_2^{2+} + mH_2O(l) \rightleftharpoons (PuO_2)_n(OH)_m^{2n-m} + mH^+ \tag{11.9}$$

The potentiometric data analysis was supported by spectroscopic evaluation of the changes in absorbance fingerprints with increasing pH and Pu(VI) concentrations. Two polynuclear solution species, $(PuO_2)_2(OH)_2^{2+}$ and $(PuO_2)_2(OH)_4(aq)$, were sufficient to fit the potentiometric data at Pu concentrations above $10^{-3}$ M, for which Reilly and Neu calculated $\log_{10}{}^{*}K_{2,2} = -(7.79 \pm 0.20)$ and $\log_{10}{}^{*}K_{2,4} = -(19.3 \pm 0.5)$. At [Pu(VI)] $\leq 10^{-4}$ M only monomeric species were observed and the authors calculated $\log_{10}{}^{*}K_{1,1} = -(5.76 \pm 0.07)$ and $\log_{10}{}^{*}K_{1,2} = -(11.69 \pm 0.05)$ for $PuO_2(OH)^+$ and $PuO_2(OH)_2(aq)$, respectively. The authors stated that there was no evidence that supports the presence of $(PuO_2)_3(OH)_5^+$ or $(PuO_2)_4(OH)_7^+$, species that are very important in the U(VI) hydrolysis system at low uranium concentrations. With the SIT ion-interaction parameters, the authors calculated the thermodynamic hydrolysis constants $\log_{10}{}^{*}K^{o}_{1,1} = -(5.51 \pm 0.16)$ and $\log_{10}{}^{*}K^{o}_{1,2} = -(11.48 \pm 0.05)$ for the monomeric Pu(VI) hydrolysis species, and $\log_{10}{}^{*}K^{o}_{2,2} = -(7.56 \pm 0.20)$ and $\log_{10}{}^{*}K^{o}_{2,4} = -(18.8 \pm 0.5)$ for the two Pu(VI) dinuclear species. The values of $\log_{10}{}^{*}K^{o}_{1,1}$ and $\log_{10}{}^{*}K^{o}_{2,2}$ agree very well with those accepted in the NEA TDB, however, the second

hydrolysis constant $\log_{10}{}^{*}K^{\circ}_{1,2}$ differs by about 1.5 logarithmic units. The data reported by Reilly and Neu indicate that the Pu(VI) hydroxo complexes are weaker than the corresponding U(VI) and Np(VI) hydrolysis products. The value $\log_{10}{}^{*}K^{\circ}_{1,2} = -(13.20 \pm 1.50)$ selected in [2001LEM/FUG] is based on a spectrophotometric study reported in [1995PAS/KIM]. Reilly and Neu suggested that the second hydrolysis constant is overestimating the concentration of $PuO_2(OH)_2(aq)$ due to the presence of other species such as $PuO_2(OH)_3^-$. The addition of an estimated constant of $\log_{10}{}^{*}K^{'}_{1,3} \sim -22$ results in a good fit of the titration data over the entire pH range, while not affecting the $\log_{10}{}^{*}K^{\circ}_{1,2}$ value. Pashalidis *et al.* [1995PAS/KIM] prepared their Pu(VI) solutions by dissolving and converting $PuO_2CO_3(s)$ to $PuO_2(OH)_2(s)$ under experimental conditions at pH 4.5-9.5. It is very likely that residual carbonate was present that form Pu(VI) carbonate complexes in the neutral pH range.

Cho and co-workers ([2010CHO/JUN], [2010CHO/JUN2]) studied the formation and stability of Pu(VI) hydroxo complexes in the absence and presence of NaOCl as oxidising agent. In the absence of this redox buffer, the initial pH of 5.62 shifted to 5.33 within one month and $(PuO_2)_2(OH)_2^{2+}$ decomposed to $PuO_2^+$ and $PuO_2^{2+}$, which remained as solution species [2010CHO/JUN]. At the initial pH of 7.33, the $PuO_2^{2+}$ fraction was reduced to $PuO_2^+$, while the Pu(VI) hydrolysis products were more resistant towards reduction and remained present even after 14 months. The authors reported the conditional equilibrium constant $\log_{10}{}^{*}K^{\circ}_{2,2} = -(7.34 \pm 0.22)$ for the equilibrium

$$2PuO_2^{2+} + 2H_2O(l) \rightleftharpoons (PuO_2)_2(OH)_2^{2+} + 2H^+ \qquad (11.10)$$

which was converted to $\log_{10}{}^{*}K^{\circ}_{2,2} = -(7.25 \pm 0.22)$ by using the SIT. The $\log_{10}{}^{*}K^{\circ}_{2,2}$ value was averaged over three data determined at pH 5.20 ($\log_{10}{}^{*}K^{\circ}_{2,2} = -7.09$), pH 5.62 ($\log_{10}{}^{*}K^{\circ}_{2,2} = -7.45$), and pH 5.71 ($\log_{10}{}^{*}K^{\circ}_{2,2} = -7.48$) in 0.01 M $NaClO_4$. The experiments conducted with 0.1-0.12 mM Pu did not show any evidence of the formation of $PuO_2OH^+$, which is in contrast to the identification of $PuO_2OH^+$ at [Pu(VI)] ≤ 0.2 mM reported in [2006REI/NEU]. Due to inconsistencies in the spectral analysis, this review does not consider these data in the data selection.

In a subsequent experiment, Cho *et al.* [2010CHO/JUN2] maintained the oxidation state Pu(VI) by the addition of NaOCl and reported the conditional hydrolysis constants $\log_{10}{}^{*}\beta_{1,n}$ according to the equilibrium (11.11):

$$PuO_2^{2+} + nH_2O(l) \rightleftharpoons PuO_2(OH)_n^{2-n} + nH^+ \qquad (11.11)$$

with $n$ = 1-3: $\log_{10}{}^{*}\beta_{1,1} = -(5.8 \pm 0.3)$ for $PuO_2OH^+$, $\log_{10}{}^{*}\beta_{1,2} = -(13.4 \pm 0.2)$ for $PuO_2(OH)_2(aq)$, and $\log_{10}{}^{*}\beta_{1,3} = -(24.3 \pm 0.8)$ for $PuO_2(OH)_3^-$ in 0.01 M $NaClO_4$. In absence of the absorbance at about 845 nm, which is characteristic of $(PuO_2)_2(OH)_2^{2+}$, the absorbance features were assigned to only monomeric Pu(VI) hydrolysis species. The thermodynamic Pu(VI) hydrolysis constants were derived by using the SIT and the ion-interaction coefficients for the analogous U(VI) species with $ClO_4^-$: $\log_{10}{}^{*}\beta^{\circ}_{1,1} =$

– (5.6 ± 0.3), $\log_{10}{}^{*}\beta^{o}_{1,2}$ = – (13.1 ± 0.2), and $\log_{10}{}^{*}\beta^{o}_{1,3}$ = – (24.0 ± 0.8). The $\log_{10}{}^{*}K^{o}_{1,1}$ value is consistent with the data reported in [2006REI/NEU] and in the NEA TDB, but the hydrolysis constant for $PuO_2(OH)_2$(aq) differs significantly from that reported in [2006REI/NEU]. This difference is manifested in the molar extinction coefficients used for calculating the concentration of $PuO_2(OH)_2$(aq), $\varepsilon_{850}$ = (436 ± 33) L·mol$^{-1}$·cm$^{-1}$ in [2010CHO/JUN2] and $\varepsilon_{845}$ = (270 ± 10) L·mol$^{-1}$·cm$^{-1}$ in [2006REI/NEU]. The hydrolysis constant $\log_{10}{}^{*}\beta^{o}_{1,3}$ = – (24.0 ± 0.8) is associated with a large uncertainty, since the concentrations of $PuO_2(OH)_3^-$ present in most sample solutions were only at trace levels.

Rao and co-workers [2011RAO/TIA] reported the temperature-dependence of the Pu(VI) hydrolysis reactions in 1.0 M $NaClO_4$. Spectroscopic data indicated that Pu(VI) hydrolysis begins at $\log_{10}[H^+] < 10^{-3}$ mol·L$^{-1}$ and experimental data were best interpreted with a mixture of mono- and polynuclear hydrolysis species, $PuO_2OH^+$, $(PuO_2)_2(OH)_2^{2+}$ and $(PuO_2)_3(OH)_5^+$ that form according to the equilibrium Reactions (11.12), (11.10), and (11.13), respectively.

$$PuO_2^{2+} + H_2O(l) \rightleftharpoons PuO_2OH^+ + H^+ \quad (11.12)$$

$$3PuO_2^{2+} + 5H_2O(l) \rightleftharpoons (PuO_2)_3(OH)_5^+ + 5H^+ \quad (11.13)$$

From the conditional equilibrium constants the authors calculated enthalpies, Gibbs energies and entropies of reaction. With increasing temperature, the hydrolysis of Pu(VI) was found to increase. Rao *et al.* reported the Gibbs energies of reaction at 298.15 K, $\Delta_r G^o_m$ (11.12) = (33.39 ± 0.80) kJ·mol$^{-1}$, $\Delta_r G^o_m$ (11.10) = (44.01 ± 1.37) kJ·mol$^{-1}$, $\Delta_r G^o_m$ (11.13) = (116.27 ± 1.26) kJ·mol$^{-1}$, and the enthalpies of reaction for the hydrolysis reactions $\Delta_r H^o_m$ (11.12) = (35.0 ± 3.4) kJ·mol$^{-1}$, $\Delta_r H^o_m$ (11.10) = (65.4 ± 1.0) kJ·mol$^{-1}$, $\Delta_r H^o_m$ (11.13) = (127.7 ± 1.7) kJ·mol$^{-1}$. The thermodynamic hydrolysis constants $\log_{10}{}^{*}K^{o}$ ($PuO_2OH^+$, 298 K) = – (5.85 ± 0.49) and $\log_{10}{}^{*}K^{o}$ ( $(PuO_2)_2(OH)_2^{2+}$, 298 K) = – (7.71 ± 0.24) are in agreement with the data selected in [2001LEM/FUG]. The constant $\log_{10}{}^{*}K^{o}$ ( $(PuO_2)_3(OH)_5^+$, 298 K) = – (20.37 ± 0.22) follows the trend of the analogous U(VI) and Np(VI) values selected in [2001LEM/FUG] and [2003GUI/FAN], $\log_{10}{}^{*}K^{o}$ ( $(UO_2)_3(OH)_5^+$, 298 K) = – (15.50 ± 0.12) and $\log_{10}{}^{*}K^{o}$ ( $(NpO_2)_3(OH)_5^+$, 298 K) = – (17.120 ± 0.220). This review has not accepted the data reported by Rao *et al.* due to the internal inconsistencies in the analysis of potentiometric and spectrophotometric data.

In summary, the experimental studies of the Pu(VI) hydrolysis system confirm that the Pu(VI) hydrolysis is less complex compared to its chemical analogue U(VI) and fewer Pu(VI) hydroxo complexes are needed to interpret the experimental data reported to date. The new experimental data confirm the existence of the three Pu(VI) hydrolysis species $PuO_2OH^+$, $PuO_2(OH)_2$(aq), and $(PuO_2)_2(OH)_2^{2+}$. The reported thermodynamic data for $PuO_2OH^+$ and $(PuO_2)_2(OH)_2^{2+}$ are in good agreement with $\log_{10}{}^{*}K^{o}_{1,1}$ = – (5.50 ± 0.50) and $\log_{10}{}^{*}K^{o}_{2,2}$ = – (7.50 ± 1.00) selected in [2001LEM/FUG] and [2003GUI/FAN]. The reported data on the second monomeric Pu(VI) complex,

$PuO_2(OH)_2$(aq), are less consistent. The hydrolysis constant for $PuO_2(OH)_2$(aq) reported in [2006REI/NEU] is about 1.5 orders of magnitude larger than the value $\log_{10}{}^{*}K^{\circ}_{1,2}$ = – (13.200 ± 1.500) selected in [2001LEM/FUG] and data reported since that review. The differences are reflected in the different molar extinction coefficients of the Pu(VI) hydrolysis species for $PuO_2(OH)_2$(aq) and $(PuO_2)_2(OH)_2^{2+}$ used to analyse spectrophotometric data. Major inconsistencies remain regarding the polynuclear species $(PuO_2)_4(OH)_7^{+}$ and $(PuO_2)_3(OH)_5^{+}$ used in the data analysis. The inability to model both potentiometric and spectrophotometric data with $PuO_2OH^{+}$, $PuO_2(OH)_2$(aq), and $(PuO_2)_3(OH)_5^{+}$ in [2011RAO/TIA] disqualifies the proposed set of complexes for data selection. Reilly and Neu preferred the complex $(PuO_2)_2(OH)_4$(aq) but did not find any evidence or preference for $(PuO_2)_3(OH)_5^{+}$ or $(PuO_2)_4(OH)_7^{+}$ in their data analysis. However, the set of hydrolysis species proposed by Reilly and Neu, $PuO_2OH^{+}$, $PuO_2(OH)_2$(aq), $(PuO_2)_2(OH)_2^{2+}$, and $(PuO_2)_2(OH)_4$(aq), could successfully fit both experimental potentiometric and spectrophotometric data in the $-\log_{10}[H^{+}]$ range 3.7-7.8.

In the absence of further reliable evidence of the formation of $(PuO_2)_4(OH)_7^{+}$ and $(PuO_2)_3(OH)_5^{+}$, we do not select the corresponding equilibrium constants. This review acknowledges the relevance of $PuO_2(OH)_3^{-}$ based on the studies by [2006REI/NEU] and [2010CHO/JUN2] and selects the hydrolysis constant reported in [2010CHO/JUN2] with an increased uncertainty to take into account the difference to the estimate by Reilly *et al.*:

$$\log_{10}{}^{*}K^{\circ}_{1,3}\ ((11.11), 298.15\ \mathrm{K}) = \mathbf{-\ (24.00 \pm 1.60)}.$$

Hence the Gibbs energy for Reaction (11.11) with $n = 3$ is $\Delta_r G^{\circ}_m(11.11)$ = **(136.993 ± 9.133)** kJ·mol$^{-1}$. Using the thermodynamic data in [2003GUI/FAN] for $PuO_2^{2+}$ and $H_2O$(l), we obtain $\Delta_f G^{\circ}_m(PuO_2(OH)_3^{-}, 298.15\ \mathrm{K})$ = – (**1336.780 ± 9.559**) kJ·mol$^{-1}$. Due to the inconsistencies of experimental data and analysis, we do not include equilibrium constants reported in [2011RAO/TIA] even though one of the constants agrees with previous NEA selections. The reported value of $\Delta_r H^{\circ}_m(11.12)$ = (35.0 ± 3.4) kJ·mol$^{-1}$ agrees reasonably well with the selected data in the NEA TDB ($\Delta_r H^{\circ}_m(11.12)$ = (28.000 ± 15.000) kJ·mol$^{-1}$), and we provide the reported value of $\Delta_r H^{\circ}_m(11.10)$ = (65.4 ± 1.0) kJ·mol$^{-1}$ for information only.

Table 11-5: Experimental constants for the equilibrium $m PuO_2^{2+} + n OH^{-} \rightleftharpoons (PuO_2)_m(OH)_n^{2m-n}$. The correction to zero ionic strength was conducted with the SIT and associated parameters in the NEA TDB.

| *n*:*m* | *T* /K | Method | *I*(medium) | $\log_{10}\beta'_{n,m}$ | $\log_{10}\beta^{\circ}_{n,m}$ | Reference |
|---|---|---|---|---|---|---|
| 1:1 | (294 ± 2) | spectr | 0.2 M $NaClO_4$ | (7.95 ± 0.12) | (8.38 ± 0.12) | [2003YUS/FED] |
| 2:1 | (294 ± 2) | spectr | 0.2 M $NaClO_4$ | (14.54 ± 0.24) | (14.98 ± 0.24) | [2003YUS/FED] |
| 2:2 | (294 ± 2) | spectr | 0.2 M $NaClO_4$ | (19.60 ± 0.30) | (20.04 ± 1.00) | [2003YUS/FED] |

Table 11-6: Experimental equilibrium constants for the reaction $m\mathrm{PuO_2^{2+}} + n\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{PuO_2})_m(\mathrm{OH})_n^{2m-n} + n\mathrm{H^+}$.

| *n*:*m* | *T* /K | Method | *I*(medium) | $\log_{10}{}^{*}K_{n,m}$ | $\log_{10}{}^{*}K^{\circ}_{n,m}$ | Reference |
|---|---|---|---|---|---|---|
| 1:1 | 298.15 | spectr | 0.1 M $NaNO_3$ | | – (5.62 ± 0.12) | [2003YUS/FED] |
| 2:1 | 298.15 | spectr | 0.1 M $NaNO_3$ | | – (13.02 ± 0.24) | [2003YUS/FED] |
| 2:2 | 298.15 | spectr | 0.1 M $NaNO_3$ | | – (7.96 ± 1.00) | [2003YUS/FED] |
| 1:1 | 298.15 | spectr | 0.1 M $NaNO_3$ | – (5.76 ± 0.07) | – (5.51 ± 0.16) | [2006REI/NEU] |
| 2:1 | 298.15 | spectr | 0.1 M $NaNO_3$ | – (11.69 ± 0.05) | – (11.48 ± 0.05) | [2006REI/NEU] |
| 2:2 | 298.15 | spectr | 0.1 M $NaNO_3$ | – (7.79 ± 0.20) | – (7.56 ± 0.20) | [2006REI/NEU] |
| 4:2 | 298.15 | spectr | 0.1 M $NaNO_3$ | – (19.3 ± 0.5) | – (18.8 ± 0.5) | [2006REI/NEU] |
| 2:2 | 294 ± 2 | spectr | 0.01 M $NaClO_4$ | – (7.34 ± 0.22) | – (7.08 ± 0.22) | [2010CHO/JUN] |
| 1:1 | 294 ± 2 | spectr | 0.01 M $NaClO_4$ | – (5.8 ± 0.3) | – (5.6 ± 0.3) | [2010CHO/JUN2] |
| 2:1 | 294 ± 2 | spectr | 0.01 M $NaClO_4$ | – (13.4 ± 0.2) | – (13.1 ± 0.2) | [2010CHO/JUN2] |
| 3:1 | 294 ± 2 | spectr | 0.01 M $NaClO_4$ | – (24.3 ± 0.8) | – (24.0 ± 0.8) | [2010CHO/JUN2] |
| 1:1 | 283.15 | spectr | 1 M $NaClO_4$ | – (6.34 ± 0.23) | – (6.32 ± 0.48) | [2011RAO/TIA] |
| 1:1 | 298.15 | spectr | 1 M $NaClO_4$ | – (5.88 ± 0.25) | – (5.85 ± 0.49) | [2011RAO/TIA] |
| 1:1 | 313.15 | spectr | 1 M $NaClO_4$ | – (5.49 ± 0.12) | – (5.45 ± 0.44) | [2011RAO/TIA] |
| 1:1 | 323.15 | spectr | 1 M $NaClO_4$ | – (5.60 ± 0.22) | – (5.54 ± 0.48) | [2011RAO/TIA] |
| 1:1 | 343.15 | spectr | 1 M $NaClO_4$ | – (5.26 ± 0.20) | – (5.19 ± 0.47) | [2011RAO/TIA] |
| 2:2 | 283.15 | spectr | 1 M $NaClO_4$ | – (8.37 ± 0.08) | – (8.02 ± 0.13) | [2011RAO/TIA] |
| 2:2 | 298.15 | spectr | 1 M $NaClO_4$ | – (8.07 ± 0.21) | – (7.71 ± 0.24) | [2011RAO/TIA] |
| 2:2 | 313.15 | spectr | 1 M $NaClO_4$ | – (7.76 ± 0.18) | – (7.39 ± 0.21) | [2011RAO/TIA] |
| 2:2 | 323.15 | spectr | 1 M $NaClO_4$ | – (7.25 ± 0.12) | – (6.87 ± 0.16) | [2011RAO/TIA] |
| 2:2 | 343.15 | spectr | 1 M $NaClO_4$ | – (6.97 ± 0.17) | – (6.57 ± 0.20) | [2011RAO/TIA] |
| 3:5 | 283.15 | spectr | 1 M $NaClO_4$ | – (22.35 ± 0.05) | – (21.32 ± 0.22) | [2011RAO/TIA] |
| 3:5 | 298.15 | spectr | 1 M $NaClO_4$ | – (21.43 ± 0.06) | – (20.37 ± 0.22) | [2011RAO/TIA] |
| 3:5 | 313.15 | spectr | 1 M $NaClO_4$ | – (20.60 ± 0.09) | – (19.50 ± 0.23) | [2011RAO/TIA] |
| 3:5 | 323.15 | spectr | 1 M $NaClO_4$ | – (19.51 ± 0.06) | – (18.37 ± 0.22) | [2011RAO/TIA] |
| 3:5 | 343.15 | spectr | 1 M $NaClO_4$ | – (18.73 ± 0.09) | – (17.55 ± 0.23) | [2011RAO/TIA] |

Yusov and co-workers [2002YUS/FED] determined spectroscopically that two ternary Pu(VI)-Al(III)-OH complexes form in the presence of $Al(NO_3)_3$. In the absence of Al(III), hydrolysis of Pu(VI) is observed at pH > 4 and $3.44 \times 10^{-4}$ M Pu, but the authors do not provide hydrolysis constants in this study. At pH below 4 and in the presence of $Al(NO_3)_3$, the appearance of a new absorption band at 838 nm is interpreted with the formation of a mixed Pu(VI)-Al(III)-OH solution complex, which is in equilibrium with $\mathrm{PuO_2^{2+}(aq)}$. Yusov *et al.* suggested the stoichiometry $(\mathrm{H_2O})_3\mathrm{PuO_2}(\mu\text{-}\mathrm{OH})_2\mathrm{Al(OH)(H_2O)_3^{2+}}$ or $(\mathrm{H_2O})_4\mathrm{PuO_2OAl(OH)(H_2O)_4^{2+}}$ for the mixed Pu(VI)-Al(III)-OH complex with a reported equilibrium constant of $\log_{10}\beta' = (33.82 \pm 0.06)$ for equilibrium reaction (11.14):

$$\mathrm{PuO_2^{2+}} + \mathrm{Al^{3+}} + 3\mathrm{OH^-} \rightleftharpoons \mathrm{PuO_2OAlOH^{2+}} + \mathrm{H_2O(l)} \qquad (11.14)$$

This review does not select this value because of the uncertainty of the proposed composition of this complex, and it is provided for information only.

Table 11-7: Thermodynamic constant for the formation of the Pu(VI)-Al(III) hydroxide complexes, $(H_2O)_4PuO_2OAl(OH)(H_2O)_4^{2+}$, according to equilibrium (11.14).

| $T$ /K | Method | $I$(medium) | $\log_{10}\beta_{VI,(2,1)1}$ | Reference |
|---|---|---|---|---|
| (293 ± 2) | spectr | 0.02 M $Al(NO_3)_3$ | (33.82 ± 0.06) | [2002YUS/FED] |

The new experimental studies have provided additional insights into the hydrolysis of Pu(VI). In contrast to the hydrolysis of U(VI), the hydrolysis of Pu(VI) involves less species and thermodynamic data have been developed for four Pu(VI) hydroxo complexes. The formation of mononuclear Pu(VI) hydrolysis products of general formula $PuO_2(OH)_n^{2-n}$ has been established for $n$ = 1-3. There remains some uncertainty regarding the interpretation of spectroscopic data, including the determination of the molar extinction coefficient of $PuO_2(OH)_2$(aq). This uncertainty translates in uncertainties in the different equilibrium constants as illustrated in the studies of [2006REI/NEU] and [2010CHO/JUN], [2010CHO/JUN2]. The uncertainties in the composition and equilibrium constants for the formation of polynuclear species are much larger. The thermodynamic data for the Pu(VI) hydrolysis system in aqueous solution are retained from prior reviews and selected in the present review (Table 11-8).

Table 11-8: Thermodynamic data for Pu(VI) hydrolysis reactions selected in this review (in italics) and former NEA TDB reviews. The Gibbs energies of formation refer to the Pu(VI) hydrolysis species formed in the reaction.

| Reaction | $\log_{10}{}^{*}K^{\circ}_{n,m}$ | $\Delta_r G^{\circ}_m$ /kJ·mol$^{-1}$ | $\Delta_f G^{\circ}_m$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $PuO_2^{2+} + H_2O(l) \rightleftharpoons PuO_2OH^+ + H^+$ | **– (5.50 ± 0.50)** | **(31.394 ± 2.854)** | **– (968.099 ± 4.013)** |
| $PuO_2^{2+} + 2H_2O(l) \rightleftharpoons PuO_2(OH)_2(aq) + 2H^+$ | **– (13.20 ± 1.50)** | **(75.346 ± 8.562)** | **– (1161.287 ± 9.015)** |
| $PuO_2^{2+} + 3H_2O(l) \rightleftharpoons PuO_2(OH)_3^- + 3H^+$ | ***– (24.00 ± 1.60)*** | ***(136.993 ± 9.133)*** | ***– (1336.780 ± 9.559)*** |
| $2PuO_2^{2+} + 2H_2O(l) \rightleftharpoons (PuO_2)_2(OH)_2^{2+} + 2H^+$ | **– (7.50 ± 1.00)** | **(42.810 ± 5.708)** | **– (1956.176 ± 8.026)** |

### 11.2.1.2 Plutonium(V) hydroxide complexes

There are only few studies on the hydrolysis of Pu(V) due to the difficulties to maintain the +V oxidation state in near-neutral and alkaline conditions. A set of Pu(V) hydrolysis studies were evaluated in [2001LEM/FUG] and one study was discussed in [2003GUI/FAN]. The upper estimate for the equilibrium constant for the formation of $PuO_2OH$(aq) was selected in [2001LEM/FUG] and retained in [2003GUI/FAN]:

$$PuO_2^+ + H_2O(l) \rightleftharpoons PuO_2OH(aq) + H^+,\ \log_{10}{}^{*}K^{\circ}_{1,1} \leq -9.730.$$

No new experimental studies on the hydrolysis of Pu(V) have been published since the last reviews. In a recent theoretical study, Odoh and co-workers [2013ODO/BYL] evaluated the coordination of Pu (III), Pu(IV), Pu(V) and Pu(VI) with water and their hydrolysis reactions by using classical molecular dynamics with a density functional theory approach. The authors used the energetics and coordination of

the assumed predominant aquo complex, $PuO_2(H_2O)_4^+$, to calculate the Gibbs free energy of the first Pu(V) hydrolysis reaction to be 54.68 kJ mol$^{-1}$ and a $pK_a$ of 9.51.

In the absence of new experimental data, this review retains the previously selected upper estimate for the equilibrium constant for the formation of $PuO_2OH(aq)$ as noted above.

#### 11.2.1.3 Plutonium(IV) hydroxide complexes

The hydrolysis of Pu(IV) has been studied in detail and both structural information and thermodynamic data are available for several solution complexes. The determination of equilibrium constants for the hydrolysis of Pu(IV) is complicated due to the extensive hydrolysis even at quite low pH, the low solubility of Pu(IV) hydrous oxides and the formation of colloids. The hydrolysis of Pu(IV) has been extensively reviewed in [2001LEM/FUG] and [2003GUI/FAN]. The reviewers selected the Pu(IV) hydrolysis constants mainly based on the data from solvent extraction studies reported in [1972MET/GUI] and selected the following thermodynamic data in the NEA TDB:

$$Pu^{4+} + H_2O(l) \rightleftharpoons PuOH^{3+} + H^+, \ \log_{10}{}^*K^o_{1,1} = (0.600 \pm 0.200)$$

$$Pu^{4+} + 2H_2O(l) \rightleftharpoons Pu(OH)_2^{2+} + 2H^+, \ \log_{10}{}^*K^o_{2,1} = (0.600 \pm 0.300)$$

$$Pu^{4+} + 3H_2O(l) \rightleftharpoons Pu(OH)_3^{+} + 3H^+, \ \log_{10}{}^*K^o_{3,1} = -(2.300 \pm 0.400)$$

$$Pu^{4+} + 4H_2O(l) \rightleftharpoons Pu(OH)_4(aq) + 4H^+, \ \log_{10}{}^*K^o_{4,1} = -(8.500 \pm 0.500).$$

Since the past reviews, a number of semi-empirical modelling and experimental studies have been published. In his reviews on the redox chemistry of Pu(VI), Haschke ([2004HAS], [2007HAS]) interpreted the $[Pu(IV)]^3$ and $[H^+]^{-3}$ dependence of the disproportionation rate of Pu(IV) with the formation of the intermediate $[Pu(OH)]_3^{9+}$, a trimeric hydroxo-bridged Pu(IV) species. The $[Pu(OH)]_3^{9+}$, is supposed to form by the combination of $Pu^{3+}$ and $PuOH^{2+}$ and a protonated aqueous Pu(VI) species $Pu(OH)_2^{4+}$. The present review considers the formation of a species with charge of 9+ as highly speculative until there is experimental support. Moriyama and co-workers [2005MOR/SAS] used the effective charge of solution complexes to predict Pu(IV) hydrolysis constants for potential monomeric and polynuclear hydrolysis species according to Equation (11.15):

$$Pu(H_2O)_8^{4+} + mOH^- \rightleftharpoons Pu(H_2O)_{8-m}(OH)_m^{4-m} + mH_2O(l) \qquad (11.15)$$

Except for the first hydrolysis constant, $\log_{10}\beta^o_{1,1} = 14.51$, which agrees well with the NEA TDB value $\log_{10}\beta^o_{1,1} = (14.600 \pm 0.200)$, the calculated constants differ by several orders of magnitude from those selected in past reviews. In another evaluation, Odoh and co-workers [2013ODO/BYL] performed MD DFT calculations to model the coordination of water with Pu(III), Pu(IV), Pu(V) and Pu(VI) and their hydrolysis reactions. The authors used the energetics and coordination of the octahydrated Pu(IV) ion, $Pu(H_2O)_8^{4+}$, to calculate the Gibbs energy of 0.59 kJ·mol$^{-1}$ and the p$K_a$ value of

0.17 for the first hydrolysis reaction of Pu(IV). The reported hydrolysis constant is in fair agreement with some experimental studies (*e.g.* [2007YUN/CHO]), but does not agree with the NEA TDB selection.

Three experimental studies have been published that provide additional insight into solution speciation and the spectroscopic features of Pu(IV) and its hydrolysis products. Walther and co-workers [2007WAL/CHO] investigated the main absorbance band of Pu(IV) at 470 nm which has been used to determine hydrolysis and complex formation reactions of Pu(IV). In the absence of colloidal Pu(IV), the Pu(IV) absorbance at 470 nm is found to be independent of pH, which means that the absorbances of $Pu^{4+}$ and the hydrolysis species $PuOH^{3+}$ and $Pu(OH)_2^{2+}$ overlap and the molar extinction coefficients do not vary for these species. The lack of additional distinct absorbance bands or a shift of the maximum absorbance in past spectroscopic studies was also mentioned in [2003GUI/FAN]. Changes to the absorption peak at 470 nm are attributed to either the formation of colloidal or polymeric Pu(IV) species or redox reactions of Pu(IV). This is in stark contrast to other studies, which interpreted changes in the absorbance at 470 nm as hydrolysis reactions. Yusov *et al.* [2004YUS/FED] determined spectroscopically the first hydrolysis constant from changes in the 470 nm band at pH 1-1.34 and calculated the single component spectrum of $PuOH^{3+}$ according to the reaction:

$$Pu^{4+} + H_2O(l) \rightleftharpoons PuOH^{3+} + H^+ \qquad (11.16)$$

Polymerisation of Pu(IV) and Np(IV) was found to start at $-\log_{10}[H^+] = 1.5$ for Pu(IV) and 2.2 for Np(IV) at about $10^{-4}$ M actinide concentration. In solutions of $-\log_{10}[H^+] < 1.4$ at $I = 0.1$ and 0.5, the conditional Pu(IV) equilibrium constants ( ${}^*K_{1,1}$ ) for Reaction (11.16) were determined ( ${}^*K_{1,1} = (0.063 \pm 0.004)$ at $I = 0.1$ and ${}^*K_{1,1} = (0.027 \pm 0.005)$ at $I = 0.5$), which extrapolated to zero ionic strength results in $\log_{10}{}^*K^\circ_{1,1}(11.16) = -(0.59 \pm 0.02)$ (or $\log_{10}\beta^\circ_{1,1} = 13.41$). As in the case for Np(IV), this value differs significantly from the selected one in the NEA TDB, $\log_{10}{}^*K^\circ_{1,1}(11.16) = (0.600 \pm 0.200)$, and is opposite to the expected trend for hydrolysis constants, $\log_{10}{}^*K^\circ_{1,1}(PuOH^{3+}) > \log_{10}{}^*K^\circ_{1,1}(NpOH^{3+}) > \log_{10}{}^*K^\circ_{1,1}(UOH^{3+})$. The difference may be attributed to the erroneous interpretation of the changes in the absorbance of Pu(IV) as discussed above. Yusov *et al.* also calculated the equilibrium constant for Np(IV), $\log_{10}{}^*K^\circ_{1,1} = -(1.23 \pm 0.06)$ ( $\log_{10}\beta^\circ_{1,1} = (12.77 \pm 0.06)$), which differs even more from the selected value in [2003GUI/FAN], $\log_{10}{}^*K^\circ_{1,1}(11.16) = (0.55 \pm 0.20)$. This review does not accept the data reported in [2004YUS/FED].

Yun and co-workers [2007YUN/CHO] investigated the hydrolysis of Pu(IV) at $-\log_{10}[H^+]$ between 0.3 and 2.5 by using spectroscopic and potentiometric techniques. In accordance with [2007WAL/CHO], the authors conclude that the Pu(IV) absorbance band at 470 nm was an overlap of absorbance bands from both $Pu^{4+}$ and $Pu(OH)_n^{4-n}$. The fraction of $Pu^{4+}$ was calculated from spectroscopic data and the $Pu(OH)_n^{4-n}$ formation constants selected in [2003GUI/FAN]. An oxidation state distribution was

measured with $Pu^{3+}$, $Pu^{4+}$ and $Pu(OH)_n^{4-n}$ being the predominant species at $-\log_{10}[H^+] < 1$. At $-\log_{10}[H^+] > 1.5$, Pu(IV) colloids are in equilibrium with $Pu^{3+}$, $Pu^{4+}$ and $Pu(OH)_n^{4-n}$, $PuO_2^+$, and $PuO_2^{2+}$. By using the SIT and the NEA TDB recommended ion interaction parameters, the authors calculated conditional equilibrium constants for 0.5 NaCl: $\log_{10}{}^*K_{III/IV} = -(16.55 \pm 0.04)$, $\log_{10}{}^*K_{V/VI} = -(15.36 \pm 0.09)$, and $\log_{10}K_{IV(s)/V} = -(19.65 \pm 0.89)$. Yun *et al.* maintained $\log_{10}{}^*K_{III/IV} = -(16.55 \pm 0.04)$ and calculated from the measured $p_e$ values both conditional and thermodynamic hydrolysis equilibrium constants for $Pu(OH)_n^{4-n}$ with $n$ = 1-3 according to the reaction:

$$Pu^{4+} + nOH^- \rightleftharpoons Pu(OH)_n^{4-n} \tag{11.17}$$

The thermodynamic hydrolysis constants reported in [2007YUN/CHO] are $\log_{10}\beta^\circ_{1,1} = (14.0 \pm 0.2)$, $\log_{10}\beta^\circ_{1,2} = (26.8 \pm 0.6)$, $\log_{10}\beta^\circ_{1,3} = (38.9 \pm 0.9)$. Except the constant for the second complex, these values are in fair agreement with the values in [2003GUI/FAN], $\log_{10}\beta^\circ_{1,1} = (14.6 \pm 0.2)$, $\log_{10}\beta^\circ_{1,2} = (28.6 \pm 0.3)$, and $\log_{10}\beta^\circ_{1,3} = (39.7 \pm 0.4)$, but the authors claim that the data in the NEA TDB overestimate the Pu(IV) hydrolysis equilibria. The largest differences between the data sets are for the first, and even more pronounced, for the second hydrolysis constant, which is due to the different interpretation of the spectroscopic data. The data by Yun *et al.* are inconsistent with the expected trend $\log_{10}{}^*K^\circ(PuOH^{3+}) > \log_{10}{}^*K^\circ(NpOH^{3+}) > \log_{10}{}^*K^\circ(UOH^{3+})$, which is related to the decreasing radii from $U^{4+}$ to $Pu^{4+}$. The currently selected values, $\log_{10}{}^*K^\circ_{1,1}(PuOH^{3+}) = (0.600 \pm 0.200)$, $\log_{10}{}^*K^\circ_{1,1}(NpOH^{3+}) = (0.5500 \pm 0.200)$ and $\log_{10}{}^*K^\circ_{1,1}(UOH^{3+}) = -(0.540 \pm 0.060)$ follow this trend and we retain the thermodynamic data for the monomeric Pu(IV) hydroxide species selected in [2003GUI/FAN].

Table 11-9: Experimental constants for the equilibrium $Pu^{4+} + H_2O(l) \rightleftharpoons PuOH^{3+} + H^+$.

| $T$/K | Method | $I$ (medium) | $\log_{10}{}^*K'_{1,1}$ | Reference |
|---|---|---|---|---|
| 298 | spectr | 0.1 M | $-(1.20 \pm 0.03)$ | [2004YUS/FED] |
| 298 | spectr | 0.5 M | $-(1.57 \pm 0.09)$ | [2004YUS/FED] |

Table 11-10: Equilibrium constants for the reaction $Pu^{4+} + nOH^- \rightleftharpoons Pu(OH)_n^{4-n}$ with $n$ = 1-3 reported in [2007YUN/CHO].

| $T$/K | Method | $I$ (medium) | $\log_{10}\beta'_{1,1}$ | $\log_{10}\beta'_{1,2}$ | $\log_{10}\beta'_{1,3}$ | $\log_{10}\beta^\circ_n$ |
|---|---|---|---|---|---|---|
| (296 ± 2) | spectr | 0.5 M (H,Na)Cl | (12.7 ± 0.2) | | | (14.0 ± 0.2) |
| (296 ± 2) | spectr | 0.5 M (H,Na)Cl | | (24.5 ± 0.6) | | (26.8 ± 0.6) |
| (296 ± 2) | spectr | 0.5 M (H,Na)Cl | | | (36.0 ± 0.9) | (38.9 ± 0.9) |

New experimental data on the solubility of $An(OH)_4$(am) with An = Np and Pu in alkaline solutions containing $CaCl_2$ have been reported in [2008ALT/NEC] and [2010FEL/NEC]. In analogy to the behaviour of Th(IV), the increase in solubility at

high pH and increasing $CaCl_2$ concentration is explained with the formation of the previously unknown ternary solution complex $Ca_4[Pu(OH)_8]^{4+}$. The authors adopted the analogous Th(IV) speciation model and the corresponding SIT ion interaction parameters, $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-) = -(0.01 \pm 0.10)$ kg·mol$^{-1}$ reported in [2008ALT/NEC], and calculated the thermodynamic constants for $Ca_4[Pu(OH)_8]^{4+}$, $\log_{10}{}^{*}K^{o}_{s,(4,1,8)} = -(58.0 \pm 0.5)$ in [2008ALT/NEC] and $-(58.5 \pm 0.4)$ in [2010FEL/NEC] for the following reaction:

$$Pu(OH)_4(am) + 4H_2O(l) + 4Ca^{2+} \rightleftharpoons Ca_4[Pu(OH)_8]^{4+} + 4H^+ \qquad (11.18)$$

Applying the solubility product $\log_{10}K^{o}_{sp} = -(58.3 \pm 0.5)$ for $PuO_2$ (am, hyd), the formation constants $\log_{10}\beta^{o}_{4,1,8} = (56.3 \pm 0.7)$ in [2008ALT/NEC] and $(55.8 \pm 0.6)$ in [2010FEL/NEC] are calculated for the equilibrium (11.19):

$$Pu^{4+} + 4Ca^{2+} + 8OH^- \rightleftharpoons Ca_4[Pu(OH)_8]^{4+} \qquad (11.19)$$

[2009ALT/NEC] considered the constant $\log_{10}{}^{*}K^{o}_{s,(4,1,8)} = -(58.0 \pm 0.5)$ reported in [2008ALT/NEC] as a preliminary value. It was revised in [2009ALT/NEC] to $\log_{10}{}^{*}K^{o}_{s,(4,1,8)} = -(59.5 \pm 0.5)$ using the Pitzer equations. With the SIT-based $\log_{10}\beta^{o}_{4,1,8} = (55.8 \pm 0.6)$ in [2010FEL/NEC] and the equilibrium constant for the $Pu(OH)_4$(aq) solution complex in [2003GUI/FAN], $\log_{10}{}^{*}K^{o}_{1,4} = -(8.50 \pm 0.50)$, we derive $\log_{10}\beta^{o}_{4,(4,1,8)} = (8.30 \pm 0.60)$ for the equilibrium reaction involving the interacting species in solution:

$$Pu(OH)_4(aq) + 4Ca^{2+} + 4OH^- \rightleftharpoons Ca_4[Pu(OH)_8]^{4+} \qquad (11.20)$$

However, this data is compromised by the fact that the value $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-)$ was obtained outside the validity range of the SIT and therefore cannot be accepted. A better approach to model these very high-ionic strength data is the Pitzer formalism. This review has not selected the thermodynamic equilibrium constants calculated by Fellhauer *et al.* [2010FEL/NEC] with the Pitzer formalism, and these data are included for information only:

$$\log_{10}K^{o}_{s,(4,1,8)}((11.18), 298.15\ K) = -(59.3 \pm 0.4) \text{ and}$$

$$\log_{10}\beta^{o}_{4,1,8}\ ((11.19), 298.15\ K) = (55.0 \pm 0.6).$$

From these data we calculate $\Delta_r G^{o}_m((11.18), 298.15\ K) = (338.487 \pm 2.283)$ kJ·mol$^{-1}$, $\Delta_r G^{o}_m((11.19), 298.15\ K) = -(313.942 \pm 3.425)$ kJ·mol$^{-1}$ and $\Delta_f G^{o}_m(Ca_4[Pu(OH)_8]^{4+}, 298.15\ K) = -(4260.914 \pm 4.853)$ kJ·mol$^{-1}$.

To conclude, this review retains the thermodynamic data for the Pu(IV) hydrolysis system in aqueous solution as listed at the beginning of this section selected in the prior reviews [2001LEM/FUG] and [2003GUI/FAN]. The solution complex $Ca_4[Pu(OH)_8]^{4+}$ forms at $\log_{10}[H^+] \leq -11$ at $[CaCl_2] \geq 2.0$ M and its equilibrium constant is not selected in this review since the conditions fall outside the SIT validity range.

#### 11.2.1.4 Plutonium(III) hydroxide complexes

Trivalent plutonium is known to be stable in aqueous systems from highly reducing acidic to near-neutral conditions. The presence of any oxidant or complexing agent that forms strong complexes with Pu(IV) can stimulate the oxidation of Pu(III) to Pu(IV). The hydrolysis of Pu(III) has been extensively reviewed in [2001LEM/FUG]. The reviewers averaged the reported Pu(III) hydrolysis constants, ranging from $\log_{10}{}^{*}K^{\circ}_{1,1} = -6.73$ to $-7.06$, which derived from potentiometric measurements in the 1940s and 1950s, and selected:

$$Pu^{3+} + H_2O(l) \rightleftharpoons PuOH^{2+} + H^+, \quad \log_{10}{}^{*}K^{\circ}_{1,1} = -(6.900 \pm 0.300).$$

with $\Delta_r G^{\circ}_m$ (298.15 K) = (39.390 ± 1.710) kJ·mol$^{-1}$ and $\Delta_f G^{\circ}_m$ ($PuOH^{2+}$, aq, 298.15 K) = – (776.739 ± 3.187) kJ·mol$^{-1}$. This equilibrium constant was obtained after corrections for temperature and chloride complex formation without further explanation.

Odoh and co-workers [2013ODO/BYL] evaluated the coordination of Pu(III), Pu(IV), Pu(V) and Pu(VI) with water and their hydrolysis reactions by using classical molecular dynamics with a density functional theory approach. The authors used the $Pu(H_2O)_8^{3+}$ ion to calculate the Gibbs energy of reaction of 38.23 kJ·mol$^{-1}$ and the $pK_a$ value of 9.13 for the first hydrolysis reactions of Pu(III).

In a new experimental study, Cho *et al.* [2016CHO/YOU] used a spectrophotometric-coulometric titration to investigate the hydrolysis of Pu(III). From changes in the absorbance bands of Pu(III) in 20 samples with $-\log_{10}[H^+] \leq 6.5$, the authors calculated the conditional hydrolysis constant $\log_{10}{}^{*}K^{'}_{1,1}(11.21) = -(6.62 \pm 0.25)$ in 0.1 M $NaClO_4$.

$$Pu^{3+} + H_2O(l) \rightleftharpoons PuOH^{2+} + H^+ \qquad (11.21)$$

Cho and co-workers used laser-induced breakdown detection to verify the absence of colloids or the formation of a solid phase at $\log_{10}[H^+] \geq -6.3$. The (small) absorbance changes were interpreted with decreasing $Pu^{3+}$ concentrations and the formation of non-absorbing $PuOH^{2+}$. In the investigated pH region, only up to 20 % of the Pu(III) is hydrolysed according to their analysis of spectroscopic data. The low abundance of Pu(III) hydroxide complexes and the scatter of the experimental data points (see discussion in the Appendix A), suggest that the reported data have a larger uncertainty than the reported ± 0.25. Using the SIT ion-interaction parameters $\varepsilon(Pu^{3+}, ClO_4^-) = (0.49 \pm 0.05)$ kg·mol$^{-1}$ and $\varepsilon(PuOH^{2+}, ClO_4^-) = \varepsilon(AmOH^{2+}, ClO_4^-) = (0.39 \pm 0.04)$ kg·mol$^{-1}$ reported in [2001LEM/FUG] and [2003GUI/FAN], the authors derived $\log_{10}{}^{*}K^{\circ}_{1,1}(11.21) = -(6.18 \pm 0.25)$. This value differs from the selected value in [2001LEM/FUG]. However, applying this value to the solubility data reported in [2016CHO/YOU] and [1989FEL/RAI] results in a good agreement of the values for $\log_{10}K^{\circ}_{s,o}$ ((11.50), $Pu(OH)_3$, am) (see Section 11.2.2.2.4 $Pu(OH)_3$(am)).

This review acknowledges the uncertainties in the study by Cho *et al.*, but considers the combination of absorbance spectroscopy and LIBD measurements to

identify formation of particles and solids as a more reliable method of exploration than the ones used in previous studies. This review accepts the value reported in [2016CHO/YOU] with an increased uncertainty to take into account the data scattering and selects the hydrolysis constant:

$$\log_{10}{}^{*}K^{\circ}_{1,1}\,((11.21), 298.15\ \mathrm{K}) = \mathbf{-\ (6.18 \pm 0.50)}$$

and

$$\Delta_r G^{\circ}_m\,((11.21), 298.15\ \mathrm{K}) = \mathbf{(35.276 \pm 2.854)}\ \mathrm{kJ\cdot mol^{-1}}.$$

Thus, with $\Delta_r G^{\circ}_m$ (298.15 K) = (35.276 ± 2.854) kJ·mol$^{-1}$ and $\Delta_f G^{\circ}_m$ ($Pu^{3+}$, aq, 298.15 K) = – (578.984 ± 2.688) kJ·mol$^{-1}$ we obtain $\Delta_f G^{\circ}_m$ ($PuOH^{2+}$, aq, 298.15 K) = **– (780.848 ± 3.921)** kJ·mol$^{-1}$.

It is to note that this value has been selected in combination with the thermodynamic solubility product, $\log_{10} K^{\circ}_{s,0}$ ((11.50), $Pu(OH)_3$, am) = (14.58 ± 0.75) (see Section 11.2.2.2.4), and both data need to be used together in order to predict Pu(III) solubility data at up to about $\log_{10}[H^+] \geq -8.5$, as illustrated for the interpretation of Pu(III) solubility data reported in [1989FEL/RAI] and [2016CHO/YOU].

## 11.2.2 Solid plutonium oxides and hydroxides

### 11.2.2.1 The plutonium-oxygen system

Numerous studies were reported on the Pu-O system due to its importance for different applications in the nuclear industry. Historically, successive versions of the Pu-O phase diagram were suggested by a number of research groups ([1958HOL/MUL], [1964CHI/MCN], [1965GAR/MAR], [1968SAR/BEN], [1970DEA/BOI], [1976BOI] and [1987BES]). More recently, [2008GUE/CHA] and [2011GUE/DUP] performed a thermodynamic assessment of the Pu-O system using the CALPHAD method and relying on a critical review of literature data performed by Wriedt [1990WRI]. The phase boundaries as calculated in the work of [2011GUE/DUP] are shown in Figure 11-1 and Figure 11-2.

Plutonium metal exists in six allotropic modifications: α-Pu monoclinic (space group $P2_1/m$), β-Pu body-centred monoclinic (space group $C2/m$), γ-Pu face-centred orthorhombic (space group $Fddd$), δ-Pu (fcc in space group $Fm\bar{3}m$), δ'-Pu (bct, space group $I4/mmm$) and ε-Pu (bcc in space group $Im\bar{3}m$). [1958HOL/MUL] found a small solubility of oxygen in metallic Pu from 1273 to 1423 K (25 ± 10 ppm), but there is no data on the oxygen solubility in liquid Pu at higher temperatures. In the thermodynamic model of [2008GUE/CHA] and [2011GUE/DUP], the oxygen solubility in the different allotropic forms of Pu are not considered.

Figure 11-1: Pu-O phase diagram reported in [2011GUE/DUP]. (Reprinted with permission from *J. Nucl. Mater.*, **2011**, *419* , 145. Copyright (2011) Elsevier).

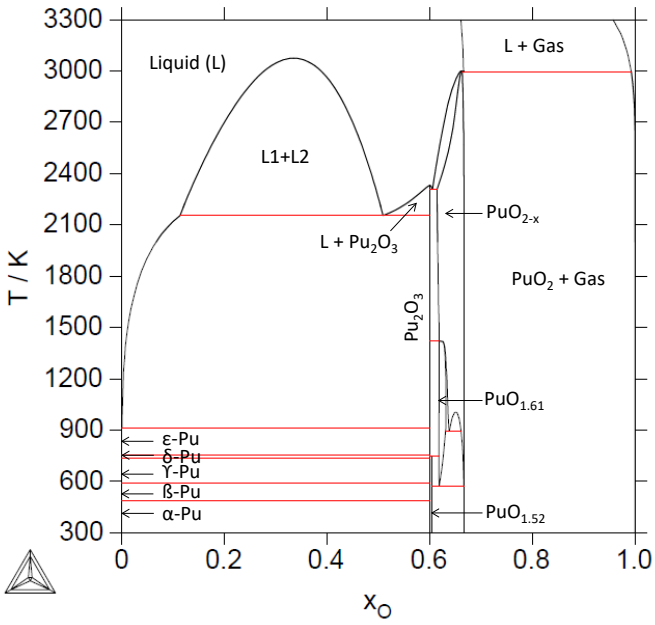
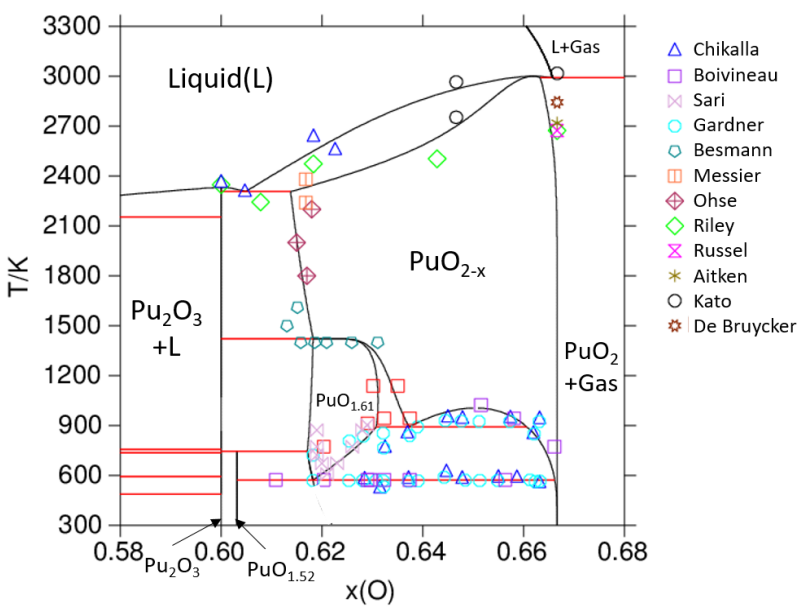



Figure 11-2: Pu-O phase diagram calculated by [2011GUE/DUP]. (Reprinted with permission from *J. Nucl. Mater.*, **2011**, *419* , 145. Copyright (2011) Elsevier).



Several oxide phases are found in this system. Plutonium dioxide $PuO_2$ has a face-centred cubic structure (space group $Fm\bar{3}m$) with a composition range from 61.3 to 66.67 atom % O (Figure 11-2). The sesquioxide $Pu_2O_3$ is hexagonal (space group $P\bar{3}m1$) with a small composition range at high temperatures. It is also denoted in the literature as β-$Pu_2O_3$ or A-phase [2008GUE/CHA]. $Pu_2O_3$ is treated as stoichiometric compound in the assessment of [2008GUE/CHA] and [2011GUE/DUP]. The body-centred cubic (bcc in space group $Ia\bar{3}$) phase, $PuO_{1.52}$, is referred to in the literature as cubic $Pu_2O_3$, α-$Pu_2O_3$ or C-phase. Finally, $PuO_{1.61}$ (bcc in space group $Ia\bar{3}$), also designated as α-$Pu_2O_3$ or C'-phase, is found above ~ 573 K with a composition range between 61.7 and 63 atom % O.

In the Pu-$Pu_2O_3$ region of the phase diagram, a miscibility gap is found in the liquid state with a monotectic reaction temperature at (2098 ± 40) K based on the results of [1969MAR/MRA]. This is consistent with the existence of similar miscibility gaps in the U-O and U-Pu-O systems. However, due to the lack of experimental data [2008GUE/CHA] and [2011GUE/DUP] could not assess the extension of the miscibility gap in detail. In the $Pu_2O_3$-$PuO_2$ region, the $PuO_{1.52}$ compound was found to decompose into $Pu_2O_3$ and $PuO_{1.61}$ at ~ 623 K. The $PuO_{1.61}$ cubic phase exists above ~ 573 K and shows a homogeneity range from $PuO_{1.61}$ to $PuO_{1.69}$. The phases $PuO_{1.61}$ and $PuO_{2-x}$ are in equilibrium from 573 to about 900 K. According to the monotectoid reaction $[PuO_{2-x}(O/Pu{\sim}1.7) \rightleftharpoons PuO_{1.98} + PuO_{1.62}]$, a small miscibility gap is found in the cubic phase, $PuO_{2-x}$, at ~ 900 K. $PuO_{2-x}$ shows a wide homogeneity range from 1650 to 2380 K covering the range ~ 1.6 < O/Pu < 2. The high temperature $PuO_{1.62}$ (bcc) phase as reported by [1964CHI/MCN], [1965GAR/MAR] and [1970RIL] is not a separate phase, but corresponds to the lower phase boundary of $PuO_{2-x}$ according to [1987BES]. The existence of hyper-stoichiometric $PuO_{2+x}$ in the $PuO_2$-O region has been the subject of controversy in recent years as discussed in [2008GUE/CHA] and [2001LEM/FUG], as detailed in Section 11.2.2.2.3.3. Hyper-stoichiometric plutonium dioxide can only form as surface species in the presence of traces of water, and its existence was not taken into account in the assessment of [2008GUE/CHA] and [2011GUE/DUP]. The solidus and liquidus curves between $Pu_2O_3$ and $PuO_2$ are uncertain. Chikalla *et al.* [1964CHI/MCN] reported that $Pu_2O_3$ melts congruently at (2358 ± 25) K.

Russel [1961RUS] found the melting point of $PuO_2$ at 2673 K. The value selected by [2001LEM/FUG], (2663 ± 40) K, is based on data in [1982GLU/GUR], while [1990WRI] recommended 2698 K. [2008GUE/CHA] calculated 2660 K for the hypostoichiometric congruently melting composition $PuO_{1.96}$. The more recent measurements of the melting temperature of plutonium dioxide by Kato *et al.* [2008KAT/MOR] using rhenium instead of tungsten crucibles suggested a liquidus temperature about 200 K higher than in previous studies. However, the authors stress the fact that the interaction with the containment material and/or changes in the O/Pu stoichiometry could affect the results. The melting temperature of plutonium dioxide selected by this review is:

$$T_{fus}(PuO_2, cr) = \mathbf{(3017 \pm 28)}\ K$$

based on the recent measurements by [2011BRU/BOB] using a quasi-containerless fast laser heating technique and multi-wavelength pyrometry. This value has been included in the diagram optimised by [2011GUE/DUP] (Figure 11-2). The CALPHAD model as presented does not consider the phase transition between hexagonal A-type $Pu_2O_3$ and H-type structure at $T_{tr}(A \rightarrow H) = (2300 \pm 50)$ K, as suggested by [2014KON/BEN] in analogy with the behaviour of the light lanthanide sesquioxides. Experimental investigations are needed to confirm the existence of this transition.

This review does not consider thermodynamic data derived from quantum chemical calculations or experimental reactions in the gas phase, however, such data may provide some validation of experimental data from studies in aqueous systems. Gibson *et al.* [2005GIB/HAI] report data on bond energies, ionisation energies and formation enthalpies derived from gas phase reactions. The ionisation energy for $PuO_2$ is reported to be IE[$PuO_2$] = (7.03 ± 0.12) eV.

The ionisation potential of the $PuO_2$ molecule was measured up to 2773 K in order to obtain the relation between the ionisation potentials of PuO and $PuO_2$, $I_o(PuO_2) = I_o(PuO) + (0.42 \pm 0.005)$ eV [2005CAP/COL]. From this equation, the authors estimated the ionisation potential for PuO of 6.2-6.6 eV. Although the upper boundary of the ionisation potential at 6.6 eV is close to the value of (7.03 ± 0.12) eV reported in [2002SAN/MAR], the paper by Capone *et al.* drew a response by Gibson *et al.* [2006GIB/SAN] challenging the assumed equilibrium achieved in the Knudsen cell. This claim is supported by calculated concentration ratios of Pu species that are quite different and incompatible with those reported in [2005CAP/COL]. Capone *et al.* also report the reaction enthalpies $\Delta_r H^\circ(11.22) = 7.1$ eV and $\Delta_r H^\circ(11.23) = 5.8$ eV for the reactions:

$$PuO(g) \rightarrow Pu(g) + O(g) \qquad (11.22)$$

$$PuO(g) \rightarrow PuO^+(g) + e^- \qquad (11.23)$$

Due to the inconsistencies in the study by Capone *et al.*, the conclusion from the present review is that these data cannot be used even for qualitative statements.

Neck and co-workers [2007NEC/ALT2] calculated a number of thermodynamic data for An(IV,V,VI) oxides and oxyhydroxides. Values of $\Delta_f G_m^\circ$ for An(VI) oxyhydroxides were converted to calculate $\Delta_f G_m^\circ$ of the corresponding binary oxides, $AnO_3$(cr, hyd). The authors estimated $\Delta_f G_m^\circ(PuO_{2.25}, cr) = -(995 \pm 3)$ kJ·mol$^{-1}$, $\Delta_f G_m^\circ(PuO_{2.5}, cr) = -(987 \pm 10)$ kJ·mol$^{-1}$ and $\Delta_f G_m^\circ(PuO_3, cr) = -(952 \pm 10)$ kJ·mol$^{-1}$ for pure and mixed valent An(IV,V,VI) oxides.

#### 11.2.2.1.1 $PuO_2$(cr)

Since the review of [2001LEM/FUG] and [2003GUI/FAN], the enthalpy increment data reported in the literature for plutonium dioxide were refitted by [2014KON/BEN]. This reassessment is based on the results in [1968KRU/SAV] from 298 to 1404 K, [1970OGA] from 1500 to 2715 K, and in [1982OET] from 354 to 1611 K. As discussed in [2001LEM/FUG], [1982OET] and [1982FIN], Ogard's measurements suggested a rapid increase in $C^{\circ}_{p,\mathrm{m}}$ above 2370 K that was attributed to partial melting of $PuO_2$ through interaction with the tungsten container. A similar increase was observed in the heat capacities of $ThO_2$, $UO_2$, and $ZrO_2$, and was explained with the formation of oxygen Frenkel pairs at high temperatures. The heat capacity function selected by [2001LEM/FUG] was calculated by refitting the values reported in [1982FIN] to an extended Kelley polynomial. In the latter analysis, the measurements of Ogard above 2370 K were given zero weight. [2014KON/BEN] refitted all the experimental data including those of Ogard, which were given a lower weight in the range 2470-2640 K. The fitted enthalpy increment and derived heat capacity function, shown in Figure 11-3 and Figure 11-4, respectively, are in reasonable agreement with the experimental data and include the upward trend associated with the formation of oxygen Frenkel pairs. The following heat capacity equation is selected in the present review:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{PuO_2},\mathrm{cr},T) = 35.2952 + 0.15225T - 129.255\times10^{-6}T^2 + 36.289\times10^{-9}T^3 - 3.47593\times10^{5}T^{-2}\ (\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$$

Note that there is a typing error in the equation reported by [2014KON/BEN], which was corrected here.

[2014KAT/UCH] measured the linear thermal expansion of hypostoichiometric plutonium dioxide, $PuO_{2-x}$, using dilatometry at a controlled oxygen partial pressure. The authors subsequently estimated the heat capacity of $PuO_{2-x}$ at constant volume $C_v$ (using a Debye function) plus the dilatational contribution $C_d$ from the experimentally determined coefficient of thermal expansion as detailed in Appendix A. The difference between the calculated ($C_v + C_d$) contributions for $PuO_{2.00}$ and the experimental heat capacity data of [1982OET] amounted to about 15 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, which was attributed to the effect of a Schottky term contributing to the experimental heat capacity.

The entropy and heat capacity values at 298.15 K for $PuO_2$(cr) recommended in this review are the same as in [2001LEM/FUG] and [2003GUI/FAN], but with slightly increased uncertainties:

$$S^{\circ}_{\mathrm{m}}(\mathrm{PuO_2},\mathrm{cr},298.15\ \mathrm{K}) = \mathbf{(66.13 \pm 0.30)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}},$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{PuO_2},\mathrm{cr},298.15\ \mathrm{K}) = \mathbf{(66.25 \pm 0.30)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Figure 11-3: Enthalpy increment data for $PuO_2$ selected by [2014KON/BEN] and [2001LEM/FUG] and comparison with experimental data

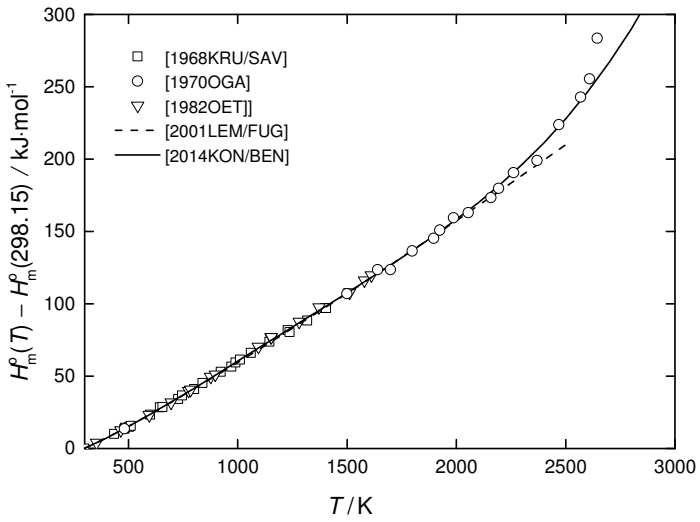
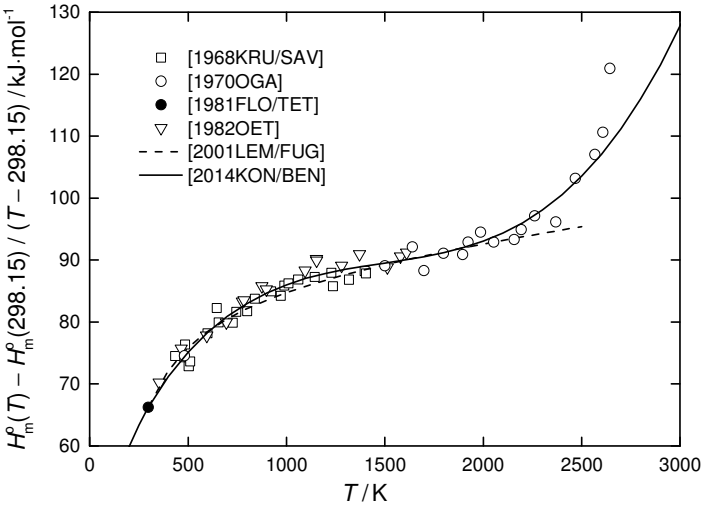



Figure 11-4: Calculated reduced enthalpy increments using the recommended equation by [2014KON/BEN] (solid line) and [2001LEM/FUG] (dashed line) in comparison with experimental data.



The data optimised by [2008GUE/CHA] and [2011GUE/DUP] are in very good agreement with the latter values. The enthalpy of formation of $PuO_2$(cr) was determined by oxygen combustion calorimetry of plutonium metal ([1957POP/IVA], [1958HOL/MUL], [1969JOH/DEV]). The value selected by [2001LEM/FUG] and [2003GUI/FAN] is retained in this review:

$$\Delta_f H^\circ_m(PuO_2, cr, 298.15\ K) = \mathbf{-\ (1055.8 \pm 1.0)}\ kJ\cdot mol^{-1}.$$

The data optimised in the thermodynamic assessment of [2008GUE/CHA] are somewhat lower, *i.e.* – (1060.3) $kJ\cdot mol^{-1}$. There are no data on the heat capacity or enthalpy of liquid $PuO_2$(cr) except for a single enthalpy measurement by [1970OGA]. In the review of [2014KON/BEN], the enthalpy of fusion was estimated assuming that the entropy of fusion of $PuO_2$(cr) is the same as for $UO_2$(cr) (24 $kJ\cdot mol^{-1}$). However, the reported result was not obtained by using the revised melting temperature. The enthalpy of fusion has thus been recalculated in the present review:

$$\Delta_{fus} H^\circ_m(PuO_2, cr, T_{fus}) = \mathbf{(72.5 \pm 6.0)}\ kJ\cdot mol^{-1}.$$

While [2001LEM/FUG] recommended $C^\circ_{p,m}(PuO_2, l, T) = 131\ J\cdot K^{-1}\cdot mol^{-1}$, [2014KON/BEN] selected

$$C^\circ_{p,m}(PuO_2, l, T) = \mathbf{70}\ J\cdot K^{-1}\cdot mol^{-1}$$

based on the data for $UO_2$(l), which shows a decrease from about 120 $J\cdot K^{-1}\cdot mol^{-1}$ near the melting point to about 84 $J\cdot K^{-1}\cdot mol^{-1}$ at 4500 K. The estimation of [2014KON/BEN] is accepted in this review.

To model the solubility of $PuO_2$(cr) in aqueous solution, Fanghänel and Neck [2002FAN/NEC] used $\log_{10} K^\circ_{sp}$ ($PuO_2$, cr) = – (64.0 ± 0.5), which was calculated from thermochemical data. This value can be used to evaluate the theoretical and experimental stabilities of Pu oxides, but it is not considered for selection by this review as it is derived from calculations.

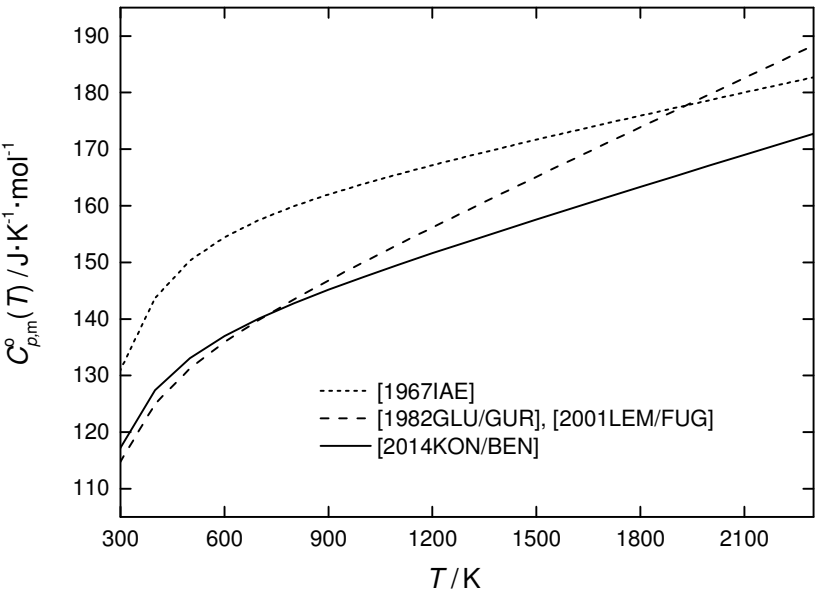
#### 11.2.2.1.2 $Pu_2O_3$(cr)

The stable phase of $Pu_2O_3$(cr) at room temperature is a hexagonal, type-A rare earth sesquioxide in space group $P\bar{3}m1$. [2014KON/BEN] assumed that the hexagonal type-A structure transformed to a H-type structure at $T_{tr}(A \rightarrow H) = (2300 \pm 50)$ K in analogy with the behaviour of the light lanthanide(III) sesquioxides. Although there is no experimental evidence for this transition, we accept this assumption in the present review.

There are no measurements of the heat capacity or enthalpy increment of $Pu_2O_3$(cr) at high temperatures. As shown in Figure 11-5, the heat capacity function recommended by [2014KON/BEN] was estimated by comparison with the actinide and lanthanide oxides, yielding values about 10 $J\cdot K^{-1}\cdot mol^{-1}$ lower than calculated by [1967IAE], [1982GLU/GUR], and [2001LEM/FUG]. The present review accepts the data of [2014KON/BEN] and selects the reported heat capacity function,

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Pu_2O_3, cr}, T) = 130.6670 + 18.4357\times10^{-3}T - 1.70530\times10^{6}T^{-2}\ (\mathrm{J\cdot K^{-1}\cdot mol^{-1}})\ .$$

Figure 11-5: Heat capacity function of hexagonal type-A $Pu_2O_3$(cr) sesquioxide.




The melting temperature of H-type $Pu_2O_3$(cr) was estimated as $T_{\mathrm{fus}}$ = (2352 ± 10) K based on the data of [1970RIL] and after correction to the International Temperature Scale of 1990 (ITS-90) by [2014KON/BEN], which is also selected in this review. This value is slightly lower than the value $T_{\mathrm{fus}}$ = (2358 ± 25) K recommended by [2001LEM/FUG] and [2003GUI/FAN] based on the data of Chikalla *et al.* [1964CHI/MCN], and rather low compared to the lanthanide sesquioxides and $Am_2O_3$ as discussed in [2014KON/BEN].

While the enthalpy of fusion of A-$Pu_2O_3$(cr) was estimated by [2001LEM/FUG] and [2003GUI/FAN] as $\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}(\mathrm{A\text{-}Pu_2O_3, cr}, T_{\mathrm{fus}})$ = (113 ± 20) kJ·mol$^{-1}$, Konings *et al.* [2014KON/BEN] considered the effect of the A→H transition at (2300 ± 50) K and suggested the following values, which are recommended by this review for scoping calculations:

$$\Delta_{\mathrm{tr}}H^{\circ}_{\mathrm{m}}(\mathrm{A\text{-}Pu_2O_3} \rightarrow H\text{-}\mathrm{Pu_2O_3}) = (32 \pm 10)\ \mathrm{kJ\cdot mol^{-1}},$$

$$\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}(\mathrm{H\text{-}Pu_2O_3, cr}, T_{\mathrm{fus}}) = (71 \pm 10)\ \mathrm{kJ\cdot mol^{-1}}.$$

The heat capacities of H-$Pu_2O_3$(cr) and $Pu_2O_3$(l) estimated by [2014KON/BEN] are also recommended by this review for scoping calculations:

$$C^{o}_{p,m}(\text{H-Pu}_2\text{O}_3, \text{cr}, T) = 165\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C^{o}_{p,m}(\text{Pu}_2\text{O}_3, \text{liq}, T) = 179\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

There are no direct measurements reported on the enthalpy of formation of $Pu_2O_3$(cr). However, this data was estimated in the literature based on the assessment by Markin and Rand [1966MAR/RAN] of the oxygen potential measurements in [1964MAR/BON] in the region between $PuO_{1.5}$ and $PuO_2$ as discussed in detail by [1990COR/KON], [1982GLU/GUR], [2001LEM/FUG], and [2014KON/BEN]. The data analysis refers to Reaction (11.24):

$$2\text{Pu}_2\text{O}_3(\text{cr}) + \text{O}_2(\text{g}) \rightleftharpoons 4\text{PuO}_2(\text{cr}) \qquad (11.24)$$

[2014KON/BEN] found $\Delta_f H^{o}_{m}(\text{Pu}_2\text{O}_3, \text{cr}, 298.15\ \text{K}) = -(1647 \pm 10)\ \text{kJ}\cdot\text{mol}^{-1}$, which is somewhat higher than $\Delta_f H^{o}_{m}(\text{Pu}_2\text{O}_3, \text{cr}, 298.15\ \text{K}) = -(1670 \pm 20)\ \text{kJ}\cdot\text{mol}^{-1}$ reported by [1982GLU/GUR] and $\Delta_f H^{o}_{m}(\text{Pu}_2\text{O}_3, \text{cr}, 298.15\ \text{K}) = -(1656 \pm 10)\ \text{kJ}\cdot\text{mol}^{-1}$ in [2001LEM/FUG]. The results of [2014KON/BEN] are based on the thermodynamic modelling assessment of [2011GUE/DUP] and cannot be retained in the present review for the reasons discussed in Appendix A. The value selected by [2001LEM/FUG] and [2003GUI/FAN] , $\Delta_f H^{o}_{m}(\text{Pu}_2\text{O}_3, \text{cr}, 298.15\ \text{K}) = -(1656 \pm 10)\ \text{kJ}\cdot\text{mol}^{-1}$, is retained in this review. The data optimised in the thermodynamic assessment of [2008GUE/CHA] are in very good agreement with the latter data.

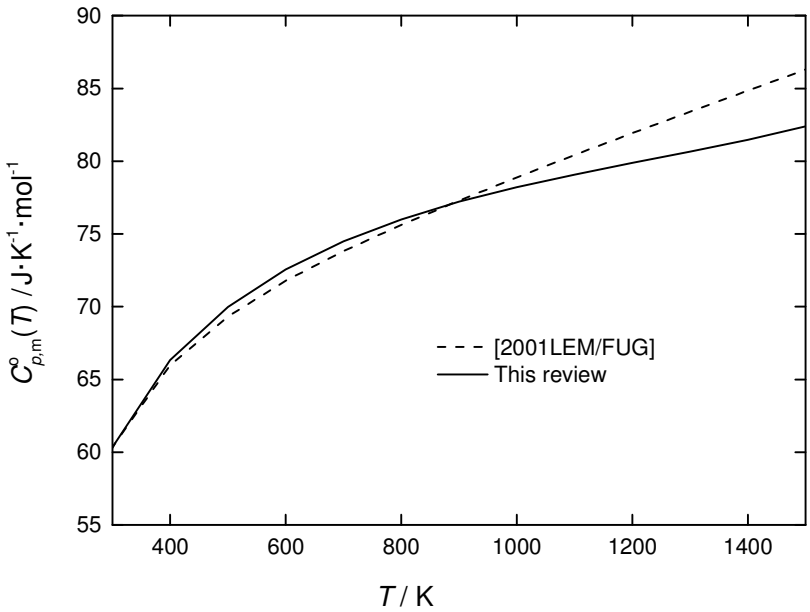
#### 11.2.2.1.3 $PuO_{1.61}$(cr)

There are no direct measurements of the thermodynamic functions of $PuO_{1.61}$(cr, bcc). The heat capacity of $PuO_{1.61}$(cr, bcc) was estimated by [2001LEM/FUG] using the weighted sum of $Pu_2O_3$(cr) and $PuO_2$(cr). Considering the newly determined heat capacity functions for $Pu_2O_3$(cr) and $PuO_2$(cr), the function for $PuO_{1.61}$(cr, bcc) is re-determined in this review as:

$$C^{o}_{p,m}(\text{PuO}_{1.61}, \text{bcc}, T) = 58.7251 + 40.6849\times10^{-3}T - 2.84361\times10^{-5}T^2 + 7.98358\times10^{-9}T^3 - 7.41537\times10^{5}T^{-2}\ (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$$

The heat capacity values calculated with this function are about 3 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ lower than previously recommended at 1300 K as shown in Figure 11-6.

Figure 11-6: Heat capacity function of $PuO_{1.61}$(cr) as recommended in this review and comparison with the data selected by [2001LEM/FUG], [2003GUI/FAN].




The enthalpy of formation and entropy of $PuO_{1.61}$(cr, bcc) were estimated in the review by [2001LEM/FUG] based on the oxygen potential measurements by Markin and co-workers ([1964MAR/BON], [1966MAR/RAN], and [1983TET]) and the partial molar enthalpies of solution of oxygen by Chereau *et al.* [1977CHE/DEA]. The final values chosen for $Pu_2O_3$(cr, bcc) and $PuO_{1.61}$(cr, bcc) were those providing the best compromise between the experimental values listed in Table 11-11 for the three Reactions (11.24)-(11.26):

$$100/11 Pu_2O_3(cr) + O_2(g) \rightleftharpoons 200/11 PuO_{1.61}(cr, bcc) \quad (11.25)$$

$$0.39 Pu_2O_3(cr) + 0.22 PuO_2(cr) \rightleftharpoons PuO_{1.61}(cr, bcc) \quad (11.26)$$

The previous analysis was re-assessed in this review to account for the newly recommended heat capacity functions for $Pu_2O_3$(cr) and $PuO_2$(cr). A good agreement between experimental and re-assessed values was obtained (see Table 11-11) as detailed in Appendix A. The enthalpy of formation and entropy values selected by [2001LEM/FUG] are therefore retained in this review:

$$\Delta_f H_m^o (PuO_{1.61}, bcc, 298.15\ K) = -(875.5 \pm 10.0)\ kJ{\cdot}mol^{-1}$$

$$S_m^o (PuO_{1.61}, bcc, 298.15\ K) = (83.0 \pm 5.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

Table 11-11: Reported thermochemical properties in $kJ{\cdot}mol^{-1}$ for interconversion reactions between plutonium oxides compared to data derived in NEA reviews.

| | $T$/K | Exp | Reference | [2001LEM/FUG] | This review |
|---|---|---|---|---|---|
| $\Delta_r G_m^o$ (11.24) | 1150 | – 624.8 | [1966MAR/RAN] | – 639.5 | – 624.1 |
| $\Delta_r H_m^o$ (11.24) | 1373 | – 875.6 | [1977CHE/DEA] | – 879.2 | – 870.1 |
| $\Delta_r H_m^o$ (11.25) | 1373 | – 826.5 | [1977CHE/DEA] | – 824.1 | – 822.5 |
| $\Delta_r G_m^o$ (11.25) | 2250 | – 547.8 | [1983TET] | – 548.0 | – 548.8 |
| $\Delta_r G_m^o$ (11.25) | 1600 | – 623.8 | [1966MAR/RAN] | – 619.2 | – 621.7 |
| $\Delta_r G_m^o$ (11.26) | 1100 | – 687.8 | [1966MAR/RAN] | – 660.0 | – 685.1 |
| $\Delta_r G_m^o$ (11.26) | 573 | – 0.2 | [1965GAR/MAR] | *ca* 0 | – 0.2 |

The values optimised in the thermodynamic assessment of [2008GUE/CHA], $\Delta_f H_m^o (PuO_{1.61}, bcc, 298.15\ K) = -867.2\ kJ{\cdot}mol^{-1}$ and $S_m^o (PuO_{1.61}, bcc, 298.15\ K) = 81.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, are in reasonable agreement with the selected data within the uncertainty limits.

#### 11.2.2.1.4 $PuO_{1.52}$ (cr)

There are no thermodynamic measurements on the pure $PuO_{1.52}$(cr, bcc) phase. Enthalpies of combustion have been reported by Chereau *et al.* [1977CHE/DEA] for uncharacterised samples with composition of O/Pu = 1.51 and 1.57, which may have contained significants amounts of the $PuO_{1.52}$(cr, bcc) phase. [2001LEM/FUG] reported $\Delta_f H_m^o (PuO_{1.52}, bcc, 298.15\ K) = -(845 \pm 10)\ kJ{\cdot}mol^{-1}$ based on the data of [1977CHE/DEA] and assuming that the uncharacterised sample $PuO_{1.57}$(cr) corresponded to a mixture of $PuO_{1.52}$(cr, bcc) and $PuO_2$(cr). The recent thermodynamic assessment by Guéneau *et al.* [2008GUE/CHA] using the CALPHAD method suggests a higher value, *i.e.*, $\Delta_f H_m^o (PuO_{1.52}, bcc, 298.15\ K) = -838\ kJ{\cdot}mol^{-1}$. Moreover, [2008GUE/CHA] found $S_m^o (PuO_{1.52}, bcc, 298.15\ K) = 80.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ using the least-squares optimisation procedure. We cannot select the latter values, which are not based on experimental determination, but recommend further investigations to solve the discrepancy regarding the enthalpy of formation and as to assess the standard entropy at 298.15 K.

#### 11.2.2.1.5 $Pu_4O_9$(cr)

Korzhavyi and co-workers [2004KOR/VIT] calculated the energy of reaction of $PuO_2$(cr) with oxygen or water by using spin-polarised, scalar-relativistic calculations of the Korringa-Kohn-Rostoker Green function method. The energy difference for the reaction

$$4PuO_2(cr) + 0.5O_2(g) \rightleftharpoons Pu_4O_9(cr) \qquad (11.27)$$

is + 1.1 eV for Pu and opposite to the exothermic reaction of U with $\Delta_r E = -0.9$ eV. Accordingly, $Pu_4O_9$(cr) is thermodynamically unstable under standard conditions and decomposes into $PuO_2$ and $O_2$. The reaction enthalpy and Gibbs energy for the reaction of $PuO_2$ with molecular oxygen is $\Delta_r H_m^o$ (11.27) = + 0.2 eV (19.3 kJ·mol$^{-1}$) and $\Delta_r G_m^o$ (11.27) = + 0.5 eV (48.2 kJ·mol$^{-1}$) compared to $\Delta_r H_m^o = -1.8$ eV (– 173.7 kJ·mol$^{-1}$) and $\Delta_r G_m^o = -1.5$ eV (– 144.7 kJ·mol$^{-1}$) for the reaction of $UO_2$ with $O_2$. This is in agreement with the general observation that higher U oxides are stable in air, while the corresponding higher Pu oxides decompose to form $PuO_2$ or $PuO_{2+x}$. Based on thermodynamic data of $UO_2$, $U_4O_9$ and $PuO_2$, the authors estimate $\Delta_f H_m^o$ ($Pu_4O_9$, cr) = – (4200 ± 15) kJ·mol$^{-1}$ and $\Delta_f G_m^o$ ($Pu_4O_9$, cr) = – (3950 ± 20) kJ·mol$^{-1}$. Similarly, the reaction

$$4PuO_2(cr) + 0.5H_2O(l) \rightleftharpoons Pu_4O_9(cr) + 0.5H_2(g) \quad (11.28)$$

is calculated to be strongly endothermic with $\Delta_r H^o$ (11.28) = + 3.2 eV (308.8 kJ·mol$^{-1}$) and $\Delta_r G^o$ (11.28) = + 2.8 eV (270.2 kJ·mol$^{-1}$), compared to $\Delta_r H^o = +1.2$ eV (115.8 kJ·mol$^{-1}$) and $\Delta_r G^o = +0.8$ eV (77.2 kJ·mol$^{-1}$) for the corresponding reaction (11.28) with U. The authors acknowledge the fact that actinide oxides such as $UO_2$ can overcome this energy barrier by reacting with oxidising agents such as radiolysis products of water. The authors calculate the reaction of $PuO_2$ with radiolytically produced atomic oxygen to be exothermic with $\Delta_r H^o$ (11.29) = – 2.3 eV (– 221.9 kJ·mol$^{-1}$) and $\Delta_r G^o$ (11.29) = – 1.9 eV (– 183.3 kJ·mol$^{-1}$) and $\Delta_r H^o$ (11.30) = – 2.8 eV (– 270.2 kJ·mol$^{-1}$) and $\Delta_r G^o$ (11.30) = – 2.9 eV (– 279.8 kJ·mol$^{-1}$).

$$4PuO_2(cr) + O(g) \rightleftharpoons Pu_4O_9(cr) \quad (11.29)$$

$$Pu_4O_9(cr) + O(g) \rightleftharpoons 4PuO_2(cr) + O_2(g) \quad (11.30)$$

The authors propose a surface-catalysed decomposition of hydrogen peroxide and a subsequent reaction of formed $Pu_4O_9$ with molecular oxygen according to

$$4PuO_2(cr) + H_2O_2(l) \rightleftharpoons Pu_4O_9(cr) + H_2O(l) \quad (11.31)$$

with $\Delta_r H^o$ (11.31) = – 0.8 eV (– 77.2 kJ·mol$^{-1}$) and $\Delta_r G^o$ (11.31) = – 0.6 eV (– 57.9 kJ·mol$^{-1}$). For the subsequent reaction

$$Pu_4O_9(cr) + H_2O_2(l) \rightleftharpoons 4PuO_2(cr) + H_2O(l) + O_2(g) \quad (11.32)$$

$\Delta_r H^o$ (11.32) = – 1.3 eV (– 125.4 kJ·mol$^{-1}$) and $\Delta_r G^o$ (11.32) = – 1.6 eV (– 154.4 kJ·mol$^{-1}$) are obtained. Based on these calculations and the endothermic nature of the oxidation of $PuO_2$(cr) by water, Korzhavy and co-workers suggest that under oxic conditions the mixed-valent $PuO_{2+x}$(cr) is only formed as an intermediate and should ultimately form stable $PuO_2$(cr). This proposition is not supported by experimental observations of the formation and stability of $PuO_{2+x}$(cr) in the presence of trace water or air ([2002HAS/OVE], [2013EKB/LAR], [2007NEC/ALT], [2007NEC/ALT2], [2007NEC/ALT3]. Ekberg and co-workers [2013EKB/LAR] report that upon contact of crystalline $PuO_2$ with water a significant shortening of the Pu–O bond distances in the

first coordination shell is observed by EXAFS, indicating that the Pu atoms in the surface of the $PuO_2$ particles become oxidised to form hyper-stoichiometric Pu(IV) oxide with oxidised Pu in the surface.

To support the first-principle calculations of [2004KOR/VIT], [2007GOU/SEI] reported a combined UV photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) study of $PuO_2$ exposed to atomic oxygen. Their results excluded possible bulk oxidation of $PuO_2$, and suggested that only the outer surface could chemisorb extra oxygen, which was moreover released when heating at 473 K. This suggested $Pu_4O_9$ to be unstable in the presence of atomic oxygen, and decomposing back to $PuO_2$ while generating molecular oxygen $O_2$ in accordance with the calculations of [2004KOR/VIT].

#### 11.2.2.2 Hydrated plutonium oxides and hydroxides

The solubility of plutonium oxyhydroxides has been discussed and evaluated in detail in [2001LEM/FUG] and in [2003GUI/FAN]. Thermodynamic data have been selected for $Pu(OH)_3$(cr), $PuO_2$(am, hyd), $PuO_2OH$(am), and $PuO_2(OH)_2{\cdot}H_2O$(cr). Fanghänel and Neck [2002FAN/NEC] applied thermodynamic data in the NEA TDB and reviewed additional experimental data to discuss the solubility of actinide oxides and oxyhydroxide phases in carbonate-free aqueous systems. Experimentally determined solubilities of actinide solid phases were evaluated as function of several parameters, such as crystallinity, particle size, pH and calculated stabilities. Since the last review, additional solubility studies have been reported with $PuO_2(OH)_2$(am) [2003FUJ/YAM] and $PuO_2{\cdot}xH_2O$(am) [2002FUJ/YAM] as the solubility-limiting solid phases. Neck and co-workers [2007NEC/ALT2] calculated a number of thermodynamic data for An(IV,V,VI) oxides and oxyhydroxides. To enable comparison with the An(IV) oxides, the $\Delta_f G_m^o$ values of oxyhydroxides of An(VI) were converted to $\Delta_f G_m^o$ values for the corresponding An(VI) binary oxides, $AnO_3$(cr, hyd). From $\Delta_f G_m^o$ ($PuO_2(OH)_2{\cdot}H_2O$, cr) = – 1442.4 kJ·mol$^{-1}$ reported in [2003GUI/FAN] the value of $\Delta_f G_m^o$ ($PuO_3$, cr, hyd) = – 968.1 kJ·mol$^{-1}$ was derived. The standard molar Gibbs energies for the hydrated phase fractions in the mixed-valent $PuO_{2+x}{\cdot}nH_2O$(cr) phase were calculated from auxiliary data in the NEA TDB for the anhydrous Pu oxides, $\Delta_f G_m^o$ ($PuO_{2.25}$, cr, hyd) ≥ – (968.4 ± 4.7) kJ·mol$^{-1}$ and $\Delta_f G_m^o$ ($PuO_{2.5}$, cr, hyd) > – (971.2 ± 5.4) kJ·mol$^{-1}$. The $\Delta_f G_m^o$ for pure $PuO_{2.5}$(cr, hyd) is estimated to be – (965 ± 7) kJ·mol$^{-1}$, which is slightly higher than the formal value of the $PuO_{2.5}$(cr, hyd) fraction in the mixed solid phase $PuO_{2+x}{\cdot}nH_2O$(s). Since these values are derived from calculations and are considered estimates, we are not considering these data in our selected data set.

##### 11.2.2.2.1 Plutonium(VI) hydrated oxides and hydroxides

Experimental data on the solubility of Pu(VI) hydroxide has been discussed in [2001LEM/FUG] and a thermodynamic equilibrium constant was selected for the reaction

$$PuO_2(OH)_2{\cdot}H_2O(cr) + 2H^+ \rightleftharpoons PuO_2^{2+} + 3H_2O(l)\ ,\ \log_{10}{}^{*}K^{o}_{s,0} = (5.500 \pm 1.000).$$

[2001LEM/FUG] assumed $PuO_2(OH)_2{\cdot}H_2O$(cr), as characterised by [1970CLE2], to be the solubility-controlling solid phase in solubility studies that were evaluated in [2001LEM/FUG]. However, none of the reported solubility studies have properly characterised the solubility-limiting solid phases. Assuming the presence of the Pu(VI) hydroxide monohydrate in all reported solubility studies is highly speculative and degrees of crystallinity and hydration may vary due to different experimental conditions. In the absence of any solid phase characterisation, the solid phase could be $PuO_2(OH)_2$(am, hyd) or a more crystalline phase such as $PuO_2(OH)_2{\cdot}nH_2O$(cr) with a variable number *n* of crystal waters. The differences in the thermodynamic properties of solid phases can be significant when exposed to high-energetic alpha-particles and radiation damage causes degradation of crystallinity. Consequentially, the assignment of solid Pu(VI) hydroxides as amorphous or crystalline phases is complicated and only of nominal value for estimating Gibbs free energies.

Fanghänel and Neck [2002FAN/NEC] used the value $\log_{10}K^{o}_{sp} = -(22.5 \pm 0.4)$ to model the solubility of $PuO_2(OH)_2$(cr). From the standard molar Gibbs energy, $\Delta_f G^{o}_{m}$ ($PuO_2(OH)_2{\cdot}H_2O$, cr) = – 1442.4 kJ·mol$^{-1}$, Neck *et al.* [2007NEC/ALT2] calculated $\Delta_f G^{o}_{m}$ ($PuO_3$, cr) = – (952 ± 10) kJ·mol$^{-1}$ for the binary Pu(VI) oxide, which is much lower than the value for the analogous U(VI) system, which ranges between – 1135.3 kJ·mol$^{-1}$ and – 1145.7 kJ·mol$^{-1}$ for the different $UO_3$(cr) phases. However, this estimated value for $PuO_3$(cr) follows the same trend as for the Np(IV), Np(V) and Np(VI) oxides and is in line with the estimated value for $\Delta_f G^{o}_{m}$ ($NpO_3$, cr).

Since the last review only one new experimental investigation of the solubility of Pu(VI) hydroxide has been reported. Fujiwara and co-workers [2003FUJ/YAM] determined solubility data for Pu(VI) hydroxide in 0.1-1 M $NaClO_4$ solutions and interpreted the measured solubility data with the dissolution equilibrium

$$PuO_2(OH)_2(am, hyd) \rightleftharpoons PuO_2^{2+} + 2OH^- \qquad (11.33)$$

The authors concluded from the reddish-gold color of the solid phase and the high redox potentials of the solutions that the solid phase is $PuO_2(OH)_2$(s). The experimentally determined solubility products (see Table 11-12) were corrected for ionic strength using the SIT. Fujiwara *et al.* derived the thermodynamic solubility product, $\log_{10}K^{o}_{sp}$ (11.33) = – (22.88 ± 0.39) and the ion-interaction parameter $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.30 \pm 0.09)$ from the SIT plot. The value of $\varepsilon(PuO_2^{2+}, ClO_4^-)$ reported in that study is slightly lower compared to the accepted value of (0.46 ± 0.05) in [2001LEM/FUG], which was derived by analogy from $\varepsilon(UO_2^{2+}, ClO_4^-)$. Assuming a more crystalline solid phase in equilibrium (11.33) and using the reported equilibrium constant $\log_{10}K^{o}_{sp}$ (11.33) = – (22.88 ± 0.39), we could obtain $\log_{10}{}^{*}K^{o}_{VI,s}$ (11.34) = (5.12 ± 0.39) assuming $PuO_2(OH)_2{\cdot}H_2O$(cr) as the solubility-controlling solid phase:

$$PuO_2(OH)_2{\cdot}H_2O(cr) + 2H^+ \rightleftharpoons PuO_2^{2+} + 3H_2O(l) \qquad (11.34)$$

which is consistent with $\log_{10}{}^{*}K^{\circ}_{\mathrm{VI,s}}(11.34) = (5.50 \pm 1.00)$ or $\log_{10}K^{\circ}_{sp}(11.33) = -(22.50 \pm 1.00)$ selected in [2001LEM/FUG].

Table 11-12: Experimental solubility constants for the dissolution equilibrium (11.33).

| $T$/K | Method | $I$ (medium) | $\log_{10}K^{'}_{sp}$ | References |
|---|---|---|---|---|
| 298 | sol | 0.1M $NaClO_4$ | – (22.27 ± 0.32) | [2003FUJ/YAM] |
| 298 | sol | 0.5M $NaClO_4$ | – (22.00 ± 0.07) | [2003FUJ/YAM] |
| 298 | sol | 1.0M $NaClO_4$ | – (22.03 ± 0.13) | [2003FUJ/YAM] |

The thermodynamic equilibrium constant selected in [2001LEM/FUG], $\log_{10}{}^{*}K^{\circ}_{\mathrm{VI,s}}(11.34) = (5.50 \pm 1.00)$, was derived as an average of four solubility data listed in Table 11-13. As in the case of the new study by Fujiwara *et al.*, all previous experimental studies lack the characterisation of the solid equilibrium phase. This review disagrees with the acceptance criteria used for the original data and the selected value in [2001LEM/FUG]. While the solubility product reported in [1984KIM/BER] appears to be estimated, the data in [1986LIE/KIM] and [1995PAS/KIM] were obtained from a series of solubility measurements under controlled conditions. The data in [1962MOS/ZAI] is based on a single measurement of ammonium plutonate after equilibration of up to six hours at room temperature. In [1973MUS/POR], details on experimental conditions and analysis methods are not provided and we cannot evaluate how the reported solubility product was obtained. Consequently, the data reported in [1973MUS/POR] and [1984KIM/BER] are not accepted by this review. This review accepts the data reported in [1962MOS/ZAI], in [1984LIE/KIM] and [1995PAS/KIM] at $I = 0.1$ mol·L$^{-1}$, and in [2003FUJ/YAM] at $I = 0.1$, 0.5 and 1 mol·L$^{-1}$ (see Figure 11-7), and we select the revised average value of:

$$\log_{10}K^{\circ}_{sp}\ ((11.33), 298.15\ \mathrm{K}) = \mathbf{-\ (22.83 \pm 0.65)},$$

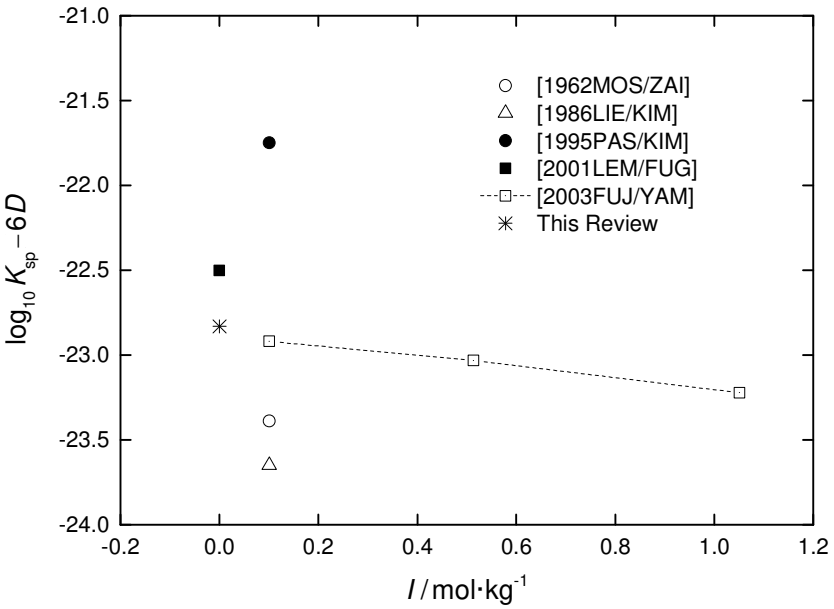
for the dissolution Reaction (11.33) and hence, $\Delta_r G^{\circ}_m(11.33) = (130.315 \pm 3.710)$ kJ·mol$^{-1}$. The corresponding revised thermodynamic equilibrium constant for Reaction (11.34) is

$$\log_{10}{}^{*}K^{\circ}_{\mathrm{VI,s}}((11.34), 298.15\ \mathrm{K}) = (5.17 \pm 0.65).$$

Table 11-13: Thermodynamic equilibrium constants for $PuO_2(OH)_2$(am, hyd) evaluated in [2001LEM/FUG] and in this review (in italics).

| $T$/K | Method | $I$ (medium) | $\log_{10}K^{\circ}_{\mathrm{VI,s}}$ (11.33) | $\log_{10}K^{\circ}_{\mathrm{VI,s}}$ (11.34) | References |
|---|---|---|---|---|---|
| *298* | *sol* | *0.1-1.0 M $NaClO_4$* | *– (22.88 ± 0.39)* | *(5.12 ± 0.39)* | *[2003FUJ/YAM]* |
| 298 | sol | 0.1 M $NaClO_4$ | – (21.7 ± 0.1) | (6.3 ± 0.1) | [1995PAS/KIM] |
| 298 | sol | | – 23.3 | | [1962MOS/ZAI] |
| 298 | sol | | – (24.04 ± 0.19) | | [1973MUS/POR] |
| 298 | sol | 0.1 M $NaClO_4$ | – 22 | | [1984KIM/BER] |
| 298 | sol | 0.1 M $NaClO_4$ | – 23.6 | 4.4 | [1986LIE/KIM] |

Figure 11-7: Extrapolation of experimental equilibrium constants to $I = 0$ using the SIT for the dissolution equilibrium of $PuO_2(OH)_2$(am, hyd) according to Eq. (11.33). The thermodynamic solubility constant, $\log_{10} K^{o}_{sp}$ (11.33) = – (22.83 ± 0.65), is compared with $\log_{10} K^{o}_{sp}$ (11.33) = – (22.50 ± 1.00) recommended in [2001LEM/FUG].




If we assume $PuO_2(OH)_2{\cdot}H_2O$(cr) as the solid equilibrium phase, we can estimate from $\Delta_r G^{o}_{m}$ (11.34) = (29.511 ± 3.710) kJ·mol$^{-1}$ the Gibbs energy of formation $\Delta_f G^{o}_{m}$ ($PuO_2(OH)_2{\cdot}H_2O$, cr) = – (1444.262 ± 2.895) kJ·mol$^{-1}$. Due to the lack of solid phase characterisation, the values for a potential $PuO_2(OH)_2{\cdot}H_2O$(cr) solid phase are not selected by this review and provided for information only. No formation data ($\Delta_f G^{o}_{m}$) are selected for the solid phase $PuO_2(OH)_2$(am, hyd) due to the unknown number of hydration water.

#### 11.2.2.2.2 Hydrated $PuO_2OH$(am, hyd)

Only few reports are available on the investigation of the solubility of Pu(V) hydroxide. The evaluation of the experimental data available in [2001LEM/FUG] resulted in the selection of the equilibrium constant for the reaction:

$$PuO_2OH(am,hyd) + H^+ \rightleftharpoons PuO_2^+ + H_2O(l),\ \log_{10}{}^{*}K^{o}_{v,s} = (5.000 \pm 0.500).$$

Fanghänel and Neck [2002FAN/NEC] compared experimental solubility data of actinide oxide and hydroxide phases with predicted solubilities calculated from thermodynamic data in the NEA TDB. To model the solubility of $PuO_2OH$(am, hyd)

Fanghänel and Neck used $\log_{10} K^{\circ}_{sp} = -(9.0 \pm 0.4)$, which is close to the selected value for the analogous Np(V) and Am(V) solid phases, $\log_{10} K^{\circ}_{sp} = -(8.7 \pm 0.5)$. This review retains the data selected in [2001LEM/FUG] and [2003GUI/FAN].

#### 11.2.2.2.3 Plutonium(IV) hydrated oxides and hydroxides

The solubility of Pu(IV) in aqueous systems in the absence of other coordinating ligands is a complex system involving hydrolysis reactions in solution, solid phase transformations associated with Pu(IV) oxide and oxyhydroxides and the formation of colloidal Pu(IV) particles. Two Pu(IV) solid phases, $PuO_2$(cr) and $Pu(OH)_4$(am, hyd) (or $PuO_2 \cdot 2H_2O$), have been identified in the past as the main solid equilibrium phases. The evaluation of the experimental data available in [2001LEM/FUG] resulted in the selection of $\log_{10} K^{\circ}_{s,IV} = -(58.0 \pm 1.0)$, which was revised in [2003GUI/FAN] to

$$PuO_2(am, hyd) + 2H_2O(l) \rightleftharpoons Pu^{4+} + 4OH^-, \quad \log_{10} K^{\circ}_{s,IV} = -(58.330 \pm 0.520).$$

In recent years, the oxidation of Pu(IV) solid phases under aerobic conditions to form a mixed-valent solid phase, $PuO_{2+x}$(cr), has been discussed ([2002HAS/OVE], [2002HAS/BAS], [2007NEC/ALT], [2007NEC/ALT2], [2007NEC/ALT3]). Since the last NEA update, two reviews on the solubility behaviour of Pu(IV) oxyhydroxides ([2002HAS/BAS] and [2002FAN/NEC]), and two experimental studies ([2013EKB/LAR] and [2004ROT/WAL]) on the formation and structure of colloidal Pu particles have been published.

Fanghänel and Neck [2002FAN/NEC] used thermodynamic data for $Pu(OH)_4$(am) and $PuO_2$(cr) to calculate the solubility behaviour of Pu(IV) in aqueous solution. The thermodynamic data for Pu oxyhydroxide solid phases used in [2002FAN/NEC] are listed in Table 11-14. The impact of colloid formation on the overall solubility of An(IV) oxyhydroxides is illustrated by the analogous Th(IV) system, but similar colloid formation is known to occur with Pu(IV).

Table 11-14: Thermodynamic solubility products for Pu oxyhydroxide solid phases used in the solubility calculations by Fanghänel and Neck [2002FAN/NEC]. The $\log_{10}{}^{*} K^{\circ}_{s}$ values are those selected in [2003GUI/FAN].

| Oxidation state | Solid phase | $\log_{10} K^{\circ}_{s}$ | $\log_{10}{}^{*} K^{\circ}_{s}$ | Reference |
|---|---|---|---|---|
| Pu(III) | $Pu(OH)_3$(am) | $-(26.2 \pm 1.5)$ | $(15.80 \pm 1.50)$ | [2002FAN/NEC] |
| Pu(IV) | $Pu(OH)_4$(am) | $-(58.5 \pm 0.7)$ | | [2002FAN/NEC] |
| Pu(IV) | $PuO_2$(cr) | $-(64.0 \pm 0.5)$ | | [2002FAN/NEC] |
| Pu(V) | $PuO_2OH$(am) | $-(9.0 \pm 0.5)$ | $(5.0 \pm 0.5)$ | [2002FAN/NEC] |
| Pu(VI) | $PuO_2(OH)_2$(s) | $-(22.5 \pm 1.0)$ | $(5.5 \pm 1.0)$ | [2002FAN/NEC] |

Haschke and Bassett [2002HAS/BAS] evaluated their thermodynamic model with respect to experimental data for the dissolution behaviour of $PuO_2$(cr) and

$Pu(OH)_4$(am) in aerobic aqueous solutions. The authors claim that the experimental observations are inconsistent with the current thermodynamic and kinetic models and that the dissolution of $PuO_2$(cr) is not an equilibrium process. The dissolution kinetics of $PuO_2$(cr) and the soluble steady-state concentrations of Pu are kinetically controlled by the rate at which Pu(V) dissolves into the solution. The authors conclude from reported solubility data that $Pu(OH)_4$(am) is a metastable phase and does not represent a thermodynamic equilibrium, as a consequence the estimated solubility can be overestimated. A transformation of both $PuO_2$(am) and $Pu(OH)_4$(am) into a more-crystalline $PuO_2$(cr) is proposed. The transformation reaction:

$$Pu(OH)_4(am) \rightarrow PuO_2(cr) + 2H_2O(l) \qquad (11.35)$$

is associated with a Gibbs energy of $\Delta G_m^o$ (298 K) = – 41 kJ·mol$^{-1}$ and this solid phase transformation reaction should result in lower soluble Pu concentrations. Although Haschke and Bassett identify a dependence of the $PuO_2$(s) dissolution rates on the formation of Pu(V), they discuss the solid phase transformation with Pu solely in its tetravalent oxidation state. The experimental data can also be explained with the formation of a mixed-valent solid phase, that releases Pu(V) into solution. Such a phase has been identified in experimental studies as $PuO_{2+x}$(cr) and is accepted to form as a solid equilibrium phase in aqueous systems under aerobic conditions.

#### 11.2.2.2.3.1 Pu(IV) colloidal particles

The polymerisation of Pu(IV) hydrolysis species results in the formation of colloidal particulates that have an important influence on solution speciation and Pu(IV) solubility. From the results of EXAFS studies, Ekberg and co-workers [2013EKB/LAR] established that the reaction of aged and freshly prepared $PuO_2$ with water results in the formation of colloidal Pu particles. Upon contact of crystalline $PuO_2$ with water, a significant shortening of the Pu-O distances in the second coordination shell is observed indicating that the Pu atoms in the surface of the $PuO_2$ particles become oxidised. With the ageing of the Pu colloids their size decreases and the resulting colloidal particles contain only 3-4 Pu atoms with a very $PuO_2$(cr)-like coordination. However, the mean Pu-O and Pu-Pu distances are shorter than in $PuO_2$(cr) due to partial oxidation.

Rothe *et al.* [2004ROT/WAL] studied the structure and stability of Pu(IV) colloidal particles by using EXAFS and LIBD. The LIBD data show two sets of mean particle diameters of about 12 and 24 nm with their solubility matching the predicted solubility calculated by using $\log_{10} K_{sp}^o = -(58.7 \pm 0.3)$. The onsets of colloid formation indicated the presence of $[Pu(OH)_2]_n^{2n+}$ species. Monomeric Pu(IV) hydroxo complexes such as $Pu(OH)_2(H_2O)_6^{2+}$ are postulated as reactants that hydrolyse and condensate to form larger charge-neutral, polymeric species. No new thermodynamic data were provided in this study.

Neck and co-workers ([2007NEC/ALT], [2007NEC/ALT2], [2007NEC/ALT3]) evaluated solubility data at pH > 4 where Pu(IV) colloids are a

significant part of the total Pu concentration in solution. The authors [2007NEC/ALT] discussed the presence of a constant amount of small Pu(IV) colloids at $\log_{10}[\text{Pu(IV)}]_{\text{coll}} = -(8.3 \pm 1.0)$ in neutral to alkaline solutions and describe the colloid formation with $\log_{10} K^{\circ}_{\text{IV,s.coll}} = -(8.3 \pm 1.0)$ for the reaction

$$\text{PuO}_2\text{(am, hyd)} \rightleftharpoons \text{PuO}_2\text{(coll, hyd)} \tag{11.36}$$

For this equilibrium reaction Neck and co-workers described $PuO_2$(coll, hyd) as polymeric Pu(IV) oxyhydroxide species. Although the exact composition of the Pu(IV) colloids are uncertain, the existence of soluble polymeric forms of Pu(IV) oxyhydroxide is confirmed by ultrafiltration studies. The redox potentials at pH > 4 are described by the postulated equilibrium between $PuO_2$(coll, hyd), $PuO_{2.5}$(am, hyd) and $PuO_2^+$(aq) with $\log_{10}{}^{*}K^{\circ} = -(11.5 \pm 1.5)$ for Reaction (11.37):

$$\text{PuO}_2\text{(coll, hyd)} + 0.5\text{H}_2\text{O(l)} \rightleftharpoons \text{PuO}_{2.5}\text{(am, hyd)} + \text{e}^- + \text{H}^+ \tag{11.37}$$

From this equilibrium constant and $\Delta_f G^{\circ}_m$ ($PuO_2$, am, hyd) = – (965.5 ± 4.0) kJ·mol$^{-1}$, Neck *et al.* calculate $\Delta_f G^{\circ}_m$ ($PuO_2$, coll, hyd) = – (918.1 ± 7.0) kJ·mol$^{-1}$. The Pu colloids in aqueous solutions contain only Pu(IV) and are in equilibrium with $PuO_2^+$ dissolved in the aqueous phase according to the proposed equilibrium Reaction (11.38):

$$\text{PuO}_2\text{(coll, hyd)} \rightleftharpoons \text{PuO}_2^+ + \text{e}^- \tag{11.38}$$

The concentration of $PuO_2^+$(aq) in (11.38) is limited by the solubility of $PuO_{2.5}$(am, hyd) in $PuO_{2+x}$(am, hyd). The equilibrium constant for Reaction (11.38), $\log_{10} K^{\circ}_{\text{IVcoll.V}} = -(11.5 \pm 1.3)$, is derived from using $\Delta_f G^{\circ}_m$ ($PuO_2$, am, hyd) = – (965.5 ± 4.0) kJ·mol$^{-1}$ and $\Delta_f G^{\circ}_m$ ($PuO_2^+$) = – (852.65 ± 2.87) kJ·mol$^{-1}$ from [2001LEM/FUG] and [2003GUI/FAN], and $\Delta_f G^{\circ}_m$ ($PuO_2$, coll, hyd) = – (918.1 ± 7.0) kJ·mol$^{-1}$.

This review has reported the average standard molar Gibbs energy of formation reported in [2007NEC/ALT3], $\Delta_f G^{\circ}_m$ ($PuO_2$, coll, hyd) = – (918.1 ± 7.0) kJ·mol$^{-1}$, and the equilibrium constant, $\log_{10} K^{\circ}_{\text{IV,s.coll}}$ ((11.36), 298.15 K) = – (8.3 ± 1.0), only for information, because of the uncertainties associated with the composition of the colloidal particles and the degree of polymerisation.

#### 11.2.2.2.3.2 $PuO_2$(am, hyd)

The solubility of Pu(IV) oxides has been subject to investigations for many years and $Pu(OH)_4$(am) (or $PuO_2 \cdot 2H_2O$) has been identified as an important solid equilibrium phase. Experimental solubility data of $Pu(OH)_4$(am) have been reviewed and a revised thermodynamic constant was selected in [2003GUI/FAN]:

$$\text{Pu}^{4+} + 4\text{OH}^- \rightleftharpoons \text{PuO}_2\text{(am, hyd)} + 2\text{H}_2\text{O(l)}\ ,\ \log_{10} K^{\circ}_s = (58.330 \pm 0.520).$$

In [2001NEC/KIM] and [2002FAN/NEC], Neck and co-workers reported the thermodynamic solubility product $\log_{10} K^{\circ}_{sp}$ ($Pu(OH)_4$, am) = – (58.5 ± 0.7), which is very close to the selected value in [2003GUI/FAN], $\log_{10} K^{\circ}_s$ ($Pu(OH)_4$, am, hyd) =

– (58.33 ± 0.52). Since this new value is within the uncertainty of the previously selected value, $\log_{10} K_s^o$ (Pu(OH)$_4$, am, hyd) = – (58.33 ± 0.52), is retained in this review.

A few new studies have been reported since the last review. The aging behaviour of Pu(IV) oxide, $PuO_2 \cdot xH_2O$, in 1-15 M NaOH solutions under air atmosphere was studied by Delegard [2013DEL]. The prepared Pu(IV) solid phases were undergoing significant particle growth from about 1.9 nm to about 5 nm within about three years. The experiments that started from Pu(VI) produced larger particle sizes of up to about 9 nm in 1 M NaOH, which is explained by radiolytic alterations of the initial Pu(VI) phases.

Felmy and co-workers in [2013FEL/MOO] studied the reduction of $^{239}PuO_2$(am, hyd) by Fe(II). The authors used data from [2001LEM/FUG] to derive $\log_{10} K$ = 15.7 for the reductive dissolution reaction:

$$PuO_2(am, hyd) + 4H^+ + e^- \rightleftharpoons Pu^{3+} + 2H_2O(l) \qquad (11.39)$$

This data is consistent with $\log_{10} K$ = 15.5 in [2002RAI/GOR] and 15.4 in [2007NEC/ALT]. The authors claim that the inclusion of the measured Fe(II) concentration and associated equilibrium with Fe(OH)$_3$(s) according to Reaction (11.40) improved the accuracy of predicted Pu(III) solubilities.

$$PuO_2(am, hyd) + H^+ + Fe^{2+} + H_2O(l) \rightleftharpoons Pu^{3+} + Fe(OH)_3(am) \qquad (11.40)$$

However, as illustrated in Figure 6a-c in [2013FEL/MOO], the solubility data predicted according to Equation (11.40) represent well the long-time Pu(III) concentrations, but do not match the total experimental Pu concentrations in the aqueous phase. The Pu solubility calculated according to Equation (11.40) is lower than the measured solubility by up to one order of magnitude. The presence of hematite had little impact on the overall solubility of $PuO_2$(am), which was predicted from measured pH and Fe(II) concentrations by using $\log_{10} K$ = – 0.6 for Reaction (11.40).

Kulyako and co-workers [2002KUL/FUJ] reported the solubility of Pu(IV) hydroxide to be about $10^{-8}$ M in simulated carbonate-free groundwater at pH 7-9. The solubility of pure Pu(IV) hydroxide is found to be below the Pu(IV) solubility of a mixed U(VI)-Pu(IV) solid phase and was measured from undersaturation to vary between (4.4-7.0) × $10^{-7}$ M. No thermodynamic data were reported in this study.

New experimental solubility data of $PuO_2 \cdot xH_2O$(s) in 0.5-2 M $NaClO_4$ and associated equilibrium constants are reported in [2002FUJ/YAM]. The solubility data obtained from both under- and oversaturation at pH < 6 were interpreted with the reaction

$$PuO_2 \cdot xH_2O(am, hyd) + e^- \rightleftharpoons Pu^{3+}(aq) + 4OH^- + (x-2)H_2O(l) \qquad (11.41)$$

due to the fact that only Pu(III) signatures were observed spectroscopically. The authors used the redox potential for the Pu(IV)/(III) couple reported by Capdevila and Vitorge [1998CAP/VIT] to calculate the solubility product for the reaction:

$$PuO_2 \cdot xH_2O(am, hyd) \rightleftharpoons Pu^{4+} + 4OH^- + (x-2)H_2O(l) \quad (11.42)$$

The conditional solubility constants obtained by Fujiwara *et al.* are listed in Table 11-15. From the SIT plot Fujiwara *et al.* derived the thermodynamic equilibrium constant $\log_{10} K^{\circ}_{s,IV}$ (11.42) = – (57.97 ± 0.24) and the SIT ion-interaction parameter $\varepsilon(Pu^{4+}, ClO_4^-) = (0.99 \pm 0.20)$. Both data are in good agreement with the values of $\log_{10} K^{\circ}_{s,IV}$ (11.42) = – (58.330 ± 0.520) and $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)$, selected in [2003GUI/FAN], which are retained in this review.

Table 11-15: Experimental solubility constants for the dissolution equilibrium $PuO_2 \cdot xH_2O(am, hyd) \rightleftharpoons Pu^{4+} + 4OH^- + (x-2)H_2O(l)$.

| $T$/K | Method | $I$ (medium) | $\log_{10} K^{\circ}_{s,IV}$ (11.37) | Reference |
|---|---|---|---|---|
| 298 | sol[(a)] | 1.0 M $NaClO_4$ | – (54.67 ± 0.24) | [2002FUJ/YAM] |
| 298 | sol[(b)] | 0.5 M $NaClO_4$ | – (55.46 ± 0.18) | [2002FUJ/YAM] |
| 298 | sol[(b)] | 1.0 M $NaClO_4$ | – (54.26 ± 0.12) | [2002FUJ/YAM] |
| 298 | sol[(b)] | 2.0 M $NaClO_4$ | – (56.01 ± 0.08) | [2002FUJ/YAM] |

(a) Experiments from oversaturation.
(b) Experiments from undersaturation.

A set of new solubility data of Pu(IV) in alkaline concentrated $CaCl_2$ and $MgCl_2$ solutions have been reported. The solubility of $Pu(OH)_4$(am) in alkaline $MgCl_2$ [2009ALT/NEC] and $CaCl_2$ ([2008ALT/NEC], [2010FEL/NEC]) solutions was studied and compared with similar studies of Th(IV) and Np(IV) conducted by the same group. The authors assumed the solid equilibrium phase to be $PuO_2 \cdot 2H_2O$(am) or $Pu(OH)_4$(am), similar to the compositions found in the hydrous oxides of Th(IV) and Tc(IV). The steep solubility increase at $-\log_{10}[H^+] \geq 11$ is described by the formation of the soluble complex $Ca_4[Pu(OH)_8]^{4+}$ in analogy with the corresponding Th(IV) system. It is of interest to note that the increase in Pu(IV) solubility due to the formation of $Ca_4[Pu(OH)_8]^{4+}$ in solution at high pH is only observed at $[CaCl_2] \geq 2.0$ M, in contrast to the formation of analogous Zr(IV) and Th(IV) complexes in solutions with $[CaCl_2] \geq 0.5$ M. The corresponding solubility behaviour of Np(IV) coincides with that of Pu(IV) and the formation of $Ca_4[Np(OH)_8]^{4+}$ is not observed in solutions containing less than 2.0 M $[CaCl_2]$. The conditional equilibrium constant for the formation of $Ca_4[Pu(OH)_8]^{4+}$ $\log_{10}{}^{*}K'_{s,(4,1,8)} = -(57.30 \pm 0.15)$ in 2 M $CaCl_2$ is determined from the dissolution Reaction (11.43) where An = Pu:

$$An(OH)_4(am) + 4Ca^{2+} + 4H_2O(l) \rightleftharpoons Ca_4[An(OH)_8]^{4+} + 4H^+ \quad (11.43)$$

As this Pu(IV) complex forms only at high ionic strength, the authors used both the SIT and the Pitzer formalism to calculate the equilibrium constant for Reaction (11.43). The SIT approach results in $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)}$ (11.43) = – (58.5 ± 0.4). The

equilibrium constant $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)}$ (11.43) is closely linked to the solubility product of $Pu(OH)_4(am)$, $\log_{10}K^{\circ}_{s,IV}$ ($Pu(OH)_4$, am) = – (58.3 ± 0.5), which was used by the authors for model calculations to derive $\log_{10}\beta^{\circ}_{s,8}$ = (55.8 ± 0.6) for Equation (11.19) (see also Section 11.2.1.3 Plutonium(IV) hydroxide complexes).

Adopting the ion-interaction parameter $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-)$ = – (0.01 ± 0.10) kg·mol$^{-1}$, Altmaier *et al.* report $\log_{10}K^{\circ}_{s,(4,1,8)}$ (11.44) = – (2.0 ± 0.5) in [2008ALT/NEC] and – (2.5 ± 0.4) in [2010FEL/NEC] for the equilibrium:

$$Pu(OH)_4(am) + 4OH^- + 4Ca^{2+} \rightleftharpoons Ca_4[Pu(OH)_8]^{4+} \qquad (11.44)$$

which is about four orders of magnitude different from $\log_{10}K^{\circ}_{s,(4,1,8)}$ ((11.44), Th) = (1.8 ± 0.5) with $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-)$ = – (0.01 ± 0.10) kg·mol$^{-1}$. However, the Th(IV) data are obtained from the SIT plot with data up to 4.5 M $CaCl_2$ ($I_m$ = 15.8), which is far outside the applicability range of the SIT method. The SIT plot including only conditional solubility constants determined in 0.5-2.0 M $CaCl_2$ solutions results in a value of $\log_{10}K^{\circ}_{s,(4,1,8)}$ closer to the one obtained by Pitzer and in a lower SIT coefficient, $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-)$ = – (0.12 ± 0.05) kg·mol$^{-1}$. However, the authors dismiss the Th(IV) ion-interaction parameter derived at $I_m \leq 3.5$ since these parameters would not be applicable for the Np(IV) and Pu(IV) system. Similarly, the data point at 4.5 M $CaCl_2$ determines the slope in the SIT plot to yield $\log_{10}K^{\circ}_{s,(4,1,8)}$ ((11.43), Th) = – (54.2 ± 0.5) and $\log_{10}K^{\circ}_{s,(4,1,8)}$ ((11.43), Pu) = – (58.5 ± 0.4). The exclusion of the data at 4.5 M $CaCl_2$ would result in quite different values for both $\log_{10}K^{\circ}_{s,(4,1,8)}$ and $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-)$. When considering only the solubility data up to 2 M $CaCl_2$, $\log_{10}K^{\circ}_{s,(4,1,8)}$ ((11.43), Th) = – (54.6 ± 0.5) is obtained. This review does not accept the values for $\log_{10}K^{\circ}_{s,(4,1,8)}$ and $\varepsilon(Ca_4[Pu(OH)_8]^{4+}, Cl^-)$ reported in [2008ALT/NEC] and [2010FEL/NEC].

To analyse the high ionic strength data for Pu(IV) (and Th(IV) and Np(IV)) in $CaCl_2$ and $MgCl_2$ solutions, the Pitzer formulism is used as the more appropriate methodology in [2009ALT/NEC] and [2010FEL/NEC]. By adopting the Th(IV)-based Pitzer ion interaction parameters, the Pu solubility increase at high $pH_m \geq 11$ is best fit with $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)}$ ((11.43), Pu) = – (59.3 ± 0.4) as reported in [2010FEL/NEC] and – (59.5 ± 0.5) reported in [2009ALT/NEC]. The Pitzer parameters determined for the $Ca_4[Th(OH)_8]^{4+}$ complex in analogy to Equation (11.43) were used to perform the regression of the Pu(IV) solubility data. The obtained constant, $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)}$ ((11.43), Pu) = – (59.3 ± 0.4), is in line with the corresponding values $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)}$ ((11.43), Th) = – (55.0 ± 0.3) and $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)}$ ((11.43), Np) = – (57.6 ± 0.4), and follows a similar trend as seen for the $An(CO_3)_5^{6-}$ series with An = Th, U, Np and Pu. It is to note that the Pitzer-derived equilibrium constant for the Th(IV) complex is in better agreement with the SIT-derived value $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)}$ ((11.43), Th) = – (54.6 ± 0.5) at $I_m \leq 3.5$ compared to the analogous Np and Pu system.

Altmaier *et al.* [2009ALT/NEC] interpreted the solubility data of $PuO_2{\cdot}nH_2O$ in alkaline $MgCl_2$ in the presence of Fe powder according to the reductive dissolution reaction

$$PuO_2{\cdot}xH_2O(am) + e^- + 4H^+ \rightleftharpoons Pu^{3+}(aq) + (2+x)\,H_2O(l) \qquad (11.45)$$

The authors calculate the equilibrium constant for Reaction (11.45) *via* $\log_{10}{}^{*}K^{o}_{IVs,III} = \log_{10}{}^{*}K^{o}_{IVs,0} - \log_{10}K^{o}_{III\text{-}IV} = -(2.33 \pm 0.52) - (-(17.69 \pm 0.04)) = (15.36 \pm 0.52)$. From this value, we calculate $\Delta_r G^o_m((11.45), 298.15\ K) = -(87.678 \pm 2.968)\ kJ{\cdot}mol^{-1}$. Using $\Delta_f G^o_m(Pu^{3+}, aq) = -(578.984 \pm 2.688)\ kJ{\cdot}mol^{-1}$ selected in [2003GUI/FAN] and assuming $x = 2$, we calculate $\Delta_f G^o_m(PuO_2{\cdot}2H_2O, am) = -965.6\ kJ{\cdot}mol^{-1}$. This value differs from the selected value, $\Delta_f G^o_m(PuO_2, cr) = -998.113\ kJ{\cdot}mol^{-1}$, which is consistent with a more amorphous hydrated solid phase $PuO_2{\cdot}nH_2O$.

Based on the similar chemical behaviour of Th(IV), Np(IV) and Pu(IV), we recommend the thermodynamic equilibrium constant $\log_{10}K^{o}_{s,(4,1,8)}((11.43), 298.15\ K) = -(59.30 \pm 0.40)$ for scoping calculations. The thermodynamic constant for equilibrium (11.43) is directly associated with the solubility product of $Pu(OH)_4$(am), $\log_{10}K^{o}_{sp}(Pu(OH)_4, am) = -(58.33 \pm 0.50)$, and any change to $\log_{10}K^{o}_{sp}(Pu(OH)_4, am)$ will affect the $\log_{10}K^{o}_{s,(4,1,8)}$ value. Although we do not select a value for the ion-interaction parameter, the value $\varepsilon(Ca_4[Pu(OH)_8]^{4+}, Cl^-) = (0.12 \pm 0.05)\ kg{\cdot}mol^{-1}$ can be used for scoping calculations.

This review retains the thermodynamic data, $\log_{10}K^{o}_{sp}(Pu(OH)_4, am) = (58.33 \pm 0.52)$ and $\Delta_r G^o_m = -(332.950 \pm 2.968)\ kJ{\cdot}mol^{-1}$, for the formation reaction of $PuO_2$(am, hyd) as selected in [2003GUI/FAN].

Table 11-16: Experimental formation constants for the equilibrium $An(OH)_4(am) + 4Ca^{2+} + 4H_2O(l) \rightleftharpoons Ca_4[An(OH)_8]^{4+} + 4H^+$ with An = Np or Pu and listed in [2010FEL/NEC].

| $T$/K | Method | Medium | $\log_{10}{}^{*}K_{s,(4,1,8)}$ Np(IV) | $\log_{10}{}^{*}K_{s,(4,1,8)}$ Pu(IV) | Reference |
|---|---|---|---|---|---|
| 295 ± 2 | sol | 2.0 M $CaCl_2$ | | – (56.98 ± 0.16) | [2008ALT/NEC] |
| 295 ± 2 | sol | 2.0 M $CaCl_2$/Fe powder | – (55.33 ± 0.22) | – (57.30 ± 0.15) | [2010FEL/NEC] |
| 295 ± 2 | sol | 3.5 M $CaCl_2$/Fe powder | | – (57.56 ± 0.29) | [2009ALT/NEC] |
| 295 ± 2 | sol | 4.0 M $CaCl_2$ | | – (57.59 ± 0.19) | [2008ALT/NEC] |
| 295 ± 2 | sol | 4.5 M $CaCl_2$/Fe powder | – (56.39 ± 0.09) | – (57.68 ± 0.19) | [2010FEL/NEC] |
| 295 ± 2 | sol | 4.5 M $CaCl_2$/$Na_2S_2O_4$ | – (56.03 ± 0.16) | | [2010FEL/NEC] |

#### 11.2.2.2.3.3 $PuO_{2+x}$(am)

Since the last review a number of studies have investigated the stability of $PuO_2$(am and cr) in aerobic aqueous solutions and its oxidation to a mixed-valent solid phase, $PuO_{2+x}$ ([2002HAS/OVE], [2002HAS/BAS], [2007NEC/ALT], [2007NEC/ALT2], [2007NEC/ALT3]). Spectroscopic measurements and solubility data confirmed the oxidation of $PuO_2$(am or cr) by water to form $PuO_{2+x}$(am), which is formulated as $(Pu(V))_{2x}(Pu(IV))_{1-2x}O_{2+x}$(am, hyd) ([2007NEC/ALT2]). The formation of $PuO_{2+x}$(am) is accompanied by an increase of the lattice parameter of the $PuO_2$ cubic structure, $a_0$(nm) = 0.53643 + 0.001764(2 + $x$) ([2002HAS/OVE], [2002HAS/BAS]). During its dissolution, $PuO_{2+x}$(am) is releasing Pu(V) into the aqueous phase since it is in equilibrium with both Pu(IV) and Pu(V). Depending on the amount of oxygen available, the fraction of oxidised Pu in the solid phase can vary between 0.5 % ($x$ = 0.003) and 10-12 % ($x$ = 0.05-0.06) under air. Neck *et al.* ([2007NEC/ALT2], [2007NEC/ALT3]) calculated the fractions of Pu(IV) and Pu(V) from the solubility product of the corresponding oxide in $PuO_{2+x}$(am, hyd) for the reaction:

$$PuO_{2.5}(am, hyd) + 0.5\,H_2O(l) \rightleftharpoons PuO_2^+ + OH^- \qquad (11.46)$$

Neck *et al.* ([2007NEC/ALT2], [2007NEC/ALT3]) report the equilibrium constant for Reaction (11.46), $\log_{10}{}^{*}K_{sp}^{o}$ ($PuO_{2.5}$ in $PuO_{2+x}\cdot nH_2O$(am, hyd)) = – (14.0 ± 0.8). As an alternative, they also report the thermodynamic equilibrium constant $\log_{10}K_{sp}^{o}$ ($PuO_{2.5}$ in $PuO_{2+x}\cdot nH_2O$(am, hyd)) = (0.0 ± 0.8) for Reaction (11.47):

$$PuO_{2.5}(am, hyd) + H^+ \rightleftharpoons PuO_2^+ + 0.5\,H_2O(l) \qquad (11.47)$$

The standard Gibbs energy for $PuO_{2+x}\cdot nH_2O$(am) is obtained from the thermodynamic solubility constants of $PuO_{2.5}$(am, hyd) in $PuO_{2+x}\cdot nH_2O$(am) ($\log_{10}K_{sp}^{o}$ = – (14.0 ± 0.8)) and $PuO_2$(am, hyd) in $PuO_{2+x}\cdot nH_2O$(am) ($\log_{10}K_{sp}^{o}$ = – (58.33 ± 0.52)) and the standard Gibbs energies for $PuO_2^+$ (– (852.65 ± 2.87) kJ·mol$^{-1}$), $Pu^{4+}$ (– (477 ± 2.70) kJ·mol$^{-1}$), $OH^-$ (– (157.22 ± 0.07) kJ·mol$^{-1}$) and $H_2O$(l) (– (237.14 ± 0.04) kJ·mol$^{-1}$). The standard molar Gibbs energy of formation of $PuO_{2+x}\cdot nH_2O$ with $x$ < 0.1 is given in [2007NEC/ALT2], [2007NEC/ALT3] as:

$$\Delta_f G_m^o(PuO_{2+x}\cdot nH_2O) = 2x(\Delta_f G_m^o(PuO_{2.5}, am, hyd))) + (1-2x)\Delta_f G_m^o(PuO_2(am, hyd)) =$$
$$= [2x(-(971.2 \pm 5.4)) + (1-2x)(-(965.5 \pm 4.0))]\ kJ\cdot mol^{-1} \qquad (11.48)$$

which results in slightly lower than $\Delta_f G_m^o$ ($PuO_2$, cr, hyd) = – (965.5 ± 4.0) kJ·mol$^{-1}$. Neck *et al.* [2007NEC/ALT2] suggest that $PuO_{2+x}$(am, hyd) with $x$ > 0.25 is not stable because its $\Delta_f G_m^o$ value is expected to be zero or slightly positive when taking into account that $\Delta_f G_m^o$ ($PuO_{2.5}$, am, hyd) = – (971.2 ± 5.4) kJ·mol$^{-1}$ calculated as a small fraction of $PuO_{2+x}$(am, hyd) includes a stabilisation energy of about 5-10 kJ·mol$^{-1}$ compared to pure $PuO_{2.5}$(am, hyd). The authors used published solubility constants and selected thermodynamic data to estimate the Gibbs energy of formation at 298.15 K, $\Delta_f G_m^o$ ($PuO_{2.25}$, cr) = – (995 ± 3) kJ·mol$^{-1}$ and $\Delta_f G_m^o$ ($PuO_{2.5}$, cr) = – (987 ± 10) kJ·mol$^{-1}$.

Using both thermodynamic equilibrium constants reported in [2007NEC/ALT2], [2007NEC/ALT3], $\log_{10} K^{\circ}_{sp}$ ($PuO_{2.5}$(am, hyd) in $PuO_{2+x}$(am, hyd), 298.15 K, (11.48)) = – (14.0 ± 0.8) and $\log_{10} K^{\circ}_{sp}$ ($PuO_2$(am, hyd) in $PuO_{2+x}$(am, hyd)) = – (58.330 ± 0.520), is just a formal way to account for the fractions of Pu(IV) and oxidised Pu in the solid equilibrium phase $PuO_{2+x} \cdot nH_2O$ and in solution. For this reason, this data is given for information only.

#### 11.2.2.2.4 $Pu(OH)_3$(am)

[2001LEM/FUG] reviewed experimental solubility data of Pu(III) hydroxide and selected the thermodynamic solubility product for a crystalline phase $Pu(OH)_3$(cr):

$$Pu(OH)_3(cr) + 3H^+ \rightleftharpoons Pu^{3+} + 3H_2O(l)\ ,\ \log_{10} K^{\circ}_{s,0} = (15.800 \pm 1.500).$$

This value is solely derived from the solubility study in [1989FEL/RAI]. It should be noted that the crystallinity of the solid equilibrium phase is uncertain due to the fact that no Bragg reflections were observed in the X-ray diffraction spectra. Thus, the selected thermodynamic data should rather be assigned to an amorphous phase, $Pu(OH)_3$(am).

Rai and co-workers [2011RAI/YUI] reviewed leaching data of actinides from doped glass and developed thermodynamic data for the Th(IV) system. The initial solubility-controlling Pu(IV) oxide solids in (or mixed with) crushed glass may not be sufficiently stable in the reducing environments of most nuclear waste repositories and may transform to Pu(III) and then form secondary Pu(III) solid phases.

Fanghänel and Neck [2002FAN/NEC] used the thermodynamic solubility product $\log_{10} K^{\circ}_{sp}$ ((11.49), $Pu(OH)_3$, am) = – (26.2 ± 1.5), which is derived from the value in [2001LEM/FUG], to model the solubility of the amorphous $Pu(OH)_3$(am).

$$Pu(OH)_3(am) \rightleftharpoons Pu^{3+} + 3OH^- \qquad (11.49)$$

The stability of Pu(III) and the relationship between $Pu(OH)_3$(am) and $PuO_2$(am, hyd) are discussed by Neck *et al.* [2007NEC/ALT]. According to the thermodynamic data presented in their study, $Pu(OH)_3$(am) should be stable only at redox conditions below (pe + pH) = – (0.4 ± 1.0). Based on $\log_{10}{}^{*} K^{\circ}_{s,0}$ ($Pu(OH)_3$, am) = (15.8 ± 0.8) from [2001LEM/FUG] for Reaction (11.50), $\log_{10}{}^{*} K^{\circ}_{s,0}$ ($PuO_2$, am, hyd) = – (2.33 ± 0.52) for the solubility equilibrium (11.51) of $PuO_2$(am, hyd) and $\log_{10} K^{\circ}_{III,IV}$ = – (17.69 ± 0.04) for the Pu(IV)/Pu(III) redox couple, Neck and co-workers concluded that $Pu(OH)_3$(am) is metastable and should convert to $PuO_2$(am, hyd) in aqueous solution.

$$Pu(OH)_3(am) + 3H^+ \rightleftharpoons Pu^{3+} + 3H_2O(l) \qquad (11.50)$$

$$Pu^{4+} + 2H_2O(l) \rightleftharpoons PuO_2(am, hyd) + 4H^+ \qquad (11.51)$$

The authors calculate $\log_{10}{}^{*} K^{\circ}_{III,IV} = (0.4 \pm 1.0)$ for the solid phase transition reaction:

$$Pu(OH)_3(am) \rightleftharpoons PuO_2(am, hyd) + H_2O(l) + H^+ + e^- \quad (11.52)$$

The stability range of $Pu(OH)_3(s)$ reported in [2007NEC/ALT] has to be considered with care due to the large uncertainty of the reported $\log_{10}{}^{*}K^{o}_{s,0}(Pu(OH)_3, am)$. The authors suggest that the stability field of $Pu(OH)_3(s)$ is located outside the stability field of water ($0 < (pe + pH) < 20.77$) and thus should not be stable in aqueous systems.

More recent experimental studies have indicated that $Pu(OH)_3(am)$ may be more stable within the stability field of water than previously assumed. Nielsson and co-workers ([2004NIL/ALB], [2013NIL/ALB]) attempted to study the solubility of $Pu(OH)_3(s)$ in 0.1 M NaCl at 50 bar $P(H_2(g))$ and in the presence of Pt wire. The measured redox potentials were higher than expected for such extremely reducing conditions and insufficient to maintain Pu(III). As a consequence, the transition of the initially blue $Pu(OH)_3(am)$ to $PuO_2(am, hyd)$ was observed over time. These observations prohibited a quantitative analysis of presented data and the determination of a solubility product for $Pu(OH)_3(am)$.

Recently, [2016CHO/YOU] studied the Pu(III) hydrolysis and solubility under reducing conditions. Cho and co-workers found the blue amorphous solid phase, assumed to be $Pu(OH)_3(am)$, to be stable over the duration of the experiment, based on the unchanged X-ray diffraction pattern after three weeks. However, this argument is meaningless as the diffraction data do not show any distinct Bragg reflections, which is typical of a highly amorphous precipitate. Any transition of amorphous solid phases would not be detected using this analytical technique. From coulometric titrations and spectroscopic data, Cho *et al.* report a conditional solubility product for $Pu(OH)_3(am)$, $\log_{10}{}^{*}K_{s,0}((11.50), Pu(OH)_3, am) = (15.23 \pm 0.50)$, in 0.1 M $NaClO_4$ solution. By using the SIT ion-interaction parameters from the NEA TDB, the authors calculate the thermodynamic solubility product, $\log_{10}{}^{*}K^{o}_{s,0}((11.50), Pu(OH)_3, am) = (14.58 \pm 0.50)$. This value is quite different from the value accepted in the [2001LEM/FUG], $\log_{10}{}^{*}K^{o}_{s,0}((11.50), Pu(OH)_3, cr) = (15.80 \pm 1.50)$, although it is within the uncertainty range of the selected value. It remains unclear how Cho *et al.* derived the solubility data as discussed in the Appendix A entry. This review assumes that the reported solubility data are related to a fresh precipitate of $Pu(OH)_3(am)$ and a very short equilibration time.

The thermodynamic solubility constants reported in [2016CHO/YOU] and [1989FEL/RAI] appear to differ by over one order of magnitude. It should be noted that the value selected in [2001LEM/FUG] originated from the solubility study performed by Felmy *et al.* in water at $pH \geq 6$, under these conditions the $Pu^{3+}$ ion undergoes hydrolysis as shown in [2016CHO/YOU] or could easily oxidise. However, Felmy *et al.* disregarded hydrolysis of Pu(III) below pH 8 based on the analogous behaviour of Am(III). Considering the hydrolysis constant for $PuOH^{2+}$ determined by Cho *et al.*, $\log_{10}\beta^{o}_{1,1} = -(6.18 \pm 0.25)$ (see also Section 11.2.1.4 Plutonium(III) hydroxide

complexes), the data in [1989FEL/RAI] can be reinterpreted with $\log_{10} K^{o}_{s,0}$ ((11.50), $Pu(OH)_3$, am) = (14.50 ± 0.50). Applying the selected value in [2001LEM/FUG], $\log_{10} \beta^{o}_{1,1}$ = – (6.90 ± 0.30), results in a thermodynamic constant $\log_{10} K^{o}_{s,0}$ ((11.50), $Pu(OH)_3$, am) = (15.10 ± 0.50) that is also close to that reported in [2016CHO/YOU].

The studies by Felmy *et al.* and Cho *et al.* indicate that Pu(III) is more stable than previously assumed and that the thermodynamic solubility product selected in [2001LEM/FUG] underestimates the stability of $Pu(OH)_3$(am) in aqueous systems. The discrepancies in the reported thermodynamic solubility products of $Pu(OH)_3$(am) can be explained with the consideration of Pu(III) hydrolysis. Despite the unknown crystallinity of the solid phase, but in light of the agreement with the data reported in [1989FEL/RAI] this review selects the equilibrium constant for Equation (11.50) with an increased uncertainty:

$$\log_{10} {}^{*}K^{o}_{s,0} \text{ ((11.50), } Pu(OH)_3\text{, am, 298.15 K)} = \mathbf{(14.58 \pm 0.75)}.$$

$$\text{and } \Delta_r G^{o}_{m} \text{ ((11.50), 298.15 K)} = \mathbf{-\ (83.223 \pm 4.281)}\ \text{kJ·mol}^{-1}.$$

Additional studies are encouraged to verify the stability of Pu(III) and $Pu(OH)_3$(s) in aqueous solutions and to reduce the uncertainties of current thermodynamic data for the Pu(III) hydroxide system.

## 11.3 Plutonium group 17 (halogen) compounds and complexes

### 11.3.1 Plutonium halide compounds

#### 11.3.1.1 Plutonium fluoride compounds

##### 11.3.1.1.1 $PuF_4$(g)

There are no new experimental data reported for $PuF_4$(g). Moskaleva *et al.* [2006MOS/MAT] used the previously reported $\Delta_f H^{o}_{m}(PuF_4, g)$ = – (1385 ± 50) kJ·mol$^{-1}$ at 0 K in DFT calculations to determine the enthalpy of formation of $PuO_2^{2+}$(g). The good agreement of the heat of formation, $\Delta_f H^{o}_{m}(PuO_2^{2+}, g)$ = (1750 ± 63) kJ·mol$^{-1}$ at 0 K, determined from reactions with $PuF_4$(g) or $PuF_6$(g) as reagents lead the authors to select the value of $\Delta_f H^{o}_{m}(PuF_4, g)$ = – (1385 ± 50) kJ·mol$^{-1}$ at 298 K compared to the previously accepted value, $\Delta_f H^{o}_{m}(PuF_4, g)$ = – 1445.3 kJ·mol$^{-1}$ recommended in [1985MOR] and used in [2003SCH/PRI]. Both of these data differ from the selected data in [2001LEM/FUG], – (1548.000 ± 22.000) kJ·mol$^{-1}$ at 298.15 K, which was calculated from sublimation and vapor pressure data. Since these

data are calculated and experimental verification is desired, we retain the data previously selected in [2001LEM/FUG].

#### 11.3.1.1.2 $PuF_6$(g)

There are no new experimental data reported for $PuF_6$(g). In DFT calculations to determine the heat of formation of $PuO_2^{2+}$(g) Moskaleva *et al.* [2006MOS/MAT] used $\Delta_f H_m^o(PuF_6, g) = -(1814.1 \pm 29.3)$ kJ·mol$^{-1}$. This value is in good agreement with the selected TDB value, $\Delta_f H_m^o(PuF_6, g) = -(1812.700 \pm 20.100)$ kJ·mol$^{-1}$. Schimmelpfennig *et al.* [2003SCH/PRI] calculated the reaction enthalpies for the gas phase Reactions (11.53) and (11.54) at 298.15 K with $PuF_6$(g) as a reacting agent.

$$PuF_6(g) + 2H_2O(g) \rightleftharpoons PuO_2F_2(g) + 4HF(g) \quad (11.53)$$

$$PuF_6(g) + 3H_2O(g) \rightleftharpoons PuO_3(g) + 6HF(g) \quad (11.54)$$

Schimmelpfennig and co-workers report $\Delta_r H_m^o(11.53) = -4$ kJ·mol$^{-1}$ and $\Delta_r H_m^o(11.54) = 222$ kJ·mol$^{-1}$, which are quite different from those calculated for the analogous reactions with U, $\Delta_r H_m^o$(U, (11.53)) = 168 kJ·mol$^{-1}$ and $\Delta_r H_m^o$(U, (11.54)) = 405 kJ·mol$^{-1}$, and Np, $\Delta_r H_m^o$(Np, (11.53)) = 158 kJ·mol$^{-1}$ and $\Delta_r H_m^o$(Np, (11.54)) = 349 kJ·mol$^{-1}$. The authors explain the differences with the weaker bonding in $PuF_6$(g).

These thermodynamic data for $PuF_6$(g) are reported for information only, but are not selected by this review. The data selected in previous reviews are retained.

## 11.3.2 Aqueous plutonium group 17 (halogen) complexes

### 11.3.2.1 Aqueous plutonium fluoride complexes

Since the last review in [2003GUI/FAN], few studies have revisited the complex formation of actinide ions with fluoride. Moriyama and co-workers [2002MOR/FUJ] evaluated the trends of the equilibrium constants of fluoride complexes by using a hard-sphere model with improved electrostatic and non-electrostatic contributions. [2010XIA/RAO] reported on the formation of Pu(IV) fluoride complexes in 2 M $HClO_4$ in the presence of HF by using solvent extraction.

#### 11.3.2.1.1 Aqueous Pu(VI) fluoride complexes

The NEA TDB review in [2001LEM/FUG] selected thermodynamic equilibrium constants for the formation of aqueous Pu(VI) fluoride complexes:

$$PuO_2^{2+} + F^- \rightleftharpoons PuO_2F^+, \ \log_{10} K_{1,1}^o = (4.560 \pm 0.200)$$

$$PuO_2^{2+} + 2F^- \rightleftharpoons PuO_2F_2(aq), \ \log_{10} K_{1,2}^o = (7.250 \pm 0.450).$$

There are no new experimental data reported since the last review. Moriyama and co-workers [2002MOR/FUJ] applied a hard-sphere model with improved electrostatic and non-electrostatic interactions to calculate thermodynamic equilibrium

constants of three Pu(VI) fluoride complexes. The calculated equilibrium constants for $PuO_2F^+$, $PuO_2F_2$(aq), and $PuO_2F_3^-$, $\log_{10}K^\circ_{1,1} = 4.30$, $\log_{10}K^\circ_{1,2} = 7.58$, and $\log_{10}K^\circ_{1,3} = 8.93$, are close to the NEA TDB values and also follow the trend of the analogous U(VI) and Np(VI) complexes.

The selected thermodynamic data in [2001LEM/FUG] are retained by this review.

#### 11.3.2.1.2 Aqueous Pu(IV) fluoride complexes

The NEA TDB review in [2001LEM/FUG] selected thermodynamic constants for the formation of two aqueous Pu(IV) fluoride complexes:

$$Pu^{4+} + F^- \rightleftharpoons PuF^{3+},\ \log_{10}K^\circ_{1,1} = (8.840 \pm 0.100)$$

$$Pu^{4+} + 2F^- \rightleftharpoons PuF_2^{2+},\ \log_{10}K^\circ_{1,2} = (15.700 \pm 0.200).$$

Moriyama and co-workers [2002MOR/FUJ] applied a hard-sphere model with improved electrostatic and non-electrostatic interactions to calculate thermodynamic formation constants of four Pu(IV) fluoride complexes, $PuF^{3+}$, $PuF_2^{2+}$, $PuF_3^+$, and $PuF_4$(aq). The corresponding equilibrium constants $\log_{10}K^\circ_{1,1} = 8.68$, $\log_{10}K^\circ_{1,2} = 16.38$, $\log_{10}K^\circ_{1,3} = 22.26$, and $\log_{10}K^\circ_{1,4} = 27.16$, show increasingly large differences from the selected NEA TDB values with fluoride coordination and are not considered by the present review.

Xia and co-workers [2010XIA/RAO] studied the complex formation of Pu(IV) with fluoride in 2.0 M $HClO_4$ by solvent extraction into TTA/toluene at 298.15, 313.15 and 328.15 K. Increasing fluoride concentration resulted in a decrease in the extraction of Pu(IV) into the organic phase, which was interpreted with the formation of two Pu(IV) fluoride complexes $PuF^{3+}$ and $PuF_2^{2+}$ in the aqueous phase. The conditional constants are listed in Table 11-17. The SIT was applied to correct the experimental equilibrium constants to $I = 0$, using $\Delta\varepsilon_{1,1} = -(0.12 \pm 0.09)$ kg·mol$^{-1}$ and $\Delta\varepsilon_{1,2} = -(0.18 \pm 0.15)$ kg·mol$^{-1}$ at 298.15 K. In this way, the equilibrium constants for the Reactions (11.55) and (11.56) were obtained at 298.15, 313.15 and 328.15 K, respectively:

$$Pu^{4+} + HF \rightleftharpoons PuF^{3+} + H^+ \quad (11.55)$$

$$Pu^{4+} + 2HF \rightleftharpoons PuF_2^{2+} + 2H^+ \quad (11.56)$$

By using the Van't Hoff equation and the known dissociation constant of HF at 298.15 K, $\log_{10}K^\circ_{HF} = (3.18 \pm 0.02)$, Xia *et al.* calculated $\log_{10}K^\circ_{HF} = (3.28 \pm 0.02)$ for 313.15 K and $\log_{10}K^\circ_{HF} = (3.38 \pm 0.02)$ at 328.15 K to derive equilibrium constants for Reactions (11.57) and (11.58).

$$Pu^{4+} + F^- \rightleftharpoons PuF^{3+} \quad (11.57)$$

$$Pu^{4+} + 2F^- \rightleftharpoons PuF_2^{2+} \quad (11.58)$$

The values of $\log_{10}\beta^{o}_{1,1}$ (11.57) = (8.86 ± 0.21) and $\log_{10}\beta^{o}_{1,2}$ (11.58) = (15.91 ± 0.21) at 298.15 K agree very well with the selected values in [2001LEM/FUG], $\log_{10}\beta^{o}_{1,1}$ = (8.84 ± 0.10) and $\log_{10}\beta^{o}_{1,2}$ = (15.70 ± 0.20). This review retains the data selected in [2001LEM/FUG].

From the equilibrium constants Xia *et al.* [2010XIA/RAO] also calculated thermodynamic properties for the Pu(IV) complexes. The enthalpies of complexation for $PuF^{3+}$ and $PuF_2^{2+}$, $\Delta_r H^o_m$ = (9.4 ± 5.0) kJ·mol$^{-1}$ and (15.0 ± 8.0) kJ·mol$^{-1}$, respectively, were calculated from the thermodynamic equilibrium constants for Equations (11.57) and (11.58) as function of 1/T. From these data and the reaction Gibbs free energies ($\Delta_r G^o_m$ (11.57) = – (50.56 ± 1.20) kJ·mol$^{-1}$ and $\Delta_r G^o_m$ (11.58) = – (90.80 ± 1.20) kJ·mol$^{-1}$), the authors calculated the entropies for the complexation reactions, $\Delta_r S^o_m$ (11.57) = (201 ± 17) J·K$^{-1}$·mol$^{-1}$ and $\Delta_r S^o_m$ (11.58) = (355 ± 27) J·K$^{-1}$·mol$^{-1}$·. The data for Equation (11.57) agree very well with those recommended in the NEA TDB, while those for Equation (11.58) are within the uncertainty of selected values. Thus, this review retains the thermodynamic data selected in [2001LEM/FUG].

Table 11-17: Experimental constants for the equilibrium reaction $Pu^{4+} + nHF \rightleftharpoons PuF_n^{4-n} + nH^+$ ($n$ = 1, 2).

| $T$/K | Method | $I$ (medium) | $\log_{10}{}^{*}\beta_1$ | $\log_{10}{}^{*}\beta_2$ | $\log_{10}{}^{*}\beta^{o}_n$ | Reference |
|---|---|---|---|---|---|---|
| 298 | solv | 2 M $HClO_4$ | (4.54 ± 0.07) | | (5.68 ± 0.21) | [2010XIA/RAO] |
| 313 | solv | 2 M $HClO_4$ | (4.50 ± 0.03) | | (5.67 ± 0.20) | [2010XIA/RAO] |
| 323 | solv | 2 M $HClO_4$ | (4.41 ± 0.03) | | (5.63 ± 0.20) | [2010XIA/RAO] |
| 298 | solv | 2 M $HClO_4$ | | (7.60 ± 0.04) | (9.55 ± 0.21) | [2010XIA/RAO] |
| 313 | solv | 2 M $HClO_4$ | | (7.45 ± 0.04) | (9.46 ± 0.20) | [2010XIA/RAO] |
| 323 | solv | 2 M $HClO_4$ | | (7.31 ± 0.04) | (9.39 ± 0.20) | [2010XIA/RAO] |

### 11.3.2.2 Aqueous plutonium chloride complexes

Although there have been several preparative studies on solid plutonium chloride compounds, thermodynamic data on aqueous plutonium chloride complexes remain rare. The study of the chloride complex formation of actinides is complicated because the complexes are very weak and high concentrations of chloride are needed to observe any ligand coordination. Spectroscopic studies have established that the coordination of chloride in the inner-sphere of the actinide ions only takes place in concentrated chloride solutions. As an example, coordination of Np(V) with chloride is not observed until [Cl] > 3 M, and Pu(III) is not coordinating chloride in solutions up to 12.3 M $Cl^-$ [1997ALL/BUC]. However, the Pu(III) and Pu(IV) anionic chloride complexes, $PuCl_6^{3-}$ and $PuCl_6^{2-}$, respectively, have been predicted from DFT calculations as the predominant complexes in molten chloride [2012BUZ/CHU], but this is a non-aqueous solvent. [2006WIL/ALM] synthesised Pu(III) chloride compounds in acidic CsCl solutions. The solid state compounds contain the bis-chloro cation, $PuCl_2(H_2O)_6^+$, and

*cis*- and *trans*-configurations of the tetra-chloro anion, $PuCl_4(H_2O)_4^-$. No thermodynamic data on these compounds are reported. Since the last NEA TDB update, the ion interaction parameter $\varepsilon(Pu^{4+}, Cl^-)$ was calculated in [2006NEC/ALT] (see also Section 11.1.4, $Pu^{4+}$) from thermodynamic data accepted by the NEA TDB and only one experimental study on the formation of the Pu(V) chloro complex, $PuO_2Cl(aq)$, has been reported in [2009TOP/AUP]. The thermodynamics of Pu(VI) chloro complexes have been discussed in [2001LEM/FUG] and [2003GUI/FAN] and are retained in this review.

#### 11.3.2.2.1 Aqueous Pu(VI) chloride complexes

As discussed in Section 11.6.1.2.1 Solid plutonium(VI) carbonates, Reilly and co-workers [2007REI/RUN] performed solubility studies of $PuO_2CO_3(s)$ in NaCl solutions. The soluble plutonium concentrations were determined from optical absorbance data, allowing to distinguish between the concentrations of $PuO_2^{2+}$, Pu(VI) chloro complexes and Pu(V) species in solution. Using the absorbances at 830 nm and 838 nm for $PuO_2^{2+}$ and $PuO_2Cl^+$, respectively, the authors calculate the formation constant for the first Pu(VI) chloro complex, $PuO_2Cl^+$. Reilly and co-workers used the SIT and report $\log_{10}\beta^{o}_{1,1}(PuO_2Cl^+) = (0.26 \pm 0.03)$ and $\Delta\varepsilon = -(0.10 \pm 0.02)\ kg \cdot mol^{-1}$. Both values agree well with the data previously reported by the same group in [1999RUN/REI], $\log_{10}\beta^{o}_{1,1}(PuO_2Cl^+) = (0.23 \pm 0.03)$ and $\Delta\varepsilon = -(0.13 \pm 0.03)\ kg \cdot mol^{-1}$ discussed in detail and selected by [2003GUI/FAN].

#### 11.3.2.2.2 Aqueous Pu(V) chloride complexes

No thermodynamic data have been selected in [2001LEM/FUG] and [2003GUI/FAN] for the complex formation of Pu(V) with chloride in aqueous solutions. Topin and co-workers [2009TOP/AUP] studied the electrophoretic mobility of Np(V) and Pu(V) in chloride media. The difference in electrophoretic mobilities of Np(V) and Pu(V) species is small and the authors report identical equilibrium constants for the monochloro complex of Np(V) and Pu(V). The reported constant for both $NpO_2Cl(aq)$ (see also Section 10.3.1.2. Aqueous neptunium chloride complexes) and $PuO_2Cl(aq)$ in 1 M NaCl is $\log_{10}\beta_1$ (11.59) $= -(0.40 \pm 0.07)$, which recalculated to zero ionic strength by using the SIT gives $\log_{10}\beta^{o}_1 = -(0.12 \pm 0.13)$.

$$PuO_2^+ + Cl^- \rightleftharpoons PuO_2Cl(aq) \qquad (11.59)$$

This data suggest that in 1 M NaCl about 40 % of the Pu(V) is coordinated with chloride as $PuO_2Cl(aq)$. This degree of Pu(V) chloride complex formation exceeds by far the results of other spectroscopic studies that showed no evidence for chloride complex formation of pentavalent actinides until higher $Cl^-$ concentrations (*i.e.*, [1997ALL/BUC]). Based on this inconsistency with spectroscopic data in the literature, this review does not recommend the data for Np(V) and Pu(V) chloride complexation reported in [2009TOP/AUP].

Table 11-18: Experimental constants for the reaction $PuO_2^+ + Cl^- \rightleftharpoons PuO_2Cl(aq)$.

| $T$ /K | Method | $I$ (medium) | $\log_{10}\beta_1$ | Reference |
|---|---|---|---|---|
| 298 ± 1 | Electrophoresis | 1 M NaCl | – (0.40 ± 0.07) | [2009TOP/AUP] |
| 298 ± 1 | Electrophoresis | 0 M NaCl | – (0.12 ± 0.13) | [2009TOP/AUP] |

#### 11.3.2.2.3 Aqueous Pu(IV) chloride complexes

In [2001LEM/FUG], Lemire *et al.* selected a thermodynamic equilibrium constant for the formation of the first Pu(IV) chloride complex:

$$Pu^{4+} + Cl^- \rightleftharpoons PuCl^{3+},\ \log_{10}K^\circ_{1,1} = (1.800 \pm 0.300).$$

In the absence of new experimental data, this value is retained by the present review. Neck and co-workers [2006NEC/ALT] have discussed the interaction parameters between $Pu^{4+}$ and $ClO_4^-$ and $Pu^{4+}$ and $Cl^-$, where the first one, $\varepsilon(Pu^{4+}, ClO_4^-)$, is derived from the redox potential and equilibrium constant for the $Pu^{4+}/Pu^{3+}$ redox Reaction (11.2).

The reported values $E^\circ(Pu^{4+}/Pu^{3+}) = (1.047 \pm 0.003)$ V and $\log_{10}K^\circ_{IV/III} = (17.69 \pm 0.04)$ are the basis for the calculated value $\varepsilon(Pu^{4+}, Cl^-) = (0.37 \pm 0.05)$ kg·mol$^{-1}$, which, in turn, is based on $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.07)$ kg·mol$^{-1}$ and $\varepsilon(Pu^{3+}, ClO_4^-) = (0.49 \pm 0.05)$ kg·mol$^{-1}$ selected in [2001LEM/FUG] and [2003GUI/FAN]. The value of $\varepsilon(Pu^{4+}, Cl^-)$ is consistent with the corresponding value in the Th(IV) system, $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)$ kg·mol$^{-1}$, also calculated by Neck and co-workers.

As discussed in Section 11.1.4, Neck and co-workers derive this value by extrapolating the experimental equilibrium constant for Reaction (11.2) in 1 M HCl reported in [1951RAB/LEM] to $I = 0$ without taking into account the presence of Pu(IV) chloro complexes in 1 M HCl. Neglecting the presence of up to 30 % $PuCl^{3+}$ in 1 M HCl causes an erroneous value of $\varepsilon(Pu^{4+}, Cl^-)$. However, the value reported by Neck and co-workers agrees reasonably well (within uncertainties) with other SIT ion interaction parameters $\varepsilon(M^{n+}, Cl^-)$. The value $\varepsilon(Pu^{4+}, Cl^-) = (0.37 \pm 0.10)$ kg·mol$^{-1}$ reported in [2006NEC/ALT] (with uncertainty increased by this review) can be used in speciation models where chloride complexes have been excluded.

## 11.4 Plutonium group 16 compounds and complexes

### 11.4.1 Aqueous plutonium sulfates

Since the last review, two additional studies have been reported on the sulfate complex formation of Pu(IV) [2007XIA/FRI] and Pu(V) [2009TOP/AUP].

#### 11.4.1.1 Aqueous plutonium(V) sulfates

No thermodynamic data have been selected in previous reviews, [2001LEM/FUG] and [2003GUI/FAN], because of the lack of experimental studies. Since then, Topin *et al.* [2009TOP/AUP] investigated the complex formation of Pu(V) by capillary electrophoresis experiments in $NaClO_4/Na_2SO_4$ at room temperature. The changes of the electrophoretic mobility of the Pu(V) species with increasing sulfate concentration was interpreted with the formation of a 1:1 Pu(V) sulfate complex according to Reaction (11.60):

$$PuO_2^+ + SO_4^{2-} \rightleftharpoons PuO_2SO_4^- \qquad (11.60)$$

Topin *et al.* measured the electrophoretic mobility of Pu(V) as function of sulfate concentration at four different ionic strengths, 0.35, 0.70, 1.0 and 1.5 M $NaClO_4/Na_2SO_4$. To correct for ionic strengths effects, they used two approaches to determine the equilibrium constants for $PuO_2SO_4^-$. Using the SIT plot, the authors obtain $\log_{10}\beta^{o}_{1,1}$ (11.60) = (1.26 ± 0.12) and $\Delta\varepsilon_{i,j}$ = (0.10 ± 0.12) kg·mol$^{-1}$, which is very similar to the corresponding values for Np(V), $\log_{10}\beta^{o}_{1,1}$ ((11.60), Np(V)) = (1.34 ± 0.12) and $\Delta\varepsilon_{i,j}$ ((11.60), Np(V)) = (0.09 ± 0.12) kg·mol$^{-1}$ (see Section 10.4.1.2 Aqueous Np(V) sulfate complexes). From the fitted $\Delta\varepsilon_{i,j}$ value, the authors calculate $\varepsilon(PuO_2SO_4^-, Na^+) = \varepsilon(NpO_2SO_4^-, Na^+)$ = (0.14 ± 0.17) kg·mol$^{-1}$. When neglecting effects caused by the replacement of the $ClO_4^-$ by $SO_4^{2-}$ in the ionic medium, the equilibrium constant for equilibrium (11.60) is slightly higher, $\log_{10}\beta^{o}_{1,1}$ (11.60) = (1.30 ± 0.06), while $\Delta\varepsilon_{i,j}$ remains unchanged, $\Delta\varepsilon_{i,j}$ = (0.10 ± 0.12) kg·mol$^{-1}$.

The lack of experimental data on Pu(V) sulfate complex formation and limited data on chemical analogues complicates the evaluation of the accuracy of the data presented in [2009TOP/AUP]. It is concerning that the authors did not verify the oxidation state stability, especially that of the Pu(V), which is highly sensitive to chemical and redox conditions. The evaluation of the Pu data relies on the comparison with data on the analogous Np(V) complex, $NpO_2SO_4^-$. The data reported by Topin *et al.*, $\log_{10}\beta^{o}_{1,1}$ (11.60) = (1.26 ± 0.12) and $\varepsilon(PuO_2SO_4^-, Na^+)$ = (0.14 ± 0.17) kg·mol$^{-1}$, are quite different from $\log_{10}\beta^{o}_{1,1}$ ((11.60), Np(V)) = (0.44 ± 0.27) selected in [2003GUI/FAN]. However, this review revised the thermodynamic data for $NpO_2SO_4^-$ and the selected $\log_{10}K^{o}$ ((10.28), 298.15 K) = (1.30 ± 0.16) (see Section 10.4.1.2 Aqueous Np(V) sulfate complexes). With the selected NEA TDB value $\Delta\varepsilon_{i,j}$ (11.60) = – (0.01 ± 0.11) kg·mol$^{-1}$ and using $\varepsilon(NpO_2^+, ClO_4^-)$ = (0.25 ± 0.05) kg·mol$^{-1}$, this review revised $\varepsilon(NpO_2SO_4^-, Na^+)$ = – (0.07 ± 0.13) kg·mol$^{-1}$. Despite the concerns about the experimental shortcomings and data analysis, this review accepts the data reported by Topin *et al.* [2009TOP/AUP], based on the agreement with the new selected value for $NpO_2SO_4^-$, and selects:

$$\log_{10}\beta^{o}_{1,1}((11.60), 298.15\ K) = (\mathbf{1.26 \pm 0.12}) \text{ and}$$

$$\Delta_r G^{o}_{m}((11.60), 298.15\ K) = \mathbf{-\ (7.192 \pm 0.685)}\ kJ\cdot mol^{-1}.$$

From this value and using $\Delta_f G_m^o(PuO_2^+, 298.15\ K) = -(852.646 \pm 2.868)$ kJ·mol$^{-1}$ and $\Delta_f G_m^o(SO_4^{2-}, 298.15\ K) = -(744.004 \pm 0.418)$ kJ·mol$^{-1}$, we obtain $\Delta_f G_m^o(PuO_2SO_4^-, 298.15\ K) =$ **– (1603.842 ± 2.978)** kJ·mol$^{-1}$.

Table 11-19: Experimental equilibrium constants for the reaction $PuO_2^+ + SO_4^{2-} \rightleftharpoons PuO_2SO_4^-$.

| $T$/K | Method | $I$ (medium) | $\log_{10}\beta_{1,1}$ | Reference |
|---|---|---|---|---|
| 298 ± 1 | Electrophoresis | 0.357 M $NaClO_4$ | (0.63 ± 0.11) | [2009TOP/AUP] |
| 298 ± 1 | Electrophoresis | 0.725 M $NaClO_4$ | (0.49 ± 0.12) | [2009TOP/AUP] |
| 298 ± 1 | Electrophoresis | 1.051 M $NaClO_4$ | (0.37 ± 0.11) | [2009TOP/AUP] |
| 298 ± 1 | Electrophoresis | 1.617 M $NaClO_4$ | (0.26 ± 0.11) | [2009TOP/AUP] |

### 11.4.1.2 Aqueous plutonium(IV) sulfates

The NEA TDB review in [2001LEM/FUG] selected thermodynamic formation constants for the 1:1 and 1:2 aqueous sulfate complexes of Pu(IV):

$$Pu^{4+} + HSO_4^- \rightleftharpoons PuSO_4^{2+} + H^+,\ \log_{10}{}^*K_{1,1}^o = (4.910 \pm 0.220)$$

$$Pu^{4+} + 2HSO_4^- \rightleftharpoons Pu(SO_4)_2(aq) + 2H^+,\ \log_{10}{}^*K_{1,2}^o = (7.180 \pm 0.320).$$

A number of experimental studies on the complex formation of Pu(IV) with sulfate have been reported and extensively reviewed in [2001LEM/FUG]. The majority of the experimental studies were performed under acidic conditions and higher ionic strength, at conditions where $HSO_4^-$ is the dominant sulfate solution species. The experimental data were interpreted with the formation of two Pu(IV) sulfate complexes, $PuSO_4^{2+}$ and $Pu(SO_4)_2(aq)$:

$$Pu^{4+} + HSO_4^- \rightleftharpoons PuSO_4^{2+} + H^+ \quad (11.61)$$

$$Pu^{4+} + 2HSO_4^- \rightleftharpoons Pu(SO_4)_2(aq) + 2H^+ \quad (11.62)$$

The conditional equilibrium constants $\log_{10}{}^*K_{1,1}^o(11.61) = (2.75 \pm 0.01)$ and $\log_{10}{}^*K_{1,2}^o(11.62) = (4.43 \pm 0.01)$ were selected in [2001LEM/FUG] as the most reliable values at $I$ = 2.2 m and 298.15 K. For the correction to zero ionic strength, the ion-interaction parameters $\Delta\varepsilon(11.61) = -(0.31 \pm 0.12)$ kg·mol$^{-1}$ and $\Delta\varepsilon(11.62) = -(0.46 \pm 0.08)$ kg·mol$^{-1}$ from [1992GRE/FUG] were used. It is to note that these values were derived from both experimental data and estimations since an independent calculation of $\log_{10}{}^*K_{1,n}^o$ and $\Delta\varepsilon_{i,j}$ was not possible. Grenthe *et al.* [1992GRE/FUG] reported the ion-interaction coefficients $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol$^{-1}$ and $\varepsilon(USO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol$^{-1}$, which were retained in [2001LEM/FUG] and [2003GUI/FAN]. From these values, we calculate $\log_{10}{}^*K_{1,1}^o(11.61) = (4.88 \pm 0.22)$ based on the analogue $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol$^{-1}$, and $\log_{10}{}^*K_{1,1}^o(11.61) = (4.75 \pm 0.22)$ when using $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.06)$ kg·mol$^{-1}$ as reported in [2003GUI/FAN]. The ionic strength correction for the equilibrium (11.62)

neglecting the ion-interaction parameter for the neutral Pu(IV) sulfate complex and relies heavily on the value for $\varepsilon(Pu^{4+}, ClO_4^-)$. The review in [2001LEM/FUG] adopted the values $\Delta\varepsilon\,(11.62) = -(0.46 \pm 0.08)$ kg·mol$^{-1}$ and $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol$^{-1}$ reported in [1992GRE/FUG] for the U(IV) analogues reaction to obtain $\log_{10}{}^{*}K^{o}_{1,2}\,(11.62) = (7.18 \pm 0.32)$. Applying the $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.06)$ kg·mol$^{-1}$ reported in [2003GUI/FAN] and maintaining $\Delta\varepsilon\,(11.62) = -(0.46 \pm 0.08)$ kg·mol$^{-1}$, we derive $\log_{10}{}^{*}K^{o}_{1,2}\,(11.62) = (7.03 \pm 0.32)$. Both values are within the accepted uncertainty range and this review retains the current values selected in [2003GUI/FAN], $\log_{10}{}^{*}K^{o}_{1,1}\,(11.61) = (4.91 \pm 0.22)$ and $\log_{10}{}^{*}K^{o}_{1,2}\,(11.62) = (7.18 \pm 0.32)$.

Xia *et al.* [2007XIA/FRI] measured the sulfate complex formation of Pu(IV) by conducting solvent extraction experiments in 2 M $HClO_4$ at different temperatures. The extraction data were interpreted with the formation of two Pu(IV) sulfate complexes according the equilibria (11.61) and (11.62). The reported experimental equilibrium constant, $\log_{10}{}^{*}K_{1,1}\,(11.61) = (2.71 \pm 0.05)$ at $I = 2$ M, can be corrected to $\log_{10}{}^{*}K_{1,1}\,(11.61) = (4.87 \pm 0.05)$ when using $\varepsilon(U^{4+}, ClO_4^-) = (0.76 \pm 0.06)$ kg·mol$^{-1}$, and $\log_{10}{}^{*}K_{1,1}\,(11.61) = (4.73 \pm 0.05)$ when using $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.06)$ kg·mol$^{-1}$. For both calculations, we applied $\varepsilon(USO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol$^{-1}$ from the NEA TDB and $\varepsilon(H^+, HSO_4^-) = (0.10 \pm 0.06)$ kg·mol$^{-1}$ reported in [2005VER/AME]. The reported $\log_{10}{}^{*}K_{1,2}\,(11.62) = (4.59 \pm 0.04)$ can be corrected to $\log_{10}{}^{*}K_{1,2}\,(11.62) = (7.17 \pm 0.05)$ by using $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.06)$ kg·mol$^{-1}$. Both values agree very well with the previously selected values and we retain the previously selected data in [2003GUI/FAN], $\log_{10}{}^{*}K_{1,1} = (4.91 \pm 0.22)$ and $\log_{10}{}^{*}K_{1,2} = (7.18 \pm 0.32)$.

The review in [2001LEM/FUG] evaluated the temperature-dependence of the formation of Pu(IV) sulfate complexes reported in four independent experimental data sets. The reported data show large differences with relatively small uncertainties for each data ranging from $-(7.1 \pm 1.7)$ kJ·mol$^{-1}$ to $(18.6 \pm 1.2)$ kJ·mol$^{-1}$ for $\Delta_r H^o_m\,(11.61)$ and from $(1.5 \pm 3.4)$ kJ·mol$^{-1}$ to $(8.6 \pm 6.8)$ kJ·mol$^{-1}$ for $\Delta_r H^o_m\,(11.62)$. The unweighted averaged data of $\Delta_r H^o_m\,(11.61) = (5.3 \pm 21.3)$ kJ·mol$^{-1}$ and $\Delta_r H^o_m\,(11.62) = (5.2 \pm 6.8)$ kJ·mol$^{-1}$ were not selected in [2001LEM/FUG], because of the lack of justification for selecting a sub-group of constants from the wide range of reported values for $\Delta_r H^o_m$. Xia *et al.* report the enthalpy of reaction $\Delta_r H^o_m\,(11.61) = (11.2 \pm 1.0)$ kJ·mol$^{-1}$ and $\Delta_r H^o_m\,(11.62) = (5.1 \pm 2.0)$ kJ·mol$^{-1}$, where $\Delta_r H^o_m\,(11.61)$ value falls in the upper half of the data available in the literature, which range from 2.4 to 18.6 kJ·mol$^{-1}$. When including the data reported in [2007XIA/FRI] the averages of all five experimental data sets are $\Delta_r H^o_m\,(11.61) = (9.3 \pm 6.4)$ kJ·mol$^{-1}$ and $\Delta_r H^o_m\,(11.62) = (5.2 \pm 5.6)$ kJ·mol$^{-1}$. This review agrees with the choice in [2001LEM/FUG], that no enthalpies of reactions can be selected, and our revised values are given for information only.

Under less acidic conditions $SO_4^{2-}$ becomes the dominant ligand that interacts with the actinide ions. By using the dissociation constants of $HSO_4^-$ ($pK_a$(2 M $H_2SO_4$) = 1.07 at 298.15 K, 1.14 at 313.15 K and 1.28 at 328.15 K) and the conditional

equilibrium constants for Reactions (11.61) and (11.62), Xia *et al.* calculated the equilibrium constants for the Reactions (11.63) and (11.64):

$$Pu^{4+} + SO_4^{2-} \rightleftharpoons PuSO_4^{2+} \quad (11.63)$$

$$Pu^{4+} + 2SO_4^{2-} \rightleftharpoons Pu(SO_4)_2(aq) \quad (11.64)$$

Xia *et al.* used $pK_a = 1.07$ at 298.15 K to obtain $\log_{10}\beta_{1,1}$ (11.63) = (3.78 ± 0.05) and $\log_{10}\beta_{1,2}$ (11.64) = (6.78 ± 0.04) at $I_M = 2$. By converting from molarity to molality and assuming $\varepsilon(USO_4^{2+}, ClO_4^-) = \varepsilon(PuSO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol$^{-1}$ and $\varepsilon(Pu^{4+}, ClO_4^-) = (0.82 \pm 0.06)$ kg·mol$^{-1}$, we calculate $\Delta\varepsilon_{i,j} = -(0.40 \pm 0.06)$ kg·mol$^{-1}$ and $\log_{10}\beta^o_{1,1}$ (11.63) = (6.61 ± 0.06) and $\log_{10}\beta^o_{1,2}$ (11.64) = (9.67 ± 0.06). It is to note that the dissociation constant of $HSO_4^-$, $pK_a = 1.07$ at 298.15 K, differs from the selected NEA TDB value by 0.24 logarithmic units. The value $pK_a = 1.07$ at $I_M = 2$ is close to $pK_a = 1.11$, which can be derived from $pK^o_a = (1.980 \pm 0.050)$ selected in the NEA TDB by using the ion-interaction parameters reported in [2005VER/AME], $\varepsilon(H^+, HSO_4^-) = (0.10 \pm 0.06)$ kg·mol$^{-1}$ and $\varepsilon(H^+, SO_4^{2-}) = -(0.03 \pm 0.06)$ kg·mol$^{-1}$. Thus, the thermodynamic data reported by Xia *et al.* for Reactions (11.63) and (11.64) are not selected by this review.

Table 11-20: Experimental equilibrium constants $\log_{10}K_{1,n}$ for the reaction $Pu^{4+} + nHSO_4^- \rightleftharpoons Pu(SO_4)_n^{4-2n} + nH^+$, and $\log_{10}\beta_{1,n}$ for the reaction $Pu^{4+} + nSO_4^{2-} \rightleftharpoons Pu(SO_4)_n^{4-2n}$.

| $T$/K | Method | $I$ (medium) | $\log_{10}K_{1,1}$ | $\log_{10}K_{1,2}$ | $\log_{10}\beta_{1,1}$ | $\log_{10}\beta_{1,2}$ | References |
|---|---|---|---|---|---|---|---|
| 298 | solv | 2.0 M $HClO_4$ | (2.71 ± 0.05) | (4.59 ± 0.04) | (3.78 ± 0.05) | (6.78 ± 0.04) | [2007XIA/FRI] |
| 313 | solv | 2.0 M $HClO_4$ | (2.79 ± 0.04) | (4.66 ± 0.04) | (3.93 ± 0.03) | (6.94 ± 0.04) | [2007XIA/FRI] |
| 323 | solv | 2.0 M $HClO_4$ | (2.87 ± 0.03) | (4.58 ± 0.04) | (4.15 ± 0.03) | (7.14 ± 0.04) | [2007XIA/FRI] |

# 11.5 Plutonium group 15 compounds and complexes

## 11.5.1 Plutonium nitrogen compounds and complexes

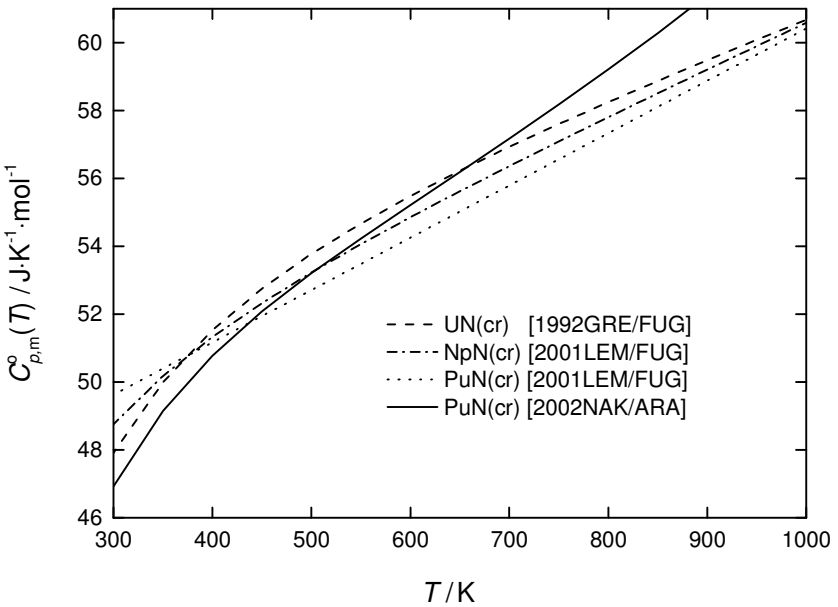
### 11.5.1.1 PuN(cr)

Since the review of [2001LEM/FUG], the heat capacity of plutonium mononitride PuN(cr) was measured by Differential Scanning Calorimetry using the scanning method in the temperature range 323-1023 K [2002NAK/ARA], yielding $C^o_{p,m}$ (PuN, cr, $T$) = (53.3-1.28 × 10$^{-3}$ $T$ + 0.24 × 10$^{-5}$ $T^2$ – 6.39 × 10$^5$ $T^{-2}$) J·K$^{-1}$·mol$^{-1}$. The calculated data are 5.6 % higher than recommended by [2001LEM/FUG] at 1000 K (see Figure 11- 8), and 5.6 % lower at room temperature, which does not satisfy the necessary constraint on $C^o_{p,m}$ (PuN, cr, 298.15 K). These data are also higher than NpN(cr) and UN(cr) above 510 and 660 K, respectively. We therefore prefer in this review to retain the equation

recommended by [2001LEM/FUG] based on the enthalpy increments data of Oetting and Leitnaker [1972OET/LEI] for the temperature range 298.15 <*T* /K < 1562:

$$C^{\circ}_{p,\mathrm{m}}\ (\mathrm{PuN, cr}, T) = (45.002 + 1.542 \times 10^{-2} T)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

Figure 11- 8: Heat capacity of the actinide mononitrides.




[2005KUR/ADA] reported a molecular dynamics (MD) study of the thermophysical properties of PuN(cr) in the temperature range 300-2500 K and pressure range 0.1MPa-1.5 GPa. The calculated ($C_V + C_d$) values (heat capacity at constant volume plus a lattice dilatation term) were found lower than the recommended data [2001LEM/FUG], with a difference of about 4 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 1400 K, which the authors attributed to the neglect of electronic contributions. [2005SED/KON] performed ab initio calculations of the enthalpies of formation of the actinide mononitrides AnN(cr) (An = Ac, Th, Pa, U, Np, Pu, Am) using the full potential linearised augmented plane wave technique modified for local orbitals (APW + lo). The calculated enthalpies of formation showed a linear decrease from UN towards AmN. However, the obtained enthalpy of formation for PuN(cr), *i.e.*, $\Delta_f H^{\circ}_{\mathrm{m}}$ (PuN, cr, 298.15 K) = – 311.9 $\mathrm{kJ \cdot mol^{-1}}$, is much lower than recommended by [2001LEM/FUG]. A good agreement was found for UN(cr) and NpN(cr), but large deviations were found for ThN(cr) and PuN(cr). The uncertainty on the calculated values is estimated to be around 15 $\mathrm{kJ \cdot mol^{-1}}$ by the present review. [2012BEN/ZAO] investigated the electronic structure, magnetic, dynamic and thermodynamic properties of PuN(cr) by ab initio pseudopotential and DFT methods

using the LDA approximation in a plane wave basis. Further details are given in Appendix A. The calculated heat capacity increased strongly below 200 K and more slowly above 600 K, approaching the Dulong-Petit limit (50 $J \cdot K^{-1} \cdot mol^{-1}$) around 1000 K. However, the data is about 10 $J \cdot K^{-1} \cdot mol^{-1}$ lower at 100 K than recommended in this review.

This review retains the data selected in [2001LEM/FUG] and [2003GUI/FAN]:

$$\Delta_f H_m^o \text{(PuN, cr, 298.15 K)} = -(299.2 \pm 2.5)\ kJ \cdot mol^{-1}$$

$$C_{p,m}^o \text{(PuN, cr, 298.15 K)} = (49.6 \pm 1.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m^o \text{(PuN, cr, 298.15 K)} = (64.8 \pm 1.5)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_f G_m^o \text{(PuN, cr, 298.15 K)} = -(273.719 \pm 2.551)\ kJ \cdot mol^{-1}.$$

### 11.5.1.2 Plutonium nitrates

#### 11.5.1.2.1 Aqueous plutonium nitrates

Despite the fact that acidic nitrate solutions are an important medium for spent nuclear fuel processing and also widely used as ionic medium electrolyte to study the properties of plutonium redox couples ([2009TKA/PRE], [2013KIM/ASA]), very few new data are available on aqueous plutonium nitrate complexes. Recent spectroscopic investigations illustrate that plutonium nitrate complexes are weak and high nitrate concentrations are necessary in order for nitrate ligands to enter the inner-coordination sphere of plutonium ions. This review assessed two studies on the Pu(IV) complex formation in 2-15 m $HNO_3/HClO_4$ solutions [1998BER/VEI] and the formation of the Pu(V) complex, $PuO_2NO_3$(aq), in 1 M $NaNO_3/NaClO_4$ [2010TOP/AUP]. Smith [2010SMI] has studied the interaction of Pu(IV) with nitrate spectroscopically, but did not provide thermodynamic data.

##### 11.5.1.2.1.1 Aqueous plutonium(V) nitrates

Topin *et al.* [2010TOP/AUP] investigated the nitrate complex formation of Pu(V) in 1 M $NaNO_3/NaClO_4$ electrolyte. The observed changes in electrophoretic ion mobility (when the majority of the background electrolyte is replaced by nitrate) are interpreted with the formation of the mono-nitrate complex, $PuO_2NO_3$(aq). The conditional stability constant is corrected to zero ionic strength by using an estimated value of $\varepsilon(AnO_2^+, NO_3^-) = (0.08 \pm 0.10)\ kg \cdot mol^{-1}$, which results in $\log_{10}\beta^o = (0.14 \pm 0.14)$ for $PuO_2NO_3$(aq). The parameter $\varepsilon(AnO_2^+, NO_3^-)$ is estimated using the empirical equation $\varepsilon(AnO_2^+, NO_3^-) = \varepsilon(Na^+, NO_3^-) + 0.12\ kg \cdot mol^{-1}$ and using $\varepsilon(Na^+, NO_3^-) = -(0.04 \pm 0.03)\ kg \cdot mol^{-1}$ from the NEA TDB. However, the data interpretation relies on the reference ion mobility of $PuO_2^+$ in 1 M $NaClO_4$ solutions, which may be different in a 0.9 M $NaNO_3$/0.1 M $NaClO_4$ solution. The replacement of 90 % of $ClO_4^-$ with $NO_3^-$ and its effect on the electrophoretic mobility of $AnO_2^+$ and the activity

coefficients of the solution species cannot be evaluated from the experimental data provided. For these reasons, this review has reported the data in [2010TOP/AUP] for information only.

Table 11-21: Experimental equilibrium constant for the reaction $PuO_2^+ + NO_3^- \rightleftharpoons PuO_2NO_3(aq)$.

| $T$/K | Method | $I$ (medium) | $\log_{10}\beta_{1,1}$ | Reference |
|---|---|---|---|---|
| 298 ± 1 | Electrophoresis | 0.9 M $NaNO_3$/0.1 M $NaClO_4$ | – (0.21 ± 0.10) | [2010TOP/AUP] |

#### 11.5.1.2.1.2 Aqueous plutonium(IV) nitrates

In [2001LEM/FUG], the NEA TDB selected the thermodynamic constant for the formation of the Pu(IV) mono-nitrate complex, $PuNO_3^{3+}$:

$$Pu^{4+} + NO_3^- \rightleftharpoons PuNO_3^{3+},\ \log_{10}K^{\circ}_{1,1} = (1.950 \pm 0.150).$$

Tkac *et al.* [2009TKA/PRE] included the Pu(IV) nitrate complexes $PuNO_3^{3+}$ and $Pu(NO_3)_2^{2+}$ to determine the amount of free Pu(IV) in 1 M $HNO_3$, which was necessary to deconvolute the electronic absorbance spectra. Smith [2010SMI] proposed the formation of multiple Pu(IV) nitrate species at 2-10 mol·L$^{-1}$ nitrate. However, he does not provide equilibrium constants or defines the composition of the solution species. [2013KIM/ASA] studied the electrochemical behaviour of Pu(III) and Pu(IV) in 1-7 M nitric acid and measured the electrochemical potentials for the Pu(IV)/Pu(III) redox couple. Spectroscopic measurements clearly identified inner-sphere complex formation of Pu(III) and Pu(IV) and the formation of multiple Pu nitrate complexes, but the authors did not explore their compositions or equilibrium constants. In an older report, not evaluated by [2001LEM/FUG] or [2003GUI/FAN], Berg *et al.* [1998BER/VEI] discussed a spectroscopic study of the reaction of Pu(IV) with nitrate, identifying two Pu(IV) nitrate complexes.

$$Pu^{4+} + NO_3^- \rightleftharpoons PuNO_3^{3+} \quad (11.65)$$

$$Pu^{4+} + 2NO_3^- \rightleftharpoons Pu(NO_3)_2^{2+} \quad (11.66)$$

The experimental data were collected up to an ionic strength of 19 m and then used together with SIT in order to correct to standard state conditions. The common SIT plot of the experimental formation constants corrected for $HNO_3$ dissociation, $\log_{10}\beta_{n,1} - \Delta z^2 D$ versus ionic strength, is linear over the investigated range of ionic strengths. The authors report the best fitting parameters as $\log_{10}\beta^{\circ}_{1,1}(11.65) = (2.12 \pm 0.20)$ and $\Delta\varepsilon_{i,j} = (0.17 \pm 0.02)$ kg·mol$^{-1}$ for $PuNO_3^{3+}$ and $\log_{10}\beta^{\circ}_{1,2}(11.66) = (3.66 \pm 0.40)$ and $\Delta\varepsilon_{i,j} = (0.36 \pm 0.03)$ kg·mol$^{-1}$ for $Pu(NO_3)_2^{2+}$ calculated over the range 2-19 m $HNO_3$. The majority of the experimental data used to establish thermodynamic data and ion-interaction parameters fall outside the applicability range of the SIT. Only the value $\log_{10}\beta_{1,1}(11.65) = 1.08$ at 2 m $HNO_3$ is within the SIT range.

The absorption spectra exhibit multiple isosbestic points indicating the presence of only two solution species and not three as used by Berg *et al.* For this reason and considering the explanations provided in Appendix A, the data for $\log_{10}\beta^{o}_{n,1}$ and $\Delta\varepsilon_{i,j}$ reported in [1998BER/VEI] have not been considered by this review.

Table 11-22: Experimental formation constants for the equilibrium: $Pu^{4+} + nNO_3^- \rightleftharpoons Pu(NO_3)_n^{4-n}$ reported in [1998BER/VEI](a). The values of $\log_{10}\beta_{n,1}$ are corrected for the $HNO_3$ dissociation and are based on the amount of free nitrate ions available.

| $T$/K | Method | $I$ (medium) | $\log_{10}\beta_{1,1}$ | $\log_{10}\beta_{1,1}$ (a) | $\log_{10}\beta_{1,2}$ | $\log_{10}\beta_{1,2}$ (a) |
|---|---|---|---|---|---|---|
| (293 ± 3) | spectr | 2 m $HNO_3/HClO_4$ | 0.48 | 1.08 | 0.49 | 1.10 |
| (293 ± 3) | spectr | 5 m $HNO_3/HClO_4$ | 0.72 | 1.63 | 0.78 | 1.74 |
| (293 ± 3) | spectr | 9 m $HNO_3/HClO_4$ | 1.14 | 2.46 | 1.42 | 3.02 |
| (293 ± 3) | spectr | 11 m $HNO_3/HClO_4$ | 1.29 | 2.90 | 1.78 | 3.88 |
| (293 ± 3) | spectr | 13 m $HNO_3/HClO_4$ | 1.26 | 2.93 | 2.04 | 4.48 |
| (293 ± 3) | spectr | 15 m $HNO_3/HClO_4$ | 1.27 | 2.91 | 2.35 | 5.07 |
| (293 ± 3) | spectr | 17 m $HNO_3/HClO_4$ | 1.27 | 2.92 | 2.66 | 5.71 |
| (293 ± 3) | spectr | 19 m $HNO_3/HClO_4$ | 1.30 | 2.93 | 3.00 | 6.33 |

(a) The values of $\log_{10}\beta_{1,n}$ are corrected for the $HNO_3$ dissociation and are based on the amount of free nitrate ions available.

## 11.5.2 Plutonium phosphorous compounds and complexes

Very few data have been reported on the aqueous plutonium phosphate system. Thermodynamic data have been selected in [2001LEM/FUG] for the Pu(III) solid compound $PuPO_4$(s, hyd), the Pu(IV) solid state compound $Pu(HPO_4)_2$(am, hyd) and the Pu(IV) aqueous complex $PuH_3PO_4^{4+}$. Since the last review, new solubility studies have been reported on the Pu(III) solid phosphate, $PuPO_4$(cr, hyd) [2010RAI/MOO], and the actinide phosphate, $(AnO_2)_3(PO_4)_2{\cdot}4H_2O$ where An = U and Pu [2005RAI/XIA].

### 11.5.2.1 Aqueous plutonium phosphates

Very few studies have been reported on the solubility or solution speciation of the Pu phosphate system. Only the thermodynamic data for the solution complex $PuH_3PO_4^{4+}$ was selected in [2001LEM/FUG] and retained in [2003GUI/FAN]:

$$Pu^{4+} + H_3PO_4(aq) \rightleftharpoons PuH_3PO_4^{4+},\ \log_{10}K^{o}_{1,1} = (2.400 \pm 0.300).$$

#### 11.5.2.1.1 Pu(VI) phosphate complexes

Rai *et al.* [2005RAI/XIA] report solubility data of Pu(VI) in phosphate-containing solutions with $(PuO_2)_3(PO_4)_2{\cdot}4H_2O$(s) as the solubility-controlling phase. The reported thermodynamic constants are summarised in Table 11-23. In the absence of solution speciation data, the authors use the analogous U(VI) phosphate solubility model to interpret Pu(VI) solubility data with the following solution species:

$PuO_2PO_4^-$, $PuO_2H_2PO_4^+$, $PuO_2(H_2PO_4)_2(aq)$, $PuO_2HPO_4(aq)$; $PuO_2H_3PO_4^{2+}$ and $PuO_2(H_2PO_4)(H_3PO_4)^+$; in addition they used the Pu(VI) hydrolysis species $PuO_2OH^+$, $PuO_2(OH)_2(aq)$, and $(PuO_2)_2(OH)_2^{2+}$. The authors made the assumption that the speciation and equilibrium constants for Pu(VI) phosphate complexes are very similar to the corresponding U(VI) species. Thus, the selected equilibrium constants for the U(VI) phosphates were used to start the data regression. The Pu(VI) solubilities predicted based on this set of Pu(VI) phosphate complexes fit very well the experimental solubility data in 0.001 m $NaH_2PO_4$ up to pH ~ 9; at higher pH, data on hydrolysis and ternary complex formation, such as $PuO_2(OH)_x(PO_4)_y^{2-x-3y}$, are uncertain, which results in an overestimate of the soluble Pu(VI) concentrations. However, in 0.01 m $NaH_2PO_4$ the speciation model agrees with experimental data at pH > 6.5, but does not match well the data at the lower solubility observed at pH < 6.5. The two solubility ranges in 0.001 m $NaH_2PO_4$ suggest that different solid phases are present in the experiments. Based on these inconsistencies and the uncertainties of the selected species, this review does not select any of the equilibrium constants for Pu(VI) phosphate solution species reported in [2005RAI/XIA].

Table 11-23: Thermodynamic equilibrium data for the Pu(VI) phosphate system.

| Method | $I$ (medium) | $\log_{10}K^o$ | Reference |
|---|---|---|---|
| $PuO_2^{2+} + PO_4^{3-} \rightleftharpoons PuO_2PO_4^-$ | | | |
| sol | 0.02 M NaCl/0.005 M $NaClO_4$-0.01 M $NaH_2PO_4$ | (11.76 ± 0.70) | [2005RAI/XIA] |
| $PuO_2^{2+} + H_2PO_4^- \rightleftharpoons PuO_2H_2PO_4^+$ | | | |
| sol | 0.02 M NaCl/0.005 M $NaClO_4$-0.01 M $NaH_2PO_4$ | 3.260 | [2005RAI/XIA] |
| $PuO_2^{2+} + 2H_2PO_4^- \rightleftharpoons PuO_2(H_2PO_4)_2(aq)$ | | | |
| sol | 0.02 M NaCl/0.005 M $NaClO_4$-0.01 M $NaH_2PO_4$ | 4.920 | [2005RAI/XIA] |
| $PuO_2^{2+} + HPO_4^{2-} \rightleftharpoons PuO_2HPO_4(aq)$ | | | |
| sol | 0.02 M NaCl/0.005 M $NaClO_4$-0.01 M $NaH_2PO_4$ | 7.241 | [2005RAI/XIA] |

#### 11.5.2.1.2 Pu(III) phosphate complexes

No thermodynamic values have been selected in previous reviews for Pu(III) phosphate solution complexes. The solution behaviour of Pu(III) in phosphate-containing solutions has been investigated by Rai and co-workers [2010RAI/MOO]. The thermodynamic equilibrium constants from this study are listed in Table 11-24. The authors assumed the interactions of phosphate with Pu(III) to be very weak based on the solubility behaviour of Pu across the pH range of 1-12, which in this respect is different from its chemical analogue Nd(III). The complex $PuPO_4(aq)$, proposed as a major Pu(III) solution species

in previous studies, was discarded by Rai and co-workers. Rai *et al.* studied the solubility of $PuPO_4$(cr, hyd) in $NaH_2PO_4$ solutions and modelled the measured Pu solubility data as function of $NaH_2PO_4$ concentration, assuming the formation of $PuH_2PO_4^{2+}$ under these conditions. The equilibrium constant $\log_{10}K^\circ = (2.2 \pm 0.6)$ was obtained for Reaction (11.67):

$$Pu^{3+} + H_2PO_4^- \rightleftharpoons PuH_2PO_4^{2+} \quad (11.67)$$

This value is in reasonable agreement with the values for the corresponding reaction in the Am(III) system, $\log_{10}K^\circ((11.75), \text{Am(III)}) = (3.00 \pm 0.50)$, selected in [1995SIL/BID] and $\log_{10}K^\circ((11.75), \text{Am(III)}) = (2.46 \pm 0.13)$ selected in the present review. Using the equilibrium constant $\log_{10}K^\circ = 2.78$, which was previously reported for the analogous Nd(III) complex $NdH_2PO_4^{2+}$ in [2003RAI/FEL], resulted in an overestimate of the Pu(III) solubility compared to the experimental data. This suggests that there are differences in the speciation and/or stability of Nd(III) and Pu(III) phosphate complexes. The associated SIT ion-interaction parameter $\varepsilon(PuH_2PO_4^{2+}, Cl^-) = 0.00$ kg·mol$^{-1}$, estimated by Rai *et al.*, is very uncertain and has no significant effect on the calculations and is not recommended by this review. Although Rai *et al.* excluded the formation of $PuPO_4$(aq) in their solubility model, they estimated an upper limit of $\log_{10}K^\circ \leq 14.4$ for the equilibrium (11.68) based on steady Pu(III) concentrations at pH > 5.

$$Pu^{3+} + PO_4^{3-} \rightleftharpoons PuPO_4(aq) \quad (11.68)$$

The estimation of this equilibrium constant coincides with the detection limit of the analytical method used and thus cannot be recommended by this review. However, this review accepts the equilibrium constant for Reaction (11.67) as reported in [2010RAI/MOO]:

$$\log_{10}K^\circ_{s,0}\ (PuH_2PO_4^{2+}, 298.15\ K) = (\mathbf{2.20 \pm 0.60}) \text{ and}$$

$$\Delta_r G^\circ_m((11.75), 298.15\ K) = \mathbf{-\ (12.558 \pm 3.425)}\ kJ{\cdot}mol^{-1}.$$

From this value and using $\Delta_f G^\circ_m(Pu^{3+}, aq, 298.15\ K) = -(578.984 \pm 2.688)$ kJ·mol$^{-1}$ and $\Delta_f G^\circ_m(H_2PO_4^-, 298.15\ K) = -(1137.152 \pm 1.567)$ kJ·mol$^{-1}$, we obtain $\Delta_f G^\circ_m(PuH_2PO_4^{2+}, 298.15\ K) = \mathbf{-\ (1728.694 \pm 4.627)}$ kJ·mol$^{-1}$.

Table 11-24: Thermodynamic equilibrium data for the Pu(III) phosphate system reported in [2010RAI/MOO].

| $T$/K | Method | $I$ (medium) | $\log_{10}K^\circ$ | Reference |
|---|---|---|---|---|
| $Pu^{3+} + PO_4^{3-} \rightleftharpoons PuPO_4(aq)$ | | | | |
| 296 ± 2 | sol | $10^{-4}$-1 M $NaH_2PO_4$ | ≤ 14.4 | [2010RAI/MOO] |
| $Pu^{3+} + H_2PO_4^- \rightleftharpoons PuH_2PO_4^{2+}$ | | | | |
| 296 ± 2 | sol | $10^{-4}$-1 M $NaH_2PO_4$ | (2.2 ± 0.6) | [2010RAI/MOO] |

### 11.5.2.2 Solid plutonium phosphorous compounds

#### 11.5.2.2.1 $(PuO_2)_3(PO_4)_2 \cdot 4H_2O$(am)

No thermodynamic data for Pu(VI) solid phases have been selected in previous reviews. [2005RAI/XIA] report solubility data of Pu(VI) in phosphate-containing solutions (0.02 M NaCl/0.005 M $NaClO_4$/0.01 M $NaH_2PO_4$) with $(PuO_2)_3(PO_4)_2 \cdot 4H_2O$(s) as the designated solubility-controlling phase. The authors assigned the composition of the solid phase in analogy to the corresponding U(VI) phase, although the absence of any peaks in the X-ray diffraction data of the solid Pu phosphate show that the phase is amorphous and EXAFS data show differences in the coordination modes between the U and Pu solid phosphate phase. However, the very similar solubility data of U(VI) and Pu(VI) at pH ≤ 4 support the assignment of the solid phase. Using the Pitzer formalism, the authors calculate $(\Delta_f G^o_m / RT)$ ($(PuO_2)_3(PO_4)_2 \cdot 4H_2O$, am) = – (2245.4 ± 1.4) and the thermodynamic solubility product $\log_{10} K^o_s$ = – (48.97 ± 0.69) for the dissolution Reaction (11.69):

$$(PuO_2)_3(PO_4)_2 \cdot 4H_2O(am) \rightleftharpoons 3PuO_2^{2+} + 2PO_4^{3-} + 4H_2O(l) \qquad (11.69)$$

The Gibbs energy of formation calculated from $\log_{10} K^o_{s,0}$ ($(PuO_2)_3(PO_4)_2 \cdot 4H_2O$, am, 298.15 K) and $(\Delta_f G^o_m / RT)$ values is $\Delta_f G^o_m$ ($(PuO_2)_3(PO_4)_2 \cdot 4H_2O$, 298.15 K) = – (5588.5 ± 3.5) kJ·mol$^{-1}$. The data are in line with the corresponding U(VI) data, $\Delta_f G^o_m$ ($(UO_2)_3(PO_4)_2 \cdot 4H_2O$, cr) = – (6137.283 ± 2.727) kJ·mol$^{-1}$ and $\log_{10} K^o_{s,0}$ ($(UO_2)_3(PO_4)_2 \cdot 4H_2O$, cr, 298.15 K) = – (49.08 ± 0.48), reported by Rai and co-workers. This data is also in good agreement with $\log_{10} K^o_{s,0}$ ($(UO_2)_3(PO_4)_2 \cdot 4H_2O$, cr, 298.15 K) = – (49.36 ± 0.30), calculated from the selected solubility product of $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr) and the dissociation constants of $H_3PO_4$(aq) in [2003GUI/FAN]. Due to the consistency with the corresponding U(VI) data, this review selects:

$\log_{10} K^o_{s,0}$ ($(PuO_2)_3(PO_4)_2 \cdot 4H_2O$, am, 298.15 K) = **– (48.97 ± 0.69)** and

$\Delta_r G^o_m$ ((11.69), 298.15 K) = (**279.523 ± 3.939**) kJ·mol$^{-1}$.

Assuming that the Pu(VI) solid phase has the same stoichiometry and number of water molecules as in $(UO_2)_3(PO_4)_2 \cdot 4H_2O$(cr) as Rai *et al.* claim, the Gibbs energy of formation calculated from the selected value of $\log_{10} K^o_{s,0}$ ($(PuO_2)_3(PO_4)_2 \cdot 4H_2O$, am, 298.15 K) and $(\Delta_f G^o_m / RT)$ = – (2245.4 ± 1.4) is $\Delta_f G^o_m$ ($(PuO_2)_3(PO_4)_2 \cdot 4H_2O$, am, 298.15 K) = – (5566.28 ± 3.47) kJ·mol$^{-1}$. Due to the amorphous character of the Pu(VI) solid phase indicated by the X-ray diffraction results and the lacking characterization of the number of hydration waters, this value is provided for information only.

#### 11.5.2.2.2 $PuPO_4$(cr) and $PuPO_4$(am,hyd)

The review in [2001LEM/FUG] discussed the only solubility study available from [1971MOS4] and selected a thermodynamic value after reinterpreting the original data:

$$PuPO_4(cr,hyd) \rightleftharpoons Pu^{3+} + PO_4^{3-},\ \log_{10}K^{o}_{s,0} = -(24.600 \pm 0.800).$$

A new solubility study of $PuPO_4$(cr, hyd) in $NaH_2PO_4$ solutions was reported by Rai *et al.* [2010RAI/MOO]. $PuPO_4$(cr, hyd) was identified as solid phase in coexistence with a less crystalline $PuPO_4$(am, hyd) phase. Due to the mixed crystallinity of the solid phase, we assign the reported data to the amorphous $PuPO_4$(am, hyd) phase. The authors applied the SIT to calculate $(\Delta_f G^{o}_m / RT)$ ($PuPO_4$, am, hyd) = – (703.144 ± 0.797) and $\log_{10}K^{o}_{sp}$ = – (24.28 ± 0.35) (Table 11-25) for the dissolution Reaction (11.70):

$$PuPO_4(am,hyd) \rightleftharpoons Pu^{3+} + PO_4^{3-} \qquad (11.70)$$

From the reported $(\Delta_f G^{o}_m / RT)$ value we calculate $\Delta_f G^{o}_m$ ($PuPO_4$, am, hyd) = – (1743.074 ± 1.976) kJ mol$^{-1}$. The reported $\log_{10}K^{o}_{sp}$ value is in good agreement with $\log_{10}K^{o}_{s}$ = – (24.790 ± 0.600) for the analogous $AmPO_4$(am, hyd) selected by the NEA TDB. Combining the $\log_{10}K^{o}_{s}$ values reported in this study and the previously selected TDB value, this review selects:

$$\log_{10}K^{o}_{s,0}\ (PuPO_4,\ am,\ hyd,\ 298.15\ K) = \mathbf{-\ (24.44 \pm 0.55)}\ \text{and}$$

$$\Delta_r G^{o}_m\ ((11.70),\ 298.15\ K) = (\mathbf{139.505 \pm 3.139})\ kJ\cdot mol^{-1}.$$

This value is very similar to $\log_{10}K^{o}_{sp}$ (11.70) = – (24.42 ± 0.38) obtained by [2010RAI/MOO] using the Pitzer formalism and also agrees well with data for the analogous Nd(III) and Am(III) phosphates. The Gibbs energy of formation calculated from the selected value of $\log_{10}K^{o}_{s,0}$ ($PuPO_4$, am, hyd, 298.15 K) and the $\Delta_f G^{o}_m$ values for $Pu^{3+}$ (– (578.984 ± 2.688) kJ·mol$^{-1}$) and $PO_4^{3-}$ (– (1025.491 ± 1.576) kJ·mol$^{-1}$) is $\Delta_f G^{o}_m$ ($PuPO_4$, am, hyd, 298.15 K) = – (1743.980 ± 3.116) kJ·mol$^{-1}$. Due to the uncertainty related to the presence of both a crystalline and amorphous phase, $\Delta_f G^{o}_m$ ($PuPO_4$, am, hyd, 298.15 K) is provided for information only and does not take into account any crystal water or water of hydration.

The low-temperature heat capacity of $PuPO_4$(cr) was measured by Thiriet *et al.* [2005THI/KON] by using relaxation calorimetry. The heat capacity and standard entropy at 298.15 K were derived as:

$$C^{o}_{p,m}(T)\ (PuPO_4,\ cr,\ 298.15\ K) = \mathbf{(114.5 \pm 2.5)}\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_m\ (PuPO_4,\ cr,\ 298.15\ K) = \mathbf{(137.0 \pm 2.7)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The high-temperature heat capacity of $PuPO_4$ was measured by Beneš *et al.* [2011BEN/POP] using a combination of drop-calorimetry (530 to 1386 K) and differential scanning calorimetry (400 to 1400 K). The results can be represented by the following equation, which is selected by the present review:

$$C^{o}_{p,m}(T) = 126.600 + 32.999\times10^{-3}(T/\mathrm{K}) - 1.9503\times10^{6}(T/\mathrm{K})^{-2} \quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}\,.$$

Table 11-25: Experimental data for the dissolution equilibrium $PuPO_4(am,hyd) \rightleftharpoons Pu^{3+} + PO_4^{3-}$

| $T$/K | Method | $I$ (medium) | $\log_{10}K^{o}_{s}$ | Reference |
|---|---|---|---|---|
| (296 ± 2) | sol | $10^{-4}$-1 M $NaH_2PO_4$ | – (24.28 ± 0.35) | [2010RAI/MOO] |

## 11.5.3 The plutonium-antimony system

### 11.5.3.1 PuSb(cr)

[2005JAV/WAS] measured the low temperature heat capacity of $^{242}$PuSb(cr) in the range 1.8-300 K using thermal relaxation calorimetry. Their results are in very good agreement with the data recommended by [2001LEM/FUG] based on the adiabatic measurements from 13 to 300 K and transient data below 20 K [1986HAL/JEF], [1990HAL/MOR]. Further details can be found in Appendix A. We retain the functions selected by [2001LEM/FUG]:

$$\Delta_f H^{o}_{m}\,(\mathrm{PuSb, cr, 298.15\ K}) = -(150.0 \pm 20.0)\ \mathrm{kJ\cdot mol^{-1}}$$

$$C^{o}_{p,m}\,(\mathrm{PuSb, cr, 298.15\ K}) = (52.8 \pm 3.5)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{o}_{m}\,(\mathrm{PuSb, cr, 298.15\ K}) = (106.9 \pm 7.5)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$\Delta_f G^{o}_{m}\,(\mathrm{PuSb, cr, 298.15\ K}) = -(152.063 \pm 20.126)\ \mathrm{kJ\cdot mol^{-1}}.$$

# 11.6 Plutonium group 14 compounds and complexes

## 11.6.1 Plutonium carbonates

### 11.6.1.1 The aqueous plutonium carbonates

Thermodynamic data for plutonium carbonate complexes in solution have been evaluated in both previous reviews, [2001LEM/FUG] and [2003GUI/FAN]. Thermodynamic data were selected for Pu(IV) ($Pu(CO_3)_4^{4-}$ and $Pu(CO_3)_5^{6-}$), Pu(V) ($PuO_2CO_3^-$ and $PuO_2(CO_3)_3^{3-}$) ), and Pu(VI) ($PuO_2(CO_3)_n^{2-2n}$ where $n$ = 1, 2 and 3) solution complexes.

In [2003VIT/CAP], Vitorge and Capdevila used reported thermodynamic data of Pu compounds to predict the Pu solubility in ground and surface waters. The authors also estimated formation constants for potential hydroxo and carbonato complexes of An(IV) and An(V), such as $Pu(OH)_x(CO_3)_y^{4-x-2y}$, in order to improve the predicted solution behaviour of actinides and to better match experimental data. In many cases the experimental evidence for the suggested complexes is not available. One experimental

study reported on the formation of the Pu(V) complexes, $PuO_2(CO_3)_n^{1-2n}$ where $n$ = 1-3 [2009TOP/AUP2].

#### 11.6.1.1.1 Pu(VI) carbonate complexes

The carbonate complex formation of Pu(VI) has been studied in detail and both structural information and thermodynamic data are available for the complexes $PuO_2CO_3(aq)$, $PuO_2(CO_3)_2^{2-}$, and $PuO_2(CO_3)_3^{4-}$. Thermodynamic data for these complexes were selected in [2001LEM/FUG] and revised in [2003GUI/FAN]:

$$PuO_2^{2+} + CO_3^{2-} \rightleftharpoons PuO_2CO_3(aq)\,,\ \log_{10}\beta_{1,1}^{o} = (9.500 \pm 0.500)$$

$$PuO_2^{2+} + 2CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_2^{2-}\,,\ \log_{10}\beta_{1,2}^{o} = (14.700 \pm 0.500)$$

$$PuO_2^{2+} + 3CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_3^{4-}\,,\ \log_{10}\beta_{1,3}^{o} = (18.000 \pm 0.500).$$

In [2001LEM/FUG], thermodynamic data have also been selected for the trimeric Pu(VI) carbonate complex, $(PuO_2)_3(CO_3)_6^{6-}$. However, the thermodynamic equilibrium constant for the Pu(VI) trimer complex was not selected in [2003GUI/FAN], claiming the lack of sufficient data compared to the analogous U(VI) or Np(VI) trimeric carbonate complex. There is experimental evidence (mainly by NMR and UV-vis-NIR absorption spectroscopy) that the Pu(VI) carbonate trimer exists, but its stability field is much more restricted compared to the analogue U(VI) or Np(VI) carbonate trimers. Since [2003GUI/FAN] did not provide any further detailed justification for not selecting the trimeric Pu(VI) carbonate species and in analogy to the U(VI) and Np(VI) system, we retain the thermodynamic equilibrium constant selected in [2001LEM/FUG]:

$$3PuO_2(CO_3)_3^{4-} \rightleftharpoons (PuO_2)_3(CO_3)_3^{6-} + 3CO_3^{2-}\,,$$
$$\log_{10}K(3.0\ \text{M NaClO}_4,\ 22\ ^\circ\text{C}) = -(7.5 \pm 0.5).$$

The combination of this equilibrium constant with $\log_{10}\beta_{1,3}^{o} = (18.0 \pm 0.5)$ revised in [2003GUI/FAN] and extrapolated to $I$ = 3.0 M $NaClO_4$ using $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)$ kg·mol$^{-1}$ and $\varepsilon(PuO_2(CO_3)_3^{4-}, Na^+) = -(0.2 \pm 0.3)$ kg·mol$^{-1}$ results in

$$3PuO_2^{2+} + 6CO_3^{2-} \rightleftharpoons (PuO_2)_3(CO_3)_6^{6-},$$
$$\log_{10}\beta_{3,6}(3.0\ \text{M NaClO}_4) = \mathbf{(51.000 \pm 2.500)}.$$

which is selected in this review without extrapolation to $I = 0$. This equilibrium constant is in line with the constants selected in [2003GUI/FAN] for U(VI), $\log_{10}\beta_{3,6}^{o}((UO_2)_3(CO_3)_6^{6-}) = (54.000 \pm 1.000)$, and selected in this review for Np(VI), $\log_{10}\beta_{3,6}^{o}((NpO_2)_3(CO_3)_6^{6-}) = (51.428 \pm 2.084)$.

Similarly, this review also retains the thermodynamic constant for the mixed-actinyl complex, $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$, reported in [2001LEM/FUG] but neglected in [2003GUI/FAN]:

$PuO_2(CO_3)_3^{4-} + 2UO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_2PuO_2(CO_3)_6^{6-} + 3CO_3^{2-}$,

$\log_{10}\beta^{o}_{(2,1),6}$ = **– (8.200 ± 1.300)**.

The value of $\Delta_f G^o_m((UO_2)_2PuO_2(CO_3)_6^{6-})$ is recalculated in this review considering the value of $\Delta_f G^o_m(PuO_2(CO_3)_3^{4-})$ = – (2448.797 ± 4.180) kJ·mol$^{-1}$ revised in [2003GUI/FAN]:

$$\Delta_f G^o_m((UO_2)_2PuO_2(CO_3)_6^{6-}) = \textbf{– (6140.119 ± 9.582)}\ \text{kJ·mol}^{-1}$$

Since the last review, no new experimental data have been reported for aqueous Pu(VI) carbonate solution complexes, but there are assessments on their structures and geometries. The modelling studies confirm the information on bonding and coordination geometries of Pu(VI) solution carbonate complexes obtained from spectroscopic and crystallographic studies. Moriyama and co-workers [2002MOR/FUJ] applied a hard-sphere model with improved electrostatic and non-electrostatic interactions to calculate thermodynamic equilibrium constants of Pu(VI) carbonate complexes and reported $\log_{10}\beta^{o}_{1,1}$ = 8.96, $\log_{10}\beta^{o}_{1,2}$ = 15.49, and $\log_{10}\beta^{o}_{1,3}$ = 17.51 for the equilibrium reactions of $PuO_2CO_3$(aq), $PuO_2(CO_3)_2^{2-}$, and $PuO_2(CO_3)_3^{4-}$, respectively:

$$PuO_2^{2+} + CO_3^{2-} \rightleftharpoons PuO_2CO_3(aq) \quad (11.71)$$

$$PuO_2^{2+} + 2CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_2^{2-} \quad (11.72)$$

$$PuO_2^{2+} + 3CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_3^{4-} \quad (11.73)$$

These estimates are quite different from the values selected in [2003GUI/FAN] and also disagree with the calculated equilibrium constants for the analogous U(VI) compounds reported in [2003GUI/FAN], $UO_2CO_3$(aq)( $\log_{10}\beta^{o}_{1,1}$ = (9.940 ± 0.030)), $UO_2(CO_3)_2^{2-}$ ( $\log_{10}\beta^{o}_{1,2}$ = (16.610 ± 0.090)), and $UO_2(CO_3)_3^{4-}$ ( $\log_{10}\beta^{o}_{1,3}$ = (21.840 ± 0.040)) and the analogous Np(VI) carbonates ( $\log_{10}\beta^{o}_{1,1}$ = (9.860 ± 0.100) and $\log_{10}\beta^{o}_{1,3}$ = (19.900 ± 0.500), see Sections 10.6.1.1.2 and 10.6.1.1.3, respectively). Balasubramanian and Chaudhuri [2008BAL/CHA] performed gas-phase calculations of the structure and vibrational spectra of the Pu(VI) bis- and tris-carbonate complexes. The authors optimised the structures of the complexes $CaPuO_2(CO_3)_2$ and $Ca_3PuO_2(CO_3)_3^{2+}$, in which the $Ca^{2+}$ cations are placed between the carbonate ligands in the equatorial plane around the Pu atom. In aqueous systems, additional coordination of water molecule(s) must be considered for the complex $CaPuO_2(CO_3)_2$. The coordination of three $Ca^{2+}$ cations in $Ca_3PuO_2(CO_3)_3^{2+}$ will require a high concentration of $Ca^{2+}$ cations and under these conditions no equilibrium constants can be selected.

#### 11.6.1.1.2 Pu(V) carbonate complexes

The Pu(V) carbonate system is discussed in [2001LEM/FUG] and thermodynamic data were selected for the complexes $PuO_2CO_3^-$ and $PuO_2(CO_3)_3^{5-}$:

$$PuO_2^+ + CO_3^{2-} \rightleftharpoons PuO_2CO_3^-,\ \log_{10}\beta_{1,1}^o = (5.120 \pm 0.140)$$

$$PuO_2^+ + 3CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_3^{5-},\ \log_{10}\beta_{1,3}^o = (5.025 \pm 0.920).$$

No thermodynamic data were added in [2003GUI/FAN] and no data were selected for the $PuO_2(CO_3)_2^{3-}$ complex. While the equilibrium constant for the formation of $PuO_2CO_3^-$ is based on experimental spectroscopic data reported in [1992BEN/HOF], [2001LEM/FUG] calculated the equilibrium constant for the limiting Pu(V) complex in carbonate, $PuO_2(CO_3)_3^{5-}$, from the recommended thermodynamic data for the formation of the Pu(VI) complex $PuO_2(CO_3)_3^{4-}$, $\log_{10}\beta_{1,3}^o = (17.7 \pm 0.9)$ and $\Delta_r G_m^o = -(101.03 \pm 5.14)$ kJ·mol$^{-1}$, and the recommended potential for the Pu(VI)/Pu(V) redox couple in acid solution, $E^\circ = (936 \pm 5)$ mV. This review rejects the selected value in [2001LEM/FUG], $\log_{10}\beta_{1,3}^o = (5.025 \pm 0.920)$, that is based on the Pu(VI)/Pu(V) equilibrium in carbonate and on the redox couple of the $PuO_2^{2+}/PuO_2^+$ aquo ions in acid. [2001LEM/FUG] state that the absence of evidence for $PuO_2(CO_3)_2^{3-}$ may be due to disproportionation reactions or a small stability of this solution species. However, the majority of the reported studies were performed at conditions that do not favour the formation of $PuO_2(CO_3)_2^{3-}$ but the limiting species $PuO_2(CO_3)_3^{5-}$, *i.e.*, electrochemical studies at $[CO_3^{2-}] \geq 0.3$ M. Under these conditions the tris-carbonato complex is the dominant Pu(VI) solution species.

Moriyama and co-workers [2002MOR/FUJ] applied a hard-sphere model with improved electrostatic and non-electrostatic interactions to calculate thermodynamic formation constants of Pu(V) carbonate complexes. The calculated equilibrium constant for $PuO_2CO_3^-$, $\log_{10}\beta_{1,1}^o = 5.12$, is identical to the value selected in [2001LEM/FUG], but is slightly different from the analogous value selected for $NpO_2CO_3^-$, $\log_{10}\beta_{1,1}^o = (4.962 \pm 0.061)$.

The formation of Np(V) and Pu(V) carbonate complexes is studied by Topin *et al.* [2009TOP/AUP2] by measuring variations in the electrophoretic mobility of the different solution species as function of pH and carbonate concentration. The authors determined equilibrium constants for $PuO_2(CO_3)_n^{1-2n}$ where $n$ = 1-3 (Table 11-26) and corrected for ionic strength by using the ion interaction parameters for the Np(V) carbonate system in [2001LEM/FUG]. Topin *et al.* report the thermodynamic equilibrium constants $\log_{10}\beta_{1,1}^o = (4.947 \pm 0.099)$ for Reaction (11.74), $\log_{10}\beta_{1,2}^o = (6.341 \pm 0.100)$ for (11.75), and $\log_{10}\beta_{1,3}^o = (5.607 \pm 0.162)$ for (11.76).

$$PuO_2^+ + CO_3^{2-} \rightleftharpoons PuO_2CO_3^- \quad (11.74)$$

$$PuO_2^+ + 2CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_2^{3-} \quad (11.75)$$

$$PuO_2^+ + 3CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_3^{5-} \quad (11.76)$$

The authors used the corresponding SIT parameters as selected in [2001LEM/FUG]. The constants reported by Topin *et al.* are consistent with those for Np(V) carbonate complexes. The value of $\log_{10}\beta_{1,1}^o = (4.95 \pm 0.10)$ is slightly lower (but

within the estimated uncertainty range) than the previously selected value of (5.120 ± 0.140) for $PuO_2CO_3^-$, and also very similar to $\log_{10}\beta^o_{1,1}$ = (4.96 ± 0.06) for $NpO_2CO_3^-$, selected in [2001LEM/FUG]. While the reported $\log_{10}\beta^o_{1,3}$ value for $PuO_2(CO_3)_3^{5-}$ also correlates well with $\log_{10}\beta^o_{1,3}$ = (5.50 ± 0.15) for $NpO_2(CO_3)_3^{5-}$ selected in [2001LEM/FUG], but both values differ significantly from $\log_{10}\beta^o_{1,3}$ ( $UO_2(CO_3)_3^{5-}$ ) = (6.950 ± 0.360) reported in [2003GUI/FAN]. The U(V) value was selected after reinterpreting data from a cyclic voltammetry study of the U(VI)/U(V) redox potential in carbonate solutions ([1993MIZ/PAR], [1999CAP/VIT]). Given the well-established analogous chemical behaviour of Np(V) in carbonate solutions, the selected constant for $UO_2(CO_3)_3^{5-}$ appears to be at least questionable and requires further experimental validation.

The stepwise formation constant, $\log_{10}\beta^o_{2,3}$ = – 0.734, for the reaction

$$PuO_2(CO_3)_2^{3-} + CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_3^{5-} \quad (11.77)$$

calculated from data in [2009TOP/AUP2] is larger than the analogous data for Np(V), $\log_{10}\beta^o_{2,3}$ = – (1.034 ± 0.110) [2003GUI/FAN]. This difference may be caused by the data analysis including both $PuO_2(CO_3)_2^{3-}$ and $PuO_2(CO_3)_3^{5-}$ complexes (see Appendix A for details). Similarly, the stepwise formation constant in [2009TOP/AUP2] for the complex $PuO_2(CO_3)_2^{3-}$, $\log_{10}\beta^o_{1,2}$ = (1.394 ± 0.100) according to the equilibrium Reaction (11.78), is slightly lower compared to the analogous Np(V) constant, $\log_{10}\beta^o_{1,2}$ = (1.572 ± 0.083) [2003GUI/FAN].

$$PuO_2CO_3^- + CO_3^{2-} \rightleftharpoons PuO_2(CO_3)_2^{3-} \quad (11.78)$$

Table 11-26: Experimental and thermodynamic equilibrium constants for the reaction $PuO_2^+ + nCO_3^- \rightleftharpoons PuO_2(CO_3)_n^{1-2n}$ with $n$ = 1-3 reported by Topin *et al.*

| $T$ /K | Method | $I$ (medium) | $\log_{10}\beta_{1,1}$ | $\log_{10}\beta_{1,2}$ | $\log_{10}\beta_{1,3}$ | Reference |
|---|---|---|---|---|---|---|
| 298 ± 1 | CE | 0.37 M $NaClO_4$ | (4.433 ± 0.089) | (6.435 ± 0.100) | (7.735 ± 0.221) | [2009TOP/AUP2] |
| 298 ± 1 | CE | 0 | (4.947 ± 0.099) | (6.341 ± 0.100) | (5.607 ± 0.162) | [2009TOP/AUP2] |

The study of Topin *et al.* [2009TOP/AUP2] provides the first set of equilibrium constants for the three major Pu(V) carbonate species in aqueous solution, although the reported constants for $PuO_2(CO_3)_2^{3-}$ and $PuO_2(CO_3)_3^{5-}$ need to be refined as discussed in the Appendix entry. We estimate that the value of $\log_{10}\beta^o_{1,2}$ is about 0.1-0.3 $\log_{10}$ units too low, which would shift the Pu(V) value closer to the reported value for $NpO_2(CO_3)_2^{3-}$. Despite the concerns regarding the data analysis in [2009TOP/AUP2], this review selects the average of the two experimental data for Reaction (11.74) reported in [1992BEN/HOF] and [2009TOP/AUP2] and selects the data in [2009TOP/AUP2] for Reactions (11.75) and (11.76) with increased uncertainties:

$\log_{10}\beta^{o}_{1,1}$ ((11.74), 298.15 K) = (**5.03 ± 0.12**) and

$\Delta_r G^{o}_{m}$ ((11.74), 298.15 K) = **– (28.711 ± 0.685)** kJ·mol$^{-1}$,

$\log_{10}\beta^{o}_{1,2}$ ((11.75), 298.15 K) = (**6.34 ± 0.20**) and

$\Delta_r G^{o}_{m}$ ((11.75), 298.15 K) = **– (36.189 ± 1.142)** kJ·mol$^{-1}$,

$\log_{10}\beta^{o}_{1,3}$ ((11.76), 298.15 K) = (**5.61 ± 0.24**) and

$\Delta_r G^{o}_{m}$ ((11.76), 298.15 K) = **– (32.022 ± 1.370)** kJ·mol$^{-1}$.

Based on these thermodynamic data and using $\Delta_f G^{o}_{m}(PuO_2^{+}, 298.15\ K)$ = – (852.646 ± 2.868) kJ·mol$^{-1}$, we can calculate the Gibbs energy of formation for the Pu(V) carbonate complexes: $\Delta_f G^{o}_{m}(PuO_2CO_3^{-}, 298.15\ K)$ = **– (1409.257 ± 2.974)** kJ·mol$^{-1}$, $\Delta_f G^{o}_{m}(PuO_2(CO_3)_2^{3-}, 298.15\ K)$ = **– (1944.635 ± 3.184)** kJ·mol$^{-1}$, and $\Delta_f G^{o}_{m}(PuO_2(CO_3)_3^{5-}, 298.15\ K)$ = **– (2468.368 ± 3.387)** kJ·mol$^{-1}$. The values agree well with the data selected in [2001LEM/FUG], $\Delta_f G^{o}_{m}(PuO_2CO_3^{-}, 298.15\ K)$ = – (1409.771 ± 3.002) kJ·mol$^{-1}$ and $\Delta_f G^{o}_{m}(PuO_2(CO_3)_3^{5-}, 298.15\ K)$ = – (2465.031 ± 6.096) kJ·mol$^{-1}$.

[2001LEM/FUG] also calculated $\Delta_r H^{o}_{m}$ ((11.76), 298.15 K) = – (19.11 ± 8.50) kJ·mol$^{-1}$ and $\Delta_r S^{o}_{m}$ ((11.76), 298.15 K) = (32.1 ± 33.5) J·K$^{-1}$·mol$^{-1}$ by using $\Delta_r H^{o}_{m}(PuO_2(CO_3)_3^{4-} / PuO_2(CO_3)_3^{5-}, 298.15\ K)$ = – (68.6 ± 5.5) kJ·mol$^{-1}$, which was derived from the one-electron reduction reaction of $PuO_2(CO_3)_3^{4-}$, the enthalpy for the $PuO_2^{2+} / PuO_2^{+}$ aquo ion couple (– (88.09 ± 6.00) kJ·mol$^{-1}$), and the enthalpy of reaction for the formation of $PuO_2(CO_3)_3^{4-}$ (– (38.6 ± 2.0) kJ·mol$^{-1}$) recommended in [2001LEM/FUG]. When we apply the new value, $\Delta_r G^{o}_{m}$ ((11.76), 298.15 K) = – (32.022 ± 1.370) kJ·mol$^{-1}$, and maintain $\Delta_r H^{o}_{m}$ ((11.76), 298.15 K) = – (19.11 ± 8.50) kJ·mol$^{-1}$, the corresponding entropy of reaction is $\Delta_r S^{o}_{m}$ ((11.76), 298.15 K) = (43.307 ± 8.610) J·K$^{-1}$ mol$^{-1}$. We do not select these calculated values because the calculation of $\Delta_r H^{o}_{m}$ in [2001LEM/FUG] relies on an estimated entropy value, $\Delta_r S^{o}_{m}(PuO_2(CO_3)_3^{4-} / PuO_2(CO_3)_3^{5-}, 298.15\ K)$ = (170 ± 48) J·K$^{-1}$·mol$^{-1}$, for the $PuO_2(CO_3)_3^{4-} / PuO_2(CO_3)_3^{5-}$ redox reaction.

The selected data for the Pu(V) carbonate system is in good agreement with the equilibrium constants for the analogous Np(V) carbonate system selected in [2001LEM/FUG] and [2003GUI/FAN], and which are retained by this review (see Section 10.6.1.1.6 Aqueous Np(V) carbonates): $\log_{10}\beta^{o}_{1,1}$ ((11.74), Np(V), 298.15 K) ((10.44), 298.15 K) = (4.962 ± 0.061), $\log_{10}\beta^{o}_{1,2}$ ((11.75), Np(V), 298.15 K) ((10.45), 298.15 K) = (6.534 ± 0.100), and $\log_{10}\beta^{o}_{1,3}$ ((11.76), Np(V), 298.15 K) ((10.46), 298.15 K) = (5.500 ± 0.150) [2001LEM/FUG]. In addition, the equilibrium constants that Topin *et al.* [2009TOP/AUP2] reported for the Np(V) carbonate system are within the range of the selected Np(V) values, which supports the selection of the thermodynamic data for Pu(V).

#### 11.6.1.1.3 Pu(IV) carbonate complexes

The characterisation of Pu(IV) carbonate complexes is limited to a few aqueous species. Both binary and ternary, mainly Pu(IV) hydroxycarbonate complexes of general formula $Pu(OH)_x(CO_3)_y^{4-x-2y}$, have been proposed to form, but there is no clear spectroscopic evidence that could support the proposed species. Thermodynamic data for two complexes were selected in [2001LEM/FUG] and revised in [2003GUI/FAN]:

$$Pu^{4+} + 4CO_3^{2-} \rightleftharpoons Pu(CO_3)_4^{4-},\ \log_{10}\beta_{1,4}^{o} = (37.000 \pm 1.100)$$

$$Pu^{4+} + 5CO_3^{2-} \rightleftharpoons Pu(CO_3)_5^{6-},\ \log_{10}\beta_{1,5}^{o} = (35.650 \pm 1.130).$$

Binary and ternary Pu(IV) solution complexes, such as $Pu(CO_3)_y^{4-2y}$ and $Pu(OH)_x(CO_3)_y^{4-x-2y}$, were used by Vitorge and Capdevila [2003VIT/CAP] to predict the solubility behaviour of Pu(IV) in natural water. The authors estimated maximum values for the stability constants of these complexes. However, there is no experimental proof of their existence, which is required before the constants can be used reliably. This review discards the data reported for the solution species proposed in [2003VIT/CAP].

Moriyama and co-workers [2002MOR/FUJ] applied a hard-sphere model with improved electrostatic and non-electrostatic interactions to calculate thermodynamic formation constants of two Pu(IV) carbonate complexes, $Pu(CO_3)_4^{4-}$ and $Pu(CO_3)_5^{6-}$. Both complexes are established Pu(IV) species that form at high carbonate concentrations. The calculated respective equilibrium constants, $\log_{10}\beta_{1,4}^{o} = 34.02$ and $\log_{10}\beta_{1,5}^{o} = 33.81$, are nearly identical suggesting that a structure with eight oxygen donors from the coordinated carbonate is more stable than the one with ten coordinated oxygen atoms, this is consistent with known structure features of An(IV) complexes. The equilibrium constants are quite different from the values selected in [2003GUI/FAN] and are not selected by this review.

#### 11.6.1.1.4 Pu(III) carbonate complexes

Ödegard-Jensen and co-workers [2004ODE/ALB] reported concentrations of $10^{-7}$ and $10^{-9}$ M Pu(III) that were measured in $NaClO_4$ solutions in the absence of carbonate and at 0.03 % $CO_2$ atmosphere with hydrogen as reducing agent. The authors suggest that the blue Pu(III) hydroxide precipitate is transforming with time to amorphous Pu(IV) oxide. No thermodynamic data were derived from the measured solubility data.

### 11.6.1.2 Solid plutonium carbonates

There are few studies reporting new experimental data on plutonium carbonate complexes in the solid state. Runde and co-workers [2007RUN/BRO] synthesised a ternary Pu(IV) carbonate-peroxide solid phase, $Na_8Pu_2(O_2)_2(CO_3)_6 \cdot 12H_2O$, that contains discrete, dimeric $Pu_2(O_2)(CO_3)_6^{8-}$ anions illustrating the potential formation of ternary Pu(IV) solid phases with more than one oxygen-donor ligand in aqueous solutions containing multiple ligands.

#### 11.6.1.2.1 Solid plutonium(VI) carbonates

The Pu(VI) carbonate solid phases relevant to aqueous environments have been discussed in [2001LEM/FUG] and [2003GUI/FAN]. The thermodynamic data selected in [2001LEM/FUG] for $PuO_2CO_3$(cr) was revised in [2003GUI/FAN] based on the new data reported in [2000REI/NEU]:

$$PuO_2CO_3(cr) \rightleftharpoons PuO_2^{2+} + CO_3^{2-},\ \log_{10}K_{sp}^{o} = -(14.650 \pm 0.470).$$

Reilly and co-workers [2007REI/RUN] reported the solubility of $PuO_2CO_3$(cr) in 0.1-5.6 m NaCl and 5.6 m $NaClO_4$ solutions. The authors monitored spectroscopically the dissolution equilibrium and used the absorbance features characteristic for Pu(V) and Pu(VI) species to determine solution speciation. The spectral data allow discrimination between Pu(VI) and Pu(V) and can in this way be used to describe the conditional solubility of $PuO_2CO_3$(cr) based on the solution concentration of Pu(VI) according to Equation (11.79).

$$PuO_2CO_3(cr) \rightleftharpoons Pu(VI)_{tot} + CO_3^{2-} \tag{11.79}$$

with the concentration of $Pu(VI)_{tot}$ being expressed by Equation (11.80):

$$[Pu(VI)]_{tot} = [PuO_2^{2+}] + \sum [PuO_2Cl_x^{2-x}] \tag{11.80}$$

The calculated conditional solubility product, $\log_{10}K_{sp}$ (11.79), considers only the carbonate complexes and does not take into account for the formation of chloride complexes. The absorbance spectra reported in [2007REI/RUN] allow to discriminate between $PuO_2^{2+}$ and $PuO_2Cl_x^{2-x}$ complexes. By using only the electronic absorbance of $PuO_2^{2+}$ at 830 nm, the true dissolution equilibrium of $PuO_2CO_3$(cr) can be calculated:

$$PuO_2CO_3(cr) \rightleftharpoons PuO_2^{2+} + CO_3^{2-} \tag{11.81}$$

In contrast to (11.79), the dissolution Reaction (11.81) explicitly excludes the contribution of chloride complexes and thus describes accurately the dissolution reaction of $PuO_2CO_3$(cr). The authors report a set of conditional solubility products and calculate from the soluble concentration of $PuO_2^{2+}$, $\log_{10}K_{sp}^{o}$ (11.81) = – (14.82 ± 0.05). The associated ion-interaction parameter $\Delta\varepsilon_{ij}$ (11.81) = (0.11 ± 0.08) kg·mol$^{-1}$ was obtained from the SIT plot, $\log_{10}K_{sp} - \Delta z^2 D$ *vs.* $I_m$. Using this value and $\varepsilon(Na^+, CO_3^{2-})$ = – (0.08 ± 0.03) kg·mol$^{-1}$, this review derives the ion-interaction parameter $\varepsilon(PuO_2^{2+}, Cl^-)$ = (0.19 ± 0.09) kg·mol$^{-1}$, which is in good agreement with the analogue vale for U(VI), $\varepsilon(UO_2^{2+}, Cl^-)$ = (0.21 ± 0.02) kg·mol$^{-1}$ selected in previous NEA TDB reviews. However, for this comparison one has to consider that the value for $\varepsilon(UO_2^{2+}, Cl^-)$ was obtained without considering the presence of U(VI) chloro complexes, which also may interact with chloride.

This review revises the data selected in [2003GUI/FAN] and selects with an increased uncertainty to accommodate for the standard deviations of the original data

$$\log_{10}K_{sp}((11.81), 298.15\ K) = \mathbf{-\ (14.82 \pm 0.12)}\ \text{and}$$

$\Delta_r G_m^o$ ((11.81), 298.15 K) = (**84.593 ± 0.685**) kJ·mol$^{-1}$.

From these values we can derive $\Delta_f G_m^o$ ($PuO_2CO_3$, cr, 298.15 K) = **– (1374.846 ± 2.929)** kJ·mol$^{-1}$, which is in agreement with – (1373.876 ± 3.912) kJ·mol$^{-1}$ reported in [2003GUI/FAN].

Table 11-27: Experimental solubility product of $PuO_2CO_3$(cr) according to the dissolution reaction $PuO_2CO_3(cr) \rightleftharpoons PuO_2^{2+} + CO_3^{2-}$ reported in [2007REI/RUN]. The values for $\log_{10} K_{sp}$ (11.81) values were calculated by this review from the original data.

| $T$/K | Method | $I$ (medium) | $\log_{10} K_{sp}$ (11.79) | $\log_{10} K_{sp}$ (11.81) | Reference |
|---|---|---|---|---|---|
| 298 | sol | 0.1 m NaCl | – (13.93 ± 0.07) | – (13.95 ± 0.07) | [2007REI/RUN] |
| 298 | sol | 0.2 m NaCl | – (13.67 ± 0.14) | – (13.71 ± 0.13) | [2007REI/RUN] |
| 298 | sol | 0.51 m NaCl | – (13.44 ± 0.06) | – (13.50 ± 0.06) | [2007REI/RUN] |
| 298 | sol | 1.02 m NaCl | – (13.19 ± 0.14) | – (13.24 ± 0.14) | [2007REI/RUN] |
| 298 | sol | 2.09 m NaCl | – (13.02 ± 0.14) | – (13.20 ± 0.14) | [2007REI/RUN] |
| 298 | sol | 3.77 m NaCl | – (13.15 ± 0.13) | – (13.60 ± 0.13) | [2007REI/RUN] |
| 298 | sol | 5.61 m NaCl | – (13.01 ± 0.13) | – (14.07 ± 0.13) | [2007REI/RUN] |
| 298 | sol | 5.6 m $NaClO_4$ | | – (15.26 ± 0.11) | [2007REI/RUN] |

## 11.6.2 Plutonium silica compounds and complexes

### 11.6.2.1 Plutonium(VI) silicate complexes

Silicates are abundant in the geosphere, but there are very few experimental data reported on the interaction of hexavalent actinides with silicate. Because $Si(OH)_4$ is a very weak acid and its complex formation reactions take place at higher pH, overlapping with hydrolysis reactions and potential silicate polymerisation, all factors which complicate the study of actinide silicate complex formation in aqueous solutions. No experimental data on the Pu(VI) silicate system were discussed in the previous reviews in [2001LEM/FUG] and [2003GUI/FAN]. For the analogous U(VI) system, [2003GUI/FAN] selected $\log_{10}{}^{*}K_{1,1}^o$ = – (1.84 ± 0.10) for the equilibrium reaction:

$$UO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons UO_2SiO(OH)_3^+ + H^+ \quad (11.82)$$

and estimated $\varepsilon(UO_2SiO(OH)_3^+, ClO_4^-)$ = 0.3 kg·mol$^{-1}$. In 2003, Yusov and co-workers [2003YUS/FED] reported an equilibrium study of the reaction of Pu(VI) with orthosilicic acid and postulated the formation of the complex, $PuO_2SiO(OH)_3^+$, in the pH range 4.5-5.5:

$$PuO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons PuO_2SiO(OH)_3^+ + H^+ \quad (11.83)$$

A second complex, $PuO_2SiO_2(OH)_2$(aq) or $PuO_2OHSiO(OH)_3$(aq), is suggested to form at pH > 6. The spectrophotometric determination of the Pu(VI) complex is complicated due to the overlap of the broad absorbance bands of $PuO_2OH^+$ and $PuO_2SiO(OH)_3^+$ and because of this, the direct quantification of $PuO_2SiO(OH)_3^+$

by spectra deconvolution is problematic. Yusov *et al.* used the spectral differences at constant [Pu(VI)] in the absence and presence of $Si(OH)_4$ at $p_cH$ = 4.5-6 and calculated $\log_{10}{}^{*}K^{o}_{1,1} = -(3.91 \pm 0.17)$ for (11.83) and $\log_{10}{}^{*}\beta_{1,1} = (5.90 \pm 0.17)$ for (11.84). In this calculation, they used the first thermodynamic dissociation constant of $Si(OH)_4$(aq), $\log_{10}K^{o}_{a} = -9.81$, which is the same value as the one selected by the NEA, $\log_{10}K^{o}_{a} = -(9.810 \pm 0.020)$.

$$PuO_2^{2+} + SiO(OH)_3^- \rightleftharpoons PuO_2SiO(OH)_3^+ \qquad (11.84)$$

The reported value for $\log_{10}{}^{*}K_{1,1}$ ((11.91), $PuO_2SiO(OH)_3^+$) is about two orders of magnitude different from the experimental value for the analogous U(VI) reaction in 0.2 M $NaClO_4$, $\log_{10}{}^{*}K_{1,1} = -(1.98 \pm 0.13)$, discussed in [1992GRE/FUG]. [2003GUI/FAN] recommended, $\log_{10}{}^{*}K_{1,1} = -(1.840 \pm 0.100)$. The differences may be a result of the problematic spectral analysis or by the partial polymerisation of silicic acid. Due to the uncertainties associated with the experiment and data analysis, we do not select the reported values, which are provided for information only.

Yusov *et al.* also suggested the formation of a second Pu(VI) silicate complex at $-\log_{10}[H^+] > 5.5$. However, the composition and charge of this complex remains speculative. Yusov *et al.* postulated the compositions $PuO_2(H_2O)_3SiO_2(OH)_2$(aq) or $PuO_2(H_2O)_3OHSiO(OH)_3$(aq) and discussed several reaction models, but the experimental data do not allow a selection between them. Due to the lack of information on the ligand and reaction stoichiometry and the increasing polymerisation of the silicic acid at high pH, the proposed formation constants for the second Pu(VI) silicate complex are not recommended by this review.

Table 11-28: Experimental equilibrium data for the plutonium(VI) silicate system.

| $T$/K | Method | $I$ (Medium) | $\log_{10}{}^{*}K$ | $\log_{10}{}^{*}\beta$ | Reference |
|---|---|---|---|---|---|
| $PuO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons PuO_2SiO(OH)_3^+ + H^+$ | | | | | |
| (294 ± 2) | spectr | 0.2 M $NaClO_4$ | – (3.91 ± 0.17) | (5.90 ± 0.17) | [2003YUS/FED] |
| $PuO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons PuO_2SiO(OH)_2(aq) + 2H^+$ | | | | | |
| (294 ± 2) | spectr | 0.2 M $NaClO_4$ | ~ – 10.5 | ~ 12.6 | [2003YUS/FED] |

### 11.6.2.2 Plutonium(IV) silicate complexes

Few studies have reported data on the complex formation between plutonium and silicate. This is mainly due to the complex chemistry of actinide-silicate systems such as the pH- and time-dependent polymerisation of silicic acid, the competing hydrolysis reactions of the actinides, and especially the formation of Pu(IV) colloids. No experimental data on the Pu(IV) silicate system were discussed in the previous reviews in [2001LEM/FUG] and [2003GUI/FAN]. Since the last review, the complex formation of Pu(IV) in aqueous silicate solutions has been investigated in [2003SHI/FED] and [2004YUS/FED]. The reported equilibrium constants are listed in Table 11-29. A solubility study by [2003SHI/FED] showed an increased solubility of amorphous

Pu(IV) hydrated oxide at pH 11 in the presence of $Na_2SiO_3$, suggesting complexation of Pu(IV) with silicate in solution. The solubility increase was explained with the formation of Pu(IV) silicate complexes:

$$\mathrm{Pu(IV)} + n\mathrm{SiO_3^{2-}} \rightleftharpoons \mathrm{Pu(SiO_3^{2-})_n} \tag{11.85}$$

The authors did not determine the stoichiometry of the complex formed, but estimated $n$ to be between 0.7 and 1.2. The reported equilibrium constants vary significantly with NaOH concentration and cannot be accepted by the present review.

Yusov and co-workers [2004YUS/FED2] investigated the complex formation of Pu(IV) (and Np(IV)) with orthosilicic acid in acidic solutions. Spectrophotometric measurements were used to assess the degree of hydrolysis and the interaction with $Si(OH)_4$ at $-\log_{10}[H^+] < 1.4$. The authors interpreted changes in the Pu(IV) absorbance spectra upon the addition of $Si(OH)_4$ with the formation of $PuSiO(OH)_3^{3+}$:

$$\mathrm{Pu^{4+}} + \mathrm{Si(OH)_4(aq)} \rightleftharpoons \mathrm{PuSiO(OH)_3^{3+}} + \mathrm{H^+} \tag{11.86}$$

In order to distinguish between silicate complex formation and hydrolysis of Pu(IV), the authors determined the first hydrolysis constant from experimental data at $I = 0.1$ mol·L$^{-1}$ and $I = 0.5$ mol·L$^{-1}$, which disagrees with the NEA TDB value and does not conform with the expected trend for hydrolysis constants, $\log_{10}{}^{*}K^{\circ}(\mathrm{PuOH^{3+}}) > \log_{10}{}^{*}K^{\circ}(\mathrm{NpOH^{3+}}) > \log_{10}{}^{*}K^{\circ}(\mathrm{UOH^{3+}})$. The use of an incorrect hydrolysis constant leads to the erroneous estimation of the fraction of Pu(IV) silicate complexes. From spectra deconvolution data the authors derived the experimental equilibrium constants $\log_{10}{}^{*}K'(11.86) = (0.99 \pm 0.06)$ at $I = 0.5$ mol·L$^{-1}$ and $\log_{10}{}^{*}K' = (1.04 \pm 0.04)$ at $I = 1.0$ mol·L$^{-1}$. In the absence of the ion interaction parameter for $PuSiO(OH)_3^{3+}$, the authors assumed this value to be the same as that for $PuOH^{3+}$ within 0.05 units, and calculated $\log_{10}{}^{*}\beta^{\circ}_{1,1}(11.86) = 2.0$. Yusov *et al.* applied the dissociation constant of $Si(OH)_4$, $\log_{10}K^{\circ} = -9.81$, and calculated from the thermodynamic equilibrium constant $\log_{10}{}^{*}\beta^{\circ}_{1,1}(11.86)$ the equilibrium constant $\log_{10}\beta^{\circ}((11.87), \mathrm{PuSiO(OH)_3^{3+}}) = 11.8$ for the equilibrium Reaction (11.87):

$$\mathrm{Pu^{4+}} + \mathrm{SiO(OH)_3^-} \rightleftharpoons \mathrm{PuSiO(OH)_3^{3+}} \tag{11.87}$$

This value is close to the analogous data reported for Np(IV), $\log_{10}\beta^{\circ}((11.87), \mathrm{NpSiO(OH)_3^{3+}}) = 11.2$. Due to the concerns associated with the Np(IV) and Pu(IV) hydrolysis constants, this review cannot recommend the data reported in [2004YUS/FED] and no thermodynamic data are selected.

Table 11-29: Experimental data for the reactions of Pu(IV) with silicate.

| $T$ /K | Method | $I$ (Medium) | $\log_{10}K$ | References |
|---|---|---|---|---|
| $Pu(IV) + nSiO_3^{2-} \rightleftharpoons PuO_2(SiO_3^{2-})_n$ | | | | |
| (294 ± 2) | spectr | 0.09 M NaOH | 2.59 | [2003SHI/FED] |
| (294 ± 2) | spectr | 0.90 M NaOH | 1.41 | [2003SHI/FED] |
| $Pu^{4+} + Si(OH)_4(aq) \rightleftharpoons PuSiO(OH)_3^{3+} + H^+$ | | | | |
| 294 | spectr | 0.14 M (H,Na)$ClO_4$ | (1.40 ± 0.04) | [2004YUS/FED2] |
| 294 | spectr | 0.5 M (H,Na)$ClO_4$ | (0.99 ± 0.06) | [2004YUS/FED2] |
| 294 | spectr | 1.0 M (H,Na)$ClO_4$ | (1.04 ± 0.04) | [2004YUS/FED2] |

# 11.7 Plutonium group 1 (alkali) compounds

## 11.7.1 Sodium compounds

Structural studies of the sodium plutonates have been reported in recent years based on X-ray diffraction [2015BYK/RAI], [2015SMI] and X-ray Absorption Spectroscopy [2016SMI/MAR] data. The compounds forming in the Na-Pu-O system are numerous, with the plutonium valence state varying between (IV) and (VII). $Na_2PuO_3$ shows partial ordering with the coexistence of a rhombohedral phase in space group $R\bar{3}m$ and a monoclinic phase in space group *C2/c*, $Na_3PuO_4$ is orthorhombic in space group *Fmmm*, $Na_5PuO_5$ is monoclinic in space group *C2/m*, $Na_4PuO_5$ is tetragonal in space group *I4/m*, $Na_5PuO_6$ is monoclinic in space group *C2/m*. The only thermodynamic data reported in the Na-Pu-O system are by [2015SMI], who measured the low temperature heat capacity of $Na_5PuO_6$ using thermal relaxation calorimetry in the temperature range 8.5 to 262.9 K. However, the sample measured was not analysed chemically and we cannot rule out the potential presence of remaining sodium or sodium oxide impurities. Their data, *i.e.*, $C_{p,m}^{o}$ ($Na_5PuO_6$, cr, 298.15 K) = (302.2 ± 9.6) $J \cdot K^{-1} \cdot mol^{-1}$ and $S_m^{o}$ ($Na_5PuO_6$, cr, 298.15 K) = (355.7 ± 8.8) $J \cdot K^{-1} \cdot mol^{-1}$ are therefore not recommended in the present review, but provided for information only.

# 11.8 Plutonium heteropolyoxo anion complexes

In a set of studies, Yusov and co-workers [2007YUS/SHI4], [2007YUS/SHI2], [2007YUS/SHI3], [2007YUS/SHI] have investigated the interactions between actinide ions and heteropolyoxo anions, determining equilibrium constants and formal redox potentials of Pu(III), Pu(IV), Pu(V) and Pu(VI). The studies are complicated because of the redox-active nature of the ligand and the difficulty to determine the composition of the actinide complex formed in the presence of the heteropolyoxo anions.

In [2007YUS/SHI4], the authors report the formal potentials of the redox couples Pu(VI)/Pu(V), Pu(V)/Pu(IV) and Pu(IV)/Pu(III). Yusov *et al.* [2007YUS/SHI2] also report the equilibrium constants (see Table 11-30) for the formation of complexes

between An(VI) with the heteropolyoxo anions $P_2W_{17}O_{61}^{10-}$, $SiW_{11}O_{39}^{8-}$ and $PW_{11}O_{39}^{7-}$, in the pH range – 0.3-5.5, reactions that involve two deprotonations according to Equation (11.88):

$$PuO_2^{2+} + H_3P_2W_{17}O_{61}^{7-} \rightleftharpoons PuO_2(HP_2W_{17}O_{61})^{7-} + 2H^+ \quad (11.88)$$

The stability of the complexes increases in the order $PuO_2(H_xPW_{11}O_{39})^{(5-x)-} > PuO_2(H_xSiW_{11}O_{39})^{(6-x)-} > PuO_2(H_xP_2W_{17}O_{61})^{(8-x)-}$. In [2007YUS/SHI3], Yusov *et al.* determined the stability of Pu(IV) in solution of near-neutral pH in the presence of $K_{10}P_2W_{17}O_{61}$. Without providing details, the authors postulated equilibrium constants for the formation of $Pu(P_2W_{17}O_{61})_2^{16-}$, $\log_{10}\beta_2' > 36.3$ in 1 M $Na^+$ solutions (pH ~ 6) and $\log_{10}\beta_2' > 14$ in 1 M $H^+$. The disproportionation of Pu(V) upon the reaction with $K_{10}P_2W_{17}O_{61}$ is investigated in [2007YUS/SHI]. The activation energy decreases with pH and is calculated to be 78.6 kJ·mol$^{-1}$ at pH 2 and 64.2 kJ·mol$^{-1}$ at pH 4.

Due to the lack of information on the stoichiometry of the Pu heteropolyoxo anion complexes and on the calculation of the equilibrium constants, together with the numerous assumptions made by the authors, this review does not accept the data reported in [2007YUS/SHI4], [2007YUS/SHI2], [2007YUS/SHI3], [2007YUS/SHI].

Table 11-30: Experimental equilibrium constants for the reaction $PuO_2^{2+} + HPA \rightleftharpoons PuO_2(HPA)$, where HPA = heteropolyoxo anion. Temperature not reported; equilibrium constants expectedly corresponding to room temperature.

| Method | *I* (Medium) | $\log_{10}\beta_1'$ ($P_2W_{17}O_{61}^{10-}$) | $\log_{10}\beta_1'$ ($SiW_{11}O_{39}^{8-}$) | $\log_{10}\beta_1'$ ($PW_{11}O_{39}^{7-}$) | Reference |
|---|---|---|---|---|---|
| spec | 0.1 M $HClO_4$ | (3.3 ± 0.2) | (3.5 ± 0.2) | (3.8 ± 0.2) | [2007YUS/SHI2] |
| spec | 0.2 M $HClO_4$ | (2.9 ± 0.2) | (3.1 ± 0.2) | (3.4 ± 0.2) | [2007YUS/SHI2] |
| spec | 0.5 M $HClO_4$ | (2.3 ± 0.2) | (2.5 ± 0.2) | (2.9 ± 0.2) | [2007YUS/SHI2] |
| spec | 1.0 M $HClO_4$ | (1.9 ± 0.2) | (2.2 ± 0.2) | (2.5 ± 0.2) | [2007YUS/SHI2] |
| spec | 2.0 M $HClO_4$ | (1.4 ± 0.2) | (1.9 ± 0.2) | | [2007YUS/SHI2] |

# Chapter 12

# Discussion of new data selection for Americium

## 12.1 Introductory remarks on the use of chemical analogues in the discussion of the chemical properties of Am(III)

The number of experimental studies of Am(III) complexes is limited because of the high radioactivity of $^{241}$Am, which is the most commonly used Am isotope. It is well established that information on the chemical behaviour of Am(III) compounds and complexes can be drawn from the properties of analogous *f*-elements. This is to a large extent due to their similar ionic radii, when in the same oxidation state, *i.e.* 1.10 Å for $Am^{3+}$ compared to 1.09 Å for $Cm^{3+}$, 1.11 Å for $Nd^{3+}$ and 1.07 Å for $Eu^{3+}$ ions (referred to a coordination number of 8) ([1976SHA], [1994CHO/RIZ]). Trends in thermodynamic data and equilibrium constants often correlate with variations in the ionic radii, *e.g.* the decrease from $La^{3+}$ to $Lu^{3+}$ and from $Ac^{3+}$ to $Cm^{3+}$. This well-established principle of oxidation state analogy is generally applied to compare the solution chemistry and stability of complexes of the tetra-, penta- and hexavalent actinides U, Np and Pu. The behaviour of Am(III) species has often been compared to that of the trivalent Cm, Nd and Eu; the chemistry of Am(V) can be compared to that of the much more stable Np(V), and the chemistry of Am(VI) is expected to be very similar to those of U(VI) and Pu(VI).

Even though there are similar trends in the chemistry of trivalent lanthanides and actinides, there are some specific differences for americium that are related to the energetic α-radiation of $^{241}$Am. The use of this isotope may result in radiation damage in solid americium compounds used in solubility studies, and in α-induced radiolytic effects in solution, especially in concentrated electrolyte solutions. The stability of Am in its different oxidation states differs significantly from that of its 4*f* analogues. Americium can be found in the +III, IV, V and VI oxidation states in aqueous solution, while lanthanide aqueous chemistry is overwhelmingly governed by its +III oxidation state. While Am(III) is very stable in aqueous solutions, Am(IV) exists only under special experimental conditions where strong complexes are formed; Am(V) is much less stable than Np(V) and is prone to disproportionation and reduction; Am(VI) (as well as Np(VI)

and Pu(VI)) can only be stabilized under highly oxidizing conditions, in contrast to the extreme stability of U(VI) in aqueous solution.

In addition, the number of tools to probe the spectroscopic properties of americium compounds is limited. With the exception of Am(III), the lower molar extinction coefficients for the electronic absorbance bands of Am(IV, V and VI) result in a low sensitivity for spectroscopic speciation. Time-resolved laser fluorescence spectroscopy, TRLFS, is a powerful method to study the chemistry of Cm(III) and Eu(III), but is far less sensitive to study the chemistry of Am(III) systems. For these reasons, it is necessary to use the information of chemical analogues to improve the understanding of the solution and solid state chemistry of americium. Good examples are the emission-active Cm(III) and Eu(III) for fluorescence studies, or Eu(III) or Nd(III) for crystallographic investigations of solid state compounds.

This generally accepted principle of oxidation state analogous chemistry has been used in previous reviews and will also be applied in the present one and experimental data on Cm(III) have been used in order to evaluate the thermodynamic data of Am(III) compounds. We have used spectroscopic data for Cm(III) to select equilibrium constants for Am(III), and to compare the chemical behaviour of Am(III) and compared these data with its chemical analogues.

### 12.1.1 Estimation of standard entropies

The standard entropies of many americium solid compounds have been revised from those suggested in [1995SIL/BID] to take into account the improved procedure suggested in [2001KON] and [2004KON]. As noted in Appendix A, in this procedure the entropy is assumed to be the sum of a lattice contribution, estimated from known values of similar actinide species, and a contribution that represents electronic effects. This scheme provides good agreement with experimental data for many lanthanide and actinide compounds, and is the basis of the existing NEA estimates for the aqueous americium ions. However, since the $^7F_0$ ground state of $Am^{3+}$ is non-degenerate and no excited states contribute to the entropy at 298.15 K, the electronic entropy is zero for most Am(III) compounds. This leads to appreciably smaller standard entropies for these species than estimated in [1995SIL/BID].

## 12.2 Elemental americium

### 12.2.1 Americium metal

Since the [2003GUI/FAN] review, there is no new data on the crystal phases of americium metal. The previous review relied on the assessment of [1990COR/KON], neglecting the experimental study of transition enthalpies and temperatures using DTA by [1992GIB/HAI]. The reported values for both $T_{trs}$ and $\Delta_{trs}H^{o}_{m}$ were much lower than

those reported in [1967WAD/WOL], [1977SEL/KOS] and [1978SEL/SHU], with the exception of the transition enthalpy (α → β), which was close to the findings of [1977SEL/KOS]. In more recent evaluations of the transition enthalpies, [2003KON] and [2010KON/BEN] rejected the previously selected values of [1967WAD/WOL], since they were found to be much larger than the trends in comparable structures of actinides and lanthanides. Therefore, we select the values of [1977SEL/KOS] and [1978SEL/SHU] for $T_{trs}$ and $\Delta_{trs}H_m^o$ for all cases (α → β, β → γ, γ → l). The selected values are listed in Table 12-1.

Table 12-1: Temperatures and enthalpies of transition for elemental americium.

| Phase transition | $T_{trs}$ /K | $\Delta_{trs}H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| α → β | (1042 ± 10) | (0.34 ± 0.10) |
| β → γ | (1350 ± 5) | (3.8 ± 0.4) |
| γ → l | (1449 ± 5) | (8.0 ± 2.0) |

#### 12.2.1.1 Heat capacity and entropy

Low temperature heat capacity measurements reviewed by [2010KON/BEN] include the work of [1976HAL/MOR] and [1980HAL/LEE] on samples of $^{241}$Am and $^{243}$Am, respectively. The selected values remain unchanged from the ones in the [2003GUI/FAN] review:

$$C_{p,m}^o\,(\text{Am, cr, 298.15 K}) = \mathbf{(25.500 \pm 1.500)}\ \text{J·K}^{-1}\text{·mol}^{-1},$$

$$S_m^o\,(\text{Am, cr, 298.15 K}) = \mathbf{(55.400 \pm 2.000)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

There is still no experimental data available for the high temperature heat capacity of americium metal, therefore previous estimates are based on observed trends in analogous systems. The most recent paper by [2003KON] introduced a more detailed method to estimate the heat capacity of americium including harmonic, dilation, electronic and magnetic components. While based on empirical correlations with lanthanides of similar structure, previous estimates reported in [1976OET/RAN] and [1986WAR/KLE] do not provide detailed arguments for their selected values. The temperature dependent heat capacity coefficients discussed by [2003KON] and reviewed in [2010KON/BEN] for all americium phases are given in the following section in Table 12-2 and selected by this review.

### 12.2.2 Americium ideal monatomic gas

#### 12.2.2.1 Heat capacity and entropy

The most recent compiled data on spectroscopic energy levels is based on the handbook by [2005SAN/MAR] and the database by [2009BLA/WYA]. These were reviewed by

[2010KON/BEN] and the thermal functions calculated include 214 electronic energy levels up to 40632 $cm^{-1}$. The calculated heat capacity of Am(g) from 298.15 to 900 K is essentially constant as shown in Table 12-2, but includes a temperature dependence at $T > 900$ K, described by the use of two polynomial equations. The selected values at 298.15 K are:

$$C^{o}_{p,m}(\text{Am, g, 298.15 K}) = \mathbf{(20.786 \pm 0.010)}\ \text{J·K}^{-1}\text{·mol}^{-1},$$

$$S^{o}_{m}(\text{Am, g, 298.15 K}) = \mathbf{(194.657 \pm 0.050)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

Thermal functions calculated using the database by [2009BLA/WYA] with the additional information provided in [2010KON/BEN] lead to slightly higher standard entropy than evaluated in [2003GUI/FAN], and the temperature dependence of the heat capacity coefficient has also been extended to 4000 K.

Table 12-2: Selected temperature coefficients for heat capacities, using the empirical function: $C_{p,m}(T) = a + bT + cT^2 + eT^{-2} + jT^3 + lT^4$ valid between temperatures $T_{min}$ and $T_{max}$ (in K). The notation E ± *n* indicates the power of 10. $C_{p,m}$ units are $J\cdot K^{-1}\cdot mol^{-1}$.

| Compound | *a* | *b* | *c* | *e* | *j* | *l* | $T_{min}$ | $T_{max}$ |
|---|---|---|---|---|---|---|---|---|
| Am(cr) | 3.0399E+01 | – 2.9053E–02 | 5.2026E–05 | 0 | – 1.8961E–08 | 0 | 298 | 1042 |
| β–Am | 8.4570E+00 | 3.3167E–02 | – 7.5870E–06 | 0 | 0 | 0 | 1042 | 1350 |
| γ–Am | 4.3000E+01 | 0 | 0 | 0 | 0 | 0 | 1350 | 1449 |
| Am(l) | 5.2000E+01 | 0 | 0 | 0 | 0 | 0 | 1449 | 3000 |
| Am(g) | 2.0786E+01 | 0 | 0 | 0 | 0 | 0 | 298 | 900 |
| Am(g) | 1.9986E+01 | 4.3365E–01 | 1.6974E–06 | 2.1403E+05 | – 1.5984E–09 | 4.4407E–13 | 900 | 2400 |
| Am(g) | 2.6881E+02 | – 1.7944E–01 | 4.5918E–05 | – 1.7767E+08 | – 3.5637E–09 | 0 | 2400 | 4000 |

### 12.2.2.2 Enthalpy of formation

The enthalpy of formation has been recalculated in the review by [2010KON/BEN] from the selected data in the solid and liquid phase along with the vapour pressures measurements of $^{241}$Am from 900-1358 K by [1976WAR/MUE] and 1200-1415 K by [1979WAR/KLE]:

$$\Delta_f H^{o}_{m}(\text{Am, g, 298.15 K}) = \mathbf{(285.5 \pm 3.0)}\ \text{kJ·mol}^{-1}$$

The reported value is selected in the present review. The calculated Gibbs energy of formation thus becomes:

$$\Delta_f G^{o}_{m}(\text{Am, g, 298.15 K}) = \mathbf{(244.0 \pm 3.0)}\ \text{kJ·mol}^{-1}$$

The $\Delta_f G^{o}_{m}(\text{Am, g, 298.15 K})$ value differs from the value selected in [2003GUI/FAN], $\Delta_f G^{o}_{m}(\text{Am, g, 298.15 K}) = (242.3 \pm 1.6)\ \text{kJ·mol}^{-1}$, but they overlap within the uncertainty ranges of the newly selected data. The selected values are consistent with the most recent review by [2010KON/BEN] and include updated thermal

functions that agree with trends seen within the lanthanide and actinide series as discussed in [2003KON].

## 12.3 Americium oxygen and hydrogen compounds and complexes

### 12.3.1 Aqueous americium and curium hydroxide complexes

#### 12.3.1.1 Aqueous Am(III) and Cm(III) hydroxide complexes

The hydrolysis of Am(III) has been discussed in previous NEA reviews, in which comparisons were made with the analogous Cm(III) hydrolysis. Equilibrium constants for the formation of three monomeric Am(III) hydrolysis species were first selected in [1995SIL/BID] and later updated in [2003GUI/FAN]. Similar hydrolysis reactions have been proposed for both Am(III) and Cm(III). Since the last review, no new experimental hydrolysis data for Am(III) have been published and the present reviewers retain the thermodynamic constants selected in [2003GUI/FAN]:

$$Am^{3+} + H_2O(1) \rightleftharpoons AmOH^{2+} + H^+,\ \log_{10} K_{11}^{o} = \mathbf{-\ (7.200 \pm 0.500)}$$

$$Am^{3+} + 2H_2O(1) \rightleftharpoons Am(OH)_2^{+} + 2H^+,\ \log_{10} K_{12}^{o} = \mathbf{-\ (15.100 \pm 0.700)}$$

$$Am^{3+} + 3H_2O(1) \rightleftharpoons Am(OH)_3(aq) + 3H^+,\ \log_{10} K_{13}^{o} = \mathbf{-\ (26.200 \pm 0.500)}.$$

In the studies discussed and reviewed in [2003GUI/FAN], no further hydrolysis reactions beyond the formation of $Am(OH)_3(aq)$ were observed. Increases in solubility data of $Am(OH)_3(s)$ at high pH were generally explained with the complexation of Am(III) with carbonate impurities and not with the formation of anionic Am(III) hydrolysis species, such as $Am(OH)_4^-$. In an earlier solubility study of Am(III) in alkaline solutions of 0-10 M KOH and in the presence of $Ca(OH)_2(s)$, Vitorge *et al.* [1991VIT/TRA] reported that the total concentration of Am(III) increased when the hydroxide concentration was above 6 M. The data from [1991VIT/TRA] were not considered by the previous reviews of [1995SIL/BID] and [2003GUI/FAN], due to the varying and very high ionic strengths used. Neck and co-workers [2009NEC/ALT] interpreted the increase of Am(III) concentration at $[OH^-] \geq 6$ M reported in [1991VIT/TRA] with the formation of $Am(OH)_4^-$ in solution and reported an equilibrium constant $\log_{10} K^{o}((12.1), 298.15\ K) = -(40.7 \pm 0.7)$ and $\log_{10} K^{o}((12.2), 298.15\ K) = -(0.5 \pm 0.4)$ for the reactions:

$$Am^{3+} + 4H_2O(1) \rightleftharpoons Am(OH)_4^- + 4H^+ \quad (12.1)$$

$$Am(OH)_3(aq) + OH^- \rightleftharpoons Am(OH)_4^- \quad (12.2)$$

However, the solubility increase is observed only in very concentrated KOH solutions, from about 6.3 M to 10.0 M KOH. Neck *et al.* [2009NEC/ALT] calculated the equilibrium constant for Reactions (12.1) and (12.2) using only two experimental data points, $\log_{10} K^{\circ}_{s,0}(Am(OH)_3, s) = -(10.6 \pm 0.8)$ and the SIT ion-interaction parameters $\varepsilon(K^+/OH^-, Am(OH)_3(aq)) = 0$ kg·mol$^{-1}$ and $\varepsilon(K^+, Am(OH)_4^-) = -(0.03 \pm 0.05)$ kg·mol$^{-1}$. This set of constants describes very well the experimental data in [1991VIT/TRA] and the increase of $[Am(III)]_{total}$ in highly alkaline solutions with $[OH^-] \geq 6$ M. However, this review does not accept the equilibrium constant for $Am(OH)_4^-$ reported by Neck and co-workers for the following reasons:

(1) Using the SIT and ion-interaction parameters to analyse data in solutions of such high ionic strength (> 6 M) is outside the applicable ionic strength range of the SIT.
(2) The existence of aged $Am(OH)_3(s)$ is not verified and a transformation of the solid phase to a quaternary K-Am(III)-OH solid phase cannot be excluded.

Since the review by [2003GUI/FAN], two experimental studies from the same research group have been published, both reporting the formation of higher hydrolysis species of M(III) (where M = Cm, Am, or Nd) in alkaline solutions containing $CaCl_2$ ([2008RAB/ALT] and [2009NEC/ALT]). The two publications describe a combined study, where both spectroscopy (Cm(III)–TRLFS, [2008RAB/ALT]) and solubility (Nd(III), [2009NEC/ALT]) data are reported.

Rabung *et al.* [2008RAB/ALT] observed new fluorescence peaks of Cm(III) at 607.5, 609.9, and 614.7 nm in solutions with $[CaCl_2] \geq 1$ M and $-\log_{10}[H^+]$ of 10.8-11.7 using TRLFS. These new bands were observed in addition to the emission peaks at 593.8, 598.8, and 603.5 nm, which were assigned by [1994FAN/KIM] to $Cm^{3+}$, $CmOH^{2+}$, and $Cm(OH)_2^+$ in NaCl/NaOH solutions. The new fluorescence bands reported in [2008RAB/ALT] were assigned to "$Cm(OH)_3(aq)$" (607.5 nm), "$Cm(OH)_4^-$" (609.9 nm), and "$Cm(OH)_6^{3-}$" (614.7 nm). Rabung *et al.* suggested the formation of ternary Ca-Cm(III)-OH complexes in order to account for the large difference in the fluorescence emission properties (the number of bands and their intensity) between the Ca-containing and Ca-free solutions and to interpret the solubility behaviour of Cm(III) in alkaline $CaCl_2$ solutions. Under analogous experimental conditions ($[CaCl_2]$ and $-\log_{10}[H^+]$) as those used in [2008RAB/ALT], Neck and co-workers [2009NEC/ALT] observed a significant and systematic increase in Nd(III) solubility with increasing $[CaCl_2]$. The combination of Nd(III) solubility and Cm(III)–TRLFS data were used by Neck, Rabung and co-workers to derive equilibrium constants based on the tested chemical models. Using SIT and Pitzer activity models they found that their experimental observations were properly explained. The thermodynamic equilibrium constants reported by the authors are summarized in Table 12-3. SIT ion-interaction coefficients determined for Ca-Nd(III)-OH complexes from solubility data were considered valid also for Cm(III): $\varepsilon(Ca[M(OH)_3]^{2+}, Cl^-) = (0.05 \pm 0.04)$ kg·mol$^{-1}$, $\varepsilon(Ca_2[M(OH)_4]^{3+}, Cl^-) = (0.29 \pm 0.07)$ kg·mol$^{-1}$ and $\varepsilon(Ca_3[M(OH)_6]^{3+}, Cl^-) = (0.00 \pm 0.06)$ kg·mol$^{-1}$.

Table 12-3: Thermodynamic equilibrium constants ($I$ = 0, 298 K) for the formation of ternary Ca-M(III)-OH complexes (M = Cm, Nd) as reported in [2008RAB/ALT] and [2009NEC/ALT]. The reported equilibrium constants describe well the experimental data in both systems.

| Reaction | Equilibrium constant |
|---|---|
| $Ca^{2+} + M^{3+} + 3H_2O(l) \rightleftharpoons Ca[M(OH)_3]^{2+} + 3H^+$ | $\log_{10}{}^{*}\beta^{o}_{1,1,3} = -(26.3 \pm 0.5)$ |
| $2Ca^{2+} + M^{3+} + 4H_2O(l) \rightleftharpoons Ca_2[M(OH)_4]^{3+} + 4H^+$ | $\log_{10}{}^{*}\beta^{o}_{2,1,4} = -(37.2 \pm 0.6)$ |
| $3Ca^{2+} + M^{3+} + 6H_2O(l) \rightleftharpoons Ca_3[M(OH)_6]^{3+} + 6H^+$ | $\log_{10}{}^{*}\beta^{o}_{3,1,6} = -(60.7 \pm 0.5)$ |

This review agrees that the set of equilibrium constants and SIT interaction coefficients reported in [2008RAB/ALT] and [2009NEC/ALT] for the ternary complexes Ca-An(III)/Ln(III)-OH provides a satisfactory interpretation of both the solubility and spectroscopic data in alkaline $CaCl_2$ solutions. However, the reported thermodynamic data are not selected for the following reasons:

(1) The ternary Ca-M-OH complexes proposed in [2008RAB/ALT] and [2009NEC/ALT] are important only in concentrated $CaCl_2$ solutions, at ionic strengths which significantly exceed the range where SIT is applicable.
(2) The stoichiometry of the proposed ternary Ca-Cm-OH complexes (especially the Ca stoichiometry) is only based on assumptions and an analogy to findings in tetravalent systems, the validity of which cannot be independently verified in the trivalent systems.

Consequently, this review does not select the thermodynamic data reported in [2008RAB/ALT] and [2009NEC/ALT], and the values of $\log_{10}{}^{*}\beta^{o}_{1,1,3}$, $\log_{10}{}^{*}\beta^{o}_{2,1,4}$, $\log_{10}{}^{*}\beta^{o}_{3,1,6}$ and corresponding SIT coefficients are provided for information only. A quantitative description of the Nd(III) solubility data reported in [2009NEC/ALT] is achieved using the Pitzer model, but these data are out of the scope of this review.

### 12.3.1.2 Aqueous Am(IV/V/VI) hydroxide complexes

The higher oxidation states of americium Am(IV), Am(V), Am(VI), and even Am(VII) have been examined by a number of investigators ([2003SHI], [2004NIK/GOG], [2004NIK/GOG3], [2005NIK/GOG], [2007YUS/SHI4], [2007YUS/SHI3] and [2012GOG/FED]). These studies discuss kinetics and mechanisms of redox reactions, with some information of interest for preparative work, and reactions between heteropolyanions such as $P_2W_{17}O_{61}^{10-}$ and actinides in different oxidation states. No new thermodynamic data are reported in these studies and we therefore only provide a brief description of their content in Appendix A. The present review does not make any new selection and the data from [1995SIL/BID] and [2003GUI/FAN] are retained.

## 12.3.2 Solid americium oxides and hydroxides

### 12.3.2.1 Americium oxides

The previously selected values of the standard entropies of $Am_2O_3$(cr) and $AmO_2$(cr) in the [2003GUI/FAN] review consisted of estimates by Konings *et al.* [2001KON] [2001KON2], which have since been revised in [2004KON] and [2005KON/MIT] and reported in a review article [2013KON/BEN]. The earlier estimates in [2003GUI/FAN] have been refined based on corrections made for entropy trends in the lanthanide and actinide series, and the values from the work of [2013KON/BEN] are selected in this review along with their estimated uncertainties.

$$S^{o}_{m}(AmO_2, cr, 298.15\ K) = \mathbf{(75.500 \pm 3.000)}\ J{\cdot}K^{-1}{\cdot}mol^{-1},$$

$$S^{o}_{m}(Am_2O_3, cr, 298.15\ K) = \mathbf{(134.200 \pm 5.000)}\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

Recently, experimental heat capacities of both $AmO_2$(cr) and $Am_2O_3$(cr) have become available for the temperature range 335-1086 K in a study by [2011NIS/ITO]. Drop calorimetry measurements were made and the enthalpy increments were fitted to a polynomial, from which the heat capacity was derived. The values for $C^{o}_{p,m}$ at 298.15 K, were found to be much lower than those reported for $UO_2$(cr), $PuO_2$(cr) and $NpO_2$(cr), as noted by the authors [2011NIS/ITO]. These data are discussed by [2013KON/BEN] and their conclusions have been accepted in this review. However, a slight adjustment was made to the $C^{o}_{p,m}$(298.15 K), which was constrained to a higher value to agree with the trends in the lanthanide and actinide oxide series. A similar procedure is applied for the measurements on $Am_2O_3$(cr), where the unreasonably low heat capacity values at room temperature in [2011NIS/ITO], was probably due to the fact that the samples were encapsulated in platinum, which might have affected the accuracy of the measurement. The selected values are those reviewed by [2013KON/BEN]:

$$C^{o}_{p,m}(AmO_2, cr, 298.15\ K) = \mathbf{(64.300 \pm 3.000)}\ J{\cdot}K^{-1}{\cdot}mol^{-1},$$

$$C^{o}_{p,m}(Am_2O_3, cr, 298.15\ K) = \mathbf{(116.500 \pm 5.000)}\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

The enthalpies of formation reviewed by [2013KON/BEN] are based on the experimental data discussed in [2003GUI/FAN] and remain unchanged after recalculation. The selected Gibbs energies of formation are thus:

$$\Delta_f G^{o}_{m}(AmO_2, cr, 298.15\ K) = \mathbf{-\ (877.000 \pm 4.300)}\ kJ{\cdot}mol^{-1},$$

$$\Delta_f G^{o}_{m}(Am_2O_3, cr, 298.15\ K) = \mathbf{-\ (1605.600 \pm 8.300)}\ kJ{\cdot}mol^{-1}.$$

### 12.3.2.2 Solid Am(III) and Am(V) hydroxides

There are no new studies of the thermodynamics of the Am(III) and Am(V) hydroxide phases since the previous review and the values selected there are retained.

# 12.4 Americium group 17 (halogen) compounds and complexes

## 12.4.1 Aqueous group 17 (halogen) complexes

### 12.4.1.1 Aqueous Am(III) and Cm(III) fluorides

There are no new studies of the thermodynamics of the Am(III)-fluoride system since the previous review. However, Skerencak *et al.* [2010SKE/PAN] studied the complex formation of Cm(III) with fluoride by TRLFS across the temperature range 293-363 K in 0.10 m $NaClO_4$ solution. The equilibrium constants determined for Reactions (12.3) and (12.4) were extrapolated to $I = 0$ using SIT. The values of $\log_{10}K^{\circ}$ ((12.3), $T$), $\log_{10}K^{\circ}$ ((12.4), $T$) and ion-interaction terms $\Delta\varepsilon_n$ reported in [2010SKE/PAN] for $T$ = 293-363 K are summarized in Table 12-4.

$$Cm^{3+} + F^{-} \rightleftharpoons CmF^{2+} \quad (12.3)$$

$$CmF^{2+} + F^{-} \rightleftharpoons CmF_2^{+} \quad (12.4)$$

Table 12-4: Equilibrium constants $\log_{10}K^{\circ}$ ((12.3), $T$) and $\log_{10}K^{\circ}$ ((12.4), $T$), and corresponding ion-interaction terms $\Delta\varepsilon_n$ reported in [2010SKE/PAN] for the formation of $CmF^{2+}$ and $CmF_2^{+}$.

| $T$ /K | $\log_{10}K^{\circ}$ ((12.3), $T$) | $\Delta\varepsilon_1$ /kg·mol$^{-1}$ | $\log_{10}K^{\circ}$ ((12.4), $T$) | $\Delta\varepsilon_2$ /kg·mol$^{-1}$ |
|---|---|---|---|---|
| 293 | (3.56 ± 0.07) | – (0.13 ± 0.01) | (2.20 ± 0.84) | – (0.11 ± 0.20) |
| 303 | (3.65 ± 0.07) | – (0.12 ± 0.01) | (2.35 ± 0.69) | – (0.17 ± 0.08) |
| 313 | (3.69 ± 0.10) | – (0.13 ± 0.01) | (2.60 ± 0.55) | – (0.19 ± 0.05) |
| 323 | (3.74 ± 0.16) | – (0.14 ± 0.01) | (2.78 ± 0.47) | – (0.18 ± 0.04) |
| 333 | (3.82 ± 0.09) | – (0.13 ± 0.01) | (2.95 ± 0.41) | – (0.16 ± 0.03) |
| 343 | (3.87 ± 0.07) | – (0.14 ± 0.01) | (3.09 ± 0.26) | – (0.14 ± 0.02) |
| 353 | (3.94 ± 0.07) | – (0.14 ± 0.01) | (3.23 ± 0.25) | – (0.13 ± 0.01) |
| 363 | (3.98 ± 0.06) | – (0.14 ± 0.01) | (3.34 ± 0.21) | – (0.13 ± 0.01) |

The equilibrium constants in [2010SKE/PAN], $\log_{10}K^{\circ}$ ((12.3), 298.15 K) = (3.60 ± 0.07) and $\log_{10}K^{\circ}$ ((12.4), 298.15 K) = (2.3 ± 0.7), agree within the reported uncertainty with $\log_{10}K^{\circ}$ ((12.3), 298.15 K) = (3.4 ± 0.3) and $\log_{10}K^{\circ}$ ((12.4), 298.15 K) = (2.4 ± 0.4) selected in [2003GUI/FAN]. The selection in [2003GUI/FAN] was based on data reported for both Am(III) and Cm(III) in four independent experimental studies ([1976CHO/UNR], [1984NAS/CLE], [1997SUG/SAT], [1997SUG/SAT2] and [1999AAS/STE]), and has been retained by the present review.

The values of $\Delta_r H_m$ for Reactions (12.3) and (12.4) were calculated in [2010SKE/PAN] from the temperature-dependence of the equilibrium constants. The stepwise stability constants showed a linear correlation with the reciprocal temperature,

and thus $\Delta_r H_m$ (12.3) and $\Delta_r H_m$ (12.4) were considered to be independent of temperature. Thermodynamic data reported in [2010SKE/PAN] are summarized in Table 12-5.

Table 12-5: Thermodynamic data at 298.15 K for the formation of $CmF^{2+}$ and $CmF_2^+$ according to Equations (12.3) and (12.4) reported in [2010SKE/PAN].

| | $Cm^{3+} + F^- \rightleftharpoons CmF^{2+}$ | $CmF^{2+} + F^- \rightleftharpoons CmF_2^+$ |
|---|---|---|
| $\Delta_r G_m^o$ (298.15 K) /kJ·mol$^{-1}$ | – (20.55 ± 0.40) | – (13.1 ± 4.0) |
| $\Delta_r H_m^o$ (298.15 K) /kJ·mol$^{-1}$ | (12.1 ± 2.2) | (33.0 ± 14.3) |
| $\Delta_r S_m^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | (109.5 ± 7.3) | (154.8 ± 49.8) |

Enthalpy data reported in [2010SKE/PAN] for $CmF^{2+}$ and $CmF_2^+$ are accepted in this review as estimates for the corresponding Am(III) complexes.

The ion-exchange study on the Eu(III) and Nd(III) fluoride systems reported by Luo and Millero [2004LUO/MIL] provides additional information. The equilibrium constants and enthalpies of reaction for the formation of $MF^{2+}$ and $MF_2^+$ are shown in Table 12-6 and are in good agreement with the data from Cm(III). Nd(III) is considered a better analogue than Eu(III), because its ionic radius is closer to that of both Cm(III) and Am(III). As discussed in Appendix A, the present review considers the uncertainties of both the equilibrium constants and the enthalpies of reaction underestimated and we propose uncertainties of 0.1 and 0.2 in $\log_{10}\beta_n$ for $MF^{2+}$ and $MF_2^+$, the corresponding uncertainties in the enthalpies of reaction are 2 and 4 kJ·mol$^{-1}$, respectively.

Table 12-6: Equilibrium constants and reaction enthalpies reported in [2004LUO/MIL] at $I$ = 0.025 M and $T$ = 298.15 K for the formation of $LnF^{2+}$ and $LnF_2^+$ complexes with Ln = Nd(III) and Eu(III). Extrapolation of $\log_{10}\beta_n$ to $I$ = 0 conducted in this review using only the Debye-Hückel term of the SIT approach because of the low ionic strength.

| Reaction | $\log_{10}\beta_n$ | $\log_{10}\beta_n^o$ | $\Delta_r H_n$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Eu^{3+} + F^- \rightleftharpoons EuF^{2+}$ | (3.72 ± 0.01) | (4.11 ± 0.01) | (8.19 ± 0.42) |
| $Nd^{3+} + F^- \rightleftharpoons NdF^{2+}$ | (3.29 ± 0.01) | (3.68 ± 0.01) | (9.38 ± 0.44) |
| $Eu^{3+} + 2F^- \rightleftharpoons EuF_2^+$ | (6.11 ± 0.01) | (6.76 ± 0.01) | (18.6 ± 1.2) |
| $Nd^{3+} + 2F^- \rightleftharpoons NdF_2^+$ | (5.66 ± 0.05) | (6.31 ± 0.05) | (20.25 ± 0.55) |

The good agreement of data reported in [2004LUO/MIL] for Eu(III) and Nd(III) with Cm(III)- and Am(III)-F data provides further confidence in the selection of thermodynamic quantities of Am(III) in [2003GUI/FAN].

Based on the selected values of $\log_{10}K^o$ ((12.3), 298.15 K), $\log_{10}K^o$ ((12.4), 298.15 K), $\Delta_r H_m^o$ ((12.3), 298.15 K) and $\Delta_r H_m^o$ ((12.4), 298.15 K), and the values of $\Delta_f G_m^o$ ($Am^{3+}$, 298.15 K) = – (598.698 ± 4.755) kJ·mol$^{-1}$, $\Delta_f H_m^o$ ($Am^{3+}$, 298.15 K) = – (616.700 ± 1.500) kJ·mol$^{-1}$, $\Delta_f G_m^o$ ($F^-$, 298.15 K) =

– (281.523 ± 0.692) kJ·mol$^{-1}$ and $\Delta_f H_m^o$ ($F^-$, 298.15 K) = – (335.350 ± 0.650) kJ·mol$^{-1}$, we have selected the following thermodynamic data:

$$\Delta_f G_m^o (AmF^{2+}, 298.15\ K) = \mathbf{-\ (899.628 \pm 5.320)}\ kJ\cdot mol^{-1},$$

$$\Delta_f H_m^o (AmF^{2+}, 298.15\ K) = \mathbf{-\ (939.950 \pm 2.741)}\ kJ\cdot mol^{-1},$$

$$S_m^o (AmF^{2+}, 298.15\ K) = \mathbf{-\ (109.125 \pm 18.404)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

and

$$\Delta_f G_m^o (AmF_2^+, 298.15\ K) = \mathbf{-\ (1194.851 \pm 5.082)}\ kJ\cdot mol^{-1},$$

$$\Delta_f H_m^o (AmF_2^+, 298.15\ K) = \mathbf{-\ (1242.300 \pm 14.604)}\ kJ\cdot mol^{-1},$$

$$S_m^o (AmF_2^+, 298.15\ K) = \mathbf{(33.708 \pm 51.063)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

It is interesting to note that Skerencak *et al.* [2010SKE/PAN] also report quantum chemical calculations and propose that the $CmF^{2+}$ complex has the constitution $[CmF(OH_2)_8^{2+}]\cdot 18H_2O$. This is a complex with nine-coordinated Cm(III), which is generally accepted as a common coordination number in Ln(III)/An(III) compounds and complexes for the elements with the largest ionic radii.

### 12.4.1.2 Aqueous Am(III) and Cm(III) chlorides

The equilibrium constants for the Am(III) chloride complexes selected in [1995SIL/BID] are based on experimental data obtained using ion-exchange and liquid-liquid distribution measurements. Americium(III) complexes with chloride are weak and it is difficult to distinguish between complex formation and effects due to variations in activity coefficients when using potentiometry, ion exchange and liquid-liquid extraction. Methods that probe the intrinsic properties of the complexes like absorption and emission spectroscopy are superior. Examples are new studies by Arisaka *et al.* [2006ARI/KIM] and Skerencak-Frech *et al.* [2014SKE/FRO], which have used Cm(III) fluorescence to analyse the complex formation with chloride.

Arisaka *et al.* [2006ARI/KIM] collected the fluorescence spectra of Cm(III) in LiCl solutions with concentrations between 0 and 14 M at 298 K, and used both spectra deconvolution and fluorescence life-times in the data analysis. The life-time provides an estimate of the number of coordinated water molecules in the complex and is an indirect measure of the number of coordinated chloride ligands. The complexes $CmCl_n^{3-n}$ (with $n$ = 1-4) were used to interpret the experimental data. The authors reported mol fractions of the different complexes, but no information on equilibrium constants was provided. From Figure 4 in [2006ARI/KIM] this review obtains a conditional equilibrium constant, $\log_{10}\beta_1 = -1.6$ in 4 M LiCl. The present review accepts the identification of three complexes with $n$ = 1-3, but not the formation of $CmCl_4^-$, for which the evidence is based on a single experimental value in 14 M LiCl.

Skerencak-Frech *et al.* [2014SKE/FRO] studied the Cm(III) chloride complexation at 298-473 K by spectroscopy at chloride molality ranging from 0.5 to 4.0 m. In addition, they also studied the structure of Am(III) chloride complexes using EXAFS. Skerencak-Frech *et al.* note a strong increase in the stability of the chloride complexes with increasing temperature and that $CmCl_2^+$ is always the predominant complex and the only one for which an equilibrium constant can be obtained. By using SIT, the conditional equilibrium constants at the different ionic strengths in [2014SKE/FRO] were used to obtain the equilibrium constant at zero ionic strength. From the temperature dependence of $\log_{10}\beta_2$ in the temperature range 373-473 K, the authors obtain the enthalpy of reaction and the equilibrium constant at 298 K. The thermodynamic data are reported in Table 12-7 and Table 12-8. The value of $\log_{10}\beta_2^o$ at 298 K is in good agreement with the selected value for $AmCl_2^+$ in [2003GUI/FAN], $\log_{10}\beta_2^o = -(0.740 \pm 0.050)$, which is based on the experimental data reported in [1995FAN/KIM] and re-evaluated in [1997KON/FAN].

Table 12-7: Thermodynamic equilibrium constants $\log_{10}\beta_2^o(T)$ for the formation of the $CmCl_2^+$ complex according to $Cm^{3+} + 2Cl^- \rightleftharpoons CmCl_2^+$, as reported in [2014SKE/FRO].

| $T$/K | $\log_{10}\beta_2^o$ |
|---|---|
| 298 | $-(0.81 \pm 0.35)$[(a)] |
| 323 | $(0.00 \pm 0.25)$ |
| 348 | $(0.62 \pm 0.21)$ |
| 373 | $(1.09 \pm 0.13)$ |
| 393 | $(1.48 \pm 0.15)$ |
| 413 | $(1.82 \pm 0.14)$ |
| 433 | $(2.17 \pm 0.11)$ |
| 453 | $(2.45 \pm 0.10)$ |
| 473 | $(2.83 \pm 0.09)$ |

(a) Value extrapolated from thermodynamic data provided in Table 12-8.

Table 12-8: Thermodynamic data for the formation of the $CmCl_2^+$ complex, $Cm^{3+} + 2Cl^- \rightleftharpoons CmCl_2^+$ as reported in [2014SKE/FRO].

| | |
|---|---|
| $\Delta_r H_m^o$ | (54.9 ± 4.5) kJ·mol$^{-1}$ |
| $\Delta_r S_m^o$ | (168.8 ± 5.5) J·K$^{-1}$·mol$^{-1}$ |
| $\Delta_r C_{p,m}^o$ | (40 ± 10) J·K$^{-1}$·mol$^{-1}$ |

Fanghänel *et al.* [1995FAN/KIM] and Könnecke *et al.* [1997KON/FAN] discussed the Cm(III) complex formation at 298 K in solutions with $CaCl_2$ concentrations ranging between 0 and 6 m. Fanghänel *et al.* reported the formation of $CmCl^{2+}$ only above 4 molal chloride, which is consistent with the observations in [2014SKE/FRO] at 298 K. Fanghänel *et al.* could determine the equilibrium constant $\beta_1$ directly from the deconvoluted spectra, but noted that the relative stability of the second complex, $CmCl_2^+$, increased with increasing $CaCl_2$ concentration. Skerencak-Frech *et al.* observed that this increase was larger at higher temperature. There are pronounced similarities between the chemistry in $CaCl_2$ and LiCl solutions, however, this review has selected the values of $\log_{10}\beta_2^o = -(0.81 \pm 0.35)$, $\Delta_r H_m^o = (54.9 \pm 4.5)$ kJ·mol$^{-1}$ and $\Delta_r C_{p,m}^o = (40 \pm 10)$ J·K$^{-1}$·mol$^{-1}$ as reported in [2014SKE/FRO], and used these data also for the Am(III)-chloride system. The following thermodynamic data have been selected

$$\Delta_f G_m^o (AmCl_2^+, 298.15\ K) = \mathbf{-\ (856.508 \pm 5.163)}\ kJ\cdot mol^{-1},$$

$$\Delta_f H_m^o (AmCl_2^+, 298.15\ K) = \mathbf{-\ (895.960 \pm 4.748)}\ kJ\cdot mol^{-1},$$

$$S_m^o (AmCl_2^+, 298.15\ K) = \mathbf{(80.827 \pm 22.313)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

The thermodynamic quantities selected in [2003GUI/FAN] for $AmCl^{2+}$ are based on the equilibrium constants for the analogous Cm(III) complexes reported in [1995FAN/KIM] and [1997KON/FAN]. The present review considers that $\log_{10}\beta_1^o$ reported by these authors still represents the best estimates available for $AmCl^{2+}$. However, the estimated uncertainty of the equilibrium constants is considered too low, and thus the experimental estimate from [2014SKE/FRO], ± 0.35 $\log_{10}$ units, has been also used for this complex.

$$\log_{10}\beta_1^o = \mathbf{(0.240 \pm 0.350)},$$

$$\Delta_r G_m^o = \mathbf{-\ (1.370 \pm 2.000)}\ kJ\cdot mol^{-1},$$

$$\Delta_f G_m^o (AmCl^{2+}, 298.15\ K) = \mathbf{-\ (731.285 \pm 5.160)}\ kJ\cdot mol^{-1}.$$

## 12.5 Americium group 16 (chalcogen) compounds and complexes

The problem to distinguish between complex formation and other types of ion-interaction is present also when analysing reactions in the Eu(III)/Am(III)/Cm(III) sulfate systems, which in part is due to the significant interactions between sulfate and the cations in the systems investigated. This problem is aggravated at higher sulfate concentrations where $M(SO_4)_2^-$ complexes are formed. Hence, methods like ion-exchange and liquid-liquid extraction are less accurate than laser-based fluorescence methods (TRLFS). The following discussion will rely mainly on fluorescence studies of Eu(III) and Cm(III) as chemical analogues for Am(III).

### 12.5.1 Americium sulfates

#### 12.5.1.1 Aqueous Am(III) and Cm(III) sulfate complexes

Equilibrium constants for the formation of Eu(III) ([2005VER/AME]) and Cm(III) ([2013SKE/PAN]) sulfate complexes determined from electro-spray mass spectroscopy and fluorescence spectroscopy are given in Table 12-9. The Cm(III) studies have been made over the temperature range 298-473 K and these data have been used to obtain equilibrium constants, enthalpies, entropies and heat capacities of reaction.

Table 12-9: Thermodynamic data for the formation of $Eu(SO_4)_n^{3-2n}$, where $n$ = 1 and 2 from [2005VER/AME], and $Cm(SO_4)_n^{3-2n}$, where $n$ = 1-3, from [2013SKE/PAN]; the uncertainties are those from the present review. The selected data from [1995SIL/BID] and [2003GUI/FAN] are included for comparison purposes. Thermodynamic quantities corresponding to the reactions $M^{3+} + nSO_4^{2-} \rightleftharpoons M(SO_4)_n^{3-2n}$ with M = Eu(III), Cm(III) and Am(III). All data reported at $T$ = 298.15 K except in [2005VER/AME] ($T$ = 296 K).

| Complex | $\log_{10}\beta_n^o$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_r C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $AmSO_4^+$ | (3.85 ± 0.03) | | | [1995SIL/BID] |
| $EuSO_4^+$ | (3.78 ± 0.20) | | | [2005VER/AME] |
| $CmSO_4^+$ | (3.45 ± 0.13) | (40 ± 4) | (280 ± 12) | [2013SKE/PAN] |
| | (3.30 ± 0.15) | | | [2003GUI/FAN] |
| $Am(SO_4)_2^-$ | (5.40 ± 0.80) | | | [1995SIL/BID] |
| $Eu(SO_4)_2^-$ | (5.28 ± 0.40) | | | [2005VER/AME] |
| $Cm(SO_4)_2^-$ | (4.57 ± 0.46) | (70 ± 7) | (430 ± 19) | [2013SKE/PAN][(a)] |
| | (3.70 ± 0.15) | | | [2003GUI/FAN] |
| $Cm(SO_4)_3^{3-}$ | (3.4 ± 1.3) | (132 ± 10) | | [2013SKE/PAN][(a)] |

(a) Thermodynamic data originally reported in [2013SKE/PAN] for step-wise reactions.

The selected equilibrium constants in [2003GUI/FAN] are $\log_{10}\beta_1^o$ = (3.30 ± 0.15) and $\log_{10}\beta_2^o$ = (3.70 ± 0.15), and are based mainly on Cm(III) fluorescence data. Neck and coworkers [1998NEC/FAN] used the Pitzer approach to extrapolate experimental data to zero ionic strength. These data were re-evaluated in [2003GUI/FAN]

using SIT, resulting in $\log_{10}\beta_1^o = (3.28 \pm 0.03)$ and $\log_{10}\beta_2^o = (3.59 \pm 0.03)$. The agreement between this value of $\log_{10}\beta_1^o$ and the one from [2013SKE/PAN] is satisfactory. A larger difference is observed between the values of $\log_{10}\beta_2^o$ reported in [1998NEC/FAN], [2005VER/AME] and [2013SKE/PAN]. We are aware of the advantage of spectroscopic methods to determine the number of complexes formed and their stoichiometry. However, the problem of extrapolation of equilibrium constants to zero ionic strength still remains, because of the significant changes in the ionic medium with increasing sulfate concentration. In the Appendix A review of [2005VER/AME], we have used solubility data from [1995RAI/FEL] for additional insights and these show that the equilibrium constants from Vercouter *et al.* are in best agreement with these solubility data.

The present reviewers have no basis to prefer one set of equilibrium constants to the other among the published data and has selected the average of the equilibrium constants for formation of $AmSO_4^+$ and $Am(SO_4)_2^-$, $\log_{10}\beta_1^o = (3.50 \pm 0.30)$ and $\log_{10}\beta_2^o = (5.0 \pm 1.0)$, respectively; both these values and their estimated uncertainty differ from previously selected values. This review selects also the values of $\Delta_r H_m^o$ and $\Delta_r C_{p,m}^o$ reported in [2013SKE/PAN] (see Table 12-9), noting that the heat capacity term becomes relevant only above 100 °C. The following thermodynamic data have been selected

$$\log_{10}\beta_1^o = \mathbf{(3.500 \pm 0.300)},$$

$$\Delta_r G_m^o = \mathbf{-\ (19.978 \pm 1.712)}\ \text{kJ·mol}^{-1},$$

$$\Delta_r H_m^o = \mathbf{(40.000 \pm 4.000)}\ \text{kJ·mol}^{-1},$$

$$\Delta_r S_m^o = \mathbf{(201.167 \pm 14.593)}\ \text{J·K}^{-1}\text{·mol}^{-1},$$

$$\Delta_f G_m^o(AmSO_4^+, 298.15\ \text{K}) = \mathbf{-\ (1362.680 \pm 5.071)}\ \text{kJ·mol}^{-1},$$

$$\Delta_f H_m^o(AmSO_4^+\ 298.15\ \text{K}) = \mathbf{-\ (1486.040 \pm 4.291)}\ \text{kJ·mol}^{-1},$$

$$S_m^o(AmSO_4^+, 298.15\ \text{K}) = \mathbf{(18.667 \pm 20.931)}\ \text{J·K}^{-1}\text{·mol}^{-1},$$

and

$$\log_{10}\beta_2^o = \mathbf{(5.000 \pm 1.000)},$$

$$\Delta_r G_m^o = \mathbf{-\ (28.540 \pm 5.708)}\ \text{kJ·mol}^{-1},$$

$$\Delta_r H_m^o = \mathbf{(70.000 \pm 7.000)}\ \text{kJ·mol}^{-1},$$

$$\Delta_r S_m^o = \mathbf{(330.505 \pm 30.294)}\ \text{J·K}^{-1}\text{·mol}^{-1},$$

$$\Delta_f G_m^o(Am(SO_4)_2^-, 298.15\ \text{K}) = \mathbf{-\ (2115.246 \pm 7.476)}\ \text{kJ·mol}^{-1},$$

$$\Delta_f H_m^o(Am(SO_4)_2^-, 298.15\ \text{K}) = \mathbf{-\ (2365.380 \pm 7.203)}\ \text{kJ·mol}^{-1},$$

$$S_m^o(Am(SO_4)_2^-, 298.15\ \text{K}) = \mathbf{(166.505 \pm 33.814)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

Skerencak *et al.* [2013SKE/PAN] provide evidence on the formation of the complex $Cm(SO_4)_3^{3-}$ at elevated temperature and high sulfate concentrations. This review notes that very minor molar fractions of this species (< 0.05) are present at $T \leq 348$ K even in rather concentrated sulfate solutions ($[SO_4^{2-}]_{total} \leq 3.65 \times 10^{-1}$ mol·kg$^{-1}$), and accordingly no thermodynamic data are selected for this complex at $T = 298$ K.

## 12.6 Americium group 15 compounds and complexes

### 12.6.1 Nitrogen compounds and complexes

#### 12.6.1.1 AmN(cr)

[2008NIS/ITO] reported for the first time the measurement of the enthalpy increments of AmN(cr) using twin-type drop calorimetry in the temperature range 354-1071 K. The AmN(cr) sample was prepared by carbothermic reduction of americium dioxide. The oxygen, nitrogen and carbon content were determined using an inert gas fusion and combustion technique. Oxygen was found at a level around 1.22 wt % and carbon around 0.21 wt %. The purity of the sample was also checked using X-ray diffraction. The corresponding lattice parameter $a = 4.998$ Å is in good agreement with literature values [1995SIL/BID]. The equations for the enthalpy increment and heat capacity in the range 354-1071 K are:

$$H_m^o(\text{AmN, cr}, T) - H_m^o(\text{AmN, cr, } 298.15\text{ K}) = 7.816 \times 10^{-6} T^2 + 0.04244\, T - 14.09 \text{ kJ·mol}^{-1}$$

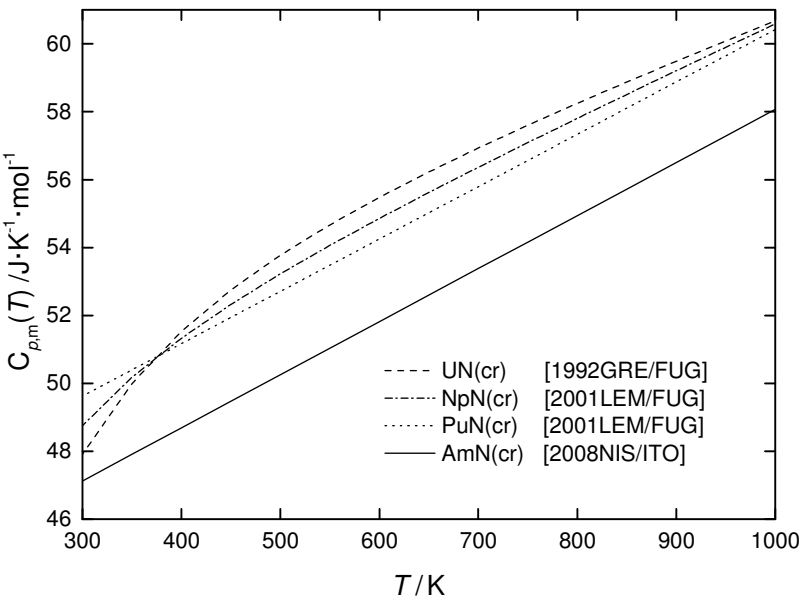
$$C_{p,m}^o(\text{AmN, cr}, T) = 42.44 + 1.563 \times 10^{-2} T \quad \text{J·K}^{-1}\text{·mol}^{-1}$$

The heat capacity for AmN(cr) is below that for PuN(cr), which is expected from the trend seen for UN(cr) and PuN(cr). The deviation is rather large, with a 4 % difference between the heat capacities for PuN(cr) and AmN(cr) at 1000 K. We accept their equation in the present review, but recommend that the measurements are repeated to confirm these results. The heat capacity obtained at 298.15 K by extrapolation is $C_{p,m}^o(\text{AmN, cr, } 298.15\text{ K}) = (47.1 \pm 3.3)$ J·K$^{-1}$·mol$^{-1}$, which is lower than for UN(cr), NpN(cr) and PuN(cr). This value is provided for information only.

[2005SED/KON] performed *ab initio* calculations of the enthalpies of formation of the actinide mononitrides AnN(cr) (An = Ac, Th, Pa, U, Np, Pu, Am) using the full potential linearized augmented plane wave technique modified for local orbitals (APW + lo), as mentioned already in Section 9.6.1.2.1. The calculated enthalpies of formation showed a linear decrease from UN(cr) to AmN(cr). A good agreement was found for UN(cr) and NpN(cr), but with large deviations for ThN(cr) and PuN(cr). The uncertainty on the calculated values is estimated to be around 15 kJ·mol$^{-1}$ by the present reviewers. The obtained enthalpy of formation for AmN(cr) is

$\Delta_f H_m^o$ (AmN, cr, 298.15 K) = – (324.6 ± 15) kJ·mol$^{-1}$. As this review does not select thermodynamic data reported in theoretical studies, this value is provided for information only. [2012BEN/ZAO] investigated the electronic structure, magnetic, dynamical and thermodynamic properties of NpN(cr), PuN(cr) and AmN(cr) by *ab initio* pseudopotential and DFT methods using the local density (LDA) approximation in a plane wave basis set. Further details are given in Appendix A. The calculated heat capacity increased strongly below 200 K, and more slowly above 600 K, approaching the Dulong-Petit limit (50 J·K$^{-1}$·mol$^{-1}$) around 1000 K for all three compounds. This is about 10 J·K$^{-1}$·mol$^{-1}$ lower at 1000 K than the value recommended in this review for NpN(cr) and PuN(cr).

Figure 12-1: Heat capacity of the actinide mononitrides.




### 12.6.1.2 Aqueous Am(III) and Cm(III) nitrate complexes

No additional studies and reports of thermodynamic data for americium nitrate complexes were reviewed in [2003GUI/FAN], which accepted the selected data in [1995SIL/BID]:

$$Am^{3+} + NO_3^- \rightleftharpoons AmNO_3^{2+}, \quad \log_{10} K_{11}^o = (1.330 \pm 0.200)$$

Tian and Shuh [2014TIA/SHU] studied the stability of the complex $AmNO_3^{2+}$ at $I$ = 1 M, at temperatures ranging between 283 and 358 K. The absorption spectra exhibit a shift in the main absorbance at 503 nm and changes in the absorbance intensity. Despite the fact that the absorbance spectra of the $AmNO_3^{2+}$ complex has two maxima at about 504 nm and 508 nm, the authors only used the 503 nm band to determine

equilibrium constants at the various temperatures. Tian and Shuh used the SIT to calculate $\log_{10} K_1^{\circ} = (1.13 \pm 0.06)$ and the Van't Hoff plot to determine $\Delta_r H_m = (2.0 \pm 0.5)$ kJ·mol$^{-1}$, and $\Delta_r S_m = (9.5 \pm 3.0)$ J·K$^{-1}$·mol$^{-1}$ at 298 K. The equilibrium constant reported by Tian and Shuh is slightly lower than data reported in the literature determined by using ion exchange or solvent extraction methods, from which the selected NEA TDB value was extracted.

Table 12-10: Experimental equilibrium constants for the reaction $Am^{3+} + NO_3^- \rightleftharpoons AmNO_3^{2+}$ at different temperatures as reported in [2014TIA/SHU].

| $T$ /K | Medium | Method | $\log_{10} K_1^{'}$ | $\log_{10} K_1^{\circ}$ |
|---|---|---|---|---|
| 283 | 1 M $HClO_4/NO_3$ | spec | (0.045 ± 0.05) | (1.09 ± 0.06) |
| 298 | 1 M $HClO_4/NO_3$ | spec | (0.063 ± 0.05) | (1.13 ± 0.06) |
| 313 | 1 M $HClO_4/NO_3$ | spec | (0.078 ± 0.05) | (1.19 ± 0.06) |
| 328 | 1 M $HClO_4/NO_3$ | spec | (0.093 ± 0.05) | (1.24 ± 0.06) |
| 343 | 1 M $HClO_4/NO_3$ | spec | (0.105 ± 0.05) | (1.30 ± 0.06) |
| 358 | 1 M $HClO_4/NO_3$ | spec | (0.125 ± 0.05) | (1.36 ± 0.06) |

There are two new experimental studies with Cm(III) reported in [2009SKE/PAN] and in [2011RAO/TIA2]. Both studies use TRLFS to investigate the complex formation in the Cm(III)-nitrate system in the temperature range 278-473 K. The experimental equilibrium constants were extrapolated to zero ionic strength, $\log_{10} K_1^{\circ}$ and $\log_{10} K_2^{\circ}$, and the corresponding ion-interaction term $\Delta\varepsilon$ was determined accordingly. The thermodynamic constants from [2009SKE/PAN] are reported in Table 12-11.

Table 12-11: Stepwise formation constants of the complexes $CmNO_3^{2+}$ and $Cm(NO_3)_2^+$ ($\log_{10} K_n^{\circ}$ at $I = 0$) and the corresponding values of $\Delta\varepsilon_n$ reported in [2009SKE/PAN].

| $T$ /K | $\log_{10} K_1^{\circ}$ | $\Delta\varepsilon_1$ /kg·mol$^{-1}$ | $\log_{10} K_2^{\circ}$ | $\Delta\varepsilon_2$ /kg·mol$^{-1}$ |
|---|---|---|---|---|
| 278 | (1.28 ± 0.07) | (0.03 ± 0.02) | – (0.50 ± 0.05) | – (0.09 ± 0.02) |
| 288 | (1.26 ± 0.06) | (0.03 ± 0.02) | – (0.47 ± 0.01) | – (0.08 ± 0.01) |
| 293 | (1.29 ± 0.06) | (0.03 ± 0.02) | – (0.36 ± 0.10) | – (0.06 ± 0.07) |
| 323 | (1.30 ± 0.03) | (0.02 ± 0.01) | – (0.30 ± 0.10) | – (0.07 ± 0.07) |
| 350 | (1.38 ±0.05) | (0.02 ± 0.02) | – (0.08 ± 0.17) | – (0.02 ± 0.05) |
| 373 | (1.58 ± 0.18) | – (0.03 ± 0.06) | – (0.07 ± 0.12) | – (0.05 ± 0.05) |
| 393 | (1.71 ± 0.30) | – (0.05 ± 0.10) | (0.07 ± 0.12) | – (0.05 ± 0.05) |
| 413 | (1.94 ± 0.18) | (0.01 ± 0.08) | (0.17 ± 0.12) | – (0.06 ± 0.05) |
| 433 | (1.99 ± 0.24) | – (0.01 ± 0.10) | (0.19 ± 0.16) | – (0.08 ± 0.05) |
| 453 | (2.03 ± 0.18) | – (0.02 ± 0.06) | (0.54 ± 0.21) | – (0.09 ± 0.07) |
| 473 | (2.08 ± 0.24) | – (0.12 ± 0.08) | (0.80 ± 0.27) | – (0.06 ± 0.10) |

Based on the temperature variation of $\log_{10} K_n^{\circ}$, Skerencak *et al.* calculated the corresponding enthalpies, entropies and heat capacities of reaction that are listed in Table 12-12 for a temperature of 298 K. It should be noted that the large temperature range makes it possible to determine a reliable value of $\Delta C_p^{\circ}$, which is rarely the case in systems

below 373 K. An important observation is that the temperature variation of $\Delta\varepsilon$ is small, less than 10 % of the value at 298 K.

Table 12-12: Thermodynamic data from [2009SKE/PAN] accepted by the present review.

| | $Cm^{3+} + NO_3^- \rightleftharpoons CmNO_3^{2+}$ | $CmNO_3^{2+} + NO_3^- \rightleftharpoons Cm(NO_3)_2^+$ |
|---|---|---|
| $\log_{10} K^o$ (298 K) | (1.28 ± 0.05) | – (0.40 ± 0.10) |
| $\Delta\varepsilon$ (298 K) /kg·mol$^{-1}$ | (0.03 ± 0.02) | – (0.07 ± 0.03) |
| $\partial_T(\Delta\varepsilon)$ /kg·mol$^{-1}$·K$^{-1}$ | – (0.5 ± 0.2)×10$^{-3}$ | (0.00 ± 0.2)×10$^{-3}$ |
| $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | – (7.30 ± 0.30) | (2.30 ± 0.60) |
| $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | (1.8 ± 1.0) | (9.0 ± 2.0) |
| $\Delta_r S_m^o$ /J·mol$^{-1}$·K$^{-1}$ | (30.5 ± 3.5) | (22.5 ± 7.0) |
| $\Delta_r C_{p,m}^o$ /J·mol$^{-1}$·K$^{-1}$ | (170 ± 20) | (80 ± 30) |

In analogy to the Am(III) study reported in [2014TIA/SHU], Rao and Tian interpreted their spectrophotometric results obtained in 1.0 M Na($ClO_4$/$NO_3$) solutions at 283-358 K with the formation of the $CmNO_3^{2+}$ complex. With increasing nitrate the luminescence emission of $Cm^{3+}$(aq) at 593 nm shifted to 594 nm with increased intensity. The authors determined the conditional equilibrium constants and used the SIT to extrapolate to $I = 0$ reporting $\log_{10} K_1^o = (1.16 \pm 0.04)$ at 298 K. Only small effects of the temperature were observed for the conditional equilibrium constants and the reaction enthalpy calculated from the Van't Hoff equation is $\Delta_r H_m^o = (0 \pm 1)$ kJ·mol$^{-1}$.

The thermodynamic data from the study by Rao and Tian have been obtained in a 1.0 M $NaNO_3$/$NaClO_4$ ionic medium over the temperature range 278-358 K, with equilibrium constants reported in the Appendix A review. Because of the lower temperatures in their study they could only identify the complex $CmNO_3^{2+}$ and report $\log_{10} K_1^o = (1.16 \pm 0.04)$ and $\Delta_r H_m^o = (0 \pm 1)$ kJ·mol$^{-1}$, both in good agreement with the values obtained by Skerencak *et al.* The present reviewers select the thermodynamic data reported in [2009SKE/PAN] as the more accurate ones because they cover a larger temperature range. The selected value of $\log_{10} K_1^o = (1.33 \pm 0.20)$ in [1995SIL/BID] is in close agreement with those reported by Skerencak *et al.* and Rao and Tian, but we find that the direct identification of complexes provides stronger support, both for the value of the equilibrium constant and its uncertainty, than the selected values in previous reviews. The present reviewers also finds strong evidence for the formation of $Cm(NO_3)_2^+$ and select the thermodynamic data reported in [2009SKE/PAN].

The following thermodynamic data have been selected

$$\Delta_f G_m^o(AmNO_3^{2+}, 298.15\ K) = \mathbf{-\ (716.798 \pm 4.782)}\ kJ\cdot mol^{-1},$$

$$\Delta_f H_m^o(AmNO_3^{2+}, 298.15\ K) = \mathbf{-\ (821.750 \pm 1.847)}\ kJ\cdot mol^{-1},$$

$$S_m^o(AmNO_3^{2+}, 298.15\ K) = \mathbf{-\ (23.758 \pm 15.406)}\ J\cdot K^{-1}\cdot mol^{-1}$$

and

$$\Delta_f G_m^o(Am(NO_3)_2^+, 298.15\ K) = \mathbf{-\ (825.309 \pm 4.868)}\ kJ\cdot mol^{-1},$$

$$\Delta_f H_m^o(Am(NO_3)_2^+, 298.15\ K) = \mathbf{-\ (1019.600 \pm 2.780)}\ kJ\cdot mol^{-1},$$

$$S_m^o(Am(NO_3)_2^+, 298.15\ K) = \mathbf{(145.471 \pm 16.868)}\ J\cdot K^{-1}\cdot mol^{-1}.$$

Herm *et al.* [2015HER/GAO] investigated the solubility of $Nd(OH)_3(s)$ and performed TRLFS studies with Cm(III) in alkaline, dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions with varying nitrate concentrations. The authors reported the formation of the complexes $Mg[M(NO_3)(OH)]^{3+}$ and $Mg[M(NO_3)(OH)_2]^{2+}$ with M = Cm(III) or Nd(III) in concentrated $MgCl_2$-$Mg(NO_3)_2$ mixtures with $[Mg^{2+}] \geq 2.8$ m. The absence of such quaternary complexes in the analogous $CaCl_2$-$Ca(NO_3)_2$ systems remains unexplained. Thermodynamic interpretation of the experimental data in [2015HER/GAO] considered also the formation of binary M(III)–hydroxide and M(III)–nitrate complexes as reported in [2009NEC/ALT] and [2009SKE/PAN], respectively. The quaternary complexes reported in [2015HER/GAO] only form at ionic strengths well beyond the applicability of SIT, and thus no thermodynamic data are selected in this review.

## 12.6.2 Phosphorus compounds and complexes

### 12.6.2.1 Aqueous Am(III) and Cm(III) phosphate complexes

There is only one new experimental study on the interaction of Cm(III) with phosphate published since the previous reviews. Moll *et al.* [2011MOL/BRE] investigated the Cm(III) phosphate complex formation in 0.1 M $NaClO_4$ solution using TRLFS at room temperature. This sensitive probe makes it possible to use small Cm(III) concentrations and thereby to avoid precipitation of insoluble Cm(III)-phosphate phases. Formation of solid phases complicated the study of the corresponding Am(III) system in [1992RAI/FEL]. Moll *et al.* report the formation of two complexes, $CmH_2PO_4^{2+}$ and $CmH_2PO_4^+$, with the equilibrium constants $\log_{10} K^o(12.5) = (22.02 \pm 0.13)$ and $\log_{10} K^o(12.6) = (18.56 \pm 0.80)$ for reactions

$$Cm^{3+} + 2H^+ + PO_4^{3-} \rightleftharpoons CmH_2PO_4^{2+} \quad (12.5)$$

$$Cm^{3+} + H^+ + PO_4^{3-} \rightleftharpoons CmHPO_4^+ \quad (12.6)$$

However, under the existing experimental conditions $PO_4^{3-}$ is not the predominant phosphate solution species. This review prefers to use the reactants that are present in significant concentrations in the test solutions, that is using Reactions (12.7) and (12.8):

$$Cm^{3+} + H_2PO_4^- \rightleftharpoons CmH_2PO_4^{2+} \quad (12.7)$$

$$Cm^{3+} + HPO_4^{2-} \rightleftharpoons CmHPO_4^+ \quad (12.8)$$

The corresponding equilibrium constants obtained using the NEA selected values for the protonation of $PO_4^{3-}$ are $\log_{10} K^\circ(12.7) = (2.46 \pm 0.13)$ and $\log_{10} K^\circ(12.8) = (6.20 \pm 0.80)$. The value of $\log_{10} K^\circ(12.7)$ is consistent within the rather large uncertainty ranges with the one selected in previous reviews, $\log_{10} K^\circ(12.7) = (3.00 \pm 0.50)$. The value reported by Moll *et al.* is based on a method that gives direct and more accurate information on the speciation in the system and for this reason we select $\log_{10} K^\circ(12.7) =$ **(2.46 ± 0.13),** assuming that this value is a good approximation for the corresponding Am(III) complex. This equilibrium constant is also in excellent agreement with those reported for trivalent lanthanides in [1995SPA/BRU]. The experimental data from Moll *et al.* provide evidence for the formation of $CmHPO_4^+$, with an equilibrium constant in good agreement with those reported for trivalent lanthanides in [1997LIU/BYR], but significantly different from the value reported by Rao *et al.* [1986RAO/MAH], $\log_{10} K^\circ(12.8) = (4.14 \pm 0.08)$, that was discussed in [1995SIL/BID]. Because of the large discrepancy in the reported constants and the possibility of precipitation of a Cm(III)-phosphate solid phase, this review does not select a value for the formation of the complex $CmHPO_4^+$, and the equilibrium constant reported by Moll *et al.* is given for information only.

Moll *et al.* [2011MOL/BRE] calculated the solubility product of amorphous Cm(III) phosphate colloids formed at pH around 5 to be – 20.1, which is 4.7 $\log_{10}$ units higher than the solubility product of $AmPO_4$(am, hyd) determined by Rai *et al.* [1992RAI/FEL] and accepted in [1995SIL/BID]. The solubility product reported in [1992RAI/FEL] was determined from long-term equilibration experiments lasting between 21 and 86 days, whereas the solubility product of the Cm(III)-phosphate colloids was determined in short-term experiments of about ten minutes. Hence the difference in stability constants for the different phases may well be the result of differences in crystallinity, particle size and water content as suggested in [2011MOL/BRE].

The present review has selected the following thermodynamic data for $AmH_2PO_4^{2+}$:

$$\log_{10} K^\circ(AmH_2PO_4^{2+}, 298.15\ \text{K}) = \mathbf{(2.460 \pm 0.130)},$$

$$\Delta_r G_m^\circ(AmH_2PO_4^{2+}, 298.15\ \text{K}) = \mathbf{-\ (14.042 \pm 0.742)}\ \text{kJ·mol}^{-1},$$

$$\Delta_f G_m^\circ(AmH_2PO_4^{2+}, 298.15\ \text{K}) = \mathbf{-\ (1749.892 \pm 5.061)}\ \text{kJ·mol}^{-1}.$$

# 12.7 Americium group 14 compounds and complexes

## 12.7.1 Carbon compounds and complexes

### 12.7.1.1 Americium carbonate compounds and complexes

#### 12.7.1.1.1 Aqueous Am(III) and Cm(III) carbonate complexes

The equilibrium constants for the formation of Am(III) and Cm(III) carbonate complexes selected in [2003GUI/FAN] are listed in Table 12-13. As discussed in that review, Cm(III) acts as a good model for the corresponding Am(III) complexes, although an important observation is that the limiting complexes are different in the two systems. Hence, an equilibrium constant for the step-wise reaction $Cm(CO_3)_3^{3-} + CO_3^{2-} \rightleftharpoons Cm(CO_3)_4^{5-}$ was reported (but not selected) in [2003GUI/FAN], $\log_{10} K_4^{\circ} = -(1.6 \pm 0.1)$, as recalculated using SIT from TRLFS data in [1999FAN/KON], but based on the new data in [2005VER/VIT], this equilibrium constant has not been accepted by the present review. It should be noted that this complex has not yet been observed for Am(III).

Table 12-13: Equilibrium constants for the formation of Am(III) and Cm(III) carbonate complexes selected in [2003GUI/FAN].

| Reaction | $\log_{10} K_n^{\circ}$ |
|---|---|
| $An^{3+} + CO_3^{2-} \rightleftharpoons AnCO_3^+$ | (8.00 ± 0.40) |
| $AnCO_3^+ + CO_3^{2-} \rightleftharpoons An(CO_3)_2^-$ | (4.90 ± 0.50) |
| $An(CO_3)_2^- + CO_3^{2-} \rightleftharpoons An(CO_3)_3^{3-}$ | (2.10 ± 0.80) |

The stoichiometry of the An(III) carbonate complexes have been discussed in papers by Vercouter, Vitorge *et al.* [2005VER/VIT], [2005VER/VIT2], and [2010PHI/VER], concluding that the limiting complexes in both the Am(III) and Cm(III) systems is $An(CO_3)_3^{3-}$, based both on new TRLFS measurements with Cm(III) [2005VER/VIT], re-interpretation of previously reported Am(III) solubility data in [1994GIF] and comparison of the stoichiometry with the corresponding lanthanide complexes ([2005VER/VIT2] and [2010PHI/VER]). This review accepts the Cm(III)–TRLFS analysis of Vercouter *et al.* [2005VER/VIT] and agrees that only two complexes can be identified and that the stepwise equilibrium constant is $\log_{10} K_3 = (2.08 \pm 0.10)$ at $I = 3$ M. However, as discussed in Appendix A, this review agrees with the conclusions of Fanghänel *et al.* [1998FAN/WEG2] that a complex with the composition $Cm(CO_3)_4^{5-}$ is formed at high carbonate concentrations. The stepwise equilibrium constants $\log_{10} K_4$ and $\log_{10} K_4^{\circ}$ are discussed in [2003GUI/FAN], but no value was selected. The re-interpretation in [2005VER/VIT] of the Am(III) solubility study by Giffaut [1994GIF] is not accepted because of the lack of solid phase characterization (see also discussion in Section 12.7.1.1.5). The authors also argue that the limiting complex in the Eu(III)

carbonate system is $Eu(CO_3)_3^{3-}$, based on solubility experiments in $NaClO_4/Na_2CO_3$ solutions. However, they note that in 3.8-4.2 M KCl solutions, $Eu(CO_3)_4^{5-}$ is the predominant complex in the range $-2 < p[CO_3^{2-}] < 0$. This observation demonstrates that the stoichiometry is depending on the counter-ion, possibly due to the formation of $M^+[Eu(CO_3)_4]^{5-}$ ion-pairs. The present reviewers do not accept the observations in [2005VER/VIT], [2005VER/VIT2] and [2010PHI/VER] as justification for the reinterpretation of the TRLFS data on Cm(III)-carbonate obtained by Fanghänel *et al.* ([1998FAN/WEG2], [1999FAN/KON]). In the Appendix A review of [2005VER/VIT], we have presented our own analysis of their data and concluded that the experimental TRLFS data from Fanghänel *et al.* provide clear evidence for the formation of $Cm(CO_3)_4^{5-}$. Unfortunately, the lack of solid phase characterization in Am(III) solubility experiments performed in the presence of high carbonate concentrations (up to $p[CO_3^{2-}] = 0$, in [1994GIF]) where $Am(CO_3)_4^{5-}$ should be expected to predominate prevents a definitive confirmation of the formation/predominance of this limiting complex for Am(III).

The analysis of experimental data requires not only the necessary mathematical/statistical tools, but also understanding of the fundamental chemistry. It is well-known that the chemistry of the 4*f* and 5*f* elements is very similar (apart from their redox properties), and also that the systematic variations in properties, like equilibrium constants, follow similar trends for both groups of elements. For this reason, a variation in the stoichiometry of the carbonate complexes between the chemically very similar Eu(III), Am(III) and Cm(III) ions is unlikely. One notes however that values of $\log_{10} K^\circ$ ((12.9), 298.15 K) summarized in Table 12-8 of [2003GUI/FAN] as derived from Am(III) solubility experiments vary significantly from 0.9 to 2.0. Possible reasons for this are the uncertainty in the experimental data and/or in the chemical model used.

$$Am(CO_3)_2^- + CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-} \tag{12.9}$$

The present reviewers have selected the equilibrium constant for the formation of $Am(CO_3)_3^{3-}$ based on the corresponding Cm(III) constant, $\log_{10}\beta_3^\circ = (15.30 \pm 0.50)$. This value, within its reported uncertainty, is close to the selected value in [2003GUI/FAN], which is therefore retained, but with a smaller uncertainty. Based on the analogous Cm(III)-system, the present review supports the proposed existence of $Am(CO_3)_4^{5-}$, but no value for $\log_{10} K_4^\circ$ can be selected; however, we note that the constant is small. A note of caution: equilibrium constants for the formation of complexes with a large negative charge are strongly dependent on the counter-ion and the selected stoichiometry and equilibrium constants at zero ionic strength may not reflect this as shown by the examples discussed in this section.

This review retains the selected thermodynamic data in [2003GUI/FAN] with a decreased uncertainty:

$$\log_{10}\beta_3^\circ = \mathbf{(15.000 \pm 0.500)}$$

$$\Delta_r G_m^o(Am(CO_3)_3^{3-}, 298.15\ K) = \mathbf{-\ (85.621 \pm 2.854)}\ kJ\cdot mol^{-1}$$

$$\Delta_f G_m^o(Am(CO_3)_3^{3-}, 298.15\ K) = \mathbf{-\ (2268.019 \pm 5.668)}\ kJ\cdot mol^{-1}.$$

#### 12.7.1.1.2 Am(III) and Cm(III) bicarbonate complexes

There is no new information on the formation of Am(III) and Cm(III) bicarbonate and mixed hydroxide-carbonate complexes.

#### 12.7.1.1.3 Am(IV) carbonate complexes

Shilov [2003SHI] has investigated the mechanism of the fast reduction of Am(IV) in $KHCO_3$-$K_2CO_3$ solutions. No thermodynamic data are reported, only a discussion of a possible reduction mechanism.

#### 12.7.1.1.4 Am(V) carbonate complexes

There is no new information on Am(V) carbonate complexes.

#### 12.7.1.1.5 Solid americium carbonates

Previous solubility data and calculations of predominance diagrams from [1994GIF] have been reanalyzed by Vercouter *et al.* in [2004VER/AME] and [2005VER/VIT]. Correcting for the possible leak of $CO_2$(g) in the original test solutions used by Giffaut, Vercouter and co-workers proposed that $Am_2(CO_3)_3$(s) and $NaAm(CO_3)_2$(s) were the solid phases controlling the solubility in the investigated systems, instead of the originally reported $Am_2(CO_3)_3$(s) and $AmOHCO_3$(s). This review considers this hypothesis plausible, but has not used the experimental data in [1994GIF] for selection of equilibrium constants because of the lack of solid phase characterization.

Vercouter *et al.* [2005VER/VIT2] studied the solubility of $NaEu(CO_3)_2\cdot 5H_2O$(cr) over a wide range of carbonate concentrations ($0.01\ M \le [Na_2CO_3] \le 2\ M$). This review notes that the equilibrium constant for Reaction (12.10), $\log_{10} K_s^o$ is very similar for $NaEu(CO_3)_2\cdot 5H_2O$(cr) and $NaAm(CO_3)_2\cdot 5H_2O$(cr), $-(20.90 \pm 0.50)$ and $-(21.00 \pm 0.50)$, respectively; the latter is selected in [2003GUI/FAN]. This observation underscores the chemical similarity between Eu(III) and Am(III).

$$NaAm/Eu(CO_3)_3\cdot 5H_2O(cr) \rightleftharpoons Na^+ + Am/Eu^{3+} + 2CO_3^{2-} + 5H_2O(l) \qquad (12.10)$$

### 12.7.2 Aqueous Am(III) and Cm(III) silicates

The study of the complex formation of Am(III) in silicate-containing solutions is complicated by the complex, pH-dependent chemistry of silicates and the formation of polynuclear silica species. At high concentration of dissolved silica, Si in solution begins to polymerize forming a variety of polynuclear species, which can complex Am(III) ions in solution ([2005WAN/FEL], [2005PAN/KIM]). However Si-NMR data from Wang *et*

*al.* [2005WAN/FEL] indicate that Si monomers are still the prominent species even at pH 12.

The complex formation between Am(III), Cm(III) and Eu(III) and aqueous silica species was studied by Thakur *et al.* [2007THA/SIN] in 0.2 to 1.0 M $NaClO_4$, and by Pathak and Choppin [2006PAT/CHO] over the temperature range (278-318 K) in 0.2 M $NaClO_4$. These two studies used a solvent extraction technique, while Panak *et al.* [2005PAN/KIM] used TRLFS to study the complex formation of Cm(III) in 0.03 M NaCl. Wang *et al.* [2005WAN/FEL] also used TRLFS to study the interactions of Cm(III) and Eu(III) in silicate-bearing solutions of high pH and concentrated $NaNO_3$. The authors used Si-NMR to obtain the speciation of silicate in sodium silicate solutions at pH 12 demonstrating the predominance of monomeric solution species. However, no equilibrium constants were reported in [2005WAN/FEL]. The equilibrium constants reported by [2005PAN/KIM] and [2007THA/SIN] are given in Table 12-14.

Table 12-14: Equilibrium constants for the formation of Eu(III) and Cm(III) silicate complexes. All data reported at $T = 298.15$ K except in [1996JEN/CHO] ($T = 297.15$ K).

| Reaction | $\log_{10}\beta_1^o$ | $\log_{10}{}^*\beta_1^o$ | Reference |
|---|---|---|---|
| $Cm^{3+} + Si(OH)_4(aq) \rightleftharpoons CmSiO(OH)_3^{2+} +$ | – | – (2.07 ± 0.10) | [2005PAN/KIM] |
| $Eu^{3+} + SiO(OH)_3^- \rightleftharpoons EuSiO(OH)_3^{2+}$ | (7.93 ± 0.20) | – | [1996JEN/CHO] |
| | (8.63 ± 0.11) | | [2007THA/SIN] |
| $Cm^{3+} + SiO(OH)_3^- \rightleftharpoons CmSiO(OH)_3^{2+}$ | (7.74 ± 0.08) | | [2005PAN/KIM] |
| | (8.60 ± 0.08) | | [2007THA/SIN] |
| $Am^{3+} + SiO(OH)_3^- \rightleftharpoons AmSiO(OH)_3^{2+}$ | (8.13 ± 0.20) | | Selected in [2003GUI/FAN] |
| | (8.13 ± 0.20) | | Selected by this review |

The average of the equilibrium constants for the formation of $MSiO(OH)_3^{2+}$ (with M = Eu(III), Cm(III) and Am(III)) in Table 12-14 is $\log_{10}\beta_1^o = (8.20 \pm 0.40)$, which is consistent with $\log_{10}\beta_1^o = (8.13 \pm 0.20)$ selected in [2003GUI/FAN]. The latter value is retained in the present review.

Reaction enthalpies for the formation of $EuSiO(OH)_3^{2+}$ and $CmSiO(OH)_3^{2+}$ have been determined from the temperature-dependence of the equilibrium constant $\log_{10}\beta_1$ in 0.20 M $NaClO_4$ and reported in Table 12-15. The table includes also the enthalpy values extrapolated to $I = 0$ as described in Appendix A. These values are assumed to be valid also for $AmSiO(OH)_3^{2+}$.

Table 12-15: Enthalpy of reaction for the formation of $EuSiO(OH)_3^{2+}$ and $CmSiO(OH)_3^{2+}$ in 0.20 M $NaClO_4$ and 298 K, as reported in [2006PAT/CHO], and extrapolated to $I = 0$ in this review.

| Metal ion | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| $Cm^{3+}$ | (15.8 ± 2.0) | (18.6 ± 4.0) |
| $Eu^{3+}$ | (14.5 ± 1.0) | (17.3 ± 3.0) |

The present review has used $\log_{10}\beta_1^o = (8.13 \pm 0.20)$ previously selected in [2003GUI/FAN] and the enthalpy of reaction available for the Cm(III) system to calculate the Gibbs energy, enthalpy and entropy of formation for $AmSiO(OH)_3^{2+}$. The enthalpy, Gibbs energy and entropy have been calculated using $\Delta_f G_m^o(Am^{3+}, 298.15\ K) = -(598.698 \pm 4.755)$ kJ·mol$^{-1}$, $\Delta_f H_m^o(Am^{3+}, 298.15\ K) = -(616.700 \pm 1.500)$ kJ·mol$^{-1}$ and $S_m^o(Am^{3+}, 298.15\ K) = -(201.000 \pm 15.000)$ J·K$^{-1}$·mol$^{-1}$ selected in 2003GUI/FAN] and $\Delta_f G_m^o(SiO(OH)_3^-, 298.15\ K) = -(1253.236 \pm 1.034)$ kJ·mol$^{-1}$, $\Delta_f H_m^o(SiO(OH)_3^-, 298.15\ K) = -(1431.753 \pm 1.352)$ kJ·mol$^{-1}$ and $S_m^o(SiO(OH)_3^-, 298.15\ K) = (91.727 \pm 3.153)$ J·K$^{-1}$·mol$^{-1}$ selected in [NEA TDB review on Auxiliary Data – to be published]:

$$\Delta_f G_m^o(AmSiO(OH)_3^{2+}, 298.15\ K) = \mathbf{-\ (1898.340 \pm 4.998)}\ \text{kJ·mol}^{-1},$$

$$\Delta_f H_m^o(AmSiO(OH)_3^{2+}, 298.15\ K) = \mathbf{-\ (2029.853 \pm 4.481)}\ \text{kJ·mol}^{-1},$$

$$S_m^o(AmSiO(OH)_3^{2+}, 298.15\ K) = \mathbf{(108.758 \pm 20.727)}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

Jensen *et al.* [1996JEN/CHO] report the formation of $Eu(SiO(OH)_3)_2^+$ in a liquid-liquid extraction and fluorescence spectroscopic study of the Eu(III)-silicate system, but this complex is inconsistent with the observations by Panak *et al.* that suggest the colloidal character of this second species. Thermodynamic data reported in [1996JEN/CHO] for the complex $Eu(SiO(OH)_3)_2^+$ is not accepted by the present review.

## 12.7.3 Aqueous Am(III) and Cm(III) borate complexes

There are no thermodynamic data for Am(III) borate complexes. The present review recognizes that such complexes may be formed in solution with polymeric boron(III) ions. There are three solubility and spectroscopic studies ([2010BOR/RIC], [2014SCH/KRE], [2015HIN/ALT]) related to the formation of Am(III) borate complexes, which involve the use of the analogous Nd(III) and Cm(III) borate systems. All these studies provide evidence on the formation of weak Nd(III)- and Cm(III)-borate aqueous complexes, although the stoichiometry of these remains ill-defined, mainly due to the very complex solution chemistry of boron. The solubility study by Hinz *et al.* [2015HIN/ALT] did not show any increase in the solubility of $Nd(OH)_3$ in the presence of borate, but indicated that the presence of borate at high concentration ( $\geq 0.16$ M) could induce a solid phase transformation. Even though the stoichiometry of the solid phase was difficult to define, the observed solubilities were similar to those reported for the well-defined $Nd(B_9O_{13}(OH)_4)$(cr) phase.

# Chapter 13

# Discussion of new data selection for Technetium

## 13.1 Elemental technetium

There are no new experimental studies focusing on the thermodynamic properties of elemental technetium. Thermodynamic data selected in [1999RAR/RAN] and [2003GUI/FAN] are retained in this review.

## 13.2 Simple aqueous technetium ions of different oxidation states

When Chemical Thermodynamics of Technetium [1999RAR/RAN] was published, there were two main solubility studies for the hydrous oxide of Tc(IV) [1991MEY/ARN2], [1992ERI/NDA] along with a few uncertain values from other studies as summarised in Table V.13 of [1999RAR/RAN]. Also, at that time there was very little evidence for polymerisation in solutions of Tc(IV) and those results were ambiguous in their interpretation. More extensive solubility data are now available along with much more evidence for polymerisation in acidic solutions of Tc(IV), especially for dimeric species. As a consequence, it is essential to reassess the speciation of Tc(IV) and solubilities of its hydrous oxides.

### 13.2.1 $TcO_4^-$ and redox potential of the $TcO_4^-/TcO_2$(am, hyd, fresh) couple

There are two general problems with the determination of the redox potential of $TcO_4^-/TcO_2(s)$. The first one is the characterisation of the $TcO_2(s)$ solid and the second that the redox process involves three electrons resulting in a major structural rearrangement. Rard *et al.* [1999RAR/RAN] analysed redox potentials for different solid/aqueous phase equilibria reported by various authors and recommended redox potentials for a solid phase, denoted $TcO_2{\cdot}xH_2O(s)$ with $x$ identified from the work of [1991MEY/ARN] as 1.6. The authors of [1999RAR/RAN] recommended a standard

potential, $E°$ = (0.746 ± 0.012) V for the $TcO_4^-/TcO_2 \cdot 1.6H_2O$(am) couple that refers to a reasonably well characterised solid phase:

$$TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO_2 \cdot 1.6H_2O(am) + 0.4H_2O\ (l)$$

This value is supported by many experimental observations (see discussion in [1999RAR/RAN]) and also the recent work of [2015YAL]. However, the value of $x$ in the precipitated solid phases of type $TcO_2 \cdot xH_2O$(am) used as electrodes, change with time (see Section 13.3.2.1.1) and in this review a distinction is made between $TcO_2$(am, hyd, fresh), $TcO_2$(am, hyd) and $TcO_2$(am, hyd, aged). In this review the value of $E°$ recommended by [1999RAR/RAN] is accepted as referring to an electrode made from a freshly formed solid $TcO_2$(am, hyd, fresh) of undefined state of hydration.

$$TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO_2\,(am, hyd, fresh) + 2H_2O(l) \qquad (13.1)$$

$$E°(13.1) = \mathbf{(0.746 \pm 0.012)}\ V$$

However, the $E°$ value for the thermodynamically meta-stable $TcO_2$ (am, hyd), obtained after prolonged storage of the amorphous phase is different and the thermodynamic data derived in this review from solubility data (*cf.* Section 13.3.2) correspond to:

$$TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO_2\,(am, hyd) + 2H_2O(l) \qquad (13.2)$$

$$E°(13.2) = (0.757 \pm 0.006)\ V$$

Only $E°$(13.1) is selected since no long-term measurements (over many weeks) for aged electrodes for $E°$(13.2) are available and this latter value is calculated from the thermodynamic data in this review. Furthermore, it has been observed [2013KOB/SCH] that due to kinetic constraints, a significant reduction of Tc(VII) in homogeneous or heterogeneous solutions occurs only at $E_h$ values about 100 mV lower than the $E_h$ corresponding to the $TcO_4^-/TcO_2$ (am, hyd, fresh) electrode. The heterogeneous reaction was more rapid than the homogeneous one, and was catalysed by adsorbed Fe(II) [2007ZAC/HEA].

## 13.2.2 Tc(IV)

This review follows the approach of [1999RAR/RAN] of using $TcO(OH)_2$(aq) as "master species" for hydrolysis schemes of Tc(IV) in aqueous solution. The reason is that most reliable thermodynamic data for simple aqueous Tc(IV) ions stem from solubility experiments. Redox potential measurements of the pair Tc(VII)/Tc(IV) reported in the previous review [1999RAR/RAN] were all derived from reactions using a freshly prepared $TcO_2$(am, hyd, fresh) electrode, and the reduction potentials were thus expressed with respect to this. Recently, redox potential determinations were performed directly for aqueous species under acid conditions ([2009VON], see Section 13.3.1.1). For discussion of corresponding phases, see Section 13.3.2.

As in [1999RAR/RAN], the present review does not select the limiting Tc(IV) species in the low pH range as "master species", since uncertainties in the stoichiometry of the polymer in this pH range are larger, and the dominance field smaller than that of $TcO(OH)_2$(aq). Importantly, the number of literature data used to constrain the stability of $TcO(OH)_2$(aq) by solubility data is also much larger than that for hydrolysis species in the low pH range. The drawback of the present choice is that variations in the degree of aging of the solid phase and the hydration state of the solubility controlling phase will have a direct impact on the magnitude and uncertainty of the equilibrium constant of $TcO(OH)_2$(aq) and on all the various hydrolysis constants that are coupled to $TcO(OH)_2$(aq).

The selected thermodynamic data of $TcO(OH)_2$(aq) are derived from solubility measurements of $TcO_2$ (am), *cf.* Section 13.3.2. The equilibrium constants of protonated and deprotonated monomer and polymer species are discussed and selected in Section 13.3.1.1.

The re-evaluation of solubility data of $TcO_2$(am, hyd) in this review (Section 13.3.2) has important consequences for the derived thermodynamic data in the Tc(IV) hydrolysis scheme: in the work of [1999RAR/RAN] the value for $\Delta_f G_m^o$ ($TcO_2 \cdot 1.6H_2O$, am) is obtained from standard potentials of the $TcO_4^-/TcO_2 \cdot 1.6H_2O$(am) electrode and the $\Delta_f G_m^o(TcO_4^-)$ value. Values for $\Delta_f G_m^o$ ($TcO(OH)_2$, aq) are then obtained from the $\log_{10} K_s^o$ value for $TcO_2 \cdot 1.6H_2O$(am). In the previous review the experimental data of [1991MEY/ARN2] were used to constrain the standard potential. In order to obtain a value for $\Delta_f G_m^o$ ($TcO(OH)_2$, aq), the implicit, but not discussed assumption was made that the solid used in the electrochemical experiments of [1991MEY/ARN2] was the same as used in solubility tests. However, potential measurements last between four hours and one day, using freshly prepared electrodes [1991MEY/ARN2] but solubility experiments are not at equilibrium after one day and establishment of equilibrium requires, according to the analysis in this review, at least 24 days (see Figure 13-5) are necessary. This may be the reason for the observation of [1999RAR/RAN] that aged electrodes sometimes have a different potential than fresh ones. The hydration number for solids formed in less than one day are three or higher [1991MEY/ARN2], indicating that the solid used in the electrochemical studies is different from the one used in solubility experiments.

The $\log_{10} K_s^o$ value of – (8.72 ± 0.40) selected by the present review (*cf.* Section 13.3.2) corresponds to a well-aged solid $TcO_2$(am, hyd, aged), which is certainly quite different from the initially formed solids used in the electrode fabrication. Indeed, the seven-day data (three-four days equilibration + three-day ageing) from [2004HES/XIA] result in a $\log_{10} K_s^o$ value of – (7.66 ± 1.22) for the reaction:

$$TcO_2(\text{am, hyd, fresh}) + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) \qquad (13.3)$$

Due to the absence of solubility or electrochemical data for well crystalline $TcO_2$(cr), this review has made an exception to the NEA rule of not providing

thermodynamic data for amorphous phases. Evidence for the existence of a $[Tc=O]^{2+}$ core in $TcO(OH)_2(aq)$ has been provided based on the combined use of X-ray Absorption Spectroscopy (XAS) and Density Functional calculations (DFT) [2009BRE/KIR]. No data exist for the solubility of solids formed after only one day, and also no data from electrochemical experiments where both potentials and Tc(IV) concentrations have been measured simultaneously. This review therefore recommends that the electrodes should be described as $TcO_4^-/TcO_2$ (am, hyd, fresh) with the electrochemically determined $\Delta_f G_m^o(TcO_2, am, hyd, fresh)$ = **– (379.055 ± 8.372)** kJ·mol$^{-1}$ calculated from Equation (13.1). This value is identical to a result calculated from the value of the $\Delta_f G_m^o(TcO_2 \cdot 1.6H_2O, am)$ of – (758.479 ± 8.372) kJ·mol$^{-1}$ of [1999RAR/RAN] after subtracting the contribution of 1.6 $H_2O$. For this solid phase obtained after seven days of equilibration/ageing, this review obtains $\log_{10} K_s^o$ = – (7.66 ± 1.22). Using this $\log_{10} K_s^o$ value and propagating uncertainties for $\Delta_f G_m^o$ for the solid, $\log_{10} K_s^o$ and water in the equation

$$\Delta_f G_m^o(TcO(OH)_2, aq) = -RT\ln(10)\cdot\log_{10} K_s^o(TcO_2, am, hyd, fresh) + \Delta_f G_m^o(TcO_2, am, hyd, fresh) + \Delta_f G_m^o(H_2O, l)\ \text{kJ·mol}^{-1}$$

the present review has selected a new value for the Gibbs energy of formation of $TcO(OH)_2(aq)$:

$$\Delta_f G_m^o(TcO(OH)_2, aq) = \textbf{– (572.471 ± 10.890)}\ \text{kJ·mol}^{-1}$$

which is slightly more negative than the value of $\Delta_f G_m^o(TcO(OH)_2, aq)$ = – (568.249 ± 8.845) kJ·mol$^{-1}$ recommended by [1999RAR/RAN]. The redox potential of a half-cell involving only aqueous "master species":

$$TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO(OH)_2(aq) + H_2O(l) \qquad (13.4)$$

results in the following selected $E°$ and $\log_{10} K^o$ values:

$$E°((13.4), 298.15\ K) = \textbf{(0.595 ± 0.046)}\ V$$

$$\log_{10} K^o((13.4), 298.15\ K) = \textbf{(30.17 ± 2.33)}.$$

### 13.2.3 $Tc^{3+}$

The study of [2009VON] has shown by slope analyses that $Tc^{3+}$ is the dominant species of Tc(III) at pH values below 3. The data of the authors were used to derive a standard potential for $Tc^{3+}$ (see Appendix A) for the Reaction (13.5), where activity coefficients and water activity are described using the SIT approach.

$$Tc_2O_2(OH)_2^{2+} + 2e^- + 6H^+ \rightleftharpoons 2Tc^{3+} + 4H_2O(l) \qquad (13.5)$$

The resulting standard potential is $E°(13.5)$ = (0.316 ± 0.037) V. [1979GRA/DEV] reported an almost identical value $E°$ = 0.319 V (Appendix A).

The value from [1979GRA/DEV] was used by [1999RAR/RAN] to obtain a minimum value of $\Delta_f G_m^o(Tc^{3+})$ of 89.6 kJ·mol$^{-1}$, corresponding to the equilibrium $Tc^{3+}/TcO^{2+}$. This value is due to the "minimum" value of the thermodynamic data of $TcO^{2+}$ given by [1999RAR/RAN], but was not recommended due to the uncertainty in the hydrolysis scheme of $Tc^{3+}$. The current analyses confirms the predominance of $Tc^{3+}$ for pH values below 3 and obtains a value for $\Delta_f G_m^o(Tc^{3+})$ of (70.1 ± 7.7) kJ·mol$^{-1}$. This value is based on giving equal weight to the evaluation of [1979GRA/DEV] and [2009VON] in Appendix A.

Uncertainties in this value were not reported for the $E°$ value of [1979GRA/DEV] but were given for the half potential as (0.286 ± 0.033) V. Converting this to standard state conditions, one obtains (0.319 ± 0.037) V. Giving equal weight to both studies the present review obtains a value of $E°(13.5)$ = (0.318 ± 0.026) V.

Using the hydrolysis scheme of Tc(IV) accepted in this review and the thermodynamic constants of the Tc(IV) dimer, we have calculated a standard potential with an estimated uncertainty and based on this, a new value for the Gibbs energy of formation:

$$\Delta_f G_m^o(Tc^{3+}) = (71.193 \pm 11.237) \text{ kJ·mol}^{-1}.$$

This value and its error range do not cover the value of 89.6 kJ·mol$^{-1}$, tentatively accepted as the lower value in the review of [1999RAR/RAN]. Also, the obtained thermodynamic constant would suggest a rather large stability field of $Tc^{3+}$ at low $E_h$/low pH conditions. Calculations have shown that this would increase the solubility of $TcO_2$(am, hyd) for values of (pe + pH) lower than 4.5. Data of [2016YAL/GAO] in the (pe + pH) range did not show such an increase of solubility. Hence, no value for $\Delta_f G_m^o(Tc^{3+})$ has been selected in the present review. The value of (71.2 ± 13.2) kJ·mol$^{-1}$ can nevertheless be used for scoping calculations of the stability domains for $Tc^{3+}$.

Further information on the Tc(III)/Tc(IV) redox boundary comes from [2014CHO/CZE] that observed the formation of a Tc(III)/Tc(IV) mixed valence dimer, similar as in [2011MAU/POI2], but not observed by [2009VON]. The presence of mixed valence dimers might add additional difficulties to locate the Tc(IV)/Tc(III) boundary.

## 13.3 Oxide and hydrogen compounds and complexes

### 13.3.1 Aqueous species formed by hydrolysis and protonation

#### 13.3.1.1 The acid/base chemistry of Tc(IV)

The following hydrolysis scheme has been used in [1999RAR/RAN] to describe the acid/base equilibria of aqueous species of Tc(IV) in non-complexing media

$$TcO^{2+} + H_2O(l) \rightleftharpoons TcO(OH)^{+} + H^{+} \quad (13.6)$$

$$TcO(OH)^{+} + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) + H^{+} \quad (13.7)$$

$$TcO(OH)_2(aq) + H_2O(l) \rightleftharpoons TcO(OH)_3^{-} + H^{+} \quad (13.8)$$

##### 13.3.1.1.1 $TcO^{2+}$

The earliest indications for the existence of a predominant hydrolysis species with charge 2+, were observed at pH < 1.3 and assigned to $TcO^{2+}$. This proposal was based on electromobility measurements of [1969GOR/KOC]. Ion exchange data using traces of $^{99m}Tc$ support the hypothesis of formation of $TcO^{2+}$ in the pH range 1.1 to 2 in perchlorate media [1977OWU/MAR]. Rard *et al.* [1999RAR/RAN] discussed a number of other observations but none of them really confirmed the existence of this species in solubility studies using $^{99}Tc$. In particular, Rard *et al.* rejected the proposition of the presence of a dimer by [1979SUN] since the impact of Tc(VII) in the data could not be neglected. The present review confirms that it is not possible to obtain thermodynamic data from the study of [1979SUN] and shares the critical evaluation of the data in [1969GOR/KOC], in which potential polymer or colloid formation were neglected but where the concentrations of Tc were not reported. The choice by Rard *et al.* [1999RAR/RAN] of hydrolysis species $TcO^{2+}$, $TcO(OH)^{+}$, $TcO(OH)_2(aq)$ and $TcO(OH)_3^{-}$ and their determination of hydrolysis constants are largely based on slope analyses of the solubility data of $TcO_2 \cdot nH_2O(am)$ from [1991MEY/ARN2], ignoring the time dependence of these slopes identified in the present review. The presence of a Tc=O core with a Tc-O distance of 1.73 Å, in the hydrolysis species of Tc(IV) was identified recently [2009BRE/KIR]. [1999RAR/RAN] attributed uncertainties in equilibrium constants to the possible formation of chloride complexes and only an upper limit for the hydrolysis constant was selected. Spectroscopic data (UV-Vis, using the absorbance peak at 329 nm) for $TcO^{2+}$ were reported by [2004HES/XIA], the equilibrium constants were determined from solubility data using their thermodynamic model. However, the presence of polymer species was neglected also in this study. The presence of the same UV-absorption at 330 nm and EXAFS analyses by [2004POI] were used as indicators for the presence of polymeric hydrolysis cations of the type $Tc_nO_y^{(4n-2y)+}$. [2008TUM/GER] assigned an absorbance peak at 400 nm to $TcO^{2+}$, but only data at wavelengths higher ≥ 400 nm were recorded and this assignment was for solutions containing peroxide ions. All this puts serious doubts on the assignment of the

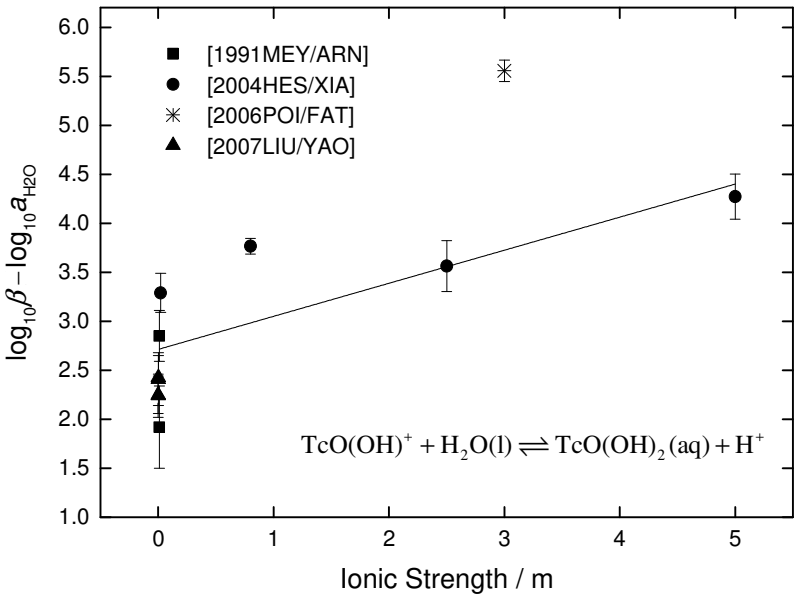
spectrum to $TcO^{2+}$. $TcO^{2+}$ may exist but at concentrations accessible for the UV-visible techniques used, polymer Tc(IV) species seem to be dominant in the low pH regime. In the present review, the apparent spectrum of $TcO^{2+}$ has been assigned as belonging to a polymer species in the study of [2004HES/XIA].

It can of course not be excluded, that at much lower concentrations than those employed experimentally, monomer species exist also in the non-complexing low pH regime. However, [2009VON] confirmed the absence of monomer hydrolysis species of Tc(IV) for Tc concentrations as low as $10^{-5}$ M. This is the case even in non-complexing very acidic solutions (up to 9 M, HTFMS (trifluoromethane sulfonic acid), "pH" < – 2 ). To complicate matters, [2013DEN] has shown that Tc(IV) polymers form complexes with triflate ions. No thermodynamic data for $TcO^{2+}$ are recommended.

#### 13.3.1.1.2 $TcO(OH)^+$

The existence of $TcO(OH)^+$ was inferred principally from slope analyses of solubility data at pH < 3 of $TcO_2 \cdot nH_2O$(am). However, a kinetic analysis of the solubility data over a period of 11 days by [2004HES/XIA] shows that in the low pH region the slopes of log (solubility) versus pH is – 2 when the solubility is approached from oversaturation, and – 1 when approached from undersaturation. The study of [2004HES/XIA] is the only one that has investigated the approach to equilibrium from both from over- and undersaturation. Most data reported by [2004HES/XIA] correspond to non-equilibrium values (see discussion of [2004HES/XIA] in Appendix A). Under long term conditions a slope of – 2 is achieved [2015YAL] also from undersaturation. Data of [1991MEY/ARN2] were determined from undersaturation over a period of three weeks. Again, as in [2004HES/XIA], a change of slope with time is observed (see discussion of data of [1991MEY/ARN2]), indicating in both cases a change of solution speciation. One may speculate that monomers are formed initially in the solubility experiments from undersaturated conditions, which then, polymerise with time. From the SIT plot one can obtain an equilibrium constant of $\log_{10}\beta^{o} = (2.7 \pm 0.8)$ for the reaction $TcO(OH)_2(aq) + H^+ \rightleftharpoons TcO(OH)^+ + H_2O(l)$, which is within the error range of the value (2.5 ± 0.3) given by [1999RAR/RAN].

Figure 13-1: SIT plot for the formation of $TcO(OH)^+$, Equation (13.7), derived from the short term solubility data following a slope of – 1.



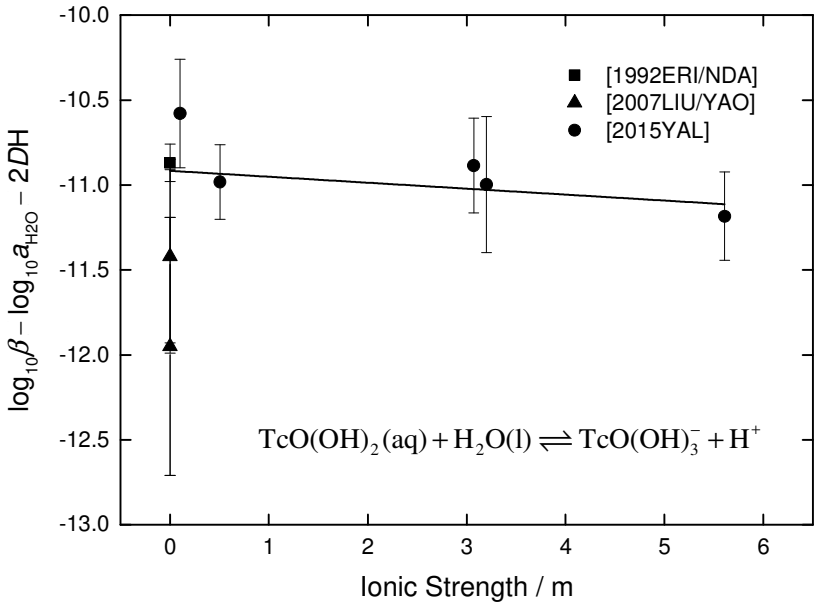

Even though the data of [2004HES/XIA] can be described with a simple hydrolysis model of $TcO(OH)^+$ and $TcO(OH)_2(aq)$, without taking into account the chloride complexes in the very acidic range, the data of [1991MEY/ARN2] and [2007LIU/YAO] give much lower stability constants of $TcO(OH)^+$. No coherent model can be obtained, and the time dependence (see discussion of [2004HES/XIA] in Appendix A) clearly indicates that the reactions appear to be kinetically controlled. The difference between the data of [2004HES/XIA] and those of [1991MEY/ARN2] and [2007LIU/YAO] is that in the former, only traces of Tc(VII) were present in the tests, while in the latter, the Tc(IV) chemistry was analysed using test solutions where a large excess of Tc(VII), had been removed by solvent extraction. It is possible that traces of Tc(IV) were co-extracted with Tc(VII). No thermodynamic data are recommended for $TcO(OH)^+$.

#### 13.3.1.1.3 $TcO(OH)_3^-$

The present review accepts the presence of $TcO(OH)_3^-$. The ionic strength dependency of this hydrolysis species, excluding data of [2007WAR/ALD] (see Appendix A for discussion), is shown in the following SIT plot that gives $\log_{10}\beta^o = -(11.03 \pm 0.24)$, based on individual determination of $\log_{10}K_s$ for each data point. Errors of the conditional constants from the individual datasets are used for weighting in the SIT plot

(Figure 13-2). The $\log_{10}\beta^{o}$ value is independent of the choice of polymer model for the cationic hydrolysis species.

Figure 13-2: SIT plot for $\Delta_f G_m^o$ formation, Equation (13.8), $\log_{10}K_s^o$ fitted using the $\log_{10}\beta^{o}$ values.




The errors are smaller when $\log_{10}K_s^o$ is not fixed globally for all datasets; if this is not done, and using different values from the different authors, every deviation in the solubility in a given dataset will contribute to the uncertainties in the equilibrium constants of the different aqueous solution species. By fixing the $\log_{10}K_s^o$ to the solid with a solubility constant of $\log_{10}K_s^o = -(8.72 \pm 0.40)$ (selected value), the following equilibrium constant for Reaction (13.8) is selected by this review:

$$\log_{10}K^o(13.8) = \mathbf{-\ (10.92 \pm 0.17)}$$

From the slope of the SIT plot and the ε-values for $H^+/Cl^-$ [1999RAR/RAN] and error propagation we obtain with the $\Delta\varepsilon$ value of (0.04 ± 0.04) kg·mol$^{-1}$:

$$\varepsilon_{Na^+/TcO(OH)_3^-} = \mathbf{-\ (0.08 \pm 0.04)}\ \text{kg·mol}^{-1}$$

The $\Delta_f G_m^o$ of $TcO(OH)_3^-$ is calculated as

$$\Delta_f G_m^o(TcO(OH)_3^-) = \mathbf{-\ (747.279 \pm 10.933)}\ \text{kJ·mol}^{-1}.$$

#### 13.3.1.1.4 Polymeric Tc(IV) hydrolysis species

The more recent spectroscopic observations of Tc(IV) solutions in acid media demonstrate the predominance of polymer formation in chloride [2002VIC/OUV], [2004POI], [2006POI/FAT], [2006POI/FAT2], sulfate [2003VIC/FAT], [2013DEN], and non-complexing [2001VIC], [2009VON], [2013DEN] media. Vichot [2001VIC] suggested a nuclearity of three (and four coordinated oxygens) and therefore a core structure 3(μ-O) in analogy with the one in molybdenum $Mo_3O_4^{4+}$ but these results are not consistent with EXAFS data which show symmetric arrangement of oxygen atoms around central $Tc^{4+}$ atoms resulting in the formation of [Tc(μ-O)$_2$Tc] bridges similar to those in precipitated $TcO_2$(am). This suggests a general stoichiometry of the type $Tc_nO_y^{(4n-2y)+}$ [2004POI].

The observed polymers of Tc(IV) show $[Tc(\mu\text{-}O)_2Tc]^{4+}$ or $[Tc(\mu\text{-}O)Tc]^{6+}$ bonding motifs. For example, a polymer $Tc_nO_y^{(4n-2y)+}$ of not yet identified nuclearity was observed at pH 1.5 and Tc concentrations of 0.005 M by using XAS spectroscopy both in chloride and in sulfate media [2001VIC], [2002VIC/OUV]. Differences between the two media were very small and bond distances and coordination numbers indicate close similarity to the structure of $TcO_2 \cdot nH_2O$(am). Polymer species of tetravalent Tc were also observed in non-complexing 1 M and 3 M HTFMS (trifluoromethane sulfonic acid). No other Tc(IV) species was observed, indicating absence of detectable amounts of $TcO^{2+}$.

The observed predominance of cationic polymeric hydrolysis species of Tc(IV) in the low pH range is inconsistent with the model of [1999RAR/RAN]. Hence, a reinterpretation of the entire set of solubility data for $TcO_2 \cdot nH_2O$(am) and the associated hydrolysis model for Tc(IV) is necessary. For this purpose solubility data of [1991MEY/ARN2] were reinterpreted to obtain an overall fit together with more recent solubility data [2004HES/XIA], [2015YAL], [2016YAL/GAO] and testing a number of different hydrolysis schemes, including formation of mono- and bi-charged dimer and trimer cationic hydrolysis species. The errors for fitting different stoichiometries of the polymer hydrolysis species are given in Table 13-1. As in [1999RAR/RAN], $TcO(OH)_2$(aq) (13.2.2) is used as "master species" and the base for the hydrolysis scheme of Tc(IV) and identification of solution species in non-complexing aqueous media in the pH range 3 to 10. The increase of solubility at lower pH is due to the formation of hydrolysis species of Tc(IV) by protonation, deprotonation or polymerisation reactions. The spectroscopic data [2004POI], [2006POI/FAT], [2006POI/FAT2], [2006POI/FAT3] indicate absence of monomers but the nuclearity and charge of the solubility controlling polymer is not known.

Considering only solubility data obtained for reaction times longer than 24 days and fitting each dataset in the pH range 1 to 14 to obtain a $\log_{10}Q$-value ($Q^\circ = a_{H_2O} / a_{TcO(OH)_2(aq)}$) (resulting values are included in Table 13-1), for each dataset a stability constant for $TcO(OH)_3^-$ was obtained (data included in Figure 13-2), and

different stoichiometry models with dimers and trimers, with charge +1 and +2 were tested for the solubility limiting complex at low pH. The plot in Figure 13-3 has been obtained using the selected formula $Tc_2O_2(OH)_2^{2+}$. Each data point corresponds to a fit of a series of solubility data for a given author at a given ionic strength. These errors were used to define the weight in the overall fit in the SIT plot according with the NEA TDB guidelines.

Table 13-1: $Q_s^o$ values are defined as $Q_s^o = TcO(OH_2)(aq)/a_{H2O}$ (Detailed conditions for each dataset are given in Table 13-3).

| Ionic strength | Time /days | $\log_{10} Q_s^o$ | 1σ | *n* | Conditions | Reference |
|---|---|---|---|---|---|---|
| 0.1-2.6 | 24 | – 8.46 | 0.24 | 14 | NaCl | [1991MEY/ARN2] |
| 0.1-1 | 24 | – 8.48 | 0.33 | 10 | electro-deposited | [1991MEY/ARN2] |
| 0 | ? | – 8.17 | 0.04 | 5 | electro-deposited | [1992ERI/NDA] |
| 0.1 | > 180 | – 8.92 | 0.44 | 24 | 0.1 M NaCl | [2015YAL] |
| 0.5 | > 180 | – 8.55 | 0.06 | 3 | 0.5 M NaCl | [2015YAL] |
| 1 | > 180 | – 8.8 | 0.26 | 11 | 1 M NaCl | [2015YAL] |
| 3 | > 180 | – 8.89 | 0.2 | 4 | 3 M NaCl | [2015YAL] |
| 5 | > 180 | – 9.41 | 0.02 | 2 | 5 M NaCl | [2015YAL] |
| 0.75 | > 180 | – 8.93 | 0.57 | 9 | 0.25 M $MgCl_2$ | [2015YAL] |
| 0.75 | > 180 | – 8.85 | 0.04 | 17 | 0.25 M $CaCl_2$ | [2015YAL] |
| 3 | > 180 | – 8.85 | 0.1 | 3 | 1 M $CaCl_2$ | [2015YAL] |
| 6 | > 180 | – 9.16 | 0.44 | 3 | 2 M $CaCl_2$ | [2015YAL] |
| 13.5 | > 180 | – 9.17 | 0.43 | 3 | 4.5 M $CaCl_2$ | [2015YAL] |
| 3 | 110 | – 8.71 | fixed | 2 | undersaturation | [2004POI], [2006POI/FAT2] |
| 0 | about 90 | – 8.39 | 0.14 | 4 | centrifugation anaerobe, DIW, Tc(tot) 1E-6M | [2007LIU/YAO] |
| 0 | 90 | – 8.56 | 0.2 | 3 | UF, anaerobe, DIW, Tc(tot) 1E-6 M | [2007LIU/YAO] |
| 1.00E-03 | 90 | – 8.54 | 0.36 | 3 | Centrifuge, anaerobe, GW, Tc(tot) 1E-6 M | [2007LIU/YAO] |
| 1.00E-03 | 90 | – 8.6 | 0.49 | 4 | UF, anaerobe, GW, Tc(tot) 1E-6 M | [2007LIU/YAO] |
| 0-5 | 60-69 | – 8.74 | 0.4 | 5 | over and undersaturation | [2004HES/XIA] |

(Continued on next page)

Table 13-1 (continued)

| Ionic strength | Time /days | $\log_{10} Q_s^o$ | 1σ | *n* | Conditions | Reference |
|---|---|---|---|---|---|---|
| 0-5 | 25-33 | – 8.48 | 0.35 | 7 | undersaturation | [2004HES/XIA] |
| 0-5 | 11-18 | – 7.84 | 0.48 | 7 | undersaturation | [2004HES/XIA] |
| 0-5 | 3-4 | – 7.66 | 0.62 | 5 | undersaturation | [2004HES/XIA] |

Figure 13-3: SIT plot for formation of $Tc_2O_2(OH)_2^{2+}$ (13.9) based on the interpretation of solubility data ($\log_{10} K_s^o = -(8.72 \pm 0.40)$) using a hydrolysis model composed of $TcO(OH)_2(aq)$, $TcO(OH)_3^-$ and a binuclear bi-charged polymer cation; the weights of datasets are based on their estimated uncertainty.

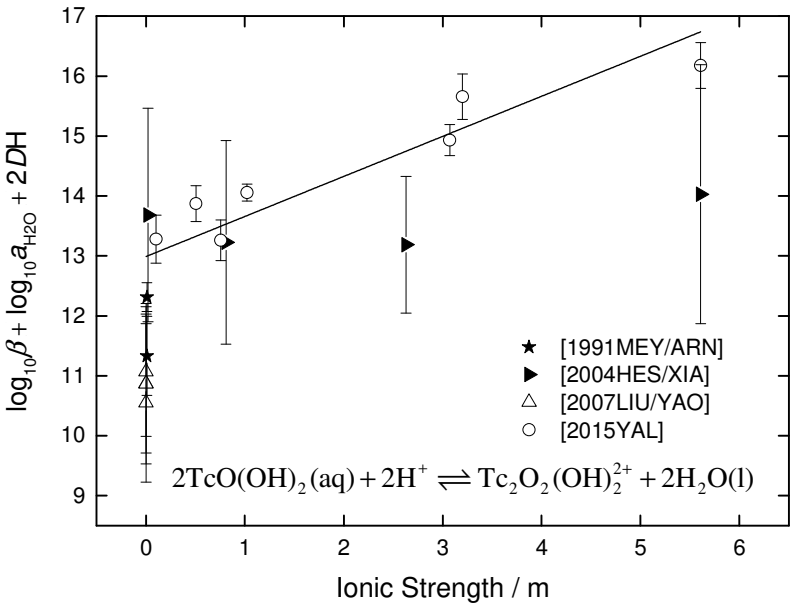



Table 13-2 provides a comparison of the uncertainty analyses of the four models. The results are not conclusive and a choice of stoichiometry cannot be based on error analyses.

Table 13-2: Comparison of uncertainty of four models on stoichiometry of limiting positively charged polymer hydrolysis complex of Tc(IV)

| Stoichiometry | Σσ (slope = f(I)) | Σσ ($\log_{10}K$) |
|---|---|---|
| $Tc_2O_2(OH)_3^+$ | 0.13 | 0.32 |
| $Tc_2O_2(OH)_2^{2+}$ | 0.10 | 0.21 |
| $Tc_3O_4(OH)_3^+$ | 0.13 | 0.29 |
| $Tc_3O_5^{2+}$ | 0.13 | 0.32 |

Additional observations that have guided the analysis of the present review:

- There are abundant observations of dimer formation of Tc(IV) in the literature: [2014POI/FOR], [2011MAU/POI], [1990ALB/AND], [1989LIN/DEW], 1981BUE/AND].
- The proposition of a trimer analogous to $Mo_3O_5^{2+}$ [2002VIC/OUV], [2003VIC/FAT] was not confirmed by spectroscopic data [2004POI], [2006POI/FAT4]. Spectroscopic observations favour a dimer with [Tc($\mu$-O)$_2$Tc] core structure, but a linear trimer cannot be excluded.
- If there is a choice between two qualitatively equivalent models, we have selected the simplest one, which is the one with a dimer.

The information which may constrain the charge of the dimer remains to be assessed: Errors are large because of inclusion of phases with very different stability in the fit of datasets. By using each dataset separately, the errors are lower and the choice between a charge of + 1 and + 2 becomes clear. In most cases a slope analysis of solubility *vs.* pH is performed to identify the charge of the solubility controlling hydrolysis species. However, a more detailed analysis reveals a time dependency in the data: as an illustration, in the diagram for 5 M NaCl (Figure 13-10) short term data (11 days, from undersaturation) of [2004HES/XIA] are compared with data of [2015YAL], clearly indicating a change in slope. The change of slope with time is indicative of time-dependent change in solution speciation, characteristic for polymerisation reactions of Tc(IV) as summarised by [2004POI], [2006POI/FAT2] along with, for solutions at very low pHs with higher chloride concentrations, changes in the relative amounts of chloride complexes. Short term data would then correspond to monomer speciation, long term data to polymer formation. The data of [2015YAL], [2016YAL/GAO] indicate presence of a +2-charged polymer hydrolysis species and the arguments presented above by the present review favour the formation of a binuclear hydrolysis species rather than a trinuclear, in contrast to what has been proposed by [2015YAL], [2016YAL/GAO]. The presence of monomeric hydrolysis species like in [1999RAR/RAN] might be indicated by the slope of one in the pH dependent short term solubility data (< 14 days ageing/equilibration) obtained from undersaturation by [2004HES/XIA]. However, these data were not used in the present review since uncertainties are rather high and time dependency of polymerisation could not be assessed with the limited amount of data. In conclusion this review recommends the use

of the stoichiometry of a +2-charged dimer as the reference hydrolysis species in non-complexing solutions at low pH.

In conclusion, the present review has chosen as the reference stoichiometry of a polymeric cationic hydrolysis species $Tc_2O_2(OH)_2^{2+}$ formed by the reaction:

$$2\ TcO(OH)_2(aq) + 2H^+ \rightleftharpoons Tc_2O_2(OH)_2^{2+} + 2H_2O(l) \qquad (13.9)$$

The selected equilibrium constant is

$$\log_{10} K\ (13.9) = \mathbf{(12.99 \pm 0.41)}.$$

From the slope of the SIT plot and the corresponding $\Delta\varepsilon$ value of $-(0.67 \pm 0.11)$ kg·mol$^{-1}$, the ε-value for $H^+/Cl^-$ [1999RAR/RAN], $\varepsilon(TcO(OH)_2(aq), Na^+, Cl^-) = 0$ (by definition in SIT) and error propagation analysis, we obtain:

$$\varepsilon(Tc_2O_2(OH)_2^{2+}, Cl^-) = \mathbf{-\ (0.43 \pm 0.11)}\ \text{kg·mol}^{-1}.$$

The selected Gibbs energy of formation is then

$$\Delta_f G_m^o(Tc_2O_2(OH)_2^{2+}) = \mathbf{-\ (744.809 \pm 21.905)}\ \text{kJ·mol}^{-1}.$$

Conditional standard potentials of Tc(VII)/Tc(IV) polymer were reported by [2009VON] as $(0.751 \pm 0.062)$ V SHE for 1 M HTFMS, $(0.770 \pm 0.029)$ V SHE for 3 M HTFMS and 0.614 and 0.989 V at 6 M HTFMS. From the equilibrium reaction:

$$10H^+ + 2TcO_4^- + 6e^- \rightleftharpoons Tc_2O_2(OH)_2^{2+} + 4H_2O(l) \qquad (13.10)$$

and the corresponding measured potential $E$ and measured concentrations of $TcO_4^-$ and of the polymer of Tc(IV):

$$E\ (13.10) = E^o\ (13.10) + \frac{2.3026RT}{6F}\left(\log_{10}\frac{[TcO_4^-]^2[H^+]^{10}}{[Tc_2O_2(OH)_2^{2+}]a_{H_2O}^4} + \log_{10}\frac{\gamma_{TcO_4^-}^2\gamma_{H+}^{10}}{\gamma_{Tc_2O_2(OH)_2^{2+}}}\right)$$

a mean value of $E^o(TcO_4^-/Tc_2O_2(OH)_2^{2+})\ (13.10) = (0.735 \pm 0.088)$ V was deduced (see discussion in Appendix A). This value agrees well with the value of $(0.731 \pm 0.011)$ V, obtained directly from the thermodynamic data for Reaction (13.10), derived from solubility studies in the present review. The comparison indicates that, within the reported uncertainties, both values are consistent, demonstrating the consistency of the present interpretation of solubility data of tetravalent Tc in the low pH region based on the +2-charged hydrolysis dimer. A lower value of $E° = 0.57$ V can be obtained from the $E_{1/2}$ data reported by [2012CHO/CZE] for 293 K, but this value is not recommended due to partial irreversibility of the reaction (see discussion in Appendix A).

The $E°$ value of 0.735 V is very similar to the recommended [1999RAR/RAN] $E°$ value of $(0.746 \pm 0.012)$ V for the $TcO_4^-/TcO_2 \cdot 1.6H_2O$(s) electrode.

#### 13.3.1.1.5 Ternary complexes

[2016YAL/GAO] observed an increase of the solubility, $\log_{10}S$ *vs.* pH of $TcO_2$(am, hyd, aged) in 4.5 M $MgCl_2$ and $CaCl_2$ solutions in the pH range 7-11, with a slope of +3. Based on DFT and model calculations, the predominance of ternary Mg-Tc(IV)-OH and Ca-Tc(IV)-OH aqueous species has been proposed by the authors in concentrated alkaline solutions. Stability constants and ion interaction parameters have been derived for these ternary species by the authors:

$$\log_{10} K^{o}_{s\ Ca_3TcO(OH)_5^{3+}} = -(41.53 \pm 0.59)$$

$$\varepsilon(Ca_3[TcO(OH)_5]^{3+},Cl) = -(0.37 \pm 0.20)\ kg\cdot mol^{-1}$$

and

$$\log_{10} K^{o}_{s\ Mg_3TcO(OH)_5^{3+}} = -(40.55 \pm 0.98)$$

$$\varepsilon(Mg_3[TcO(OH)_5]^{3+},Cl) = \varepsilon(Ca_3[TcO(OH)_5]^{3+},Cl)\,.$$

However, due to the high ionic strength employed, the SIT model cannot be used and these data were not selected in the present review.

### 13.3.1.2 Mixed Tc(III)/Tc(IV) aqueous species

In an attempt to obtain metallic Tc by strong reduction of Tc(VII) with borohydride in acetate media ([2011MAU/POI] and [2011MAU/POI2]) it was observed that no metal was obtained but an aqueous species with a $[Tc(\mu\text{-}O)_2Tc]^{3+}$ core structure, probably a dimer in a mixed (III/IV) oxidation state. Using the sum of bond-valences, as described in [2005WES/HES], based on published EXAFS data and an average unit-valence parameter $R_o$ value of 1.8945 Å for Tc(III/IV), an average oxidation state of 3.50 was obtained. Formation of mixed Tc(III/IV) polymers was also suggested to explain UV spectra observed during strong electrochemical reduction of Tc(VII) in non-complexing 6 M HTFMS solutions. Confirmation of a Tc(III)/Tc(IV) mixed valence dimer with absorption band at 502 nm was given by [2014CHO/CZE]. However, no such spectra were observed in solutions of lower acidity [2009VON]. Tc(III/IV) polymers seem to reoxidise rapidly [2009VON] and it is not expected that these polymers have to be taken into account when analysing solubility data of $TcO_2$(s).

### 13.3.1.3 The acid/base chemistry of Tc(VII)

Detailed conditions for the formation of $HTcO_4$ and description of its structure were reported [2010POI/WEC]. EXAFS and density functional calculations show the formation of "$HTcO_4$" with the formula $TcO_3(OH)(H_2O)_2$(aq) at 12 M $H_2SO_4$. In contrast, $TcO_4^-$ remains stable in 6 M $H_2SO_4$. A good fit of the experimental data was obtained with $pK_a$ of $-4.9$, the Hammet acidity, $H_o$ for $H_2SO_4$ and the

equation $\log_{10}([HTcO_4]/[TcO_4^-]) = pK_{HTcO_4} - H_0$. However, based on the EXAFS data of the authors, the correct reaction should be:

$$TcO_4^- + H^+ + 2H_2O(l) \rightleftharpoons TcO_3(OH)(H_2O)_2(aq)$$

Hence, in contrast to the approach of the authors, water activity needs to be taken into account, to obtain meaningful thermodynamic constants. However, the formation of $HTcO_4$ occurs only at very high $H_2SO_4$ concentration, outside the range of applicability of the SIT theory. Therefore, no thermodynamic constant is proposed in the present review.

#### 13.3.1.4 Peroxocomplexes

##### 13.3.1.4.1 Peroxocomplexes of Tc(VII)

Red solutions of diperoxo pertechnetic acid, $TcO(O_2)_2(H_2O)(OH)(aq)$ can be obtained for example in $HNO_3$ solutions more than 7 M and 4.25 M $H_2O_2$ [2013POI/WEC2] or in 6 M $H_2SO_4$ and $H_2O_2$ above 2.12 M [2015POI/GER]. $^{99}Tc$ NMR spectra were consistent with a Tc(VII) species with lower symmetry than $TcO_4^-$. These complexes are still detectable at 9 M $H_2SO_4$ but they are absent at higher acidity. A conditional equilibrium constant can be obtained from the dependency of the UV-visible spectra on $H_2O_2$ concentration published by [2015POI/GER]:

$$TcO_4^- + H^+ + 2H_2O_2(l) \rightleftharpoons TcO(O_2)_2(H_2O)(OH)(aq) + H_2O(l)$$

$$\log_{10}K = \log_{10}[TcO(O_2)_2(H_2O)(OH)] - \log_{10}[TcO_4^-] - 2\log_{10}[H_2O_2] - \log_{10}[H^+]$$

The value of $\log_{10}K$ in 6 M $H_2SO_4$ is (4.65 ± 0.50).

At sulfuric acid concentrations > 9 M, [2015POI/GER] observed the formation of a red and a blue peroxo complexes of Tc(VII). UV-visible spectra are different in 13 and 18 M $H_2SO_4$, indicating the formation of different peroxo complexes. Various hypotheses were formulated, suggesting that the blue species can either be a $Tc^{VII}$ peroxosulfate complex, a $Tc^{VII}$ monoxo or tri-peroxo complex.

Both red (see [2013POI/BUR]) and blue solutions are unstable and decompose in few minutes by release of oxygen and transformation of the peroxo species into $TcO_3(OH)(H_2O)_2(aq)$. As shown in [2013POI/BUR], $TcO_3(OH)(H_2O)_2(aq)$ is predominant and thermodynamically stable at very high sulfuric acid concentrations.

##### 13.3.1.4.2 Peroxocomplexes of Tc(V) and Tc(VI)

Peroxocomplexes of Tc(V) and (VI) are extremely unstable intermediates in the oxidation of Tc(IV) to Tc(VII) by hydrogen peroxide. [2008TUM/GER] could stabilise these species by suppressing the complete oxidation using the very low water activity in solutions of anhydrous concentrated (16 M) sulfuric acid.

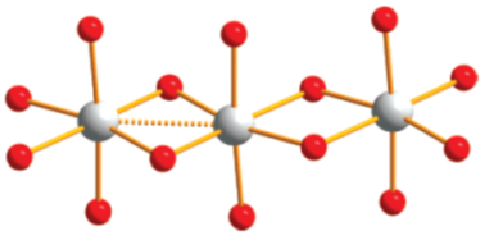
## 13.3.2 Solid technetium oxides and their hydrates

### 13.3.2.1 $TcO_2$(cr)

#### 13.3.2.1.1 General properties

The structure of water free crystalline $TcO_2$(cr) corresponds to a distorted rutile structure with one-dimensional straight chains of edge sharing $TcO_6$ octahedra [2007ROD/POI]. The various chains are cross-linked by shared corners to form a three-dimensional structure. The rutile structure is distorted by first order metal-metal bonds between two neighbouring Tc atoms. Nearest neighbour distance of 2.61 Å was reported by [1995ALM/BRY], but the more recent analyses of [2007ROD/POI] by neutron diffraction and by molecular modeling give two different Tc-Tc distances: one at (2.622 ± 0.001) the other at (3.076 ± 0.001) Å. Recommended thermodynamic data for $TcO_2$(cr) are those discussed in [1999RAR/RAN], no additional data have been reported.

Figure 13-4: Structure of $TcO_2$(cr) as reported in [2007ROD/POI]. (Reprinted with permission from *J. Am. Chem. Soc.* **2007**, 129, 10244. Copyright (2007) American Chemical Society).



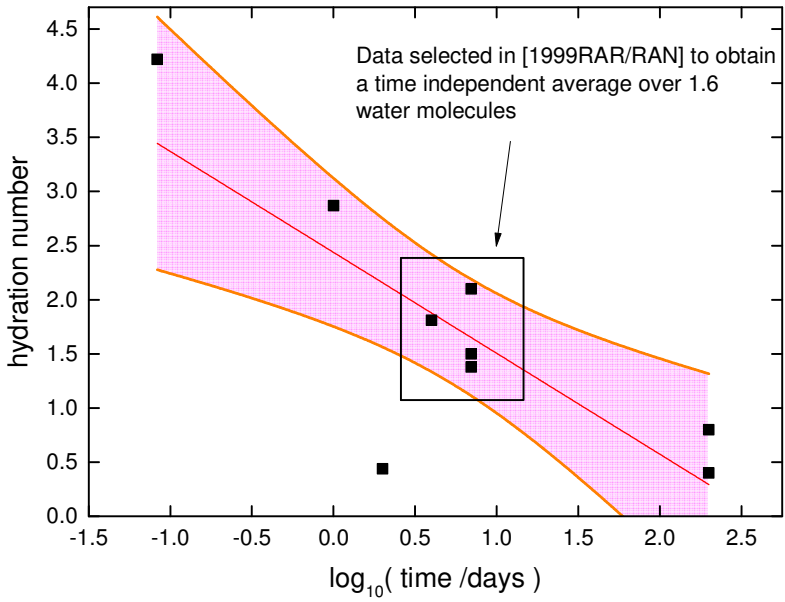
### 13.3.2.2 $TcO_2$(am, hyd)

#### 13.3.2.2.1 General properties

[1991MEY/ARN2] determined the water content of $TcO_2 \cdot xH_2O$(am) as $x = (1.63 \pm 0.55)$ both for a solid electro-deposited from acid and base solutions that had been drying for four to seven days. [1999RAR/RAN] estimates that the $TcO_2 \cdot 1.6H_2O$(am) formula is the most reasonable one. They confirmed that the exact value of water molecules in this oxide depends not only on the method of preparation (electrochemistry, hydrolysis) but also on the pH. [1999RAR/RAN] concluded: "*… since the exact value of x is of no importance in aqueous chemistry, a notation such as $TcO_2$(s, hyd) for this compound would not be unreasonable. However, in order to visibly indicate in the chemical formula that the solid phase in question is hydrated, we prefer to use the formula $TcO_2 \cdot 1.6H_2O$(s) as 1.6 seems to be a reasonable average hydration number in spite of possible larger variations*".

However, more recent results indicate that the degree of hydration decreases with time. An average value of only 0.4-0.8 water molecules was observed for equilibrium times > 6 months [2015YAL], [2016YAL/GAO]. The diagram in Figure 13-5 summarises the evolution of the hydration number with time, using data from [1991MEY/ARN2] and [2015YAL], [2016YAL/GAO].

Figure 13-5: Degree of hydration of $TcO_2 \cdot xH_2O$(am) as a function of time (drying time, equilibrium time) with 95% confidence band, according to data obtained from [1991MEY/ARN2] (all data below 10 days) and [2016YAL/GAO] (all data above 100 days). The "outlier" at 2 days is from the work of 1991MEY/ARN2].



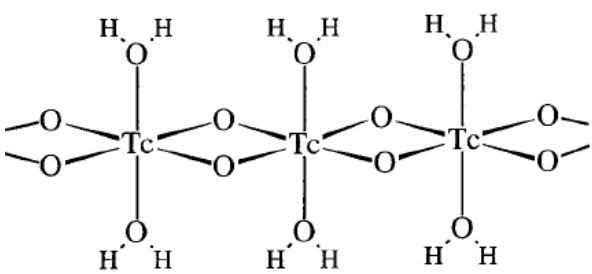

Looking at Figure 13-5, the choice of 1.6 water molecules for $x$ seems arbitrary, since the value of $x$ tends towards zero in few years.

The solubility constant and the Gibbs energy of reaction do not depend strongly on the value of $x$, but this is not true for the Gibbs energy of formation. It is only true that the use of a fixed hydration number $x$ has no impact in the calculation of solubilities, as long as its variation is ignored. If explicitly included in the stoichiometry of the solid, variations of $x$ have a very strong influence on the $\Delta_f G_m^\circ$ value, but not necessarily with the measured solubility and Gibbs energy of reaction. This review

notes that in the neutral pH range the solubility does not depend on ionic strength (Figure 13-8).

No information on particle size and crystallinity is given. Even though $TcO_2$(am) is amorphous, even after two months of ageing [2015YAL], [2016YAL/GAO], the particle size may increase with time resulting in a decrease of solubility with time. Nevertheless, the local structure of the phase is well defined, as confirmed by very similar data obtained by XAS spectroscopy by many authors [2016YAL/GAO], [2002VIC/OUV], [2002LUK/BUC], [2004HES/XIA], [1995ALM/BRY]. The XAS results reveal a single coordination geometry in the technetium centre that is typical in distorted rutile structures, with four oxygen neighbours at 1.98-2.07 Å identified by all studies. [2002LUK/BUC] showed that these oxygen atoms are co- planar. The distances of two remaining oxygens, identified in [2002LUK/BUC] as water molecules (see Figure 13-6), show larger variation in Tc-O distances between 1.98 and 2.7 Å. In some cases ([2016YAL/GAO], [1995ALM/BRY] and the radiolysis sample of [2002LUK/BUC]) these oxygens have similar distances like the ones in the plane. [2002LUK/BUC] proposed that different ratios of bridging oxo- and trans- water ligands and variations of Debye Waller factors indicate different degrees of hydration, but no systematic study has been performed on this. Finally there are two technetium neighbours at 2.53-2.61 Å. The proposed coordination geometry of technetium is consistent with a one-dimensional chain structure consisting of edge-sharing $TcO_6$ octahedra with *trans*-water ligands. If the *trans*- water ligands are replaced by the bridging oxo ligands of the neighbouring chains, one obtains the chains that are present in crystalline $TcO_2$(cr). Both Tc-O distances and Tc-Tc distances are similar for $TcO_2$(am) and $TcO_2$(cr).

Figure 13-6: Structure of $TcO_2 \cdot xH_2O$(am) as reported in [2002LUK/BUC]. (Reprinted with permission from *Environ. Sci. Technol.*, **2002**, 36, 1124. Copyright (2002) American Chemical Society).



[2002VIC/OUV] excluded Tc = O bonds in the structure since they expected bond distances at 1.63-1.64 Å for such a bond.

Analyses of [1976SPI/KUZ] of precipitated $TcO_2 \cdot xH_2O$(am) by IR spectroscopy showed no signature of bound water molecules in the structure indicating that water could easily be removed from the solid prior to analyses and that it was not hydration water. On the other hand, the XAS data indicate that the degree of hydration of the solid has an influence on the local coordination environment of Tc and on the interlinkage between structural chains. This indicates that the IR study is not conclusive and a better characterisation of the state of water in the solid is highly recommended.

The present review recommends the stoichiometry of $TcO_2 \cdot xH_2O$(am) as $TcO_2$(am), allowing to distinguish between stability constants for (i) $TcO_2$(am, hyd, fresh) assigned to freshly prepared solids such as used in electrodes, (ii) $TcO_2$(am, hyd) for solids with an unidentified degree of hydration, including essentially the solids of all solubility studies except those of [2015YAL], [2016YAL/GAO], and (iii) $TcO_2$(am, hyd, aged) for a well-aged solid, typical of those encountered in the study of [2015YAL], [2016YAL/GAO]. The general term $TcO_2$(am) is used in this review to cover in a single term all different degrees of aging and hydration in the solids. The variation of $\Delta_f G_m^o$ for the different degrees of hydration/ageing amounts to about $\pm$ 3 kJ·mol$^{-1}$. The dehydration of $TcO_2$(am), therefore, can in no way be interpreted as indication that the system transforms towards the formation of crystalline $TcO_2$(cr). Even if thermodynamically favoured, and despite the structural similarity between the amorphous and the crystalline phase, the rate of crystallisation at room temperature is too slow to be observed experimentally, even in experiments lasting several years.

#### 13.3.2.2.2 Thermodynamic data

The present review of the solubility of $TcO_2$(am) data shows that both the hydration number $x$ and the solubility are time dependent. Table 13-3 summarises the considered solubility studies and the experimental conditions used in the various datasets:

Table 13-3: Experimental conditions of the solubility studies with different preparations of $TcO_2$(am) evaluated in this review.

| | Approach to equilibrium | Method of solid preparation | Alteration time of solid or ageing of solution before test | Time of equilibrium | Starting concentration | Method of separation solid/ solution | Precaution Tc(VII) |
|---|---|---|---|---|---|---|---|
| [2015YAL], [2016YAL/GAO] | Undersaturation | Electro-chemical, $Na_2S_2O_4$, pH 12.5 | 2 months | Many months, < 600 d | 0 | Ultrafiltration | TPPC |
| [1991MEY/ARN2] | Undersaturation | hydrazine | 1 week | 2-3 weeks | 0 | Centrifugation | Tc(VII/IV) ratio < 200, Separation tetraphenyl arsonium |
| [1991MEY/ARN2] | Undersaturation | Electro-deposition | 1 week | 2-3 weeks | 0 | Centrifugation | Tc(VII/IV) ratio < 200, Separation tetraphenyl arsonium |
| [2007LIU/YAO] | Oversaturation | $SnCl_2$ | – | 3-7 months | $3 \times 10^{-6}$ M | Centrifugation, ultrafiltration | Tc(VII/IV) ratio < 20, Separation tetraphenyl arsonium |
| [2004HES/XIA] | Undersaturation | $Na_2S_2O_4$, pH 12 | 3 days | 3 to 69 days most data: 11 days | 0 | Centrifugation, ultrafiltration | TPPC |
| [2004HES/XIA] | Oversaturation | $Na_2S_2O_4$, hydrazine | 11 days | < 69 days | $5.6 \times 10^{-5}$ pH 0.44 $8.3 \times 10^{-6}$ pH 0.79 | Centrifugation, ultrafiltration | TPPC, Tc(VII/IV) < 0.05 |
| [1992ERI/NDA] | Undersaturation | Electrodeposition | – | Waiting until constant concentration (daily measurement) | $5 \times 10^{-4}$ M (before electro-depos.) | none | Separation by Tetraphenyl arzonium, Tc(VII/IV) ratio < 20 |
| [2004POI], [2006POI/FAT2] | Undersaturation | Solubilisation of $TcCl_6^{2-}$ and pH increase to 6 | – | 110 days | 0 | filtration | Tc(VII/IV) ratio (0.02) determined spectroscopically |



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In non-complexing solutions over a large pH range from 3 to 10, the solubility of $TcO_2$(am) is constant. This review follows the proposal of Rard *et al.* [1999RAR/RAN] that considered a neutral complex of the type $TcO(OH)_2$(aq) as the dominant complex in this pH range, even though it cannot be excluded that a neutral polymer species is formed, as suggested by [1991MEY/ARN].

The solubility reported in [2004HES/XIA] in the pH range from 3 to 10 decreases with time (see data discussion in Appendix A). This may be explained either by Ostwald ripening or by partial dehydration of initially formed precipitates/deposits of $TcO_2$(am), but one cannot distinguish between these mechanisms, since [2004HES/XIA] did not analyse, neither the temporal evolution of solubility, nor the water content of their solid phase. No other data exists, either for studying the water content as a function of aging time, or for studying the temporal evolution of the structure of the solid using modern methods such as Rietveld analysis. By comparing data from long duration experiments [2015YAL], [2016YAL/GAO] with data from short time experiments [2004HES/XIA] and [1991MEY/ARN2], one can conclude that there is a link between hydration number and solubility: short-term data have higher solubility and higher hydration number, long-term data have lower values. A presentation of the apparent solubility data of [2004HES/XIA] together with other solubility data as a function of time is given in Figure 13-7, where only data between pH 4 and ten have been used. Solubility data of the various datasets (see Table 13-1) are expressed as ion activity product $Q = TcO(OH)_2(aq)/a_{H2O}$ are calculated for various ionic strength (0-5 M NaCl) and water activity.

Data of [1992ERI/NDA] of relative high solubility (see Table 13-1) were not included in the diagram, since equilibrium times are not reported and are expected to be rather short (a few days). Despite the uncertainty, there is a clear trend of decreasing $Q_s^o$ value with time. For the data of [2015YAL] and [2016YAL/GAO] a very low average value of $\log_{10} K_s^o = -(8.92 \pm 0.42)$ was obtained for very long equilibrium times > 180 days. It is tempting to use this latter value as the long term equilibrium constant. Still, excluding the short term data of [2004HES/XIA] and considering the uncertainties, the distinction between the average values for all datasets obtained for time periods > 24 days ("long term" in Figure 13-7) is not sufficiently large to discard any of the other datasets as non-equilibrium values. Hence, all datasets > 24 days were used to fix a selected value for $\log_{10} K_s^o$ for an aged solid $TcO_2$(am, hyd, aged).

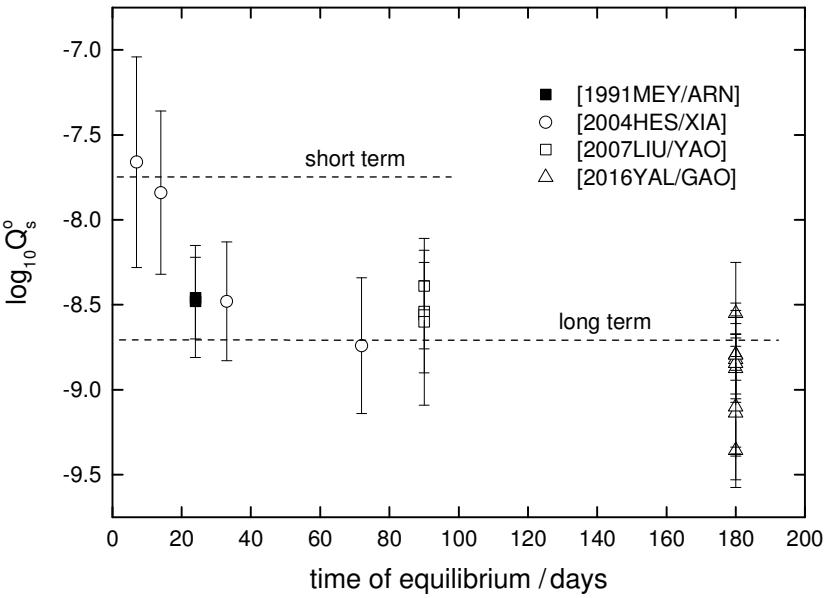
For reaction:

$$TcO_2(am, hyd, aged) + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) \qquad (13.11)$$

the selected solubility constant is

$$\log_{10} K_s^o(13.11) = \mathbf{-(8.72 \pm 0.40)}.$$

Figure 13-7: Time dependency of solubility data for $TcO_2$(am), with $\log_{10} Q_s^o = \log_{10} a_{TcO(OH)_2(aq)} - \log_{10} a_{H_2O}$.




This value is lower than the previously recommended value – (8.4 ± 0.5) of [1999RAR/RAN], although both values agree within their uncertainties. This difference arises as a result of excluding short term equilibration data in our new evaluation and by including more recent measurements.

The Gibbs energy of formation of $TcO_2$(am, hyd, aged) can be obtained using the new selected value of $TcO(OH)_2$(aq) (see Section 13.2.2) together with the $\log_{10} K_s^o$ (13.11) value:

$$\Delta_f G_m^o(TcO_2, am, hyd, aged) = -RT\ln(10)\cdot\log_{10} K_s^o(TcO_2, am, hyd, aged) - \Delta_f G_m^o(TcO(OH)_2, aq) + \Delta_f G_m^o(H_2O, l)\ \text{kJ·mol}^{-1} \quad (13.12)$$

after error propagation one obtains the selected value:

$$\Delta_f G_m^o(TcO_2, am, hyd, aged, (13.12)) = -\ \mathbf{(385.105 \pm 11.127)}\ \text{kJ·mol}^{-1}.$$

Without the data of [2004HES/XIA] and [2015YAL], [2016YAL/GAO] the solubility constant would be $\log_{10} Q_s^o(\text{average}) = \log_{10} K_s^o = -(8.51 \pm 0.36)$ ((13.12)) slightly lower than the value recommended by [1999RAR/RAN], but the difference is not large enough to select a new value.

Hence, we interpret $\log_{10} K_s^o = -(8.4 \pm 0.5)$ from the review of [1999RAR/RAN] as that of a solid obtained in solubility studies, lasting typically a few weeks, which corresponds to Reaction (13.13).

$$TcO_2(am, hyd) + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) \quad (13.13)$$

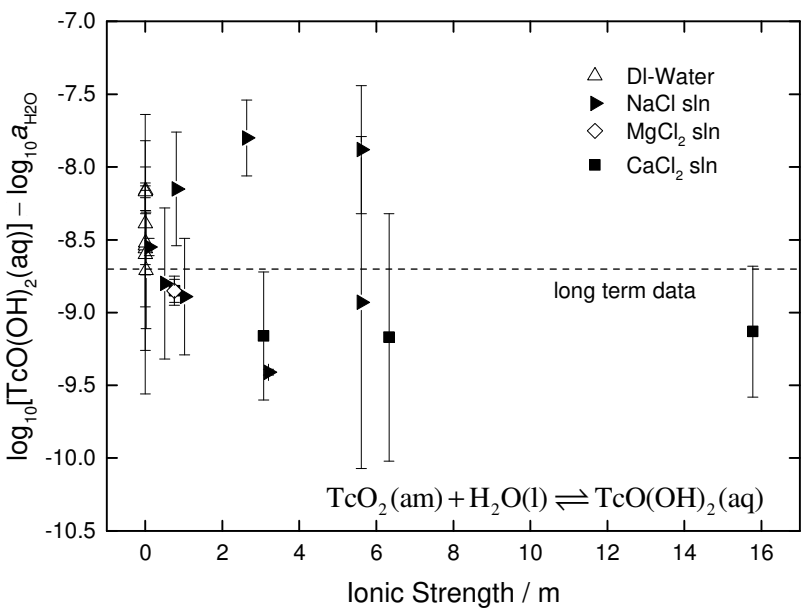
$$\Delta_f G_m^o(TcO_2, am, hyd) = -RT\ln(10)\cdot\log_{10} K_s^o(TcO_2, am, hyd) - \Delta_f G_m^o(TcO(OH)_2, aq) + \Delta_f G_m^o(H_2O, l)\ kJ\cdot mol^{-1} \quad (13.14)$$

giving

$$\Delta_f G_m^o(TcO_2, am, hyd, (13.14)) = -(383.28 \pm 11.72)\ kJ\cdot mol^{-1}.$$

This value is situated between that for $TcO_2$(am, hyd, fresh) and $TcO_2$(am, hyd, aged) and due to the transitionary character of this phase, this value is not included in the list of selected values. Within the range of uncertainty, the $Q_s^o$ values are independent on ionic strength (Figure 13-8). The figure shows, that there is no variation of the solubility constant as a function of ionic strength and of chloride concentration, indicating solubility control by an uncharged chloride free aqueous species.

Figure 13-8: Solubility data of $TcO_2$(am, hyd) as a function of ionic strength. High ionic strength data are from $CaCl_2$ systems [2015YAL], [2016YAL/GAO].



#### 13.3.2.2.3 Solubility pH dependency in dilute and high ionic strength solutions

Solubility data of $TcO_2$(am, hyd) in diluted aqueous solutions are shown in Figure 13-9, using the hydrolysis model including the three hydrolysis species $TcO(OH)_2(aq)$, $TcO(OH)_3^-$ and the dimer $Tc_2O_2(OH)_2^{2+}$. Uncertainty ranges (1.96σ) are shown as well. The plot includes also data which were rejected in the fit of the hydrolysis model (*e.g.* data of [2007WAR/ALD] or [1992ERI/NDA]).

Figure 13-9: Comparison of solubility data of $TcO_2$(am, hyd) or $TcO_2$(am, hyd, aged) in dilute solutions with present hydrolysis model and model of [1999RAR/RAN].

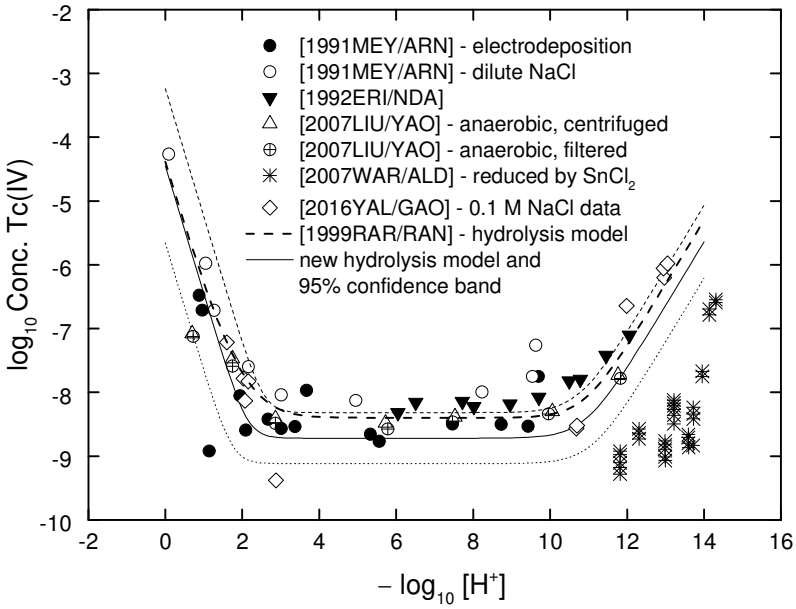



Figure 13-9 shows that selected low ionic strength data ($I < 0.1$) are well described using both the model of Rard *et al.* [1999RAR/RAN] and the model developed in the present review. Some high solubility data in the pH range 9-10 from the dataset of [1991MEY/ARN] were excluded from the overall fit as described in the Appendix A entry. The data of [2007WAR/ALD] are inconsistent with all other data in the alkaline range. This is also the case for data at much higher ionic strength. The data of [2007WAR/ALD] are internally inconsistent as data in the presence of $Fe^{2+}$ as reductant (not shown) are lower than those in the presence of $Sn^{2+}$. As the total amounts of Tc in these experiments are rather low, the Tc concentrations may decrease as a result of sorption to values lower than those required by solubility constraints. No solid phase

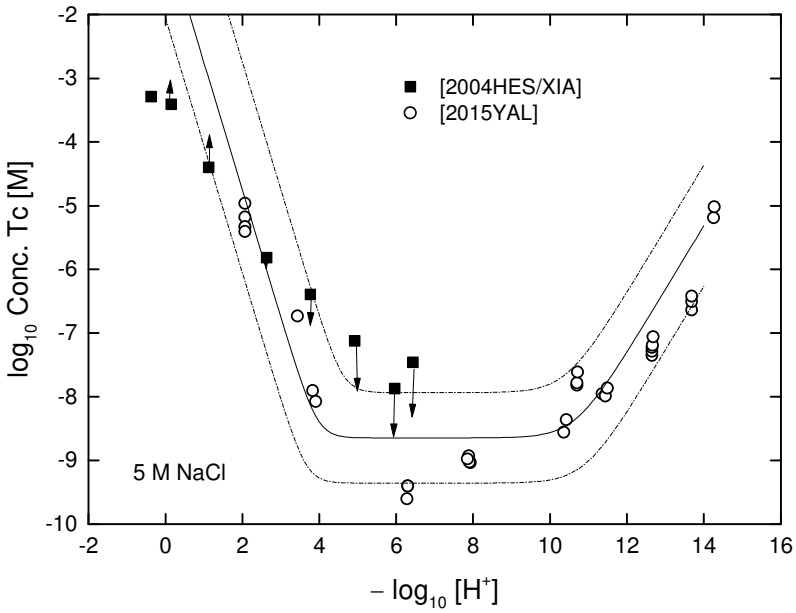
characterisation was performed. This review gives zero weight to the data of [2007WAR/ALD].

The data of [1992ERI/NDA] are higher than the predicted ones, probably due to the short equilibrium times. Since equilibrium times were not reported, no weight is given to these data.

A kinetic analysis of the solubility data of [2004HES/XIA] (see detailed evaluation of data in Appendix A) shows that in the low pH region the slopes of solubility versus pH is – 2 when approaching solubility from oversaturation and – 1 from undersaturation over as much as 29 days.

The study of [2004HES/XIA] is the only one where the approach to equilibrium has been studied from both over- and undersaturation. Most data reported by [2004HES/XIA] correspond to non-equilibrium values (see discussion of [2004HES/XIA] in Appendix A). After a longer equilibration time [2015YAL], [2016YAL/GAO] obtained a slope of – 2 also from undersaturation. Data reported in [1991MEY/ARN2] were determined from undersaturation over a time of three weeks. Again, as in [2004HES/XIA], a change of slope with time is observed, indicating in both cases a change of solution speciation. One may speculate that in solubility experiments, approaching equilibrium from initially undersaturated conditions, initially formed monomers of dissolved Tc(IV) species are polymerised with time. Figure 13-10 describes the application of the recommended hydrolysis model to solubility data in 5 M NaCl: The data obtained after 11 days [2004HES/XIA] and data from long duration experiments [2015YAL]. The arrows link the 11-day data with the ones for 29 days. The data show that equilibrium is not attained after 11 days in [2004HES/XIA] and that the solution concentrations evolve with time towards the long term data of [2015YAL], [2016YAL/GAO] and the recommended solubility curve. The slope of pH *vs.* Tc concentration increases with time for the data of [2004HES/XIA]. For example in tests performed for 11 days, and pH values smaller than 2, the solution concentrations were found to increase with time, while concentrations decrease with time for experiments performed at larger pH. Two parallel time dependent processes may explain this behaviour: dimerisation of dissolved monomer hydrolysis species ($TcO(OH)^+$) and Oswald ripening of the solubility controlling solid. At low pH, increasing concentrations with time correspond to fast dimerisation in solution at high monomer concentration, as observed by [2004POI], [2006POI/FAT2] in 3 M NaCl (pH 1.5) dominating over continuing Oswald ripening. Decrease of solution concentrations with time at larger pH indicate that slower dimerisation at lower monomer concentration is counter balanced by Oswald ripening of the solubility controlling solid. The change of slope (concentration *vs.* pH) and the agreement of the long term data of [2015YAL], [2016YAL/GAO] to the hydrolysis model confirm the change in solution speciation with time and the validity of the final state (dimer in equilibrium with very weakly soluble solid) of the proposed approach.

Figure 13-10: Comparison of solubility data in 5 M NaCl obtained by [2004HES/XIA] and [2015YAL], [2016YAL/GAO]. The arrows indicate the evolution of solution concentration in the experiments of [2004HES/XIA] between 11 and 29 days.




The short term data (11 days) in the low pH region follow a slope of one and can be explained by a monomer hydrolysis model with $TcO(OH)^+$ as dominant species similar as in [1999RAR/RAN].

#### 13.3.2.3 $TcO_2$ colloids

##### 13.3.2.3.1 General properties

$TcO_2$ often precipitates in colloidal form. The particle diameter of the Tc colloids are found to be 20-40 nm by analysis of TEM observations in reducing supercritical water [2007YAM/YUB], 30-50 nm if prepared by reduction by tin(II) [1998NAI/SEK] and that of 30–130 nm by bremsstrahlung irradiation [2002SEK/NAR], [2004SEK/NAR]. Colloids may enhance the apparent solubility of Tc if solutions are not properly filtered. Colloidal suspensions remain stable for at least two months if solution concentrations of Tc(IV) remain lower than $5 \times 10^{-8}$ M [1998NAI/SEK]. The colloid particle was found as aggregates (30-130 nm) of very small particles of 2-3 nm in diameter and data suggests that polymeric Tc(IV) species was a precursor of $TcO_2 \cdot nH_2O$ colloids [2004SEK/NAR]. No thermodynamic quantities are selected in this review for $TcO_2$ colloids.

# 13.4 Group 17 (halogen) compounds and complexes

## 13.4.1 Chlorine, bromine and iodine compounds and complexes

### 13.4.1.1 Aqueous technetium chlorides, bromides and iodides

#### 13.4.1.1.1 Aqueous Tc(IV) halides

##### 13.4.1.1.1.1 $TcCl_4(aq)$, $TcCl_5^-$ and $TcCl_6^{2-}$

$TcCl_6^{2-}$ can easily be produced by dissolution of $K_2TcCl_6$ in concentrated HCl solutions and is well characterised spectroscopically and stable between 3 and 12 M HCl.

[2004HES/XIA] determined the molar Gibbs free energy of formation of $TcCl_4(aq)$ and $TcCl_6^{2-}$. The spectrophotometric identification of $TcCl_4(aq)$ in solubility tests has not been accepted by the present review (see Appendix A). $TcCl_6^{2-}$ may indeed exist in short duration solubility experiments, conducted by the authors, but polymerisation is expected with time.

Considering molarity/molality conversion, a stability constant $\log_{10}K^\circ = -(0.101 \pm 0.197)$ was derived by [1999RAR/RAN] by extrapolating high temperature data (< 90 °C) of [1976KAW/KOY] for 4 M Cl for the reaction:

$$TcCl_6^{2-} \rightleftharpoons TcCl_5^- + Cl^- \qquad (13.15)$$

This reaction was confirmed by electrophoretic measurements in [2005LIU/POI] but no thermodynamic data were derived. Equilibration times are very long and depend on the presence or absence of light. [1999BEN] derived a $\log_{10}K$ value of 0.097 for this reaction in 1 M HCl but equilibrium times were probably too short and the value has been given zero weight (see Appendix A). In darkness and after one month of equilibration, [2004POI] obtained a stability constant $\log_{10}K$ ((13.15), 3 M, HCl) = (0.37 ± 0.1) (after molality/molarity conversion). For the presence of normal laboratory light conditions ($0.45 \times 10^{-10}$ einst·min$^{-1}$) and after nine months of equilibration in 3 M HCl and molality/molarity conversion, a $\log_{10}K$ = (0.50 ± 0.06) (two values) was derived in the present review from Table IV-1 of the authors. Considering the small number of data and their uncertainties, this review recommends a common value for experiments made in darkness and light of $\log_{10}K$ ((13.15), 3 M HCl) = (0.44 ± 0.17).

Extrapolating the data in a SIT plot (not shown) to zero ionic strength gives $\log_{10}K^\circ$ (13.15) = (2.44 ± 1.16) with $\Delta\varepsilon$ = (0.46 ± 0.35) kg·mol$^{-1}$.

As only two values of constants at different ionic strengths are available (the average value of [2004POI] measured in darkness and the value derived by [1999RAR/RAN]), the uncertainty of the value of $\Delta\varepsilon$ and of the constant at zero ionic strength is very high. However, the order of magnitude of the $\Delta\varepsilon$ value appears to be correct, since it is within the error range of the estimated value of $\Delta\varepsilon$ = 0.38, obtained by

analogy between $\varepsilon(TcCl_5^-, H^+)$ and $\varepsilon(TcCl_6^{2-}, H^+)$ with $\varepsilon(ClO_4^-, H^+)$ and $\varepsilon(SO_4^{2-}, Na^+)$. This is an additional argument for not using the data of [1999BEN], since its inclusion would give a $\Delta\varepsilon$ value close to unity. Without more accurate $\varepsilon$-values being available, this review therefore suggests to use the $\Delta\varepsilon$ value of 0.38 with $\varepsilon(TcCl_5^-, H^+) = \varepsilon(ClO_4^-, H^+) = 0.14$ kg·mol$^{-1}$ and $\varepsilon(TcCl_6^{2-}, H^+) = \varepsilon(SO_4^{2-}, Na^+) =$ – 0.12 kg·mol$^{-1}$.

Fixing $\Delta\varepsilon = 0.38$ kg·mol$^{-1}$ with the measured uncertainty of $\Delta\varepsilon$ of ± 0.35 kg·mol$^{-1}$ we obtain as selected value $\log_{10}K^\circ(13.15)$ = **(2.08 ± 1.29)**.

[2004POI] showed that $TcCl_5^-$ can be produced fast by photochemical reaction of $TcCl_6^{2-}$. It is sufficiently stable to allow electrophoretic separation, allowing recording spectrophotometric data for both species, correcting as well for presence of $Tc_2OCl_{10}^{4-}$ by spectrophotometric measurements. Irradiation by light also stabilises $TcCl_5^-$ against $TcCl_6^{2-}$ [2004POI], [2006POI/FAT].

#### 13.4.1.1.1.2 Polymeric Tc(IV) chloride complexes

Monomer Tc(IV) chloride complexes are only stable at rather low concentrations, and at pH ≤ 0 [2004POI], [2006POI/FAT].

At Tc concentrations higher than about $10^{-4}$ m, and/or higher pH, the monomer chloride complexes are dimerised to give $Tc_2OCl_{10}^{4-}$. An equilibrium constant $\log_{10}K$ ($I$ = 3 M) = (4.67 ± 0.07) has been derived by [2004POI] for reaction:

$$2TcCl_5^- + H_2O(l) \rightleftharpoons Tc_2OCl_{10}^{4-} + 2H^+ \qquad (13.16)$$

No data are available for this reaction at another ionic strength for the photosensitive $Tc_2OCl_{10}^{4-}$. The experiments of [2006POI/FAT] allow to establish the predominance ranges of $TcCl_5^-$ and $Tc_2OCl_{10}^{4-}$ (Figure 5 of the authors) under light irradiation between pH = 0 and pH = 1.3 at 3 M (Na, H)Cl solutions.

Whereas in the absence of light $TcCl_5^-$ is the dominant solution species of Tc(IV) only at pH < 0.2 in solutions of 3 M chloride and $1.2 \times 10^{-4}$ M Tc(IV) (as deduced from Fig. IV-1 in [2004POI]), its predominance extends for similar concentrations of $0.83 \times 10^{-4}$ M Tc(IV) well beyond pH 1 under light ($\varphi = 1.77 \times 10^{-6}$ einst·min$^{-1}$, see Figure 5 in [2006POI/FAT]).

The stability of $TcCl_6^{2-}$ at higher pH has been studied by [2001VIC], [2002VIC/OUV] in mixed chloride/sulfate media and by [2004POI] in chloride media. These studies have shown that, at pH > 1.5, $TcCl_6^{2-}$ transforms to polymer hydrolysis species of the type $Tc_nO_y^{(4n-2y)+}$. The present review has interpreted this polymer species as $Tc_2O_2(OH)_2^{2+}$.

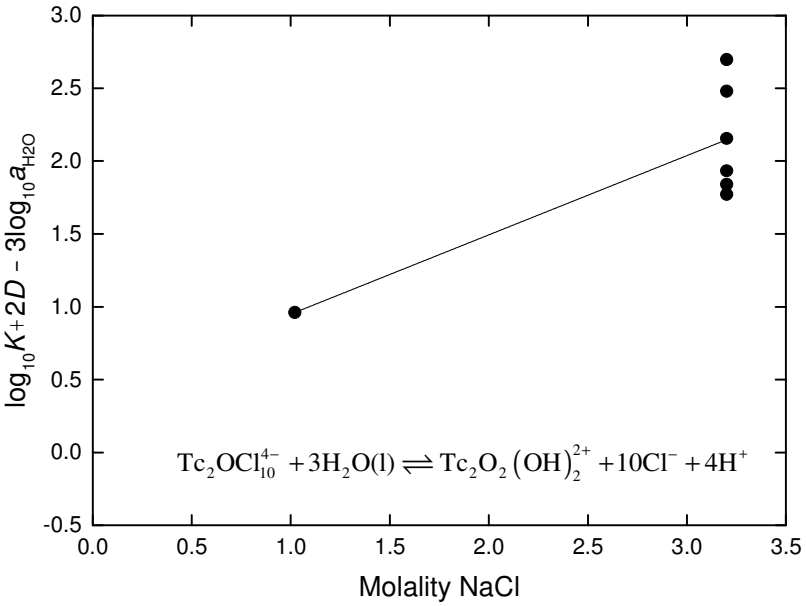
In [2004POI], the author showed that none of the monomer or polymer chloride complexes of Tc(IV) stays stable at pH > 1.5. In this pH range only species of

the type $Tc_nO_y^{(4n-2y)+}$ ($\equiv$ "$Tc_2O_2(OH)_2^{2+}$") are stable. Transformation of $TcCl_6^{2-}$ to $Tc_nO_y^{(4n-2y)+}$ is slow and takes as much as three months [2006POI/FAT2].

Spectroscopically constrained speciation diagrams have been derived in [2004POI] for two total Tc(IV) concentrations and Cl concentrations of either 1 or 3 M. These diagrams were analysed in the present review (see Appendix A) to obtain conditional constants for reaction:

$$Tc_2OCl_{10}^{4-} + 3H_2O(l) \rightleftharpoons Tc_2O_2(OH)_2^{2+} + 10Cl^- + 4H^+ \qquad (13.17)$$

Figure 13-11: SIT plot for Reaction (13.17) based on conditional equilibrium constants obtained from experimental data in [2004POI].




An equilibrium constant of $\log_{10}K^{\circ}(13.17)$ = **(0.4 ± 1.1)** was obtained with a $\Delta\varepsilon$ = – (0.54 ± 0.37) kg·mol$^{-1}$ (see Figure 13-11). This constant provides the necessary link between the hydrolysis scheme of the present review and chloride complex formation. It is now possible to derive values for the Gibbs free energy of the studied chloride complexes, see below.

Using the $\Delta\varepsilon$ value together with the $\varepsilon$-values for $H^+/Cl^-$, $Na^+/Cl^-$ [1999RAR/RAN], the $\varepsilon$-value for $Tc_2O_2(OH)_2^{2+}/Cl^-$ derived from the analyses of solubility data and error propagation we obtain $\varepsilon(Tc_2OCl_{10}^{4-}, Na^+)$ = (0.89 ± 0.40) kg·mol$^{-1}$.

Using this $\varepsilon$-value, based on the hypothesis that $\varepsilon(Tc_2OCl_{10}^{4-}, Na^+) = \varepsilon(Tc_2OCl_{10}^{4-}, H^+)$ and the $\varepsilon$ values of $TcCl_5^-$ obtained by analogy (see above) of $\varepsilon(ClO_4^-, H^+)$, the hypothesis of equal uncertainties of the epsilon values of H/$TcCl_5$ and H/$TcCl_6$ together with error propagation analysis one obtains a $\Delta\varepsilon$ value for Reaction (13.16) of $\Delta\varepsilon$ = (0.85 ± 0.40) kg·mol$^{-1}$.

Using this value together with the above mentioned conditional stability constant of (4.67 ± 0.07) for Reaction (13.16) in 3 M HCl, one obtains the selected constant for this reaction. The uncertainty is large:

$$\log_{10} K^\circ(13.16) = \mathbf{(3.53 \pm 1.29)}.$$

In summary, the following system of equilibrium reactions was obtained:

$TcCl_6^{2-} \rightleftharpoons TcCl_5^- + Cl^-$ (13.15) with $\log_{10} K^\circ(13.15) = (2.08 \pm 1.29)$

$2TcCl_5^- + H_2O(l) \rightleftharpoons Tc_2OCl_{10}^{4-} + 2H^+$ (13.16) with $\log_{10} K^\circ(13.16) = (3.53 \pm 1.29)$

$Tc_2OCl_{10}^{4-} + 3H_2O(l) \rightleftharpoons Tc_2O_2(OH)_2^{2+} + 10Cl^- + 4H^+$ (13.17) with $\log_{10} K^\circ(13.17) =$ (0.4 ± 1.1).

By combining these equations with Reaction (13.9) a link is provided between the chloride and hydroxide complexes of Tc(IV), resulting in the selected values of $\Delta_f G_m^\circ$:

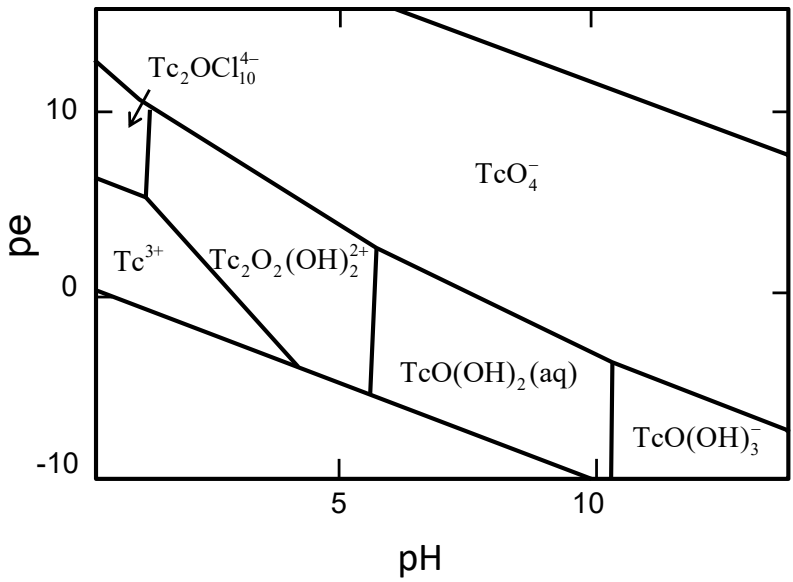
$$\Delta_f G_m^\circ(TcCl_5^-) = \mathbf{-\ (542.994 \pm 11.988)}\ \text{kJ·mol}^{-1}$$

$$\Delta_f G_m^\circ(TcCl_6^{2-}) = \mathbf{-\ (662.338 \pm 14.069)}\ \text{kJ·mol}^{-1}$$

$$\text{and } \Delta_f G_m^\circ(Tc_2OCl_{10}^{4-}) = \mathbf{-\ (1343.276 \pm 22.817)}\ \text{kJ·mol}^{-1}.$$

It shall finally be mentioned that the formation of Tc(IV)(-OH-) chloro-complexes was considered by [2016YAL/GAO] in high ionic strength solutions, based on EXAFS data showing Cl-Tc bonding at pH 2 in 4.5 M $MgCl_2$ solution. The present model of formation of chloro complexes is not applicable at this high ionic strength. A typical $E_h$/pH diagram illustrating the coupling of chloride speciation with the hydrolysis scheme of Tc(IV) in the present review is given in Figure 13-12.

Figure 13-12: $E_h$/pH diagram at $T$ = 298.15 K for solution species of Tc in 3 M (Na, H) Cl solutions and total Tc concentrations of 0.18 mM, in which the presence of solid phases was excluded. The stability field of $Tc^{3+}$ is given only as indication. It has been drawn using the thermodynamic data of $Tc^{3+}$ derived in this review.




### 13.4.1.2 Solid technetium chlorides, bromides and iodides

#### 13.4.1.2.1 Binary halides

To interpret solubility data in a strongly acid reducing environment, [2004HES/XIA] proposed the formation of $TcCl_4$(am). XRD and EXAFS data showed differences in the solid phase compared to $TcO_2 \cdot xH_2O$(am) but the new phase has not been characterised chemically. No weight is given in this review to the thermodynamic data derived by the authors for this solid.

#### 13.4.1.2.2 Ternary halides

Only reaction data for formation of the K and $NH_4$ salts of $TcCl_6^{2-}$ were reported in [1999RAR/RAN] and using these data together with $\Delta_f G_m^o(TcCl_6^{2-})$, the value $\Delta_f G_m^o$ ($M_2TcCl_6$, cr) can be derived:

Considering the reaction $M_2TcCl_6(cr) \rightleftharpoons 2M^+ + TcCl_6^{2-}$, the following $\log_{10} K_s^o$ values are given:

$$M = NH_4: -(7.988 \pm 1.000)$$

M = K: – (9.61 ± 1.00)

M = Rb: – (11.12 ± 1.00)

and M = Cs: – (11.43 ± 1.00)

This review obtains and selects:

$\Delta_f G_m^o$ ($(NH_4)_2TcCl_6$, cr) = **– (866.730 ± 15.193)** kJ·mol$^{-1}$

$\Delta_f G_m^o$ ($K_2TcCl_6$, cr) = **– (1282.212 ± 15.185)** kJ·mol$^{-1}$

$\Delta_f G_m^o$ ($Rb_2TcCl_6$, cr) = **– (1293.829 ± 15.186)** kJ·mol$^{-1}$

$\Delta_f G_m^o$ ($Cs_2TcCl_6$, cr) = **– (1310.493 ± 15.220)** kJ·mol$^{-1}$.

The uncertainties in these thermodynamic data are large, principally due to the uncertainty in the data of $TcCl_6^{2-}$.

# 13.5 Group 16 compounds and complexes

## 13.5.1 Sulfur compounds and complexes

### 13.5.1.1 Technetium sulfides

#### 13.5.1.1.1 Binary Technetium(IV) sulfides

Two binary Tc-sulfide compounds have been reported in the literature, $TcS_2$ and $Tc_2S_7$. The oxidation state of Tc in these solid phases was not addressed in [1999RAR/RAN]. Available solubility data were not considered reliable, and no thermodynamic data were selected for these compounds. Technetium data were discussed in [2003GUI/FAN], but no thermodynamic data were selected.

Recent work [2005LUK/BUC], [2013FER/KER], [2014FER] has clarified the oxidation state of Tc in the binary Tc-sulfide system using XANES. Ferrier and co-workers confirmed that Tc is in +IV redox state both in $Tc_2S_7$ and in $TcS_2$ [2013FER/KER] and [2014FER]. $TcS_2$ can also be formed by precipitation using nano-particles of zerovalent Fe, although this synthetic path results always in the co-existence of $TcO_2$. The ratio $TcS_2$:$TcO_2$ strongly depends on the initial S:Fe ratio [2013FAN/ANI]. In the structure of $Tc_2S_7$ there are −S−S− disulfide ligands explaining the reduction of Tc(VII) to Tc(IV) with only little change in Tc:S stoichiometric ratio that remained close to the value within the interval of 3.3-3.5 [2005LUK/BUC], [2016GER/OBR]. Despite the existence of some solubility data for $Tc_2S_7$ [2015GER/SHI], [2016GER/OBR], no thermodynamic data could be obtained due to unclear solution speciation and predominance of colloids of the general formula ($[Tc_3(\mu^3\text{-}S)(\mu^2S_2)_3(S_2)_{(3n-1)/n}]_n$) [2016GER/OBR].

#### 13.5.1.1.2 Oxosulfides of Tc(IV)

##### 13.5.1.1.2.1 Aqueous species

According to [2014FER], $TcO_3S^-$ formation was observed in acetonitrile solution in the reaction of $(Bu_4N)TcO_4$ and $(Me_3Si)_2S$ with a ratio Tc:S = 1:200. This compound undergoes a fast reduction and/or polymerisation reaction, and consequently no thermodynamic data were obtained.

### 13.5.1.2 Sulfate complexes of Tc

No formation of sulfate complexes of Tc(VII) was observed in [2010POI/WEC]. [2013POI/WEC] studied the formation of sulfate complexes of Tc(V). The initial reactants were $HTcO_4$ and MeOH in 13 M $H_2SO_4$, where $HTcO_4$ was reduced to Tc(V) with redox titrations using cerium(III). EXAFS analyses of the resulting aqueous complexes are consistent with the stoichiometry of $TcO(HSO_4)_2(H_2O)_2(OH)$ and/or $[TcO(HSO_4)_3OH]^-$. DFT calculations suggest that these complexes are stable and the calculated bond distances agree to those measured by EXAFS. No thermodynamic data could be obtained.

[2014FER] observed in 3, 6, 9 and 12 M $H_2SO_4$ solutions the presence of polymeric species containing the Tc-O-Tc unit coordinated to sulfate, water and/or hydroxide ligands. In 15 M $H_2SO_4$, a monomeric compound was formed in which the central technetium atom is surrounded by sulfate, water and/or hydroxide ligands. The species identified in 18 M $H_2SO_4$ contained the $Tc_2(\mu\text{-}O)_2$ unit coordinated to monodentate sulfate, water and/or hydroxide ligands. The mechanism of polymerisation was described as successive reduction of $Tc^{VII}O_3(H_2O)_2(OH)$ to $Tc^{V}O(HSO_4)_3(OH)^-$ and to Tc(IV) complexes (*i.e.*, $Tc(HSO_4)_2(H_2O)(OH)_2(aq)$ and $Tc_2O(HSO_4)_4(H_2O)_2(OH)_2(aq)$). These oxosulfate and sulfate complexes started to polymerise and form colloids.

## 13.6 Group 14 compounds and complexes

### 13.6.1 Carbon compounds and complexes

#### 13.6.1.1 Technetium(IV) carbonates

The selection of carbonate complexes by the review of [1999RAR/RAN] followed the experimental work of Eriksen *et al.* [1992ERI/NDA], [1993ERI/NDA]. The authors deduced from the increase in solubility of $TcO_2{\cdot}nH_2O(am)$ in carbonate media in the pH range 6.26 to 8.56 the formation of two hydroxide-carbonate complexes, a neutral and an anionic one:

$$TcO(OH)_2(aq) + CO_2(g) \rightleftharpoons TcCO_3(OH)_2(aq) \quad (13.18)$$

$$TcO(OH)_2(aq) + CO_2(g) + H_2O(l) \rightleftharpoons TcCO_3(OH)_3^- + H^+ \quad (13.19)$$

with $\log_{10} K^{o}(13.18) = (1.1 \pm 0.3)$ and $\log_{10} K^{o}(13.19) = -(7.2 \pm 0.6)$ [1999RAR/RAN].

The present review accepts the data of the authors. New potentiometric determinations of Tc(IV) carbonate complexes have been reported by [2009ALL/ALL] *cf.* Appendix A, and the constants agree with those of [1992ERI/NDA], but since the authors did not demonstrate absence of precipitation, no weight has been given to their data.

Due to the new formation constant of $TcO(OH)_2(aq)$ determined in the present review, also the Gibbs free energy of formation of the two complexes has been modified. The present review selects the following values:

$$\Delta_f G_m^o (TcCO_3(OH)_2, aq) = \mathbf{-\ (973.123 \pm 11.025)}\ kJ \cdot mol^{-1}$$

$$\Delta_f G_m^o (TcCO_3(OH)_3^-) = \mathbf{-\ (1162.886 \pm 11.417)}\ kJ \cdot mol^{-1}.$$

# Chapter 14

# Discussion of new auxiliary data selection

In several places in the main text and in Appendix A we refer to the comprehensive reviews of high-quality thermodynamic data from the former Soviet Union under the direction of Academician Glushko V.P., best known as a designer of rocket engines. Several dozen researchers contributed to the project, including prominent Soviet specialists in thermodynamics such as V.A. Medvedev, L.V. Gurvich, I.L. Khodakovsky, I.V. Veits and others.

Two series of handbooks have been produced. The first one "The Thermal Constants of Substances" was published in Russian in 1965-1982 in ten volumes, each consisting of one to three parts: Vol. I [1965GLU/MED], Vol. II [1966GLU/MED], Vol. III [1968GLU/MED], Vol. IV, Part 1 [1970GLU/MED], Vol. IV, Part 2 [1971GLU/MED], Vol. V [1971GLU/MED], Vol. VI, Part 1 [1972GLU/MED], Vol. VI, Part 2 [1973GLU/MED], Vol. VII Part I and II published in 1974 [1974GLU/MED], Vol. VIII Part I and II published in 1978 [1978GLU/MED], Vol. IX [1979GLU/MED], Vol. X, Parts 1 and 2 [1981GLU/MED], and Vol. X, Part 3 [1982GLU/MED]. We will refer to this work as the Glushko/Medvedev Tables. The scope was similar to that of the NBS project [1982WAG/EVA]: it covered nearly all chemical elements and contained data for compounds in the gaseous, solid, liquid and dissolved states, including aqueous compounds. However, the major differences between the 1982 version of the NBS Tables and the Glushko/Medvedev Tables are the facts that the latter provided uncertainty estimates and bibliographic references for primary data sources (but no explanation of the data selection). In 1999, the Glushko/Medvedev Tables were published by Wiley (ISBN: 978-0-471-31855-2) as Thermal Constants of Substances, 8 Volume Set, V. S. Yungman (Editor), V. P. Glushko (Founding Editor), V. A. Medvedev (Founding Editor), L. V. Gurvich (Founding Editor).

The second review “Thermodynamic Properties of Individual Substances” was published in Russian in 1978-1982 in four volumes, each consisting of two parts dealing with a selected number of elements and their compounds: Vol. 1 [1978GLU/GUR], Vol. 2 [1979GLU/GUR], Vol. 3 [1981GLU/GUR], and Vol. 4 [1982GLU/GUR]. We will refer to this work as the Glushko/Gurvich Tables and they are the ones listed in

Table 14-3. This compilation contained thermodynamic data for compounds in condensed and gaseous state, and treated a smaller number of elements compared to the Glushko/Medvedev handbook. Its scope is very similar to the JANAF table, but the treatment of the gaseous compounds was in several cases more advanced. Data for aqueous species were not discussed but it appears that data in that work were consistent with CODATA recommendations, as V.A. Medvedev participated in the CODATA project. A strong feature of the Glushko/Gurvich review was the detailed discussion of data selection. Please note that data in the two reviews are not always identical, as several errors have been corrected (for example, the enthalpy of formation of $P_4O_{10}$(cr)) and additional literature sources have been included in the latter project. Generally values from these two sources should not be mixed together. In 1989-1994, the first three volumes of the Glushko/Gurvich Tables have been translated into English and published by Hemisphere Publishing Corporation as "Thermodynamic properties of individual substances", L.V. Gurvich, I.V. Veyts, C.B. Alcock (Editors). Vol. 4, containing data for the actinides Th, U and Pu, as well as alkali metals, was not translated and is available only in Russian as [1982GLU/GUR].

It should be noted that the CODATA values used in the NEA reviews have not been given an independent evaluation by the NEA teams. The reason is that these compilations have been made by a group of eminent international experts and the NEA teams were convinced that an additional review was not necessary. In the present review we have for the same reason used thermodynamic data from the Glushko tables, only those reported in Table 14-3, also without an independent review.

The selected auxiliary data are based on evaluations made by the present review both using available literature information, and the Glushko tables. In some cases, the selected data from the earlier versions of the tables have been updated and we have then used these [1982GLU/GUR]. The selected data are given in bold in the following tables.

## 14.1 Data for auxiliary vanadium compounds

### 14.1.1 $V_2O_5$(cr)

The enthalpy of formation of $V_2O_5$(cr) has been determined in several studies—see the Russian IVTAN review http://www.chem.msu.su/rus/tsiv/V/table.V.T7.html. That review has concluded—see http://www.chem.msu.su/rus/tsiv/V/V2O5_c.html—that the most reliable results have been obtained by combustion calorimetry by Mah and Kelley [1961MAH/KEL] and by Lavut and Chelovskaya, [1989LAV/CHE] that report $\Delta_f H^o_m(V_2O_5, cr) = -(1550.8 \pm 2.1)$ kJ·mol$^{-1}$, and $\Delta_f H^o_m(V_2O_5, cr) = -(1557.4 \pm 1.7)$ kJ·mol$^{-1}$, respectively; the final recommendation was made to select $\Delta_f H^o_m(V_2O_5, cr) = -(1556.0 \pm 3.0)$ kJ·mol$^{-1}$. This choice is accepted by the present review. The same IVTAN review recommends for the molar heat capacity and the molar entropy of

$V_2O_5$(cr) at 298.15 K: $C^\circ_{p,m}$ (298.15 K) = (127.60 ± 0.20) J·K$^{-1}$·mol$^{-1}$ and $S^\circ_m$ (298.15 K) = (130.30 ± 0.20) J·K$^{-1}$·mol$^{-1}$; both values are accepted by the present review. The Gibbs energy of formation of $V_2O_5$(cr), $\Delta_f G^\circ_m$ ($V_2O_5$, cr) = – (1424.84 ± 3.01) kJ·mol$^{-1}$, is obtained using the enthalpy of formation and the entropy of formation, $\Delta_f S^\circ_m$ ($V_2O_5$, cr) = (439.92 ± 0.63) J·K$^{-1}$·mol$^{-1}$, the latter from the molar entropies of V(cr) and $O_2$(g), equal to $S^\circ_m$ (V, cr) = (28.67 ± 0.30) J·K$^{-1}$·mol$^{-1}$, from [1982GLU/GUR] and the online IVTAN review—see http://www.chem.msu.su/rus/tsiv/V/V_c.html, and the NEA selected value $S^\circ_m$ ($O_2$, g) = (205.15 ± 0.003) J·K$^{-1}$·mol$^{-1}$.

## 14.1.2 Enthalpy, entropy and Gibbs energy of formation of $VO_2^+$ and $VO_4^{3-}$

The enthalpy, Gibbs energy and entropy of formation of $VO_2^+$ are based on Reaction (14.1):

$$V_2O_5(cr) + 2H^+(aq, HClO_4) \rightleftharpoons 2VO_2^+(aq, HClO_4) + H_2O(l, aq, HClO_4) \quad (14.1)$$

The Gibbs energy of reaction, $\Delta_r G^\circ_m$ (14.1) has been determined by LaSalle and Cobble, [1955SAL/COB], using solubility experiments in 0.122-0.543 M $HClO_4$ and extrapolated the resulting solubility constant, ${}^*K^\circ_s = [VO_2^+]^2 / [H^+]^2$ to zero ionic strength. As there are no details on the extrapolation, the present review has re-analyzed the data and finds, $\log_{10} {}^*K^\circ_s = -(1.25 \pm 0.10)$ as compared to the value from La Salle and Cobble, $\log_{10} {}^*K^\circ_s = -(1.37 \pm 0.044)$. The selected Gibbs energy of reaction is, $\Delta_r G^\circ_m$ = (7.14 ± 0.57) kJ·mol$^{-1}$; the value reported in [1955SAL/COB] is $\Delta_r G^\circ_m$ = (7.82 ± 0.25) kJ·mol$^{-1}$.

The Gibbs energy of formation, calculated from the calorimetric data for $V_2O_5$(cr) and the recalculated Gibbs energy of reaction from this review, is $\Delta_f G^\circ_m(VO_2^+) = -(590.28 \pm 1.53)$ kJ·mol$^{-1}$.

The enthalpy of reaction, $\Delta_r H^\circ_m$ (14.1) has been measured calorimetrically in [1955SAL/COB] and [1966BER/STA], but with different results, the present review finds the data from the latter study more reliable and has used the reported average value, $\Delta_r H^\circ_m$ (14.1) = – (33.5 ± 1.0) kJ·mol$^{-1}$ to calculate the enthalpy of formation, $\Delta_f H^\circ_m(VO_2^+) = -(651.84 \pm 1.58)$ kJ·mol$^{-1}$; the corresponding entropy of reaction is, $\Delta_f S^\circ_m(VO_2^+) = -(206.5 \pm 7.4)$ J·K$^{-1}$·mol$^{-1}$, in good agreement with our recalculated value in the Appendix A review of [1955SAL/COB].

Our selected values are:

$$\Delta_f H^\circ_m(VO_2^+) = \mathbf{-\ (651.840 \pm 1.580)}\ \text{kJ·mol}^{-1},$$

$$\Delta_f G^\circ_m(VO_2^+) = \mathbf{-\ (590.280 \pm 1.530)}\ \text{kJ·mol}^{-1},$$

$$\Delta_f S^\circ_m(VO_2^+) = \mathbf{-\ (206.500 \pm 7.400)}\ \text{J·K}^{-1}\text{·mol}^{-1},$$

$$S^{o}_{m}(VO^{+}_{2}) = \mathbf{-\ (38.000 \pm 7.400)}\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

The Gibbs energy of formation of $VO^{3-}_{4}$ has been calculated from the Gibbs energy of formation of $VO^{+}_{2}$ and the Gibbs energy of reaction, $\Delta_r G^{o}_{m}$ (14.6), based on the analysis in [1976BAE/MES], who in "The Hydrolysis of Cations", have made an extensive review of published data on the hydrolysis of the vanadyl-ion, $VO^{+}_{2}$ and their reported equilibrium constants have been accepted by the present review as follows:

$$VO^{+}_{2} + 2H_2O(l) \rightleftharpoons H_3VO_4(aq) + H^{+} \quad (14.2)$$

$$\log_{10} K\ ((14.2),\ 0.5\ M\ NaClO_4) = -\ (3.20 \pm 0.09)$$

$$H_3VO_4(aq) \rightleftharpoons H_2VO^{-}_{4} + H^{+} \quad (14.3)$$

$$\log_{10} K\ ((14.3),\ 0.5\ M\ NaClO_4) = -\ (3.78 \pm 0.09)$$

$$H_2VO^{-}_{4} \rightleftharpoons H_2VO^{2-}_{4} + H^{+} \quad (14.4)$$

$$\log_{10} K\ ((14.4),\ 0.5\ M\ NaCl) = -\ (7.8 \pm 0.1)$$

$$H_2VO^{2-}_{4} \rightleftharpoons VO^{3-}_{4} + H^{+} \quad (14.5)$$

$$\log_{10} K\ ((14.5),\ 3.0\ M\ NaClO_4) = -\ (13.2 \pm 0.1)$$

$$VO^{+}_{2} + 2H_2O(l) \rightleftharpoons VO^{3-}_{4} + 4H^{+} \quad (14.6)$$

$$\log_{10} K^{o}\ (14.6) = -\ (30.0 \pm 0.2)$$

The reported equilibrium constants have been extrapolated to zero ionic strength by Baes and Mesmer with a SIT method and these values, listed below, have been selected by the present review.

$$\log_{10} K^{o}\ (14.2) = \mathbf{-\ (3.3 \pm 0.1)};$$

$$\log_{10} K^{o}\ (14.3) = \mathbf{-\ (4.0 \pm 0.1)};$$

$$\log_{10} K^{o}\ (14.4) = \mathbf{-\ (8.55 \pm 0.15)};$$

$$\log_{10} K^{o}\ (14.5) = \mathbf{-\ (14.26 \pm 0.1)};$$

$$\log_{10} K^{o}\ (14.6) = \mathbf{-\ (30.0 \pm 0.2)};$$

$$\Delta_r G^{o}_{m}\ (14.6) = \mathbf{(171.3 \pm 1.1)}\ kJ{\cdot}mol^{-1}.$$

The Gibbs energies of formation reported by Glushko *et al.* [1974GLU/MED], are $\Delta_f G^{o}_{m}(VO^{3-}_{4}) = -\ (889.5 \pm 5.0)\ kJ{\cdot}mol^{-1}$ and $\Delta_f G^{o}_{m}(VO^{+}_{2}) = -\ (588.3 \pm 5.0)\ kJ{\cdot}mol^{-1}$, which result in $\Delta_r G^{o}_{m}\ (14.6) = (173.1 \pm 7.1)\ kJ{\cdot}mol^{-1}$, which is consistent with the value obtained from the equilibrium constant. The present review has used our selected value for the Gibbs energy of formation $\Delta_f G^{o}_{m}(VO^{+}_{2}) = -\ (590.28 \pm 1.53)\ kJ{\cdot}mol^{-1}$, and selects a slightly different value:

$$\Delta_f G^{o}_{m}(VO^{3-}_{4}) = \mathbf{-\ (892.750 \pm 1.910)}\ kJ{\cdot}mol^{-1}.$$

Table 14-1: Selected auxiliary data for Gibbs energies ($\Delta_f G^o_m$), enthalpies of formation ($\Delta_f H^o_m$), molar entropies ($S^o_m$), and heat capacities ($C^o_{p,m}$). All data refer to 298.15 K and 1 bar.

| Compound | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| V(cr) | – | – | (28.67 ± 0.30) | – | http://www.chem.msu.su/rus/tsiv/V/V_c.html |
| $V_2O_5$(cr) | **– (1424.840 ± 3.010)** | **– (1556.000 ± 3.000)** | **(130.300 ± 0.200)** | **(127.600 ± 0.200** | http://www.chem.msu.su/rus/tsiv/V/table.V.T7.html |
| $VO_2^+$ | **– (590.280 ± 1.530)** | **– (651.840 ± 1.580)** | **– (38.000 ± 7.400)** | – | This review |
| $VO_4^{3-}$ | **– (892.750 ± 1.910)** | – | – | – | This review |
| $NaVO_3$(cr) | **– (1067.480 ± 1.520)** | **– (1149.140 ± 1.500)** | (113.81 ± 0.84) | | [1960KOE], [1961KIN/WEL], [1967BER/HEP] |
| $KVO_3$(cr, rhomb) | – | – (1169.9 ± 5.9) | – | – | [1981GLU/MED], vol.X |
| $RbVO_3$(cr) | – | – (1147.4 ± 1.6) | – | – | [1988FOT/SLO] |
| $CsVO_3$(cr) | – | − (1148.2 ± 1.6) | – | – | [1988FOT/SLO] |
| $KNbO_3$(cr) | – 1267.8 | – | – | – | [1981GLU/MED], vol.X |
| $KTaO_3$(cr) | – 1632.2 | – 1419.99 | (119.2 ± 12.6) | – | [1981GLU/MED], vol.X |
| $Mg_2V_2O_7$(cr) | **– (2650.170 ± 3.240)** | **– (2841.000 ± 3.210)** | **(200.410 ± 1.260)** | | [1962KIN/KOE], [1962WEL/KIN] corrected |
| $Ba_2V_2O_7$(cr) | | – (3115.0 ± 10.3) | 280 estimated | 212 estimated | [1988FOT/SLO] |
| $Ca(VO_3)_2$(cr) | **– (2174.750 ± 3.280)** | **– (2334.350 ± 3.230)** | (179.08 ± 1.67) | 166.8 | [1962KIN/KOE], [1962WEL/KIN] corrected |
| $Mg_3(VO_4)_2$(cr) | | – (3464.3 ± 7.1) | (219.9 ± 2) | (239.2 ± 0.5) | [1988FOT/SLO] |

(a) Selected values in bold. Non-bold values for information only.

### 14.1.3 Final consideration of the experimental values of $\Delta_f H_m^o$ (NaVO3, cr, 298.15 K)

The values for $\Delta_f H_m^o$ ($NaVO_3$, cr, 298.15 K): – (1148.65 ± 1.53) kJ·mol$^{-1}$ [1960KOE] and – (1149.85 ± 1.83) kJ·mol$^{-1}$ [1967BER/HEP], are consistent within the claimed uncertainties and the present review has selected weighted average value – (1149.140 ± 1.170), however, but increased the uncertainty to 1.5 kJ·mol$^{-1}$.

Values of $S_m^o$ and $C_{p,m}^o$ are quoted from [1962KIN/WEL] (measured at 50-298 K, extrapolated below 50 K).

## 14.2 Data for auxiliary boron compounds

### 14.2.1 Auxiliary data for the borate section

Table 14-2: Selected auxiliary data for Gibbs energies ($\Delta_f G_m^o$), enthalpies of formation ($\Delta_f H_m^o$), molar entropies ($S_m^o$), and heat capacities ($C_{p,m}^o$). All data refer to 298.15 K and 1 bar.

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| B(cr) | **0.000** | **0.000** | **(5.900 ± 0.080)** | **(5.900 ± 0.080)** | [2003GUI/FAN] |
| $B_2O_3$(cr) | **– (1194.324 ± 1.404)** | **– (1273.500 ± 1.400)** | **(53.970 ± 0.300)** | **(62.761 ± 0.300)** | [2003GUI/FAN] |
| $B(OH)_3$(aq) | **– (969.268 ± 0.820)** | **– (1094.800 ± 0.800)** | **(89.950 ± 0.600)** | **(86.060 ± 0.400)** | [2003GUI/FAN] |
| **$CaB_2O_4$(cr)** | **– (1924.561 ± 1.723)** | **– (2031.500 ± 1.700)** | **(105.020 ± 0.840)** | **(104.000 ± 0.300)** | [1947TOR/SHO], [1948KEL/TOD] |
| $NaBO_2$(cr) | **– (920.203 ± 2.501)** | **– (976.500 ± 2.500)** | **(73.530 ± 0.200)** | **(65.940 ± 0.300)** | [1982GLU/GUR] |

## 14.3 Other auxiliary species

### 14.3.1 $CO_2$(g)

The thermodynamic data for $CO_2$(g) at 298.15 K used in this review are those selected previously [2003GUI/FAN]. The heat capacity at high temperatures was taken from [1998CHA2].

$$C_{p,m}^o(CO_2, g, T) = 31.5503 + 0.034520T - 1.1354\times10^{-5}T^2 - 3.31758\times10^5 T^{-2}\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

## 14.3.2 Group 2 (alkaline-earth) auxiliary data

### 14.3.2.1 Strontium auxiliary data

#### 14.3.2.1.1 SrO(cr)

The enthalpy of formation of SrO(cr) used in this review is that selected previously in [1992GRE/FUG], [2003GUI/FAN]. The heat capacity and entropy values at 298.15 K have been updated since our last review, however. The data recommended in [2003GUI/FAN], *i.e.*, $S^{o}_{m}$ (SrO, cr, 298.15 K) = (55.440 ± 0.500) J·K$^{-1}$·mol$^{-1}$ was based on the assessment of Busenberg, Plummer and Parker [1984BUS/PLU], which selected the low temperature heat capacity results of Gmelin [1969GME] from 1.4 to 310 K. Those data are systematically higher, however, than the results of Anderson [1935AND] from 58 to 298 K, and those of Cordfunke *et al.* [1994COR/LAA] from 5 to 350 K. Because the results of Anderson and Cordfunke *et al.* are in good agreement and cover a larger temperature range, we prefer to retain the latter data:

$$C^{o}_{p,m}\,(\mathrm{SrO, cr, 298.15\ K}) = \mathbf{(45.150 \pm 0.100)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{o}_{m}\,(\mathrm{SrO, cr, 298.15\ K}) = \mathbf{(53.630 \pm 0.100)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The Gibbs energy of formation has been recalculated for the newly selected enthalpy of formation and entropy:

$$\Delta_f G^{o}_{m}\,(\mathrm{SrO, cr, 298.15\ K}) = \mathbf{-\ (559.400 \pm 0.903)}\ \mathrm{kJ\cdot mol^{-1}}.$$

### 14.3.2.2 Barium auxiliary data

#### 14.3.2.2.1 Ba(cr)

The thermodynamic data for Ba(cr) at 298.15 K used in this review are those selected previously [2003GUI/FAN]. The heat capacity from 298.15 to 1000 K is that recommended in the review of [1993ALC/CHA]:

$$C^{o}_{p,m}(\mathrm{Ba, cr}, T) = 23.059 + 16.941\times10^{-3}\,T\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

#### 14.3.2.2.2 Ba(l)

The enthalpy of fusion of Ba(l) selected in this review is 7.12 kJ·mol$^{-1}$ as recommended in the review of [1993ALC/CHA], and the heat capacity is taken constant, equal to:

$$C^{o}_{p,m}\,(\mathrm{Ba, l}, T) = (40.000 \pm 2.000)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

#### 14.3.2.2.3 Ba(g)

All data for Ba(g) in our previous review [2003GUI/FAN] were taken from the assessment by Glushko *et al.* [1981GLU/GUR], which are based on early CODATA

compatible data. In this review, we have retained the heat capacity and entropy selected previously, but have preferred the enthalpy of formation selected by [1990COR/KON], namely:

$$\Delta_f H_m^o \text{ (Ba, g, 298.15 K)} = \mathbf{(179.000 \pm 3.000)} \text{ kJ·mol}^{-1}.$$

The latter value was derived from third law analysis of thirteen vapour pressure studies, applying the most weight to the studies of [1974KAR/TOT] and [1976KUL/DAD] which show a good second/third law agreement. It should be pointed out that the latter value is significantly different from that previously selected, *i.e.*, $\Delta_f H_m^o$ (Ba, g, 298.15 K) = (185.0 ± 5.0) kJ·mol$^{-1}$.

The heat capacity at high temperatures was taken from [1998CHA2].

$$C_{p,m}^o(\text{Ba, g}, T) = 20.7860 \text{ J·K}^{-1}\text{·mol}^{-1}$$
(298.15-700 K)

$$C_{p,m}^o(\text{Ba, g}, T) = 28.0338 + 0.01155T + 5.16075\times10^{-6}T^2 - 8.29311\times10^{5}T^{-2} \text{ J·K}^{-1}\text{·mol}^{-1}$$
(700-1300 K)

$$C_{p,m}^o(\text{Ba, g}, T) = 48.9833 - 0.03718T + 1.7771\times10^{-5}T^2 - 4.53290\times10^{6}T^{-2} \text{ J·K}^{-1}\text{·mol}^{-1}$$
(1300-3000 K)

#### 14.3.2.2.4 BaO(cr)

The enthalpy of formation selected by [1992GRE/FUG], [2003GUI/FAN] for BaO(cr) is retained. The heat capacity and entropy values selected in this review were taken from the measurements by Cordfunke *et al.* covering the temperature range 5 to 350 K [1994COR/LAA]:

$$C_{p,m}^o \text{ (BaO, cr, 298.15 K)} = \mathbf{(47.060 \pm 0.100)} \text{ J·K}^{-1}\text{·mol}^{-1}$$

$$S_m^o \text{ (BaO, cr, 298.15 K)} = \mathbf{(70.010 \pm 0.100)} \text{ J·K}^{-1}\text{·mol}^{-1}.$$

The Gibbs energy of formation has been recalculated for the newly selected enthalpy of formation and entropy:

$$\Delta_f G_m^o \text{ (BaO, cr, 298.15 K)} = \mathbf{-(519.780 \pm 2.513)} \text{ kJ·mol}^{-1}.$$

The entropy value adopted by [1992GRE/FUG], [2003GUI/FAN], *i.e.*, $S_m^o$ (BaO, cr, 298.15 K) = (72.070 ± 0.380) J·K$^{-1}$·mol$^{-1}$, was based on the measurements of [1935AND] and [1969GME] that covered more limited temperature ranges, *i.e.*, 56-299 K and 1.4-310 K, respectively. While the results of [1935AND] and [1994COR/LAA] are in good agreement, those of [1969GME] deviate from the aforementioned studies below 50 K and above 250 K.

Regarding the heat capacity at high temperature for this compound, we select the data of Cordunke *et al.* [1994COR/LAA], who measured the enthalpy increments in the temperature range 470-877 K by drop calorimetry.

$$C^{o}_{p,m}(\mathrm{BaO,\ cr},\ T) = 41.3004 + 0.029079T - 2.100919\times10^{-5}T^{2} + 5.20615\times10^{-9}T^{3} - 1.04319\times10^{5}T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

#### 14.3.2.2.5 $BaCO_3$(cr)

The thermodynamic data for $BaCO_3$(cr) at 298.15 K used in this review are those selected by [1995PAR].

$$\Delta_f H^{o}_{m}(\mathrm{BaCO_3,\ cr,\ 298.15\ K}) = \mathbf{-\ (1213.030 \pm 2.000)}\ \mathrm{kJ\cdot mol^{-1}}$$

$$S^{o}_{m}(\mathrm{BaCO_3,\ cr,\ 298.15\ K}) = \mathbf{(112.100 \pm 2.000)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^{o}_{p,m}(\mathrm{BaCO_3,\ cr,\ 298.15\ K}) = \mathbf{(85.983 \pm 0.600)}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The heat capacity at high temperatures and transition enthalpies, 17.56 $kJ\cdot mol^{-1}$ at 1079 K and 3.13 $kJ\cdot mol^{-1}$ at 1241 K were taken from [1995BAR].

$$C^{o}_{p,m}(\mathrm{BaCO_3,\ cr,\ 298.15\ K}) = 85.7928 + 0.052710T - 1.42536\times10^{6}T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$
(298.15-1079 K)

$$C^{o}_{p,m}(\mathrm{BaCO_3,\ cr,\ 298.15\ K}) = 154.8080\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$
(1079-1241 K)

$$C^{o}_{p,m}(\mathrm{BaCO_3,\ cr,\ 298.15\ K}) = 158.9920\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$
(>1241 K).

## 14.4 Group 1 (alkali) auxiliary data

### 14.4.1 Lithium auxiliary data

#### 14.4.1.1 $Li_2O$(cr)

The heat capacity at 298.15 K used in this review for the estimations based on Neumann Kopp's rule is that selected by [1998CHA2], *i.e.*, $C^{o}_{p,m}(\mathrm{Li_2O,\ cr,\ 298.15\ K}) = 54.087\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

## 14.5 Additional auxiliary data used

Table 14-3: Selected auxiliary data for Gibbs energies ($\Delta_f G_m^o$), enthalpies of formation ($\Delta_f H_m^o$), molar entropies ($S_m^o$), and heat capacities ($C_{p,m}^o$). All data refer to 298.15 K and 1 bar. The errors in the heat capacity data are estimated to 0.5 % by this review. The data from the Glushko tables have not been reviewed, but are accepted for the reasons given in the introduction to this chapter.

| Compound | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| LiF(cr) | **– 590.019** | **– 618.300** | **35.660** | **41.800** | [1982GLU/GUR] |
| | **± 0.703** | **± 0.700** | **± 0.120** | | |
| NaF(cr) | **– 546.327** | **– 576.600** | **51.160** | **46.820** | NEA |
| | **± 0.704** | **± 0.700** | **± 0.150** | | [2001LEM/FUG] |
| KF(cr) | **– 540.212** | **– 569.900** | **66.500** | **48.990** | [1982GLU/GUR] |
| | **± 0.706** | **± 0.700** | **± 0.200** | | |
| LiCl(cr) | **– 384.273** | **– 408.540** | **59.270** | **47.990** | [1982GLU/GUR] |
| | **± 0.213** | **± 0.200** | **± 0.150** | | |
| NaCl(cr) | **– 384.221** | **– 411.260** | **72.150** | **50.500** | NEA |
| | **± 0.147** | **± 0.120** | **± 0.200** | | [2001LEM/FUG] |
| KCl(cr) | **– 408.539** | **– 436.461** | **82.570** | **51.300** | NEA |
| | **± 0.151** | **± 0.129** | **± 0.170** | | [2005GAM/BUG] for $\Delta_f H_m^o$ and [1982GLU/GUR] for $S_m^o$ and $C_{p,m}^o$ |
| RbCl(cr) | **– 407.465** | **– 435.220** | **95.230** | **52.260** | [1982GLU/GUR] |
| | **± 0.219** | **± 0.160** | **± 0.400** | | |
| CsCl(cr) | **– 413.807** | **– 442.310** | **101.170** | **52.470** | NEA |
| | **± 0.208** | **± 0.160** | **± 0.200** | | [2001LEM/FUG] |
| $NH_4Cl$(cr) | **– 203.658** | **– 315.120** | **94.860** | **86.440** | CODATA + [1965PAR][(a)] $S_m^o$ and $C_{p,m}^o$ from [1998CHA2] |
| | **± 1.350** | **± 0.500** | **± 4.200** | | |
| $LiNO_3$(cr, hex) | **– 384.712** | **– 482.700** | **104.000** | **890** | [1982GLU/GUR] |
| | **± 3.024** | **± 0.500** | **± 10.000** | | |
| $NaNO_3$(cr) | **– 366.676** | **– 467.580** | **116.400** | **93.050** | NEA |
| | **± 0.424** | **± 0.410** | **± 0.300** | | [2003GUI/FAN] for $\Delta_f H_m^o$, and [1982GLU/GUR] for $S_m^o$ and $C_{p,m}^o$ |
| $KNO_3$(cr) | **– 394.027** | **– 494.000** | **132.900** | **95.060** | [1982GLU/GUR] |
| | **± 0.517** | **± 0.500** | **± 0.400** | | |
| $RbNO_3$(cr) | **– 394.697** | **– 494.700** | **144.900** | **99.000** | [1982GLU/GUR] |
| | **± 0.516** | **± 0.500** | **± 0.300** | | |
| $CsNO_3$(cr) | **– 405.140** | **– 505.000** | **153.830** | **96.140** | [1982GLU/GUR] |
| | **± 0.522** | **± 0.500** | **± 0.300** | | |
| $Sr(NO_3)_2$(cr) | **– 783.146** | **– 982.360** | **194.600** | – | [2003GUI/FAN] |
| | **± 1.018** | **± 0.800** | **± 2.100** | | |
| $Li_2CO_3$(cr) | **– 1130.145** | **– 1214.100** | **90.120** | **98.320** | [1982GLU/GUR] |
| | **± 1.011** | **± 1.000** | **± 0.300** | | |

(Continued on next page)

Table 14-3 (continued)

| Compound | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| $Na_2CO_3$(cr) | **– 1045.450** | **– 1129.250** | **135.000** | – | NEA TDB review on Ancillary Data – to be published |
| | **± 0.345** | **± 0.300** | **± 0.400** | | |
| $K_2CO_3$(cr) | **– 1065.833** | **– 1151.500** | **155.500** | **114.430** | [1982GLU/GUR] |
| | **± 2.018** | **± 2.000** | **± 0.800** | | |
| $CaCO_3$(cr, calcite) | **– 1128.983** | **– 1207.500** | **91.710** | – | NEA TDB review on Ancillary Data – to be published |
| | **± 1.207** | **± 1.200** | **± 0.210** | | |
| $SrCO_3$(cr) | **– 1144.913** | **– 1226.000** | **97.200** | **82.420** | [1994GUR/VEY] |
| | **± 2.088** | **± 2.000** | **± 2.000** | | |
| $BaCO_3$(cr) | **– 1134.367** | **– 1213.030** | **112.100** | **85.983** | [1995PAR] |
| | **± 2.101** | **± 2.000** | **± 2.000** | **± 0.600** | |
| $Na_2SiO_3$(cr) | – 1461.842 | – 1555.86 | 113.8 | 111.800 | [1971NAU/RYZ] |
| | ± 2.117 | ± 2.1 | ± 0.8 | | Corrected value[(b)] |
| $KH_2PO_4$(cr) | – | **– 1574.500** | – | – | This review |
| | | **± 2.000** | | | |
| $KH_2AsO_4$(cr) | – | **– 1181.300** | – | – | This review |
| | | **± 4.200** | | | |
| $K_2SO_4$(cr) | **– 1319.585** | **– 1437.700** | **175.560** | **131.460** | [1982GLU/GUR] |
| | **± 0.544** | **± 0.500** | **± 0.600** | | |
| $Pb(NO_3)_2$(cr) | **– 256.90** | **– 451.750** | **217.900** | – | [1970GLU/MED], Vol. 4 |
| | **± 1.7** | **± 1.200** | **± 6.700** | | |
| α-$NiSO_4{\cdot}6H_2O$ | **– 2225.467** | **– 2683.817** | **334.450** | **327.900** | NEA |
| | **± 1.059** | **± 1.014** | **± 1.000** | **± 1.000** | [2005GAM/BUG] |
| β-$NiSO_4{\cdot}6H_2O$ | **– 2224.915** | **– 2677.287** | **354.500** | – | NEA |
| | **± 1.815** | **± 1.034** | **± 5.000** | | [2005GAM/BUG] |
| $CuSO_4$(cr) | **– 662.185** | **– 771.400** | **109.200** | – | CODATA |
| | **± 1.206** | **± 1.200** | **± 0.400** | | [1989COX/WAG] |
| $CuSO_4{\cdot}5H_2O$(cr) | **– 1880.699** | **– 2280.380** | **301.250** | – | [1971NAU/RYZ] |
| | **± 1.314** | **± 1.290** | **± 0.840** | | Corrected value[(c)] |
| $FeSO_4{\cdot}7H_2O$(cr) | **– 2507.710** | **– 3012.512** | **409.118** | – | NEA |
| | **± 0.652** | **± 0.602** | **± 0.825** | | [2013LEM/BER] |
| $CoSO_4{\cdot}6H_2O$(cr) | **– 2238.215** | **– 2685.170** | **367.610** | **353.400** | [1973GLU/MED], |
| | **± 2.106** | **± 2.090** | **± 0.840** | **± 0.600** | Vol. VI |
| Co(cr) | – | – | **30.040** | – | [1972GLU/MED], |
| | | | **± 0.170** | | Vol.VI |
| $Co^{2+}$ | **– 53.640** | **– 56.610** | **– 110.500** | – | [1972GLU/MED], |
| | **± 0.380** | **± 1.920** | **± 6.300** | | Vol. VI |
| Mn(cr) | – | – | **32.010** | – | [1972GLU/MED], |
| | | | **± 0.130** | | Vol. VII |
| $Mn^{2+}$ | **– 230.960** | **– 220.160** | **– 62.300** | – | [1972GLU/MED], |
| | **± 1.260** | **± 0.630** | **± 4.600** | | Vol. VII |
| $ZnSO_4{\cdot}7H_2O$(cr) | **– 2561.620** | **– 3076.850** | **388.690** | **381.460** | [1971NAU/RYZ] |
| | **± 0.770** | **± 0.670** | **± 1.260** | | Corrected value[(d)] |
| $CdSO_4{\cdot}8/3H_2O$(cr) | **– 1464.983** | **– 1729.300** | **229.650** | – | CODATA |
| | **± 0.810** | **± 0.800** | **± 0.400** | | [1989COX/WAG] |
| $Na_2O$(cr) | **– 375.770** | **– 414.570** | **75.040** | **69.120** | [1982GLU/GUR] |
| | **± 0.344** | **± 0.300** | **± 0.400** | | |

(Continued on next page)

Table 14-3 (continued)

| Compound | $\Delta_f G^\circ_m$ /kJ·mol$^{-1}$ | $\Delta_f H^\circ_m$ /kJ·mol$^{-1}$ | $S^\circ_m$ /J·K$^{-1}$·mol$^{-1}$ | $C^\circ_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| $K_2O$(cr) | **– 321.171** | **– 361.700** | **96.000** | **72.000** | [1982GLU/GUR] |
| | **± 4.383** | **± 4.000** | **± 6.000** | | |
| CaO(cr) | **– 603.296** | **– 634.920** | **38.100** | **42.049** | [2003GUI/FAN] |
| | **± 0.916** | **± 0.900** | **± 0.400** | **± 0.400** | |

(a) V. Parker [1965PAR] based on available data recommended for reaction $NH_4Cl(cr) \rightleftharpoons NH_4^+ + Cl^-$ $\Delta_r H^\circ_m = (14.78 \pm 0.06)$ kJ·mol$^{-1}$ ($(3.533 \pm 0.015)$ kcal·mol$^{-1}$). Combining this value with the CODATA-based [1989COX/WAG] enthalpies of formation of $NH_4^+$ – $(133.26 \pm 0.25)$ and $Cl^-$ – $(167.08 \pm 0.10)$, we calculate for $NH_4Cl$(cr) $\Delta_f H^\circ_m$ (298.15 K) = – $(315.12 \pm 0.28)$ kJ·mol$^{-1}$. The final uncertainty was increased to ± 0.5 kJ·mol$^{-1}$.

(b) The handbook [1971NAU/RYZ] based on available data recommends for reaction $Na_2CO_3(cr) + SiO_2(quarz) \rightleftharpoons Na_2SiO_3(cr) + CO_2(g)$ the value $\Delta_r H^\circ_m$ (298.15 K) = $(90.58 \pm 0.96)$ kJ·mol$^{-1}$ ($(21.65 \pm 0.23)$ kcal·mol$^{-1}$). Combining this value with the CODATA-based [1989COX/WAG] enthalpies of formation of quartz – $(910.7 \pm 1.0)$ and $CO_2$(g) – $(393.51 \pm 0.13)$, and the enthalpy of formation of $Na_2CO_3$(cr) from [NEA TDB review on Ancillary Data – to be published] – $(1129.25 \pm 0.30)$, this review calculates for $Na_2SiO_3$(cr) $\Delta_f H^\circ_m$ (298.15 K) = – $(1555.86 \pm 2.1)$ kJ·mol$^{-1}$, leaving the uncertainty given for the [1971NAU/RYZ] value.

(c) The handbook [1971NAU/RYZ] based on available data recommends for reaction $CuSO_4(cr) + 5H_2O(l) \rightleftharpoons CuSiO_4 \cdot 5H_2O(cr)$ the value $\Delta_r H^\circ_m$ (298.15 K) = – $(79.83 \pm 0.42)$ kJ·mol$^{-1}$ (– $(19.08 \pm 0.1)$ kcal·mol$^{-1}$). Combining this value with the CODATA-based [1989COX/WAG] enthalpies of formation $CuSO_4$(cr) (– $(771.4 \pm 1.2)$) and $H_2O$(l) (– $(285.83 \pm 0.04)$), we calculate for $CuSO_4 \cdot 5H_2O$(cr) $\Delta_f H^\circ_m$ (298.15 K) = – $(2280.38 \pm 1.29)$ kJ·mol$^{-1}$.

(d) The handbook [1971NAU/RYZ] based on available data recommends for reaction $ZnSO_4 \cdot 7H_2O(cr) + 5H_2O(l) = Zn^{2+} + SiO_4^{2-} + 5H_2O(l)$ the value $\Delta_r H^\circ_m$ (298.15 K) = $(13.31 \pm 0.42)$ kJ·mol$^{-1}$ ($(3.18 \pm 0.1)$ kcal·mol$^{-1}$). Combining this value with the CODATA-based [1989COX/WAG] enthalpies of formation of $Zn^{2+}$ (– $(153.39 \pm 0.20)$) and $SO_4^{2-}$ (– $(909.34 \pm 0.40)$) and $H_2O$(l) (– $(285.83 \pm 0.04)$), we calculate for $ZnSO_4 \cdot 7H_2O$(cr) $\Delta_f H^\circ_m$ (298.15 K) = – $(3076.85 \pm 0.67)$ kJ·mol$^{-1}$.

# Appendices

# Appendix A

# Discussion of selected references for Uranium

## A-1.1 Uranium aqua-ions

**[2003DAV/VOK]**

David and Vokhmin have used a semi-empirical model mainly based on structure data and bond distances as described in their previous publications (listed in [2003DAV/VOK]), to propose Gibbs energies of hydration and molar entropies for $An^{3+}$ and $An^{4+}$ aqua-ions. The current paper is an update of [2001DAV/VOK], where the thermodynamic quantities have been recalculated using a revised value of the Gibbs enthalpy of hydration of $H^+$ ( $\Delta G^{o}_{hydr}$ ) = – 1096 kJ·mol$^{-1}$, instead of – 1056 kJ·mol$^{-1}$.

Table A-1 summarises the calculated thermodynamic data and also how they compare with experimental ion entropies. David and Vokhmin have also calculated $An^{4+}$ / $An^{3+}$ redox potentials and a comparison with the experimental values selected in [2003GUI/FAN] is given in Table A-2.

The agreement between the calculated thermodynamic quantities and experimental data is satisfactory considering the experimental and model uncertainties. The data from David and Vokhmin are based on models and they have not been used in the selection of thermodynamic data.

**[2004PRI/MAC]**

The rates and mechanisms of outer- and inner-sphere mediated electron self-exchange between U(VI)-U(V) complexes in solution were studied using quantum chemical methods. The outer-sphere model was tested on the aqua-ions and the inner-sphere model using hydroxide, fluoride and carbonate as bridging ligands. The lower limit for the rate constant in the outer-sphere model was 26 $M^{-1}\cdot s^{-1}$ and for the inner-sphere model $2 \times 10^4$ to $4 \times 10^6$ $M^{-1}\cdot s^{-1}$. There are no thermodynamic data in this paper

Table A-1: The calculated hydration entropy ΔS(hyd), the entropies of gaseous ion $S°$gas and of the aquo ion $S°$aq, the difference $\delta S° = S°aq(pub.) - S°aq(calc)$, the formation entropy, $\Delta S_f$, in $J \cdot K^{-1} \cdot mol^{-1}$, the standard redox potentials $E°(3/0)$, $E°(4/0)$, $E°(4/3)$, the calculated radius $R_2$ of the aquo ion, the Stokes radius $R_s$ in Å and equivalent conductivity $\lambda_o$ in $S \cdot cm^2 \cdot eq^{-1}$, c. and a. indicate conventional and absolute scales respectively.

| | ΔS(hyd) calc, a. | $S°$ (gas) calc | $S°$ (aq) calc, c. | $S°$ (aq) exp, c. | $\delta S°$ calc | $\Delta S_f$ calc, c. | $E°(3/0)$ /V | $E°$ (4/0) /V | $E°$ (4/3) /V | $R_2$ /Å | $R_s$ /Å | $\lambda_o$ /S·cm²·eq⁻¹ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Ac^{+3}$ | – 411 | 176 | – 168 | – 180 | – 12 | – 33 | – 2.222 | | | 4.52 | 3.94 | 67.1 |
| $Th^{+3}$ | – 421 | 192 | – 163 | | | – 20 | | | | 4.52 | 3.95 | 66.9 |
| $Pa^{+3}$ | – 426 | 195 | – 164 | | | – 20 | | | | 4.53 | 3.96 | 66.9 |
| $U^{+3}$ | – 441 | 196 | – 178 | – 175 | 3 | – 32 | – 1.656 | | | 4.54 | 3.98 | 66.7 |
| $Np^{+3}$ | – 444 | 195 | – 183 | – 194 | – 11 | – 37 | – 1.783 | | | 4.54 | 3.98 | 66.7 |
| $Pu^{+3}$ | – 451 | 192 | – 193 | – 185 | 8 | – 53 | – 1.991 | | | 4.55 | 3.99 | 66.6 |
| $Am^{+3}$ | – 454 | 186 | – 201 | – 201 | 0 | – 59 | – 2.069 | | | 4.55 | 4.00 | 66.6 |
| $Cm^{+3}$ | – 459 | 195 | – 198 | – 188 | 10 | – 74 | – 2.049 | | | 4.56 | 4.02 | 66.4 |
| $Bk^{+3}$ | – 464 | 199 | – 199 | – 188 | 11 | – 81 | – 1.993 | | | 4.59 | 4.08 | 66.1 |
| $Cf^{+3}$ | – 469 | 201 | – 202 | | | – 86 | – 1.905 | | | 4.65 | 4.19 | 64.9 |
| $Es^{+3}$ | – 475 | 201 | – 207 | | | – 100 | – 1.973 | | | 4.69 | 4.28 | 63.8 |
| $Fm^{+3}$ | – 479 | 201 | – 212 | | | – 107 | – 2.056 | | | 4.71 | 4.31 | 63.5 |
| $Md^{+3}$ | – 483 | 199 | – 217 | | | – 108 | – 1.737 | | | 4.72 | 4.33 | 63.3 |
| $No^{+3}$ | – 486 | 195 | – 224 | | | – 93 | – 1.258 | | | 4.72 | 4.34 | 63.2 |
| $Lr^{+3}$ | – 489 | 178 | – 244 | | | – 103 | – 2.060 | | | 4.73 | 4.34 | 63.2 |
| $Th^{+4}$ | – 703 | 177 | – 438 | – 423 | 15 | – 230 | | – 1.815 | | 5.02 | 4.86 | 72.7 |
| $U^{+4}$ | – 717 | 195 | – 433 | – 414 | 19 | – 222 | | – 1.361 | – 0.473 | 5.10 | 4.99 | 71.8 |
| $Np^{+4}$ | – 704 | 196 | – 420 | – 426 | – 7 | – 209 | | – 1.280 | 0.231 | 5.23 | 5.18 | 70.5 |
| $Pu^{+4}$ | – 693 | 195 | – 409 | – 415 | – 6 | – 204 | | – 1.242 | 1.007 | 5.26 | 5.23 | 69.9 |

Table A-2: Comparison of calculated and experimental redox potentials for $An^{4+}/An^{3+}$ couples. The value for the $Pu^{4+}/Pu^{3+}$ couple has been obtained from the experimental value 0.982 V discussed in [2003GUI/FAN] and recalculated by the present review to zero ionic strength using the specific ion-interaction model, with ion interaction parameters from Appendix B.

| Redox couple | Redox potential, $E°(An^{4+}/An^{3+})$, in V. Values from [2003GUI/FAN] within parenthesis |
|---|---|
| $U^{4+}/U^{3+}$ | – 0.473 (– 0.553) |
| $Np^{4+}/Np^{3+}$ | 0.231 (0.219) |
| $Pu^{4+}/Pu^{3+}$ | 1.007 (1.047) |

**[2004MOS/KRU]**

This is a quantum chemistry study of the role of solvation for the reduction of $UO_2^{2+}$ to $UO(OH)^{2+}$ and $U(OH)_2^{2+}$. Information on structures, solvation and reaction energies are given but these theory based quantities have not been included in the present review.

**[2005CAO/BAL]**–Also discussed in the Pu section.

Cao and Balasubramaniam have made a detailed quantum chemistry study of $UO_2(H_2O)_n^{2+}$, $NpO_2(H_2O)_n^{+}$ and $PuO_2(H_2O)_n^{2+}$, $n$ = 4-6, with information on structures, relative energies and vibration frequencies in gas-phase and a CPCM model of aqueous solution. They report structures that are in good agreement with those in other studies and most importantly, they find that complexes with $n$ = 5 are the most stable ones; they also note that the energy difference between $UO_2(H_2O)_6^{2+}$ and $UO_2(H_2O)_5^{2+}\cdot H_2O$ is small, which is consistent with an associative mechanism for the water exchange. There is an extensive discussion on hydration energies in the paper, but this information is of no direct interest for the present review as the difference between the values reported and the experimental data in [2005GIB/HAI] is large. The vibration spectra, *i. e.* the symmetric and asymmetric stretch frequencies of the hydrated ions are in good agreement with experimental information for $UO_2(H_2O)_5^{2+}$, $NpO_2(H_2O)_5^{+}$.

**[2005GIB/HAI]**–Also discussed in the Pu section.

Gibson *et al.* have used resonance mass spectroscopy to study the thermodynamics and kinetics of reactions between $An^{2+}$, $AnO^{+}$, $AnOH^{2+}$ and $AnO_2^{2+}$ (An = Th, U, Np, Pu and Am) and $N_2O$, ethylene oxide, $H_2O$, $O_2$, $CO_2$, NO and $CH_2O$ in gas phase. Gas-phase reactions of this type are outside the scope of the present review, but the experimental enthalpy of formation $\Delta_f H^o(AnO^{2+}, g)$, An = U, Np is of interest because it allows an assessment of the enthalpy of formation $\Delta_f H^o(AnO_2^{2+}, g)$, which in turn can be used to estimate the enthalpy of solvation of these ions. Gibson *et al.* report $\Delta_f H_m^o(UO_2^{2+}, g) = (1524 \pm 63)$ kJ·mol$^{-1}$, which when combined with the enthalpy of

formation of $UO_2^{2+}(aq)$ selected in [2003GUI/FAN] results in the enthalpy of hydration, $\Delta_{hydr}H_m^o(UO_2^{2+},g) = -(1665 \pm 64)$ kJ·mol$^{-1}$. Rösch *et al.* [2004MOS/KRU] have used quantum chemistry methods to determine the electronic hydration energy, $\Delta_{hydr}E_m^o(UO_2^{2+},g) = -1766$ kJ·mol$^{-1}$. Gibson *et al.* have used the following relationship to calculate the corresponding enthalpy of hydration:

$$\Delta_{hydr}H^o(UO_2^{2+},g) = \Delta_{hydr}E^o(UO_2^{2+},g) + \Delta^*(UO_2^{2+},g) + T\Delta_{hydr}S \quad (A.1)$$

$\Delta^*(UO_2^{2+},g) \approx 209$ kJ·mol$^{-1}$ is the estimated difference between the calculated electronic hydration energy and the Gibbs energy at 298 K. Using $\Delta_{hydr}S_m^o(UO_2^{2+}) = 400$ J·K$^{-1}$·mol$^{-1}$, they find an enthalpy of hydration, $\Delta_{hydr}H_m^o(UO_2^{2+},g) = -1676$ kJ·mol$^{-1}$, in excellent agreement with the experimental value, but very different from that reported by Marcus and Loewenschuss, [1986MAR/LOE], – 1345 kJ·mol$^{-1}$, based on semi-empirical methods.

Gibson *et al.* have also corrected the enthalpy of hydration from Hildenbrand *et al.* [1985HIL/GUR] and report $\Delta_f H_m^o(UO_2^{2+},g) = (115 \pm 50)$ kJ·mol$^{-1}$ and used this value to calculate the enthalpy of hydration, $\Delta_{hydr}H_m^o(UO_2^{2+},g) = -(709 \pm 50)$ kJ·mol$^{-1}$. The present review reports the $\Delta_{hydr}H_m^o(UO_2^{2+},g)$ and $\Delta_{hydr}H_m^o(UO_2^{+},g)$ from Gibson *et al.* for information, but these data are not included among the selected values as the NEA reviews do not include thermodynamic data for ions in gas phase. Gibson *et al.* also discuss bond dissociation and ionisation energies but these fall outside the scope of the present review.

**[2005MOS/MAT]**

Moskaleva *et al.* have used DFT methods to calculate the enthalpy of formation of $UO_2^{2+}$ in gas-phase at 0 K, and report $\Delta_{hydr}H$ (g, 0 K) = (365 ± 10) kcal·mol$^{-1}$, which differs significantly from an estimate by Marcus [1975MAR], 289 kcal·mol$^{-1}$. These values are not included in the present review.

**[2006TSU/WAH]**

The redox potential for the $AnO_2(OH_2)_5^{2+} / AnO_2(OH_2)_5^{+}$ couples, An = U, Np, Pu, Am, were studied using quantum chemical methods at the MP2, CASPT2 and CCSD(T) levels by taking spin-orbit effects into account; the solvent was described as a dielectric continuum with a macroscopic dielectric permittivity. Structures and reaction energies are reported, and the redox potentials are summarized in Table A-3.

Table A-3: Calculated redox potentials in V *vs.* the normal hydrogen electrode for the $AnO_2(OH_2)_5^{2+} / AnO_2(OH_2)_5^{+}$ couples in solution.

| | CASPT2 | CCSD(T) | Experiment |
|---|---|---|---|
| U | 0.003 | 0.082 | 0.088 |
| Np | 1.525 | | 1.159 |
| Pu | 0.730 | | 0.936 |
| Am | 1.894 | | 1.591 |

This study is of interest mainly from a methodological point of view and the data reported have not been considered when selecting thermodynamic data.

**[2009BRE/BAN]**

Brendebach *et al.* have made XANES and EXAFS studies of tri- and tetravalent actinides in 1.0 and 0.1 M HCl solutions. The preparation of test solutions and the analysis of the experimental data are well described. The authors report XANES spectra and energy shifts for An(III), An = U, Np, Pu and An(IV), An = U, Np. The EXAFS data are consistent with the stoichiometry $An(OH_2)_9^{3+}$ for U(III), Np(III) and Pu(III). The number of coordinated water, CN, can in general only be determined within 10 % for the An(IV) systems, which indicates that the uncertainties in the following results for U(IV): 1 M HCl, CN = $(12.6 \pm 0.5)$; 0.10 M HCl, CN = $(10.9 \pm 0.3)$, are underestimated. The An-$OH_2$ distances are consistent with those found in a number of other studies. There is an indication of an "actinide contraction" in the An(III)-$OH_2$ distances that decrease from 2.52 to 2.49 Å, between U(III) and Pu(III).

**[2009FRI/PRI]**

Frick *et al.* have used the method described in [2010FRI/HOF] to explore the structure and dynamics of the $U^{4+}$(aq) ion using molecular dynamics simulations. In this way they find that the number of water in three shells surrounding the uranium are 9, 14 and 44 respectively. The U-$OH_2$ distance is 2.45 Å, in good agreement with experimental LAXS and EXAFS data, 2.44 and 2.42 Å, respectively and the same is true for the coordination number 9 that is consistent with CN 8 suggested by LAXS data and $(10 \pm 1)$ from EXAFS. The U-$OH_2$ distance in the second coordination sphere is 4.80 Å and in the diffuse third shell 6.80 Å; these observations demonstrate the large polarisation of the solvent by the $U^{4+}$ ion.

**[2010FRI/HOF]**

Frick *et al.* have studied the structure of $UO_2^{+}$(aq) using quantum mechanical charge field dynamics (QMCF-MD), a "pure" *ab initio* method that does not rely on empirical

solute-solvent potentials. The method offers a more realistic description of the water solvent than the continuum methods. The authors find that $UO_2^+$ is surrounded by four coordinated water ligands at 2.51 Å and they also identify a second coordination sphere around the equatorial water ligands that contains an average of 12 water molecules; in addition there is water hydrogen bonded to the uranyl oxygen atoms, presumably a result of their negative charge. One should note that quantum chemical models based on the use of a continuum model for the solvent, results in coordination of five water ligands, illustrating the uncertainty that is related to the choice of model. Atta-Fynn *et al.* [2012ATT/JOH] have studied the same system using Car-Parrinello molecular dynamics simulations (CPMD) but find slightly different results.

**[2011CHA/DIA]**

Chaboy and Díaz-Moreno have used X-ray near edge structure (XANES) and previous EXAFS studies, in connection with quantum chemical modelling, to suggest a tri-capped trigonal prism structure, $An(OH_2)_9^{4+}$, for the Th(IV), U(IV) and Np(IV) aqua-ions; they also provide compelling evidence for the structural similarity of these ions.

**[2012ATT/JOH]**

Atta-Flynn *et al.* have used Car-Parrinello *ab initio* molecular dynamics simulations at 300 K to deduce structures of U(IV), U(VI) and U(V) aqua-ions and to determine their first hydrolysis constants. In the $U^{4+}$(aq) ions there are eight or nine coordinated water in the first coordination sphere at a distance of 2.45 Å, which is in good agreement with previous EXAFS data. The second coordination sphere is composed of 15.2 water molecules at a distance of 4.65 Å from uranium; the first and second coordination spheres are linked by hydrogen bonds with O-O distance of 2.81 Å. The first coordination spheres of $UO_2^+$(aq) and $UO_2^{2+}$(aq) both contain five coordinated water, resulting in very similar coordination geometry; this is in agreement with known data from other quantum chemical studies and with experimental observations. The second coordination shell is clearly visible and contains 15.4 water in the equatorial plane at a distance of 4.55 Å from uranium. The coordinated water is strongly polarised as indicated by the computed dipole moments, 4.2, 3.5 and 4.1 Debye, for $U^{4+}$(aq), $UO_2^+$(aq) and $UO_2^{2+}$(aq), respectively. One effect of this strong polarisation is the rather large acid strength of these aqua-ions. The modeling results in the following equilibrium constants that are in good agreement with experimental data from [2003GUI/FAN] within parenthesis.

$$U(OH_2)_8^{4+} + H_2O \rightleftharpoons U(OH)(OH_2)_7^{3+} + H^+; \quad \text{(A.2)}$$

$$\log_{10} K^o\,(\text{A.2}) = -0.93\ (-0.54);$$

$$UO_2(OH_2)_5^{2+} + H_2O \rightleftharpoons UO_2(OH)(OH_2)_4^{+} + H^+; \quad \text{(A.3)}$$

$$\log_{10} K^{o}(\text{A.3}) = -4.95\ (-5.25);$$

$$UO_2(OH_2)_5^+ + H_2O \rightleftharpoons UO_2(OH)(OH_2)_4 + H^+; \qquad \text{(A.4)}$$

$$\log_{10} K^{o}(\text{A.4}) = -8.51.$$

These results are slightly different from the ones reported by Frick *et al.* [2009FRI/PRI], [2010FRI/HOF].

**[2013POM/TIW]**–Also discussed in the Pu section.

In this study of the constitution of $AnO_2^+(aq)$ and $AnO_2^{2+}(aq)$, An = U, Np, Pu and Am, Pomogaev *et al.* have used quantum chemistry methods to develop intermolecular force-field parameters for the interaction between the actinyl-ions and water. Based on these, they have performed molecular dynamics simulations and find that all ions have the constitution $AnO_2(OH_2)_5^+$ and $AnO_2(OH_2)_5^{2+}$.

These papers [2004MOS/KRU], [2005MOS/MAT], [2005CAO/BAL], [2005GIB/HAI], [2012RAI/TIW], [2005SHA/SCH] are all based on different quantum chemical methods and provide information on the constitution of $AnO_2^{2+}(aq)$ and $AnO_2^+(aq)$ complexes, the enthalpy and free energy of solvation and on the redox potential of $AnO_2^{2+}/AnO_2^+$ couples.

The quantum chemistry methods are based on geometry optimisation in gas-phase followed by a calculation of the energy in a solvent using continuum models ([2004MOS/KRU], [2005MOS/MAT], [2005SHA/SCH]). An alternative method is discussed in [2013POM/TIW], where the continuum solvent is replaced by discrete water molecules (1000 molecules in a square box) into which $AnO_2^{2+}$ and $AnO_2^+$ are inserted. The interactions between solvent and solute are described by pair potentials. The result is information on the geometry and the number of coordinated water ligands in addition to the free energy of hydration, a quantity that can be compared with experimental data. These data are given in the following table, where $\Delta G^{o}_{exp}(\text{hydr})$ is estimated from the experimental enthalpy and entropy of hydration.

Table A-4: Calculated and experimental Gibbs energies of hydration and experimental enthalpies of hydration of $AnO_2^+$ and $AnO_2^{2+}$ ions in kJ·mol$^{-1}$.

| $AnO_2^{n+}$ | $\Delta G^{o}$ (hydr) /kJ·mol$^{-1}$ | $\Delta G^{o}_{exp}$ (hydr) /kJ·mol$^{-1}$ | $\Delta H^{o}_{exp}$ (hydr) /kJ·mol$^{-1}$ |
|---|---|---|---|
| $UO_2^{2+}$ | – 1702 | – 1546 | – 1665 |
| $NpO_2^{2+}$ | – 1703 | – 1565 | – 1687 |
| $PuO_2^{2+}$ | – 1697 | – 1549 | – 1671 |
| $AmO_2^{2+}$ | – 1644 | > – 1774 | > – 1896 |
| $UO_2^+$ | – 716 | – 613 | – 709 |
| $NpO_2^+$ | – 709 | – 658 | – 754 |
| $PuO_2^+$ | – 670 | – 649 | – 746 |
| $AmO_2^+$ | – 639 | – 682 | – 776 |

The enthalpy of hydration for $UO_2^{2+}$ can be compared with the information in [2004MOS/KRU], [2005MOS/MAT], [2005SHA/SCH], where the first study reports $\Delta G^o$ (hydr) = – 1758 kJ·mol$^{-1}$, that was changed to – 1548 kJ·mol$^{-1}$, taking estimated systematic errors into account. In the following study Moskaleva *et al.* revise this value to – (1528 ± 42) kJ·mol$^{-1}$ and note that this in in good agreement with an experimental value from [2005GIB/HAI]. Shamov and Schreckenbach [2005SHA/SCH] report a free energy of solvation $\Delta G^o$ ($UO_2^{2+}$, hydr) that varies with the number of water molecules in the second coordination sphere; for $UO_2(OH_2)_5^{2+}$, $[UO_2(OH_2)_5^{2+}](H_2O)_5$ and $[UO_2(OH_2)_5^{2+}](H_2O)_{12}$, they report $\Delta G^o$ ($UO_2^{2+}$, hydr) equal to – 1607, – 1779 and – 1739 kJ·mol$^{-1}$, respectively. The corresponding free energy of solvation are – 606, – 641 and – 686 kJ·mol$^{-1}$, respectively. From both studies it is clear that even slight modifications of the solvent model results in large changes in the free energy of solvation.

The present review has not made a systematic study of the various quantum chemical methods used to study the properties of actinide aqua-ions but notes that the geometric parameters and the number of water ligands in the first coordination sphere, in general agree very well with experimental data. Computed energies of reaction, on the other hand, are not yet sufficiently accurate even for scoping calculations. Hay *et al.* [2000HAY/MAR] and Shamov and Schreckenbach [2005SHA/SCH] have estimated the redox potential of the $AnO_2^{2+}$ (aq)/ $AnO_2^{+}$ (aq) couples and report the following data, where the experimental values are from [2003GUI/FAN] and the calculated data using two different estimates of the solvation energy. It is obvious that the theory based redox potentials are too uncertain to be of use in the modeling of chemical reactions; they do, however, reproduce the experimental trends.

Table A-5: Experimental and calculated redox potentials for $AnO_2^{2+}$ - $AnO_2^{+}$ redox couples, An = U, Np and Pu. Data for two different models are reported.

| Redox couple | Redox potential *vs.* NHE in V, exp. data | Calculated redox potential, model 1 | Calculated redox potential, model 2 |
|---|---|---|---|
| $UO_2^{2+}$ (aq)/ $UO_2^{+}$ (aq) | 0.088 | – 0.10 | – 0.51 |
| $NpO_2^{2+}$ (aq)/ $NpO_2^{+}$ (aq) | 1.16 | 1.72 | 0.87 |
| $PuO_2^{2+}$ (aq)/ $PuO_2^{+}$ (aq) | 0.94 | 0.91 | 0.43 |

## A-1.2 Compounds and complexes in the uranium hydroxide, oxide and peroxide systems

**[1975MAR]**

Based on an evaluation of the lattice energy of $UO_2F_2$(cr), Marcus has estimated the enthalpy of formation of $UO_2^{2+}$ (g) and reports $\Delta_f H_m^o$ ($UO_2^{2+}$, g, 298.15 K) = 1210 kJ·mol$^{-1}$. This value is significantly different from the experimental value of Gibson *et al.* [2005GIB/HAI], $\Delta_f H_m^o$ ($UO_2^{2+}$, g, 298.15 K) = (1524 ± 63) kJ·mol$^{-1}$.

**[2002DES/GIA]**

Potentiometry using an $H^+$-glass electrode was used to study the hydrolysis of $UO_2^{2+}$ in aqueous NaCl (0.1-4.5 mol·$L^{-1}$) and $NaNO_3$ (0.1-1 mol·$L^{-1}$) solution with pH < 6 at $T = 25$ °C. The data were fitted with a model including $UO_2OH^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, and $(UO_2)_3(OH)_7^-$ species. Equilibrium constants were obtained for the NaCl and $NaNO_3$ media at different ionic strengths. The constants at infinite dilution were calculated by extrapolation using a Debye-Hückel type equation including a polynomial expression of the ionic strength ($L(I) = CI + DI^{1.5} + EI^2$), where $C$, $D$ and $E$ are empirical parameters obtained by fitting. For $\beta_{qp} = [(UO_2)_p(OH)_q^{2p-q}][H^+]^q[UO_2^{2+}]^{-p}$, $\log_{10}{}^*\beta^o_{1,1} = -(5.19 \pm 0.05)$, $\log_{10}{}^*\beta^o_{2,2} = -(5.76 \pm 0.04)$, $\log_{10}{}^*\beta^o_{4,3} = -(11.82 \pm 0.08)$, $\log_{10}{}^*\beta^o_{5,3} = -(15.89 \pm 0.06)$, and $\log_{10}{}^*\beta^o_{7,3} = -(29.26 \pm 0.10)$.

The experimental approach is technically sound and the experiments seem to be carefully performed. The equilibrium constants at different ionic strengths from this study are re-analysed by using the "standard" SIT plot of the conditional equilibrium constants *vs.* the ionic strength. The result is shown in Figure 9-1, Figure 9-2 and Figure 9-3 in the main text, in which the equilibrium constants at zero ionic strength turn out to be the same as found by [2002DES/GIA]. As chloride and nitrate complex formation are not taken into account, the values of $\Delta\varepsilon$ are empirical parameters and cannot be used to deduce individual ion interaction coefficients for the reactants/products; the equilibrium constants at zero ionic strength are correct.

De Stefano *et al.* note that there are some differences in hydrolysis between the chloride and nitrate systems and in their Table 2, they present species distribution data at different ionic strengths. In their analysis, De Stefano *et al.* have used an empirical method where the term $L(I) + CI^{1.5} + EI^2$ has been added to the Debye-Hückel term. $L$, $C$, and $E$ are empirical parameters that are fitted in the extrapolation procedure. The present review finds it hard to judge the reliability of this method, but we note that it provides the same values of the constants at zero ionic strength as the "traditional" SIT method used in the present review. The SIT values of $\Delta\varepsilon$ cannot be used to deduce individual ion-interaction parameters as chloride and nitrate complex formation is not taken into account. It is also not possible to use the value of $\Delta\varepsilon = -(0.248 \pm 0.022)$ kg·$mol^{-1}$ from Figure B.1 in [1992GRE/FUG] to calculate the conditional equilibrium constants for chloride complex formation that are necessary to correct the data in [2002DES/GIA]; the reason is that this $\Delta\varepsilon$ is obtained in mixed chloride/perchlorate media and not in a pure chloride medium as in the study by De Stefano *et al.* [2002DES/GIA]. For the same reason it is not possible to make corrections for nitrate complex formation.

**[2002FAN/NEC]**

This is not an experimental study, but an overview of the solubility behaviour of actinide oxides/hydroxides. Analogies among actinides of the same oxidation state and systematic trends were discussed.

**[2002FUJ/YAM]**

The solubility of $UO_2 \cdot nH_2O$ was determined at $pC_H$ about 3, 25 °C, and different ionic strengths ($I$ = 0.1, 0.5, 1.0, and 2.0 M NaCl) in aqueous solutions (from "over-saturation" direction). The hydrolysis constants of U(IV), $\beta_n$ ($n$ = 1 and 2) where $\beta_n = [U(OH)_n^{4-n}]/\{[U^{4+}][OH^-]^n\}$, were determined by a solvent extraction method, using $^{233}U$ as the radiotracer and thenoyltrifluoroacetone (TTA) as the extractant in xylene solvent. The experiments were made in test solutions at $I$ = 1.0 M (H/Na)$ClO_4$. Using SIT, the hydrolysis constants at $I = 0$ were calculated to be: $\log_{10} \beta_1^o = (14.71 \pm 0.53)$ and $\log_{10} \beta_2^o = (28.28 \pm 0.42)$. The values of $\log_{10} \beta_3^o$ and $\log_{10} \beta_4^o$ were estimated by a semi-empirical model previously developed by the authors to be $\log_{10} \beta_3^o = (39.18 \pm 0.45)$ and $\log_{10} \beta_4^o = (48.88 \pm 0.59)$. The model used is a simple hard sphere approach based on the trends of mononuclear hydrolysis constants of actinide ions, whereby the effective charges of actinide ions are taken into account.

Using the hydrolysis constants determined in this study, the solubility data were analysed and the value of $K_{sp}^o$ ($I = 0$) was calculated to be – (55.78 ± 1.00). This value is more than one order of magnitude lower the value selected by NEA TDB, namely, – (54.500 ± 1.000), although the two values overlap within uncertainties.

The hydrolysis constants and the solubility product were determined in different ionic media ((H/Na)$ClO_4$ *vs.* NaCl) using solubility experiments at 25 °C. No temperature is reported for the solvent extraction experiments and this review assumes that they refer to 25 °C.

The data from this study are not accepted by this review, because the same group determined different hydrolysis constants at additional ionic strengths ($I$ = 0.1, 0.5, and 1.0 M (H/Na)$ClO_4$) and in a re-evaluation of the solubility data in a later study [2003FUJ/YAM2] with the new hydrolysis constants. Further discussions are provided under [2003FUJ/YAM2].

**[2002KUL/FUJ]**

A semi-quantitative study that reports solubilities but no speciation and no thermodynamic data.

**[2002BAI/CHA]**

Oxygen partial pressures of hypostoichiometric $UO_{2-x}$ at the phase boundary with the liquid metal are measured by KEMS. It uses twin cells with a reference (of $UO_2$) to account for mass loss due to various vapour species (*i.e.*, U(g), UO(g) and $UO_2$(g)). Therefore, two cells within the same isothermal block are loaded with the material under study and pure $UO_2$ for reference. This method assure that accuracy and sensitivity of the KEMS is optimised and the resulting $\Delta G(O_2)$ and $p(O_2)$ as a function of temperature are used in subsequent papers for the construction of the O/U phase diagram. The paper discusses the congruency that is reached between the vapor and solid phase at high temperatures, which leads to an under stoichiometric composition. While the reference thermodynamic data used to calculate the partial pressures is consistent with this review, the paper is not relevant for waste management.

**[2003FUJ/YAM2]**

This is an additional investigation that follows a previously published study on the hydrolysis of U(IV) and solubility of $UO_2 \cdot nH_2O$ [2002FUJ/YAM]. The hydrolysis constants of U(IV) were determined in this study with a solvent extraction method, using $^{233}U$ as the radiotracer and thenoyltrifluoroacetone (TTA) as the extractant in xylene. The distribution coefficients of U(IV) were determined as a function of the acidity ($pC_H$ = 1-4) and ionic strength ($I$ = 0.1, 0.5, and 1.0 M (H/Na)$ClO_4$) in the aqueous phase (in contrast to the solvent extraction study at a single ionic strength of 1.0 M (H/Na)$ClO_4$ in [2002FUJ/YAM]). Using SIT and the ion interaction parameters selected by the NEA TDB [1992GRE/FUG], the hydrolysis constants ($\log_{10}\beta_n$, where $\beta_n = [U(OH)_n^{4-n}]/\{[U^{4+}][OH^-]^n\}$) at $I$ = 0 were calculated to be: (13.71 ± 0.31) ($n$ = 1), (26.12 ± 0.21) ($n$ = 2), and (36.85 ± 0.36) ($n$ = 3). These values are between one and two orders of magnitude lower than corresponding values of $\log_{10}\beta_n$ ($n$ = 1-3) obtained in [2002FUJ/YAM]. The value of $\log_{10}\beta_4^o$ was estimated to be (45.44 ± 0.40), by a semi-empirical "hard-core" model.

Using the newly determined hydrolysis constants from this study, the solubility data of the previous study [2002FUJ/YAM] were re-evaluated to determine $\log_{10}K_{sp}$ at $I$ = 0.1, 0.5, 1.0, and 2.0 M $NaClO_4$ for the reaction $UO_2 \cdot xH_2O \rightleftharpoons U^{4+} + 4OH^- + (x-2)H_2O$. Using SIT and ion interaction parameters selected by the NEA TDB [1992GRE/FUG], the value of $K_{sp}^o$ ($I$ = 0) was calculated to be – (53.93 ± 0.20), which overlaps with the value selected by the NEA TDB – (54.500 ± 1.000) within the reported uncertainties.

**[2003HUG/HEL]**

The standard enthalpy of formation of studtite, $\Delta_f H_m^o(UO_4{\cdot}4H_2O, cr, 298\ K)$ was measured to be $-(2344.7 \pm 4.0)\ kJ{\cdot}mol^{-1}$ by high-temperature oxide-melt solution calorimetry. The solubility product of $UO_4{\cdot}4H_2O(cr)$ for the reaction:

$$(UO_2)O_2(H_2O)_4(cr, 298\ K) + 2H^+(aq, 298\ K) \rightarrow$$
$$UO_2^{2+}(aq, 298\ K) + H_2O_2(aq, 298\ K) + 4H_2O(l, 298\ K)$$

was determined to be $K_s^o = 1.34 \times 10^{-3}$ (*i.e.*, $\log_{10} K_s^o = -2.87$) based on data with the concentration of $H_2O_2$ varied from $7.57 \times 10^{-7}$ to $9.99 \times 10^{-3}$ M over a pH range 2.91-3.37. It was noted that the reaction is influenced by the presence of cations [1992SUN/SHO] and that a continuous supply of $H_2O_2$ is necessary in order to avoid decomposition of the studtite. The measurements by calorimetry and solubility seem to be well conducted and the data seem reliable.

To assess if studtite is stable relative to the common uranyl oxide hydrate alternate phase, dehydrated schoepite, $UO_3{\cdot}0.8H_2O$, the enthalpy of the reaction:

$$UO_3(H_2O)_{0.8}(cr, 298\ K) + 2.2H_2O(l, 298\ K) + H_2O_2(l, 298\ K) \rightleftharpoons$$
$$(UO_2)O_2(H_2O)_4(cr, 298\ K)$$

was determined to be $\Delta_r H_m^o(298\ K) = -(58.2 \pm 4.3)\ kJ{\cdot}mol^{-1}$. Based on the exothermic enthalpy of this reaction, the authors conclude that studtite is stable relative to dehydrated schoepite because the entropy of this reaction is expected to be small (no $O_2(g)$ is involved). This review cannot confirm this conclusion because the corresponding Gibbs energy of reaction is not available.

The enthalpies of formation of studtite and meta-studtite have also been studied using quantum chemical methods in [2007OST/ZEL] and [2007OST/ZEL2].

**[2003LAB/DUG]**

This paper is the first in a series of reviews on the thermodynamics of the O-U system, which assesses pertinent data of oxygen potentials (part I), composition ranges (part II), including the congruent composition (part IV) and an overall assessment of information that leads to the construction of a phase diagram and thermodynamic model. In this part, the composition range of $UO_2$-$U_3O_8$ is reviewed. The authors give an extensive review of the available experimental findings up to the publication date, which is the same as the last NEA update [2003GUI/FAN], therefore few, if any new papers are discussed. The authors do consider various corrections to the discussed data, to account for discrepancies among the experimental methods, for which there are two main causes. First, the main correction is made with the findings of Ackermann and Chang [1973ACK/CHA], who assert that $U_3O_8$ at temperatures above 873 K

and pressures more oxidising that $p(O_2) = 0.21$ atm, the oxide is actually understoichiometric. Second, the composition of O/U can be described by the following equation up to 1500 K:

$$O/U = 1.3752 + 0.0046875T - 6.1855\times10^{-6}T^2 + 3.5194\times10^{-9}T^3 - 7.3925\times10^{-13}T^4$$

The effects of $N_2$ during heat treatment is also considered as a large source of error that is attributed to samples heated in air or other non-inert atmospheres. Results from the following authors were possibly affected by these factors including [1989SRI/YAD], [1981FUJ/TAG], [1965GER/DOD], by oxidation of air *in situ* so that the O/U values are actually more deficient than reported. Many EMF experiments are considered, even though much of the data is scattered and are not consistent across composition or temperature ranges. The uncertainty is evaluated at each stage. As none of the described data is new compared to [2003GUI/FAN], and the main selected data in this work consist of oxygen pressures, the reader is addressed to reference Tables 6 and 7 in [2003LAB/DUG] for the dependence of temperature and composition on oxygen potentials.

**[2003LAB/DUG2]**

The stability range of $UO_{2+x}$, $U_4O_{9-y}$ and $U_3O_8$ is discussed in great detail applying the same or similar corrections as the above paper (first in the series). Again, no new papers are discussed from the previous NEA TDB update book [2003GUI/FAN]. Notable findings include the oxygen rich limit of $UO_{2+x}$ with $U_4O_9$, in which the shape of the phase limit is in question, since there are anomalies at 1250-1350 K and 800-850 K, which are accounted for by the phase transitions of $U_4O_9$; regardless these temperatures are at the limit of, or above the consideration of this review. The phase transitions of $U_4O_9$ are discussed and the data of Westrum are selected. Additionally, low temperature phase transitions are discarded on the basis of a metastable state, since nothing in the heat capacity showed a magnetic component. XRD methods were considered to account for the increased entropy at the transition temperature (350 K), which was eventually attributed to a rearrangement of the metal cations that agree with adiabatic calorimetry and electrical conductivity measurements. The thermodynamic functions used are in agreement with the values of NEA TDB. The transitions of $U_3O_8$ are also discussed and in agreement with our selected values.

**[2003RAI/YUI]**

The solubility and solubility product of $UO_2$(cr) were determined at 22 °C (equilibrated at 90 °C for 24 days, then at 22 °C for one day) in chloride solutions (pH = 0.221-1.474, [chloride] = 0.052-0.651 m) from over-saturation. The reducing conditions were maintained by using $Eu^{2+}$ to reduce the $O_2$ fugacity in the solubility experiments.

Using the Pitzer approach including the Pitzer parameters for the interactions of ($U^{4+}$, $Cl^-$) and ($UOH^{3+}$, $Cl^-$) from a previous study, the upper limit of the $\log_{10} K^\circ$ value for the dissolution of $UO_2$(cr) ($UO_2(cr) + 2H_2O \rightleftharpoons U^{4+} + 4OH^-$) was set at – (60.20 ± 0.24), which is consistent with the selected value of – (60.86 ± 0.30) by NEA TDB [1992GRE/FUG]. The hydrolysis constant ($\log_{10} {}^*K_4^\circ$ for the reaction $U^{4+} + 4H_2O(l) \rightleftharpoons U(OH)_4(aq) + 4H^+$) was estimated in this study to be < – 11.6. This upper-limiting value is a few orders of magnitude lower than the previous value (– 4.0) reported by Bruno *et al.* [1986BRU/FER] and the value – (4.54 ± 1.4) calculated from $\Delta_f G_m^\circ$ for $U(OH)_4$(aq) and $H_2O$(l) [1992GRE/FUG]. The authors attributed the difference to the presence of U(VI) solid phase resulting from poor control of the redox potential in previous solubility studies.

**[2003SAW/SHA]**

This is an experimental study of the hydrolysis of Th(IV) and U(VI) by potentiometry. The data on Th(IV) hydrolysis were reviewed in [2008RAN/FUG]. Only the data for U(VI) hydrolysis are discussed in the present review.

The hydrolytic behaviour of U(VI) was studied at 25 °C, in 1 M $NaClO_4$, in the absence as well as in the presence of small concentrations of fluoride in the pH range of 2.0 to 5.5. The authors claimed that using small amounts of fluoride (~ 1 % of uranium concentration) was helpful in suppressing the early polymerisation and colloid formation at the metal ion concentrations investigated; the addition of fluoride did not seem to affect the response of glass electrode significantly. The well-established $(UO_2)_3(OH)_5^+$ species was not included in the speciation of the U(VI) system, casting doubts on the validity of the speciation model used.

From the experiments in the absence of fluoride, the log values of $^*\beta_{2,2}$, $^*\beta_{6,4}$, and $^*\beta_{7,4}$ were calculated to be – (6.15 ± 0.05), – (18.43 ± 0.09), and – (23.36 ± 0.07), respectively. The hydrolysis constants obtained in the presence of fluoride are about 0.1-0.3 logarithm units higher than those in the absence of fluoride.

The authors compared the values at 1 M $NaClO_4$ with other experimental values in the literature. However, due to the absence of necessary ion interaction parameters, the data were not converted to the values at $I$ = 0 with SIT. The chemical model used in [2003SAW/SHA] is very different from the ones used in similar studies. The authors do not seem to have tested other models and the present review finds the neglect of the well established (5,3) complex surprising. The present review does not consider the reported chemical model and the equilibrium constants reliable.

**[2004CLA/PAB2]**

The formation of studtite during oxidative dissolution of $UO_2$(s) by hydrogen peroxide was studied at pH = 5.8 and $H_2O_2$ concentrations of $5 \times 10^{-6}$ and $5 \times 10^{-4}$ M. The formation of secondary phases was investigated using scanning surface force microscopy. It was found that the steady state concentrations of U(VI) and $H_2O_2$ are [U(VI)] = $1.3 \times 10^{-6}$ M and [$H_2O_2$] = $4 \times 10^{-4}$ . Results seem to suggest that studtite is more stable than dehydrated schoepite, consistent with the finding in [2003HUG/HEL]. No thermodynamic data were derived from the study.

**[2004CRE/DES]**

Calorimetric studies were performed to study the hydrolysis of $UO_2^{2+}$ in different ionic media (1.0 m $NaClO_4$ and 0.1 to 1.02 m NaCl) at 25 °C. In the NaCl system, hydrolysis species ((1,1), (2,2), (4,3), (5,3), and (7,3)) were included and the enthalpies of hydrolysis at variable ionic strengths were calculated by using the hydrolysis equilibrium constants obtained in a previous study [2002DES/GIA]. In the $NaClO_4$ system, hydrolysis species ((1,1), (2,2), and (5,3)) were included and the enthalpies of hydrolysis in 1.0 m $NaClO_4$ were calculated by fitting the calorimetric data either simultaneously for $\log_{10}{}^{*}\beta$ and $\Delta H$, or only for $\Delta H$ using the hydrolysis equilibrium constants from a private communication the source of which was not given in the original publication.

The dependence of enthalpy on the ionic strength (for the NaCl system, $I$ = 0.1 to 1.02 m) was expressed by simple linear equations: $H_{pq} = H^{\circ}_{pq} + aI^{1/2}$, where $a$ is an empirical parameter obtained by linear regression. Results show that $H^{\circ}_{pq}$ (kJ·mol$^{-1}$) = (42.5 ± 1.8), (47.9 ± 0.6), (99.7 ± 0.8), (120.4 ± 11.7), and (179.2 ± 19.5), and $a$ = – 5.6, – 4.2, – 9.7, – 11.7, and – 19.5, for hydrolysis species (1,1), (2,1), (4,3), (5,3), and (7,3), respectively. The enthalpies of hydrolysis from this study are re-analysed and corrected to $I$ = 0 using the SIT approach outlined in the discussion under [2004ZAN/DIB].

**[2004GAS/BUK]**

This is a modeling study on the solubility of $UO_2$(s) under conditions of underground disposal of nuclear waste and spent nuclear fuel, using the [1992GRE/FUG] and Nagra/PSI data bases. No new thermodynamic information was obtained.

**[2004GIA/HER]**

This study was focused on the influence of $Na^+$ and $Cs^+$ on the solubility of uranyl oxide hydrate and the transformation of meta-schoepite to a clarkeite phase. Clarkeite $NaUO_2(O)(OH)\cdot 3H_2O$ is stoichiometrically equivalent with $1/2Na_2U_2O_7\cdot 3H_2O$. The

authors find significant differences between their experimental solubility product and published data; references are given to [1992GRE/FUG] and [1992SIL].

**[2004GIA/MIL]**

Hydrolysis and chemical speciation of $UO_2^{2+}$ were studied by potentiometry in simulated sea water, and in a large number of different ionic media (NaCl, $NaNO_3$, LiCl, $CaCl_2$, $MgCl_2$, $Na_2SO_4$, and mixtures of $(Ca/Mg)Cl_2$ and $Na_2SO_4$/NaCl, $Na_2SO_4$/$NaNO_3$). The activity corrections have been made using the method in [2002DES/GIA] and using the Pitzer model. The data for the binary NaCl and $NaNO_3$ systems are from [2002DES/GIA] and discussed by this review under [2002DES/GIA]. The data for the binary LiCl, $CaCl_2$, and $MgCl_2$ are re-analysed with SIT in this review without taking into consideration the formation of U(VI)/chloride complexes, and the hydrolysis constants at $I = 0$ are obtained (Table A-6). In general, the values of $\log_{10}{}^{*}\beta^{\circ}_{n,m}$ (298.15 K) from this work are in good agreement with values from other studies and the values selected by previous NEA TDB reviews. However, the experiments with $CaCl_2$ and $MgCl_2$ were conducted at only three ionic strengths and some of the linear fits by SIT are not satisfactory (*e.g.*, the (5,3) species from the $CaCl_2$ media, and the (7,3) species from the $CaCl_2$ and $MgCl_2$ media). As a result, this review accepts only the data for the LiCl media for further analysis and comparison with other data. The data from $CaCl_2$ and $MgCl_2$ are not accepted by this review.

In the above-mentioned analysis, the effect of chloride on the hydrolysis was considered only through ion interactions and the formation of U(VI)/chloride complexes was not taken into account. Therefore, the $\Delta\varepsilon$ values developed in our analysis reflect the specific ion interactions between the cationic species ($UO_2^{2+}$, $UO_2Cl^+$, $H^+$) and chloride.

For the same reason as described for the data of [2002DES/GIA] in Appendix A, it is not possible to use the values of $\Delta\varepsilon$ derived from the data of [2004GIA/MIL] or [2002DES/GIA] to determine individual ion interaction coefficients for the system.

Figure A-1: SIT analysis of U(VI) hydrolysis data from [2004GIA/MIL] excluding the formation of U(VI) chloride complexes.

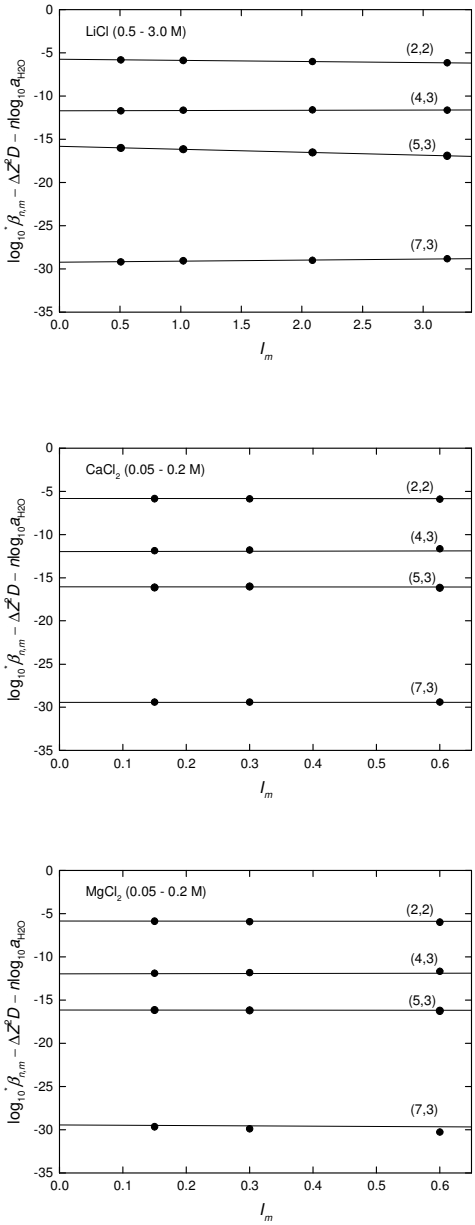


Table A-6: $\log_{10} {}^{*}\beta^{o}_{n,m}$ (298.15 K) and $\Delta\varepsilon$ obtained from different ionic media from [2004GIA/MIL].

| | LiCl (0.5-3.0 M) | | $CaCl_2$ (0.05-0.20 M) | | $MgCl_2$ (0.05-0.20 M) | |
|---|---|---|---|---|---|---|
| | $\log {}^{*}\beta^{o}_{n,m}$ | $\Delta\varepsilon$ | $\log {}^{*}\beta^{o}_{n,m}$ | $\Delta\varepsilon$ | $\log {}^{*}\beta^{o}_{n,m}$ | $\Delta\varepsilon$ |
| (2,2) | – (5.75 ± 0.02) | (0.12 ± 0.01) | – (5.83 ± 0.03) | (0.13 ± 0.12) | – (5.84 ± 0.01) | (0.25 ± 0.03) |
| (4,3) | – (11.69 ± 0.11) | – (0.03 ± 0.07) | – (11.96 ± 0.03) | – (0.52 ± 0.15) | – (11.97 ± 0.03) | – (0.49 ± 0.15) |
| (5,3) | – (15.81 ± 0.13) | (0.34 ± 0.07) | – (16.05 ± 0.14) | (0.14 ± 1.30) | – (16.12 ± 0.01) | (0.19 ± 0.02) |
| (7,3) | – (29.22 ± 0.08) | (0.12 ± 0.03) | – (29.41 ± 0.03) | – (0.02 ± 0.07) | – (29.44 ± 0.08) | (1.39 ± 0.22) |

**[2004KIR/KIM]**

This study examines the fluorescence properties of U(VI) aqueous solutions ($5 \times 10^{-5}$ M uranium(VI) in 0.5 M $NaClO_4$ at pH 3.8-6.0) at elevated temperatures (up to 100 °C) and pressures (0.1-40 MPa). Using the DQUANT equation and the data of $\Delta_r S^{o}_{m}$ (298.15 K) and $\Delta_r H^{o}_{m}$ (298.15 K) from the literature, the hydrolysis constants at zero ionic strength in the temperature range of 25 to 100 °C were calculated (the effect of pressure is insignificant). The calculated equilibrium constants were used to construct speciation diagrams for U(VI) at different temperatures. It was found that the emission spectra and the fluorescence lifetime could be well deconvoluted into components assigned to the hydrolysis species including $UO_2OH^+$, $(UO_2)_2(OH)_2^{2+}$, and $(UO_2)_3(OH)_5^+$.

No new equilibrium hydrolysis constants of U(VI) were determined experimentally in this study.

**[2004MAS/MIK]**

The stoichiometry of U(VI) hydrolysis reactions was studied by using oxygen exchange kinetics. No thermodynamic data or speciation information were reported.

**[2004NEU/SOD]**

X-ray scattering was used to determine the hydration number of $UO_2^{2+}$. No thermodynamic data were reported in this study.

**[2004SPA/DEV]**

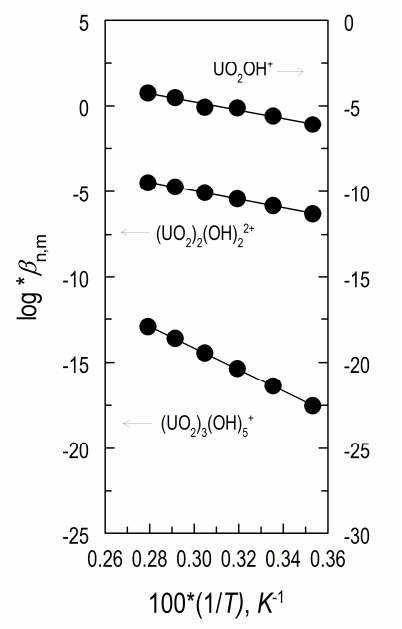
No thermodynamic data on aqueous uranium hydroxide were determined in this study.

**[2004ZAN/DIB]**

Zanonato *et al.* have determined the equilibrium constants and enthalpies of reactions for the formation of uranyl(VI) hydroxide complexes in the temperature range 10-85 °C, using potentiometry and titration microcalorimetry. The experiments have been conducted in a 0.10 M tetra-ethyl ammonium perchlorate medium and all details on the experiments, including primary data are reported. Spectroscopic information on optical absorption and fluorescence spectra/lifetimes of the excited states are also reported in this paper.

The analysis of the data is satisfactory and includes the complexes $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^{+}$, consistent with the findings in most experimental studies. It is noted that the enthalpies of hydrolysis calculated by the van't Hoff equation using the equilibrium constants of hydrolysis in the temperature range (10-85 °C) are in good agreement with those determined by calorimetry at 298.15 K. The van't Hoff plots of the data are shown in Figure A-2, the "average" enthalpies of hydrolysis at 10-85 °C are calculated to be (47.6 ± 2.6) kJ·mol$^{-1}$ and (120.0 ± 3.7) kJ·mol$^{-1}$ for $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^{+}$, respectively. The enthalpy of hydrolysis for the (1,1) species, $UO_2OH^+$, was determined to be (46.5 ± 3.7) kJ·mol$^{-1}$ from the temperature-dependent data in [2004ZAN/DIB].

Figure A-2: log $*\beta^{o}_{n,m}$ *vs.* 1/*T* [2004ZAN/DIB].



This review accepts the experimental enthalpies of hydrolysis at 298.15 K determined by calorimetry from this study, but has made a minor correction of the enthalpies of reaction from ionic strength 0.10 M to zero ionic strength using the method described in *Modelling in Aquatic Chemistry*, Section IX.10 [1997GRE/PLY2], Eqn. (IX. 72) on p. 412.

$$\Delta_r H_m - rL_1 = \Delta_r H_m^o + \frac{3}{4}\frac{A_L \Delta(z^2)\sqrt{I_m}}{(1+1.5\sqrt{I_m})} - RT^2 m\Delta\varepsilon_L \qquad \text{(A.5)}$$

The relative partial enthalpy of the solvent is obtained from Equation (A.6)

$$L_1 \approx \frac{M_W}{1000}\left[-\frac{3A_L}{2(1.5^3)}\left(t - 2\ln t - \frac{1}{t}\right)\right], \text{ where } t = (1+1.5\sqrt{I_m}) \qquad \text{(A.6)}$$

The values of $L_1$ for a number of common electrolyte solutions were calculated and tabulated in *Modelling in Aquatic Chemistry* [1997ALL/BAN], Table IX.14, p.409. The table shows that the absolute values of $L_1$ for common electrolyte solutions decrease as the ionic strength is decreased from 6.0 to 0.5 mol·kg$^{-1}$, approaching the magnitude of $|L_1| = 0.001$ kJ·mol$^{-1}$ when $I = 0.5$ mol·kg$^{-1}$. Therefore, we expect that the values of $L_1$ for an electrolyte solution with $I = 0.1$ mol·kg$^{-1}$ are very close to zero and can be neglected when we correct the experimentally determined enthalpies of hydrolysis at $T = 298.15$ K and $I = 0.1$ M from [2004ZAN/DIB] to obtain the enthalpies of hydrolysis at 298.15 and infinite dilution. In addition, we have neglected the third term on the right side of Equation (A.5). The second term on the right side of Equation (A.5) is an ionic strength term. For the ionic strength of 0.1 m, the ionic strength term in Equation (A.5) is calculated to be – 0.64 kJ·mol$^{-1}$ for the $(UO_2)_2(OH)_2^{2+}$ hydrolysis reaction ($\Delta Z^2 = -2$), and – 1.92 kJ·mol$^{-1}$ for the $(UO_2)_3(OH)_5^{+}$ hydrolysis reaction ($\Delta Z^2 = -6$).

This is the only study in the literature where enthalpies of hydrolysis ($\Delta^* H_{22}$ and $\Delta^* H_{53}$) were determined at different temperatures so that the heat capacities of hydrolysis were calculated. The values of $\Delta_r C_p$ for the $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^{+}$ species are accepted by this review. The concentration of the (1,1) species, $UO_2OH^+$, is small at low temperatures, which explains why the enthalpy of reaction for $UO_2OH^+$ (46.5 ± 3.7) kJ·mol$^{-1}$ from the van't Hoff method has a fairly large uncertainty. The corresponding entropy for $UO_2OH^+$ (reaction 4 in the paper) is (53 ± 13) J·K$^{-1}$·mol$^{-1}$.

In a later study on the formation of ternary U(VI)-OH-peroxide complexes [2012ZAN/DIB], Zanonato *et al.* also fitted the data (covering a p$C_H$ region up to 12) with the equilibrium constants of the binary U(VI) hydroxide species, including (1,1), (2,2), (4,3), (5,3), (6, 3), (7,3), (8,3), and (3,1) species, with the equilibrium constants of – (5.20 ± 0.10), – (5.95 ± 0.03), – (12.25 ± 0.08), – (16.43 ± 0.02), – (22.68 ± 0.23), – (28.95 ± 0.12), – (38.91 ± 0.17), and – (18.75 ± 0.22), respectively, at 25 °C in

0.100 M tetramethylammonium nitrate. The constants for the (1,1), (2,2) and (5,3) species are consistent to those obtained in [2004ZAN/DIB]. The (6,3) and (7,3) species were found to form in significant amounts at p$C_H$ = 5.4 and 5.7, respectively. Since the p$C_H$ of the potentiometric experiments is below 5.5 in the present study [2004ZAN/DIB], the (6,3) and (7,3) species should be insignificant.

**[2005CRE/MIL]**

The formation of ternary U(VI)-Cu(II)-hydroxide and U(VI)-$(C_2H_5)_2Sn^{2+}$-hydroxide complexes were investigated by potentiometry within the pH range 2.4-5.4. While fitting the data, binary U(VI) hydroxide complexes including (1,1), (1,2), (2,2), (4,3), (5,3), and (7,3) at $T = 25$ °C and $I$ = 0.16 M $NaNO_3$ were also obtained. Using SIT and the values of Δε derived from [2002DES/GIA], the binary hydrolysis constants at $I = 0$ are calculated in this review: $\log_{10}{}^{*}\beta^{o}_{n,m}$ (298.15 K) = – (5.58 ± 0.12), – (4.08 ± 0.05), – (5.73 ± 0.03), – (12.31 ± 0.10), – (15.60 ± 0.03), and – (28.16 ± 0.07), for the (1,1), (1,2), (2,2), (4,3), (5,3), and (7,3) species, respectively. These values are compared with the values from other studies and the values selected by NEA TDB, and discussed in the main text.

**[2005DJO/CUC]**

Djogić *et al.* studied the precipitation of U(VI) peroxide in $NaClO_4$ and reported a solubility product $[UO_2^{2+}][O_2^{2-}] = 1.32 \times 10^{-36}$ M$^2$. This result is obviously in error as it is not possible to determine the second dissociation constant for hydrogen peroxide experimentally in aqueous solution. The authors used an equilibrium constant for the reaction $H_2O_2 \rightleftharpoons 2H^+ + O_2^{2-}$ equal to $10^{-36.65}$ based on an earlier study [1949EVA/URI]. However, such information was not found in that paper. Instead, it is just stated in ref. 28 of [2005DJO/CUC] that "we would expect the second dissociation of $H_2O_2$ to be extremely small".

To further check the validity of the results from this work, the experimental data in Table II (p.578) of [2005DJO/CUC] were used by this review, in order to estimate the solubility product for the reaction $(UO_2(O_2)(s) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2)$ for comparison of the data from [2005DJO/CUC] with those from [2003HUG/HEL]. Details of the calculation are shown in Table A-7. In the calculation, $[H^+] \approx 10^{-4.8}$ M, and $[H_2O_2(l)] = [H_2O_2(l)]_{total}$ at pH 4.8.

Table A-7: Estimate of the solubility constant $\log_{10}{}^{*}K_{sp}$ for the reaction $UO_2(O_2)(s) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2$.

| pH | $[UO_2^{2+}]_{free} \times 10^6$ /M | $[H_2O_2(l)] \times 10^3$ /M | $\log_{10}{}^{*}K_{sp}$ |
|---|---|---|---|
| 4.8 | 0.16 | 9.0 | 0.76 |
| 4.8 | 0.25 | 6.0 | 0.78 |
| 4.8 | 0.31 | 5.0 | 0.79 |
| 4.8 | 0.45 | 3.5 | 0.80 |
| 4.8 | 0.53 | 3.0 | 0.80 |
| 4.8 | 0.82 | 2.0 | 0.81 |
| 4.8 | 2.0 | 0.90 | 0.85 |
| 4.8 | 2.3 | 0.80 | 0.86 |
| 4.8 | 2.7 | 0.70 | 0.88 |
| 4.8 | 2.0 | 0.60 | 0.68 |
| 4.8 | 4.0 | 0.50 | 0.90 |
| 4.8 | 5.4 | 0.40 | 0.93 |

The calculation shows that the logarithm of the solubility product ($\log_{10}{}^{*}K_{sp}$) for the reaction ($UO_2(O_2)(s) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O_2$) ranges from 0.75 to 0.93, substantially higher than the value of – 2.87 from [2003HUG/HEL]. Such discrepancy could be due to the difference in the degree of crystallinity of the solid phases in the two studies. It is noted that the solid phase was checked by powder X-ray diffraction, but the crystallinity of the solid is unknown in [2005DJO/CUC].

Due to the unsubstantiated use of an unknown equilibrium constant for the reaction $H_2O_2 \rightleftharpoons 2H^+ + O_2^{2-}$ and the lack of information on the crystallinity of the solid phase, data from [2005DJO/CUC] are not accepted by the present review.

**[2005FUJ/YAM]**

This is an extended solubility study related to two previous studies on the solubility of $UO_2$(am) in [2002FUJ/YAM], [2003FUJ/YAM2]. In this study, the solubility was measured from oversaturation at higher pH (12-14) and in the presence of $Na_2S_2O_4$ as a reducing agent. The higher order hydrolysis constants ($\log_{10}\beta_n^{o}$ for the reaction $U^{4+} + nOH^- \rightleftharpoons U(OH)_n^{4-n}$ where $n$ = 5 and 6) were determined by modeling the solubility data using the solubility product obtained in a previous study ($\log_{10} K_{sp}^{o} = -53.93$ [2003FUJ/YAM2]). The values of $\log_{10}\beta_5^{o}$ (< 48.10) and $\log_{10}\beta_6^{o} = (48.95 \pm 1.01)$ were obtained in conjunction with two ion interaction parameters $\varepsilon(Na^+, U(OH)_5^-) < 0.63$ mol·kg$^{-1}$, and $\varepsilon(Na^+, U(OH)_6^{2-}) = (1.01 \pm 0.712)$ mol·kg$^{-1}$.

Considering the extreme difficulty to maintain the U(IV) state in solutions of very high pH, the higher order hydrolysis constants ($\log_{10}\beta_5^{o}$ and $\log_{10}\beta_6^{o}$) from this study are questionable. The interaction parameters from this work, $\varepsilon(Na^+, U(OH)_5^-) < 0.63$ mol·kg$^{-1}$ and $\varepsilon(Na^+, U(OH)_6^{2-}) = (1.01 \pm 0.712)$ mol·kg$^{-1}$, seem unreasonably

high for the interactions between $Na^+$ and anions with – 1 or – 2 charges, which is also an indication that the presence of higher order hydrolysis species and the reliability of the hydrolysis constants need further investigation. It should also be pointed out, as the authors did in the paper, that the solubility of tetravalent oxides of Th, Np, or Pu remain constant in the pH region up to 13-14, suggesting the absence of $M(OH)_5^-$ or $M(OH)_6^{2-}$ species (where M = Th, Np, and Pu). As a result, the values of $\log_{10} \beta_5^o$ and $\log_{10} \beta_6^o$ are not selected by this review.

**[2005FUJ/YAM2]**

This is a careful experimental study of the solubility of U(VI) hydrous oxide in the $pC_H$ range from 4 to 6 at 25 °C in 0.1-1.0 M $NaClO_4$. The equilibrium was reached from both over- and undersaturation. The solid phase was identified as a mixture of $UO_3 \cdot 2H_2O$(s) and $UO_2(OH)_2$(s) by XRD. Hydrolysis reactions including hydrolysis species of (1,1), (2,1), (1,2), (2,2), (4,3), (5,3), and (7,4) were considered in analysing the solubility data, but only the data in the $pC_H$ range < 5 were used in order to reduce the uncertainty introduced by the chemical model when calculating $K_{sp}$. All hydrolysis constants and ion interaction parameters were taken from the NEA TDB [2003GUI/FAN]. The $\log_{10} K_{sp}^o$ value of $-(22.46 \pm 0.10)$ is slightly higher than the value for $UO_3 \cdot 2H_2O$(s) selected by the NEA TDB $-(23.19 \pm 0.43)$ [2003GUI/FAN]. The difference in $\log_{10} K_{sp}^o$ could be attributed to the difference in the solid phase, a mixture of $UO_3 \cdot 2H_2O$(s) and $UO_2(OH)_2$(s) in this study.

**[2006BAT/KAL]**

Sorption study and modelling of $UO_2$(s) interactions with ground water, no new thermodynamic data.

**[2006BAI/CHA]**

The third article of the series concerning the O-U system thermodynamics this paper touches on the hyperstoichiometric range at high temperatures. This paper introduces the congruent vaporisation composition (azeotropic) of the solid as it approaches the melting point and becomes reduced. The laser pulse method is reviewed as a technique to measure the melting behaviour. The most recent results by [2002MAN/RON] and [2003MAN/RON] are rejected for the liquidus and solidus temperatures, citing that a metastable phase with large quenching speed or time limited segregation leads to an oxygen enriched liquid where the exact composition is unknown. The incongruency of the liquid ($UO_{2-x}$) is also discussed, but it is of little relevance to this review. The paper discusses the corrections made to the work of [2003MAN/RON], where the melting temperatures and congruent compositions are accounted for. However, the corrections

are neglible, and the authors therefore select the melting point and liquidus/solidus curves of [1970LAT/FRY].

**[2006BAI/CHA2]**

The last of a series of critical reviews on the O-U system, this paper covers the limited range of U-$UO_{2.01}$, most importantly covering the thermodynamic properties at high temperatures, including the Bredig or λ transition that includes anomalous increases of the enthalpy increment. Techniques that minimise the effect of vaporisation of the material at high temperatures are discussed, including laser heating at high pressures and the effect of Knudsen surface layers that drive a stoichiometric sample to hypostoichiometric congruent compositions through gas diffusion. The general thermodynamic properties ($\Delta_f G_m^o$, $\Delta_f H_m^o$, $S_m^o$, and $C_{p,m}^o$) are unchanged from [1992GRE/FUG] at 298.15 K as listed in the compiled data tables. Discrepancies however arise in the liquid phase, which is beyond the scope of this review, similar to the chemical potential measurements considered by [2006BAI/CHA] that detail the behaviour of oxygen potential with respect to composition. The authors are skeptical of the high temperature model that details heat capacity values up to 8000 K, with a decrease above the melting point up to about 4000 K, and then an increase up to the $T$ = 8000 K. However, relatively few papers new to this review are introduced in this more than thorough review.

**[2006JAN/DEM]**

This is a solubility study of $UO_3 \cdot nH_2O$(s). By comparing a few sets of thermodynamic hydrolysis constants and solubility products, it was found that the solubility data were represented most accurately by using the hydrolysis constants from Langmuir [1978LAN] with schoepite ($\log_{10}{}^* K_{sp}^o$ = 5.39) as the solubility limiting phase for solutions with low to intermediate initial degrees of supersaturation. This value of $\log_{10}{}^* K_{sp}^o$ is higher than that selected by NEA TDB ($\log_{10}{}^* K_{sp}^o$ = (4.93 ± 5.39) for β-$UO_2(OH)_2$(s) [1992GRE/FUG], [2003GUI/FAN]), leading to a difference of 2.63 kJ·mol$^{-1}$ in $\Delta_f G_m^o$ (β-$UO_2(OH)_2$ , s). The value of $\log_{10}{}^* K_{sp}^o$ = 5.39 from this work is not accepted by this review.

**[2006KUB/BUR]**

Crystal chemistry of uranyl peroxides with no thermodynamic information.

**[2006KUB/UNR]**

This is not an experimental study. Using the standard enthalpies of formation for becquerelite and studtite from the literature, and the standard enthalpies of formation for

$H_2O_2$, and CaO, the enthalpy of reaction for the conversion from becquerelite to studtite was calculated to be negative. On the assumption that the reaction entropy is small (no $O_2$ gas involved), the Gibbs free energy of the reaction is estimated to be negative (identical to the enthalpy), and studtite is expected to be more stable than becquerelite. No useful thermodynamic data are obtained for this review.

**[2006MAN/CAR]**

This is a potentiometric study using a cell containing inert metal sponge and glass electrodes to determine the hydrolysis constants of U(IV) in the absence of a solid phase. The experiments were conducted in 3 mol·dm$^{-3}$ $NaClO_4/HClO_4$ aqueous solutions in the p$C_H$ (= $\log_{10}[H^+]$) range from 0.5 to 1.8. The lower value of p$C_H$ = 0.5 was chosen to avoid large corrections for the liquid junction potential (the diffusion potential is determined by the difference in $[H^+]$ between the reaction cell and the reference cell and this information is not given in the paper), the upper value of p$C_H$ = 1.8 was imposed by the precipitation of $UO_2$(s). The values of $\log_{10}{}^{*}\beta_1$ and $\log_{10}{}^{*}\beta_4$ were determined to be – (1.62 ± 0.02) and – (7.70 ± 0.04) at $I$ = 3 mol·dm$^{-3}$ $NaClO_4$. Using SIT, the values of $\log_{10}{}^{*}\beta_1^{o}$ and $\log_{10}{}^{*}\beta_4^{o}$ were calculated to be – (0.49 ± 0.18) and – (4.93 ± 0.35), respectively. These values correspond to the values of $\log_{10}\beta_n^{o}$ (13.51 ± 0.18) for $n$ = 1 and (51.07 ± 0.35) for $n$ = 4. The value of $\log_{10}\beta_1^{o}$ (13.51 ± 0.18) is consistent with that selected by the previous NEA TDB update book (13.46 ± 0.06) [1992GRE/FUG], but the value of $\log_{10}\beta_4^{o}$ (51.07 ± 0.35) is significantly higher than that selected by the previous NEA TDB update review (46.0 ± 1.4) [2003GUI/FAN]. The authors claim that the value of $\log_{10}{}^{*}\beta_4^{o}$ from this work, – (4.93 ± 0.35), agrees with previous literature values related to crystalline $UO_2$(s). However, a previous solubility study [2003RAI/YUI] using $UO_2$(cr) in fact suggests $\log_{10}{}^{*}\beta_4^{o} < -11.6$ (or $\log_{10}\beta_4^{o} < 44.4$).

**[2006MOR/SAS]**

An electrostatic model with the effective charges on the actinide atoms (U, Np, and Pu) in the hexavalent actinyl ions ( $AnO_2^{2+}$ ) was applied to calculate the hydrolysis constants of polynuclear species. No new experimental data are determined.

**[2006PER/KUL]**

This is a study of the solubility of uranium and neptunium hydroxide with mixed valences, *i.e.* U(IV/VI) and Np(IV/V) in simulated ground water and 0.1 M $NaClO_4$. No thermodynamic information is extracted from this work.

**[2006SCH/HAW]**

The dissolution of becquerelite was studied. The focus is on the characterisation of solid phase(s). No thermodynamic data were reported.

**[2006SCH/MAN]**

A study similar to [2006SCH/HAW]. The dissolution of curite was studied.

**[2007LUC/BOR]**

The concentrations of Nd(III) and U(VI) in WIPP (Waste Isolation Pilot Plant, New Mexico, USA) brines were experimentally determined. Results indicate that the concentration of U was orders of magnitude lower than that expected from the WIPP thermodynamic database. Due to the lack of the characterisation of the solid phase, it is difficult to comment on the reason for the difference between the observed and the calculated concentrations of U.

**[2007OPE/WEI]**

This appears to be a carefully conducted study by coulometric titration to determine the solubility of U(IV) in acidic $HClO_4$/$NaClO_4$ solutions. Laser-induced breakdown detection (LIBD) is used to determine the pH values at which colloids started to form and from these to calculate the solubility product of crystalline and amorphous uranium dioxides. Crystalline $UO_2$(cr) was observed at low pH (~ 1), while amorphous hydrous oxide $UO_2{\cdot}xH_2O$(am) was found to form at pH ~ 3.

The solubility products $K_s$ were found to be dependent on the particle size of the colloids determined by LIBD, so that the experimentally obtained values of $K_s$ should be corrected for the effect of particle size. SIT was used to correct the values to the infinite dilution ($I$ = 0). The hydrolysis species of $U(OH)_n^{(4-n)}$ were considered in the calculation of the solubility products, with the hydrolysis constants taken from [2001NEC/KIM]. Among the hydrolysis constants used in this study, only those of the species with $n$ = 1 and 4 were selected by the NEA TDB [1992GRE/FUG], [2003GUI/FAN]. The values of the species with $n$ = 2 and 3, though quite reasonable, were not the selected, but were the estimated values from [2001NEC/KIM].

The value of $\log_{10} K_s^o$ for $UO_2{\cdot}xH_2O$(am) was determined to be – (54.1 ± 1.0), consistent with the values selected by the NEA TDB – (54.500 ± 1.000) [2003GUI/FAN]. The value for crystalline $UO_2$(cr) was – (59.6 ± 1.0) after correction

of the effect of the particle size, close to that estimated from the CODATA values of $\Delta_f G_m^o$ by the previous review, – (60.860 ± 0.360) [1992GRE/FUG].

**[2007OST/ZEL]**

This is a quantum chemistry study of solid phases studtite and meta-studtite. Following the review guidelines, the values from computations are only for comparative discussions, but are not accepted by this review.

For studtite, the authors report enthalpies of formation at 0 K, $\Delta_f H_m^o(UO_4{\cdot}4H_2O, cr, 0\ K) = -2303.4\ kJ{\cdot}mol^{-1}$. In comparison, the value from [2003GUI/FAN] is $\Delta_f H_m^o(UO_4{\cdot}4H_2O, cr, 298\ K) = -(2384.7 \pm 2.1)\ kJ{\cdot}mol^{-1}$, and the value from [2003HUG/HEL] is $\Delta_f H_m^o(UO_4{\cdot}4H_2O, cr, 0\ K) = -(2344.7 \pm 4.0)\ kJ{\cdot}mol^{-1}$.

For meta-studtite, the value from this quantum chemistry study is $\Delta_f H_m^o(UO_4{\cdot}2H_2O, cr, 0\ K) = -1693\ kJ{\cdot}mol^{-1}$. In comparison, the value of $\Delta_f H_m^o(UO_4{\cdot}2H_2O, cr, 298\ K) = -(1784.7 \pm 4.2)\ kJ{\cdot}mol^{-1}$ from [2003GUI/FAN].

The difference in the enthalpies of formation between studtite and meta-studtite is 610.4 $kJ{\cdot}mol^{-1}$ in [2007OST/ZEL], and 600 $kJ{\cdot}mol^{-1}$ in [2003GUI/FAN].

**[2007OST/ZEL2]**

This is a discussion of the mechanism for the phase transformation between schoepite, meta-schoepite and dehydrated meta-schoepite based on *ab initio* molecular dynamics simulations at room temperature. There are no new thermodynamic data in this study.

**[2007RED/WOO]**

This study discusses the speciation of uranium(VI) in aqueous solution, and experiences from experiments and calculations. Solubility has been measured in the pH range 2.72-11.04 in what the authors claim are filtered solutions; the concentration of dissolved U(VI) varies surprisingly little, between – 4.72 and – 5.10 in the concentration range studied, but the data have been used to determine equilibrium constants for 17 hydroxide complexes, four carbonate complexes and five solid phases from 14 solubility measurements. The present review does neither accept the experimental data nor the data analysis.

**[2008AMO/GAM]**

The hydrolysis of U(VI) was studied at 75 and 100 °C in 3.6 $mol{\cdot}kg^{-1}$ $LiClO_4$ aqueous solutions with a coulometric-potentiometric technique. The titrations were performed in low – $\log_{10}[H^+]$ range (up to – $\log_{10}[H^+] \approx 3.2$). The authors tested 14 different chemical models to fit the data, including different combinations of (1,1), (1,2), (2,2), (3,2), (3,3),

(4,3), and (5,3) species. The selected model, included only the (2,2), (3,2) and (3,3) species with $\log_{10}{}^{*}\beta_{n,m}$ values at 75 and 100 °C resulted in comparable, or only slightly better, statistical parameters between the different models. It is noted that the concentrations of U(VI) in the experiments were quite high (from 5 mmol·kg$^{-1}$ up to 42 mmol·kg$^{-1}$), and that, with the selected hydrolysis constants, the percentages of the (3,2) and (3,3) species were less than 5 %, while that of the (2,2) species was less than 10 %. Because of the low concentrations of these two complexes, one should expect the constants to have much higher uncertainties than those provided in the paper. The hydrolysis constants from this work are not accepted by this review.

Using the van't Hoff equation with the equilibrium constants obtained at two temperatures (75 and 100 °C) from this work, the enthalpies of hydrolysis ( $\Delta H^{*}_{\mathrm{n,m}}$ ) for the (2,2), (3,2), and (3,3) species were calculated by this review to be + 45.7, + 42.7, and + 73.5 kJ·mol$^{-1}$, respectively. Even though the enthalpy value for the (2,2) species agrees with other values in the literature, this review does not accept the data from [2008AMO/GAM] because the temperature range in this study is narrow and two data points are not sufficient to determine the enthalpy of reaction.

**[2008CHO/JUN]**

Laser-induced breakdown detection technique was used to determine the solubility product of U(VI) hydrous oxide in 0.1 M $NaClO_4$. The hydrolysis constants from [2003GUI/FAN] were used in conjunction with SIT to calculate the speciation of U(VI) and obtain the [ $UO_2^{2+}$ ]. The mean solubility product $\log_{10} K^{\mathrm{o}}_{sp}$ = (23.23 ± 0.04), compared well with the previous NEA TDB selected value of (23.19 ± 0.43) for $UO_3{\cdot}2H_2O$(cr) ([1992GRE/FUG], [2003GUI/FAN]).

**[2008GOF/BRO]**

Ternary U(VI)-peroxide-carbonate complex was identified in the solid phase by crystallography and in alkaline solutions with 0.5 M $K_2CO_3$ by optical UV-VIS absorption spectroscopy. An apparent formation constant of $\log_{10} K'$ = (4.70 ± 0.02) was determined, where $K'$ = ([ $UO_2(O_2)(CO_3)_2^{4-}$ ][ $CO_3^{2-}$ ])/([ $UO_2(CO_3)_3^{4-}$ ][$H_2O_2$]$_{\mathrm{total}}$. The reason of using the apparent constant is probably the unavailability of the p$K_{\mathrm{a1}}$ of $H_2O_2$. The data of this work was re-analysed by this review as follows. Using the p$K_{\mathrm{a1}}$ of $H_2O_2$ (11.5) measured in [2012ZAN/DIB] and the experimental conditions in this work (pH ~ 11.6 ± 0.05), the equilibrium constant for the reaction $UO_2(CO_3)_3^{4-} + HO_2^{-} \rightleftharpoons [UO_2(O_2)(CO_3)_2]^{4-} + CO_3^{2-} + H^{+}$ is estimated to be – (6.6 ± 0.1) by this review. This value is reasonably close to that – (6.3 ± 0.1) obtained by [2012ZAN/DIB2].

Goff *et al.* also report molar absorbtivities for $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$ as well as a detailed description and discussion of the structure.

Also, using the p$K_{a1}$ of $H_2O_2$ (11.5) measured in [2012ZAN/DIB] and the equilibrium constant for $UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons [UO_2(CO_3)_3]^{4-}$ from [2003GUI/FAN], the equilibrium constant for the reaction $UO_2^{2+} + H_2O_2(l) + 2CO_3^{2-} \rightleftharpoons [UO_2(O_2)(CO_3)_2]^{4-} + 2H^+$ is estimated by this review to be (3.74 ± 0.10), in fair agreement with the value of (4.03 ± 0.05) in [2012ZAN/DIB2].

**[2008GOR/FEI]**

Based on measured solubility products of meta-schoepite, compreignecite, Na-compreignecite, becquerelite and clarkeite the corresponding free energies of formation for the phases have been obtained.

**[2008KEE/NOE]**

This is an electrochemical study coupling chemical oxidation in solution with cathodic reduction at $UO_2$(s) according to the following reactions:

$$2U(VI) + H_2O_2 \rightleftharpoons 2U(V) + 2OH^-$$

$$2U(V) + 2e^- \rightleftharpoons 2U(IV)$$

The focus is on mechanisms (that are not very detailed) and there is no useful thermodynamic information.

**[2008MEC/MAR]**

The dissolution of non-irradiated $UO_2$ was studied in the presence of hydrogen peroxide at alkaline pH (11, 11.5, 12, and 13). U(IV) was found to be slowly oxidised to U(VI), forming sodium uranate precipitates ($Na_2U_2O_7$). No ternary U(VI)/peroxide-hydroxide complexes or compounds were identified. No thermodynamic data are obtained.

**[2008MUL/BRE]**

This is a very careful spectroscopic study to characterise the hydroxide and carbonate complexes of U(VI) in solution of micromolar concentrations. FTIR data demonstrated discrepancies between the speciation predicted with current NEA TDB selected equilibrium constants and the speciation suggested by the IR absorption spectra of this work. The major discrepancies are two-fold: (1) the spectral data strongly suggest that the monomeric U(VI) hydrolysed species, $UO_2OH^+$, starts to form at pH as low as 2.5 and dominates the speciation at pH 3, in contradiction to the prediction that the free

aqua $UO_2^{2+}$ ion is the main U(VI) species at pH values below 4; (2) The infrared spectra do not confirm that the triscarbonato U(VI) species, $UO_2(CO_3)_3^{4-}$, is the dominant species at pH ≥ 8 as predicted by the equilibrium data in the current NEA TDB. Instead, IR spectra suggest that mixed hydroxo-carbonate U(VI) species are important in this pH region.

Results of this study clearly point out the importance of conducting more hydrolysis studies at lower U(VI) concentrations (*e.g.*, micromolar).

**[2008OLL]**

This is a "working report", not a paper published in peer-reviewed journals. The solubility of $UO_2$ was studied at high pH (9-13) and reducing conditions. The results show that the solubility is very sensitive to the redox conditions, especially at high pHs. No thermodynamic solubility products were provided. The U concentrations in 0.01 M NaCl were equal to or about one order of magnitude higher than those calculated with the data in [2003GUI/FAN] when including the hydrolysis constants of $U(OH)_4(aq)$ ($\log_{10} {}^*\beta_4^o = -10.0$). It is noted that pH, not the $p[H^+]$, was measured and no attempts were made to convert the measured pH to $p[H^+]$ in these studies.

**[2008TRO/KUL]**

The solubility of $AnO_2(s)$ powders (An = U, Np, and Pu) in simulated groundwater was measured. The reported solubility products are questionable. No thermodynamic data were reported.

**[2009KIM/BAI]**

Comparison of measured and calculated solubility of $UO_2$ and $ThO_2$ in KURT ground water. Data collected at pH 8.1-11.4 and different values of $E_H$. The solubility of U decreases with decreasing $E_H$ and the authors assume that the dissolved uranium is found in oxidation state + 6 (as carbonate complexes).

**[2009KIM/KIM]**

The dissolution of uranium dioxide and precipitation characteristics of the uranyl(VI) ions in alkaline and acid solutions have been studied in the presence of carbonate and hydrogen peroxide. The structure of the different precipitates formed under these conditions have been compared with X-ray diffractometry, SEM and thermogravimetry. The authors discuss the stoichiometry of the solids based on the known solution

chemistry. The morphology of the solids formed is discussed, but there is no new thermodynamic information.

**[2009MUL/FOE]**

U(VI) and Np(VI) hydroxide complexes were characterised by spectroscopy, but no thermodynamic data were generated.

**[2009TEK/ACA]**

Potentiometry was used to determine the hydrolysis constants of $Th^{4+}$, $UO_2^{2+}$, and $Ce^{3+}$ at three temperatures (25, 37 and 45 °C) in 0.1 M KCl.[1] For U(VI), the model included (1,1), (2,2), (4,3), and (5,3) species. The (1,1) species was not observed in any of the three temperatures. The (4,3) species was included in the model at all three temperatures, but the $\log_{10}{}^{*}\beta_{4,3}$ was found to be decreasing as the temperature was increased (– 11.21, – 11.36, – 11.81 for 25 °C, 37 °C, and 45 °C, respectively). This trend is opposite to the trends for all other hydrolysis species such as (1,1), (2,2), and (5,3) in the literature [2004ZAN/DIB], [2008AMO/GAM] where the equilibrium constants increase with increasing temperature, (see Table 1 of [2009TEK/ACA]), suggesting that the hydrolysis constant for the (4,3) complex is doubtful.This conclusion is supported by the observation that exclusion of the (4,3) results in equally good fit between model and experiment as when the complex is included.

The enthalpies of hydrolysis for (2,2) and (5,3), calculated from van't Hoff plots of the equilibrium constants at three temperatures, are significantly higher than those directly determined at 25 °C by calorimetry [2004ZAN/DIB]. The authors made the statement that direct measurement by calorimetry could produce more reliable values of enthalpy. The narrow temperature range (25-45 °C) and the limited number of points (three temperatures) in this work result in large uncertainties of the enthalpy values obtained by van't Hoff plots. It is to be noticed that, even though the hydrolysis constant of $\log_{10}{}^{*}\beta_{4,3}$ were obtained at three temperatures in this study, the authors elected not to present or discuss the enthalpy of hydrolysis for the (4,3) species by van't Hoff plots. This omission supports the assessment of this review that the hydrolysis constants of $\log_{10}{}^{*}\beta_{4,3}$ from this work are not reliable. The enthalpy of hydrolysis for the (4,3) species would be negative ("exothermic") based on the values from this work, which is the opposite to the enthalpies of hydrolysis for all other species and, very likely, is wrong. In fact, since a hydrolysis reaction involves the dissociation of water

[1] Thanks to the e-mail communication with the corresponding author of this work, a confusion on the ionic medium was clarified and it was confirmed that all the measurements were conducted in the ionic medium of 0.1 M KCl. In the paper, it is stated in the experimental section that 1 M KCl was used to adjust the ionic strength of the media, but Table 4 of the paper indicates, mistakenly, the U(VI) titrations were conducted in 1.0 M KCl.

($H_2O \rightleftharpoons H^+ + OH^-$) and the enthalpy of the dissociation of water is highly endothermic (+ 56.7 kJ·mol$^{-1}$ at 25 °C), most of the hydrolysis reactions should be endothermic, including the hydrolysis reactions of (1,1), (2,2), (5,3). In brief, the values of $\log_{10}{}^{*}\beta_{4,3}$ and its trend at different temperatures from this work are determined to be incorrect by this review. Due to above-mentioned shortcomings and the narrow temperature range in this work, this review does not accept the variable-temperature data from [2009TEK/ACA] for further analysis to obtain the enthalpies of hydrolysis.

**[2009TSI/ROI]**

This work discusses the use of electrospray ionisation mass spectrometry to quantify the speciation of U(VI) in aqueous nitrate solutions. Results indicate that the stoichiometry and quantities of the U(VI) species generated in the gas phase are highly dependent on many factors including the concentration of the solution entering the electrospray ionisation source. Attempts were made to propose an approximate relationship between the gas phase speciation and aqueous solution data with very limited success, leading to the conclusion that the U(VI) system is not ideal for such purpose. No thermodynamic data on U(VI) hydrolysis can be extracted from this work.

**[2010KIN/EDW]**

Concentrations of uranium and plutonium in alkaline Savannah River high level waste solutions were measured. No thermodynamic data were reported.

**[2011MEC/MAR]**

Complexation in the U(VI)-$H_2O_2$ system was studied at pH = 12 with spectrophotometry, by varying [U(VI)] at constant [$H_2O_2$], or varying [$H_2O_2$] at constant [U(VI)]. The experimental technique is satisfactory and similar to those in [2012ZAN/DIB] and [2014ZAN/DIB], but the model used to fit the data is different in [2011MEC/MAR] from those in [2012ZAN/DIB] and [2014ZAN/DIB]. The model in [2011MEC/MAR] includes two ternary complexes with the ratios of [$H_2O_2$]/[U(VI)] at 1:1 and 2:1, $[UO_2(O_2)(OH)_2]^{2-}$ and $[UO_2(O_2)_2(OH)_2]^{4-}$, while the model in [2012ZAN/DIB] includes the ternary complexes with the ratio of [$H_2O_2$]/[U(VI)] at 1:1, $[(UO_2)(O_2)(OH)]^-$ and $[(UO_2)_2(O_2)_2(OH)]^-$. Concerns about the data in [2011MEC/MAR] are raised by this review, all related to the analysis of the experimental data.

In the first graphical method, there seems to be an error in the mass balance for hydrogen peroxide. The mass balance in the paper is: $[H_2O_2]_{tot} = [H_2O_2]^0 + [UO_2(O_2)(OH)_2^{2-}]$. This is incorrect because it does not include the concentration of $HO_2^-$ that is the predominant peroxide species at pH = 12. The second evaluation method

in the paper uses the STAR computer program (Ref. 26 in [2011MEC/MAR]), but it is not clear from the text how the molar absorptivities of the hydroxide complexes were obtained. Because the experiments were conducted at constant pH, it is not possible to determine the number of coordinated hydroxide ions in the peroxide complexes.

Due to these concerns, the present review does not accept the chemical model and the associated equilibrium constants reported in [2011MEC/MAR].

**[2011QUI/NGU]**

A combination of three spectroscopic techniques (Raman, IR, and UV-visible spectra) was used to identify the hydrolysed U(VI) species in acidic, moderately basic ($-\log_{10}[H^+]$ = 12-13) and strongly basic solutions ($-\log_{10}[H^+] \geq 13.7$). The spectroscopic features were analysed to assign the hydrolysed species in solutions with different acidity (or basicity). The assignments of (1,1), (2,2) and (5,3) species in acidic regions agree with the generally accepted hydrolysis model. The assignments of (4,1) and (5,1) species and the suggestion of (6,1) species in strongly basic solutions ($-\log_{10}[H^+] \geq 13.7$) are reasonable. However, the interpretation of the spectroscopic features and the assignment of (8,3) and (11,3) species in the moderately basic region ($-\log_{10}[H^+]$ = 12-13) seem more speculative and highly questionable.

**[2012KIM/JUN]**

This is a study focused on identification and characterisation of species in the $Na^+$-U(VI)-$CO_3^{2-}$-$OH^-$-$H_2O_2$ aqueous system by Raman spectroscopy. No thermodynamic data were provided. In general, the assignments of Raman peaks are reasonable (*e.g.*, $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$) and the data supports previous information on the relative stability of $UO_2(CO_3)_3^{4-}$ and $UO_2(O_2)(CO_3)_2^{4-}$. However, some assignments lack justification (*e.g.*, for $UO_2(O_2)_2^{2-}$ which seems to be based on an unrealistic equilibrium constant, $\log_{10}K$ = 72 of unknown origin). This review points out that Raman and other spectroscopic tools are important in analysis of solution chemical data, but require a more comprehensive set of data than in the present study.

**[2012KIM/LEE]**

This study builds on the previous work reported in [2012KIM/JUN] and contains no thermodynamic information for the present review. The observation that the ternary uranyl(VI)-peroxide-carbonates complexes are not stable, especially at elevated temperatures, is consistent with observations in other studies.

**[2012MAL/WAL]**

Mallon *et al.* studied the behaviour of studtite covered electrodes in cyclic voltammetry experiments and noted both oxidation and reduction waves, the latter leading to the formation of $UO_2$(s). The co-precipitation and inclusion of other radionuclides were also investigated. An observation of interest was that the presence of Fe(II) prevented the formation of studtite (not unexpected from a chemical point of view). There are no thermodynamic data reported.

**[2012STE/WAL]**

Electrospray ionisation-mass spectrometry (ESI-MS) was used to detect and quantify the hydrolysed species of U(VI) in aqueous acidic solutions (pH = 3-5.3). For the systems with low [U(VI)] ($5 \times 10^{-5}$ M), the observed distributions of hydrolysed species agree with that predicted by using the equilibrium constants selected by NEA TDB [2003GUI/FAN]. The dimeric $(UO_2)_2(OH)_2^{2+}$ species was detected by ESI-MS for the first time.

**[2012TOK/KIM]**

This paper investigates the concentrations of U(VI) in solutions in equilibrium with different U(VI) minerals. Fitting the solubility data indicates that tyuyamunite ($Ca(UO_2)_2V_2O_8 \cdot 8H_2O$), uranophane ($Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$), and becquerelite ($Ca(UO_2)_6O_4(OH)_6 \cdot 8H_2O$) controlled the U concentrations.

**[2012ZAN/DIB]**

Zanonato *et al.* studied equilibria in the U(VI)-$H_2O_2$-$OH^-$ system in a 0.1 M tetra-methylammonium nitrate ($(TMA)NO_3$) ionic medium at 25 °C using potentiometry and spectrophotometry. This is a three-component system, which complicates the analysis of the data in terms of a unique chemical model; for this reason it is important to use different experimental methods. The model obtained by potentiometry includes two ternary complexes with the ratio of $[H_2O_2]/[U(VI)]$ at 1:1 (or 2:2), $[UO_2(O_2)(OH)]^-$ and $[(UO_2)_2(O_2)_2(OH)]^-$, in addition to the known binary U(VI) hydroxide complexes. The authors report for the reactions (25 °C, 0.1 M $(TMA)NO_3$)):

$$UO_2^{2+} + H_2O + HO_2^- \rightleftharpoons [UO_2(O_2)(OH)]^- + 2H^+ ;\ \log_{10}K = -(2.67 \pm 0.07)$$

$$2UO_2^{2+} + H_2O + 2HO_2^- \rightleftharpoons [(UO_2)_2(O_2)(OH)]^- + 3H^+ ;\ \log_{10}K = (7.16 \pm 0.16).$$

These equilibrium constants were used to calculate absorptivities at 386.6 nm in different test solutions and comparing them with corresponding experimental observations; the agreement was good, providing support for the chosen model and its equilibrium constants. One should note that the experiments were made in test solutions

where the total concentration of hydroxide varied from 31.2 to 3.6 mM. A spectrophotometric titration showed that only the complexes with the ratio U(VI)/peroxide equal to one formed, which is in agreement with the observation in spectrophotometric titrations by [2011MEC/MAR] that the optical absorbance remains nearly constant as the ratio of $[H_2O_2]/[U(VI)]$ is higher than 1.

The equilibrium constants for the two ternary reactions were re-evaluated in [2014ZAN/DIB] by fitting the calorimetric titration data (see [2014ZAN/DIB]).

For the binary U(VI) hydroxide complexes, the best model to fit the experimental data includes (1,1), (2,2), (4,3), (5,3), (6, 3), (7,3), (8,3), and (3,1) species, with the equilibrium constants of $-(5.20 \pm 0.10)$, $-(5.95 \pm 0.03)$, $-(12.25 \pm 0.08)$, $-(16.43 \pm 0.02)$, $-(22.68 \pm 0.23)$, $-(28.95 \pm 0.12)$, $-(38.91 \pm 0.17)$, and $-(18.75 \pm 0.22)$, respectively, at 25 °C in 0.100 M tetramethylammonium nitrate. Using the SIT approach (without taking into consideration of the specific ion interaction term due to the low ionic strength), the equilibrium constants at $I = 0$ were obtained and compared with those available in NEA TDB.

The value of $\log_{10}{}^{*}\beta^{\circ}_{7,3}(298.15\ \mathrm{K}) = -28.53$, from [2012ZAN/DIB] and [2014ZAN/DIB], obtained by potentiometry using tetraalkyl ammonium ionic media, is significantly higher than the value selected by [2003GUI/FAN], $-(32.2 \pm 0.8)$, which is mainly based on the solubility data from [1992SAN/BRU]. In the present potentiometric study, precipitation is avoided by using tetraalkyl ammonium ionic media, where the large cation prevents formation of uranates; however, the large cation may result in an ionic medium effect quite different from the ones usually used.

**[2012ZAN/DIB2]**

This is a potentiometric/spectrophotometric study similar to [2012ZAN/DIB] but investigates the ternary U(VI)-peroxide-carbonate system.

Equilibrium constants of the formation of a series of ternary U(VI)-peroxide-carbonate complexes were determined in $(0.5\ \mathrm{M\ Na^+(ClO_4^-,\ CO_3^{2-})})$, using the notation of $(p, q, r, -2q)$ for the reactions: $p\mathrm{UO_2^{2+}} + q\mathrm{H_2O_2(l)} + r\mathrm{CO_3^{2-}} \rightleftharpoons [(\mathrm{UO_2})_p(\mathrm{O_2})_q(\mathrm{CO_3})_r]^{(2p-2q-2r)} + 2q\mathrm{H^+}$.

The experimental techniques are satisfactory and the analysis of data seems reasonable. This review accepts the conditional values for the reactions of (1,1,1, – 2), (1,1,2, – 2), (2,1,2, – 2), (2,1,4, – 2), (2,2,1, – 4), and (5,5,5, – 10) for the ionic media of $0.5\ \mathrm{M\ Na^+(ClO_4^-,\ CO_3^{2-})}$, but does not make attempts to extrapolate to obtain the values at $I = 0$. Additional studies are needed in order to understand the chemistry in these systems. At present, there is only one other study [2008GOF/BRO] reporting the equilibrium constant for the $\mathrm{UO_2(O_2)(CO_3)_2^{4-}}$ species.

**[2013LUC/BOR]**

The concentration of U(VI) in carbonate-free WIPP (Waste Isolation Pilot Plant)-brine was determined. No new thermodynamic data were obtained.

**[2013MAR/MEC]**

TRLFS was used to study U(VI) speciation at alkaline pH (11-14) in the absence and presence of $H_2O_2$. Very similar equilibrium constants to those obtained by UV/Vis spectroscopy [2011MEC/MAR] were obtained by TRLFS in this study. The reported fluorescence lifetimes for the binary hydroxide complexes are in fair agreement with previous studies [1995ELI/BID]. Fitting of the fluorescence data results in an equilibrium constant of $\log_{10}K = (28.4 \pm 0.4)$ for the reaction $UO_2^{2+} + H_2O_2 + 4OH^- \rightleftharpoons [UO_2(O_2)(OH)_2]^{2-} + 2H_2O$ at the ionic strength of the experiments (either 0.01 or 0.1 M (TMA)Cl—not clear from the paper). After correcting by Debye-Hückel approximation, the value of $\log_{10} K^o = (28.7 \pm 0.4)$ was obtained. This value is in good agreement with that reported in [2011MEC/MAR], $\log_{10} K^o = (28.1 \pm 0.1)$. However, it should be pointed out that concerns on the mass balance of $H_2O_2$ and the major $H_2O_2$ species at high pH (pH > 12) are raised by this review about the model used to fit the data in [2011MEC/MAR] and the value from [2011MEC/MAR] is not accepted by the present review. The same concerns are raised to [2013MAR/MEC]. In addition, it is not clear how sensitive the fluorescence spectra and lifetime values are to the equilibrium constant in the fluorescence study. The equilibrium constants from [2013MAR/MEC] are not accepted by the present review.

**[2013ODO/SCH]**

This is a quantum chemistry study of $F^-$, $OH^-$, $CO_3^{2-}$, $NO_3^-$ and peroxide complexes using DFT. Structures and vibration spectra are reported as well as a discussion of chemical bonding. Reaction energies involving $UO_2(OH_2)_5^{2+}$ and $HO_2^-$ as reactants were also calculated and a solvent effect of more than 150 kcal·mol$^{-1}$ was found, which seems so large as to cast some doubts on the calculated energies. The authors also note that the reaction energy is exothermic for the formation of the complexes $UO_2(O_2)(OH_2)_n$ where $n$ = 2, 3, 4, but strongly endothermic for reactions where complexes with more than one peroxide is coordinated. The formation of ternary peroxide complexes was also investigated, but the reported reaction energies are not useful for the present review.

**[2013PLA/BER]**

The kinetics and mechanism for the formation of studtite at pH ~ 3 in sulfate solutions (reflecting conditions used in industry) were studied. The model is based on the speciation information with equilibrium constants from [1992GRE/FUG] and [2003GUI/FAN]. Data in Fig. 6A of this paper suggests good agreement between experiments and model (within a factor of ten) in the solubility range of $10^{-7}$ to $10^{-2}$ M. There is no other information of interest for the present review.

**[2013PRI/SAM]**

The hydrolysis of U(VI) leading to the formation of colloids was studied by UV-Vis, ATR-FTIR and light scattering. Information on particle size was reported, but there are no thermodynamic data.

**[2013ZAN/DIB]**

Zanonato *et al.* studied equilibria by $H^+$- and $F^-$-potentiometry in the $UO_2^{2+}$-$H_2O_2$- $F^-$/ $OH^-$ systems in a $NaClO_4$ ionic medium. Two models can describe the potentiometric data in this work fairly well, one includes $[(UO_2)_4(O_2)_4F]^-$ and $[(UO_2)_4(O_2)_4F_2]^{2-}$, the other includes $[(UO_2)_4(O_2)_4F]^-$ and $[(UO_2)_5(O_2)_5F_3]^{3-}$. This paper selects the second model as the best to represent the data. The technique is satisfactory and the data analysis seems reasonable. However, since this is the only such study, this review does not accept the values and recommends more studies to be conducted.

The ternary complexes $[(UO_2)_4(O_2)_4F]^-$ and $[(UO_2)_4(O_2)_4F_3]^{3-}$ might be the building blocks in the formation of the clusters $[Na_6(OH_2)_8]@[UO_2(O_2)F]_{24}^{18-}$ identified in the solid state. In the absence of fluoride, a corresponding hydroxide polymer is formed, $[Na_6(OH_2)_8]@[UO_2(O_2)OH]_{24}^{18-}$, suggesting that a hydroxide polymer, $[(UO_2)_4(O_2)_4(OH)_n]^{n-}$ is present in solutions in the presence of $Na^+$. It is also important to note that, in contrast to the previous observation of predominant monomeric $UO_2(O_2)OH^-$ species in the $(TMA)NO_3$ media [2012ZAN/DIB], no significant amounts of the corresponding monomeric species such as $UO_2(O_2)F^-$ was found to be present in the $NaClO_4$ ionic medium in the present study.

**[2014KON/BEN]**

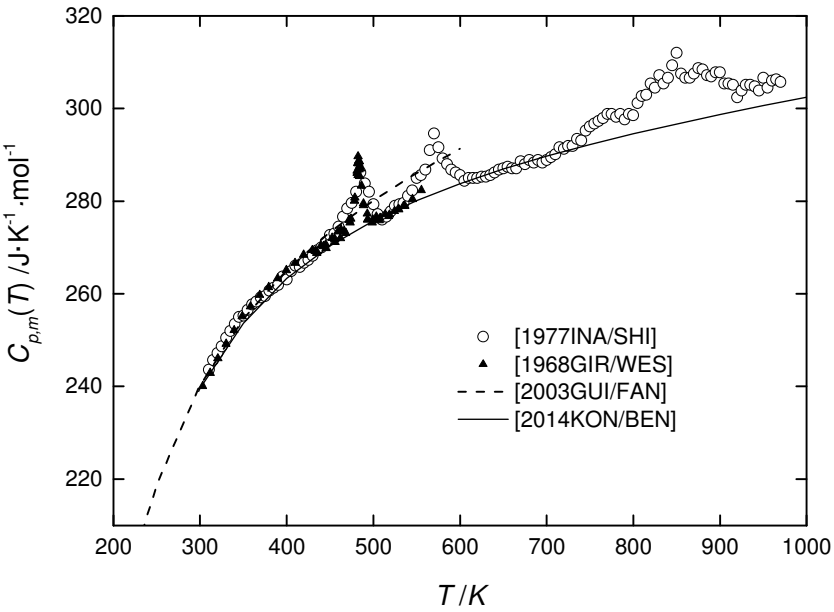
New experimental data considered for this review article for americium oxides includes new heat capacity data by [2011NIS/ITO]. A model for the Am-O phase diagram is reported by [2003THI/KON] and improved by [2011GOT/COL], using the data of [2011NIS/ITO] and the vaporisation behaviour from [2011GOT/COL3]. The data by [2011NIS/ITO] is accepted by the authors, although a higher value for the constraint at

$C_{p,\mathrm{m}}^{\mathrm{o}}(\mathrm{AmO_2}, 298.15\,\mathrm{K})$ is set to 64.3 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ as derived by [2004KON] as it better fits the trends of the lanthanide and actinide oxides and accounts for experimental error due to the encapsulation of the samples in a platinum container. The standard entropy value for $AmO_2$ from [2004KON] is accepted here, which leads to a slight decrease in the Gibbs energy of formation selected by the review, although still within the initial experimental error. Additionally for the $Am_2O_3$ sesquioxide, a slight adjustment is made to the standard entropy based on a more sound theoretical evaluation of the lanthanide series analogue in [2005KON/MIT] that slightly increases the lattice contribution to the entropy due to structural differences. The heat capacity data of [2011NIS/ITO] are also fitted with a correction for the room temperature values as is done in $AmO_2$. For the $UO_2$, the authors use mostly the same papers as the last review by [2000FIN], as discussed in [2003GUI/FAN], although the addition of previously unused data [1987INA/NAI] and the [2001AMA/UNE] are included, that complete previously missing data of [2000FIN] from 1000-2000 K. This leads to a more complete fit that is in relatively good agreement with [2000FIN] until 1300 K, where deviations in the fitted heat capacity are up to 3 % higher for (1300 K < $T$ < 2250 K) in [2014KON/BEN] and then at higher temperatures, the weighted fit from [1993HIE/HYL], [1993RON/HIE] are up to 3 % lower from 2550-3000 K. We retain the more complete dataset of [2014KON/BEN] for the $UO_2$ heat capacity in this review. Otherwise, for $UO_2$, γ-$UO_3$, $UO_{2.6667}$ = 1/3 $U_3O_8$, and $UO_{2.25}$ = ¼ $U_4O_9$ the following thermodynamic values remain unchanged from [1992GRE/FUG] and [2003GUI/FAN]:

$$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr}, 298.15\,\mathrm{K}),\ S_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr}, 298.15\,\mathrm{K}),\ C_{p,\mathrm{m}}^{\mathrm{o}}(298.15\,\mathrm{K}),\ \text{and}\ \Delta_{\mathrm{f}} G_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr}, 298.15\,\mathrm{K}).$$

The heat capacity equation for $U_4O_9$ remains unchanged. $U_3O_8$ or $UO_{2.6667}$, as discussed by [1992GRE/FUG], fits the same data as in [2014KON/BEN], however Figure A-3 indicates up to 3 % deviation from both experimental studies [1977INA/SHI] and [1968GIR/WES], while the fit by [2014KON/BEN] is within 0.5 % of the original experimental data, which we therefore retain.

Figure A-3: Heat capacity data of $U_3O_8$. Experimental data of [1968GIR/WES] and [1977INA/SHI] and fitting equations by [2003GUI/FAN] and [2014KON/BEN].




**[2014MOL/ROS]**

Theoretical calculations and XAS experiments were conducted to reveal the speciation of U(VI) and the exchange mechanism of the "yl" oxygen between $UO_2(OH)_4^{2-}$ and $UO_2(OH)_5^{3-}$.

**[2014TIF/GIL]**

A review of solid state clusters, with no thermodynamic data of interest for the present review.

**[2014ZAN/DIB]**

The major objective of this study is to use calorimetry to determine the enthalpy of the formation of two ternary U(VI)-peroxide-hydroxide complexes, $[UO_2(OH)(O_2)]^-$ and $[(UO_2)_2(OH)(O_2)_2]^-$, the equilibrium constants of which were reported in a previous publication [2012ZAN/DIB]. Enthalpies of hydrolysis for a few binary U(VI)-

hydroxide complexes were also obtained in the data analysis and compared with the data in NEA TDB.

For the binary U(VI)-hydroxide complexes, the previous potentiometric data [2012ZAN/DIB] were re-interpreted by including an additional species, $UO_2(OH)_4^{2-}$. A new set of hydrolysis constants were obtained, all of which are either identical to or slightly different from those in [2012ZAN/DIB]. The new set of hydrolysis constants was used in the analysis of the calorimetric data to obtain the enthalpy values. The enthalpies of hydrolysis for the (1,1), (2,2) and (5,3) species in 0.1 M (TMA)$NO_3$ from this work are in excellent agreement with those for the same species in 0.1 M (TEA)$ClO_4$ from [2004ZAN/DIB], and in satisfactory agreement with those for the same species in 0.5 M $NaNO_3$ [1962BAE/MEY] and 3.0 M $NaClO_4$ [1968ARN/SCH] from previous studies.

In the studies of the ternary U(VI)-$OH^-$-$H_2O_2$ complexes in 0.1 M TMA($NO_3$), Zanonato *et al.* also re-visited the binary U(VI)-$OH^-$ system and fitted the potentiometric titration data up to pH 11.5 by including the mononuclear $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$ complexes ([2012ZAN/DIB], [2014ZAN/DIB]). The equilibrium constants at $T$ = 298.15 K and $I$ = 0.1 M TMA($NO_3$), $\log_{10}{}^*\beta_{3,1}$ and $\log_{10}{}^*\beta_{4,1}$, were $-(18.81 \pm 0.17)$ and $-(31.25 \pm 0.50)$, respectively. These values were converted to infinite dilution by ignoring the ion interaction term ($\Delta\varepsilon \times I_m$) due to the low ionic strength and the unavailability of the ion interaction parameters such as $\varepsilon(TMA^+, UO_2(OH)_3^-)$ and $\varepsilon(TMA^+, UO_2(OH)_4^{2-})$. The values of $\log_{10}{}^*\beta^o_{3,1}$ and $\log_{10}{}^*\beta^o_{4,1}$ were calculated to be $-(18.81 \pm 0.17)$ and $-(31.71 \pm 0.50)$ in [2014ZAN/DIB]. Due to the shortcomings in the analysis of medium effects in tetraalkyl ammonium media discussed for [2012ZAN/DIB] in Appendix A, the value of $\log_{10}{}^*\beta^o_{3,1}$ from [2014ZAN/DIB], which is significantly higher than the selected value by previous NEA TDB review, is not accepted by the current review.

The value of $\log_{10}{}^*\beta^o_{7,3}$ (298.15 K) = $-28.53$ obtained in [2014ZAN/DIB] is essentially identical to that from [2012ZAN/DIB]. As discussed for [2012ZAN/DIB] in Appendix A, the large cation may result in an ionic medium quite different from the ones usually used, and the ion interaction parameters for this ionic medium are not available. In addition, using the value of $\log_{10}{}^*\beta^o_{7,3}$ from [2012ZAN/DIB] and [2014ZAN/DIB], the solubility of $UO_3 \cdot 2H_2O$(cr) and $Na_2U_2O_7 \cdot 2H_2O$(cr) in 0.51 m NaCl was not well described. Therefore, the value of $\log_{10}{}^*\beta^o_{7,3}$ (298.15 K) from [2014ZAN/DIB] is not selected by this review. More discussions are provided in the main text of Chapter 9.

**[2016DRO/BAU]**

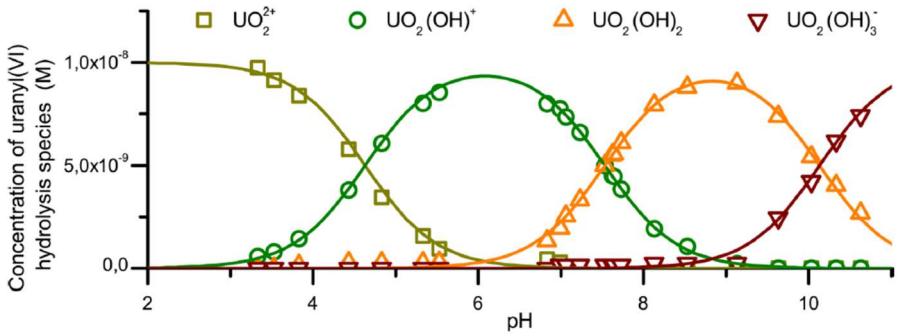
Laser-induced fluorescence spectroscopy was used to investigate the hydrolysis of U(VI) in 1.0 M $NaClO_4$ solutions at an extremely low total concentration, $[U(VI)]_{tot}$ =

$1 \times 10^{-8}$ M. The authors report data from a pH range 3 to 10.5 and precautions were taken to avoid the interference of carbon dioxide by conducting the experiments in a $N_2$-atmosphere glove box. The experiments were made as single-point measurements, where a test solution was prepared at 25 °C and its pH measured; the solution was then transferred to the spectroscopic device where the spectral data were collected at 1 °C. Analysis of the experiment requires:

- Analysis of the spectral data, involving deconvolution of the fluorescence spectra into components for each complex present, this procedure is described in detail in the publication and the supporting information;
- Accurate measurement of the pH, or rather – $\log_{10}[H^+]$, that requires a calibration of the pH-electrode. The authors have made this calibration at 25 °C and then assumed this to be valid also at 1°C (this procedure was not clear from their text, but has been provided to us in a discussion with them). This assumption is not correct and will result in a systematic error in the measured pH values.

The measurements have been made in a pH-range with small buffer capacity, which makes them sensitive to protolytic impurities, but we have been convinced that this did not have a detrimental effect on the results, assuming an uncertainty of 0.05 to 0.10 pH units. Figure A-4, taken from [2016DRO/BAU], is useful for the following discussion:

Figure A-4: Experimental data of the concentration of the different U(VI) hydroxide complexes as a function of the measured pH at 1 °C. (Reprinted with permission from *Anal. Chem.* **2016**, *88,* 3548. Copyright (2016) American Chemical Society).




The equilibrium constants at this temperature can be determined directly from Figure A-4: $\log_{10}{}^{*}\beta_1 = \log_{10}([UO_2OH^+]/[UO_2^{2+}]) + pH$; it is clear that the overall equilibrium constants $\log_{10}{}^{*}\beta_n$ are directly affected if there is a systematic error in pH and the procedure used by the authors is far from clear.

However, the stepwise constants, $\log_{10}{}^{*}K_2$ and $\log_{10}{}^{*}K_3$ are not affected by a constant error in the pH measurement and can therefore be used for comparison with the corresponding selected data from potentiometry. The values from spectroscopy and potentiometry are, $\log_{10}{}^{*}K_2$ (spectroscopy) = – (7.6 ± 0.6), and $\log_{10}{}^{*}K_2$ (potentiometry) = – (7.2 ± 0.32), respectively; these values are consistent within their estimated uncertainty. However, the corresponding constants $\log_{10}{}^{*}\beta_1$ are significantly different, $\log_{10}{}^{*}\beta_1$ (spectroscopy) = – (4.6 ± 0.3) and $\log_{10}{}^{*}\beta_1$ (potentiometry) = – (5.9 ± 0.3), respectively. This suggests that there is a constant error in the reported pH values of – 1.3 units and that the pH values in Figure A-4 should be increased by this amount. Doing this gives $\log_{10}{}^{*}\beta_1$ (spectroscopy) = – (5.9 ± 0.3), $\log_{10}{}^{*}\beta_2$ (spectroscopy) = – (13.5 ± 0.7) and $\log_{10}{}^{*}\beta_3$ (spectroscopy) = – (23.6 ± 0.9), all at 1 °C. Recalculation of these data to 25 °C gives $\log_{10}{}^{*}\beta_1^{o}$ (spectroscopy) = – (5.2 ± 0.3), $\log_{10}{}^{*}\beta_2^{o}$ (spectroscopy) = – (12.5 ± 0.7) and $\log_{10}{}^{*}\beta_3^{o}$ (spectroscopy) = – (21.1 ± 0.9). These values are in excellent agreement with the selected values in [2003GUI/FAN], $\log_{10}{}^{*}\beta_1^{o}$ = – (5.25 ± 0.24), $\log_{10}{}^{*}\beta_2^{o}$ = – (12.15 ± 0.07) and $\log_{10}{}^{*}\beta_3^{o}$ = – (20.25 ± 0.42), but with larger uncertainties, than the ones reported in previous NEA reviews.

To obtain additional support for this statement we asked professor Pier-Luigi Zanonato at University of Padova to test if the equilibrium constants proposed by Drobot *et al.* were consistent with his experimental data obtained by potentiometry; his analysis, reported at the end of this review, demonstrate that they are not.

To conclude: This is an important study because it allows determination of equilibrium constants of mononuclear complexes, $[UO_2(OH)_n]^{2-n}$ in systems where no polynuclear species are present. However, the reported equilibrium constants in [2016DRO/BAU] have to be corrected for a systematic error in pH and if this is done, the equilibrium constants are in good agreement with those obtained by potentiometry. An important implication of this finding is that it confirms that accurate values of equilibrium constants for mononuclear complexes can be obtained by potentiometry, even in the presence of much larger amounts of polynuclear complexes.

The present review has asked the authors for a comment on their uncertainty estimates and we have included their response below:

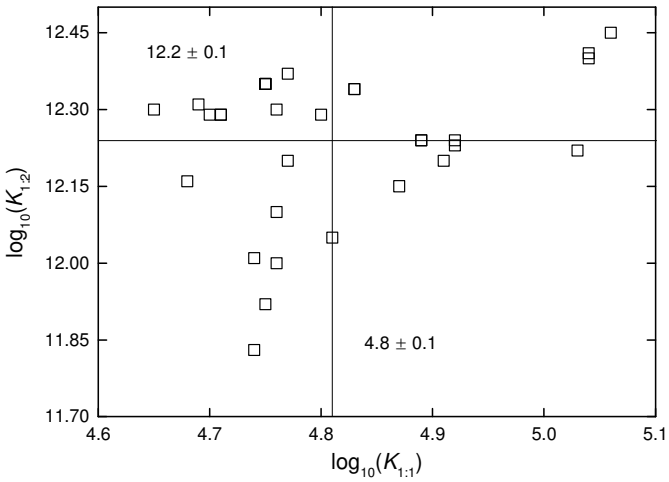
***Assessment of parameter errors and parameter correlation***

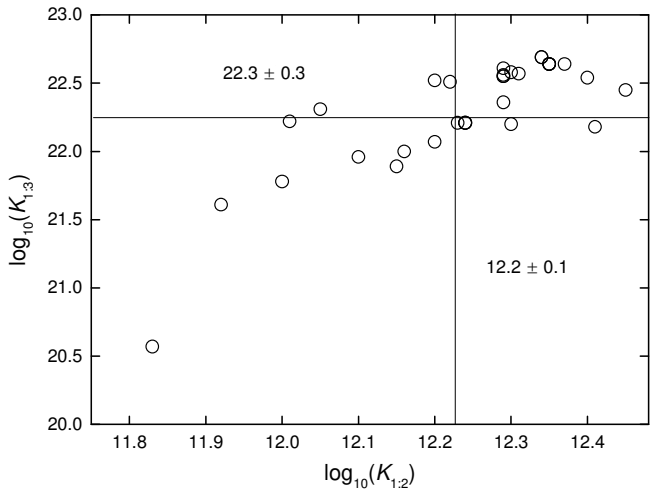
*The data processing as described in the publication has been repeated, based on the Jackknife resampling method (Tuckey 1958) and the result is given in Figure A-5(a). But this time all intermediate $log_{10}K$ sets have been screened to filter out those sets that formally deliver $log_{10}K$ values and simultaneously pure component emission spectra that show artefacts or an unsatisfactorily explained variance (Sum-of-squares > 3*Sum-of-squares of the best data deconvolution). Consequently, the derived*

*conditional* $\log_{10} \beta_{n,1}$ *values in the figures below do not shift significantly except for the 1.1 complex that still remains within the originally published error margins. The newly derived uncertainties represent one sigma.*

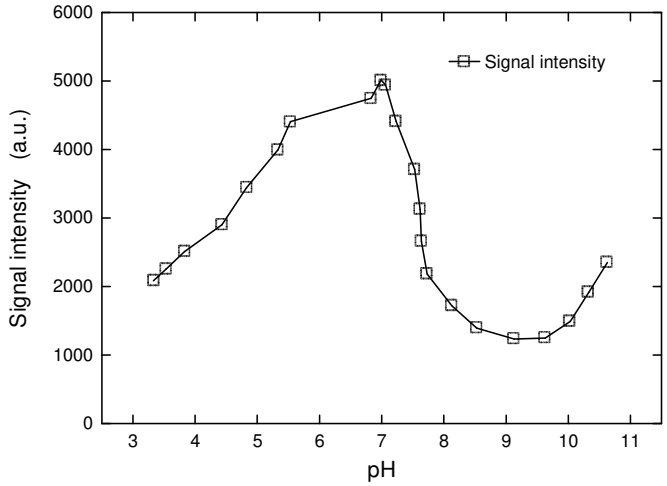
Figure A-5: Analysis of parameter correlation in Figure A-5(a) and uncertainty estimates Figure A-5(b) by Drobot *et al.*

*(a)*



*(b)*




*As a by-product, the parameter correlation is visualised in Figure A-5(a). Whereas there is no significant correlation between* $\log_{10} K_{1:1}$ *and* $\log_{10} K_{1:2}$, *one observes a slight linear dependence between* $\log_{10} K_{1:2}$ *and* $\log_{10} K_{1:3}$. *However, this is difficult to judge because for the majority of parameter sets published for subsequent hydrolysis steps no such correlations have been investigated (or at least published) at all.*

***Correlation between parameters and optical signal intensities***

*Figure A-5(b), shows the integrated intensity of the fluorescence signal as a function of pH. Each single spectrum has been normalised to the respective signal intensity before data processing in order to reach a rather homogeneous weighing of all spectra. A correlation between signal intensities (as representatives of the photon yield) and parameter values could not be observed. In addition, before re-calculating the speciation, this normalisation has been reversed to avoid any artefacts (see Fig. 2 of the paper & page 43 of the thesis).*

We have compared the analyses of experimental potentiometric data from [2004ZAN/DIB] using both their equilibrium constants reported in Table A-8 (Figure A-6) and using the equilibrium constants of Drobot *et al.* [2016DRO/BAU] (Table A-9) by using Hyperquad 2003.

Table A-8: Equilibrium constants $\log_{10}{}^{*}\beta$ for the formation of U(VI) hydroxide complexes, $m\mathrm{UO}_2^{2+} + n\mathrm{H}_2\mathrm{O(l)} \rightleftharpoons (\mathrm{UO}_2)_m(\mathrm{OH})_n^{(2m-n)} + n\mathrm{H}^+$, from [2004ZAN/DIB]. (Chi-squared = 73.63 sigma = 0.7049).

| | Value and relative standard deviation | $\log_{10}\beta$ and standard deviation | Complex |
|---|---|---|---|
| Beta A constant | $0.1660 \times 10^{-13}$ | – 13.7800 | – 1 0 |
| Beta B refined | $(0.4070 \times 10^{-16} \pm 0.0105)$ | – (16.3904 ± 0.0046) | – 5 3 |
| Beta C refined | $(0.1418 \times 10^{-5} \pm 0.0139)$ | – (5.8483 ± 0.0060) | – 2 2 |
| Beta D refined | $(0.1299 \times 10^{-5} \pm 0.3618)$ | – (5.8863 ± 0.1571) | – 1 1 |

Figure A-6: Speciation of the uranyl(VI) hydroxide system calculated using equilibrium constants in Table A-8. The difference between calculated and measured pH in [2004ZAN/DIB] shows the agreement between experimental data and model and the relative amounts of $UO_2^{2+}$ (green), $UO_2OH^+$ (dark blue), $(UO_2)_2(OH)_2^{2+}$ (green) and $(UO_2)_3(OH)_5^+$ (red).

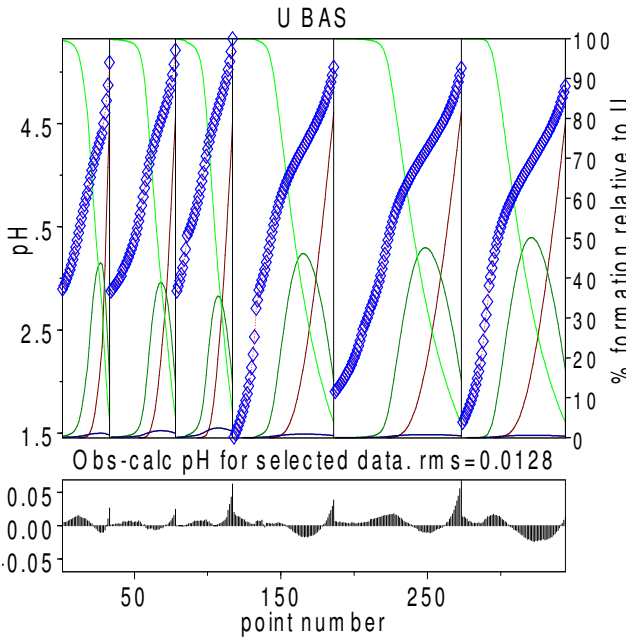
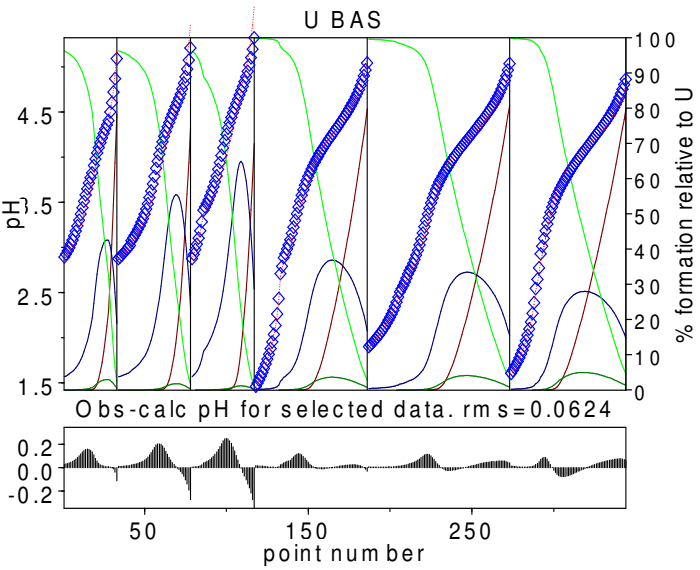


Table A-9: Equilibrium constants $\log_{10}{}^{*}\beta$ for the formation of U(VI) hydroxide as re-evaluated by Professor Pier-Luigi Zanonato based on experimental data in [2004ZAN/DIB] and with the equilibrium constant for the species (1,1) fixed with the value determined by [2016DRO/BAU] (– 4.10 – 0.18 = – 4.28). (Chi-squared = 170.19 sigma = 4.2262).

| | Value and relative standard deviation | $\log_{10}\beta$ and standard deviation | Complex |
|---|---|---|---|
| Beta A constant | $0.1660 \times 10^{-13}$ | – 13.7800 | – 1 0 |
| Beta B refined | $(0.5021 \times 10^{-16} \pm 0.063)$ | – (16.2992 ± 0.0275) | – 5 3 |
| Beta C refined | $(0.1053 \times 10^{-6} \pm 0.508)$ | – (6.9776 ± 0.2206) | – 2 2 |
| Beta D refined | $0.5248 \times 10^{-4}$ | – 4.2800 | – 1 1 |

Using the equilibrium constants in Table A-9, it was not possible to obtain convergence in the least-squares refinement and it is obvious that the equilibrium constant from [2016DRO/BAU] results in significant differences between experimental and calculated data that can amount to nearly 0.2 p[$H^+$] units and this is another reason why our revised data are selected instead of those from [2016DRO/BAU].

Figure A-7: Speciation of the uranyl(VI) hydroxide system calculated using equilibrium constants in Table A-9. The difference between calculated and measured pH in [2004ZAN/DIB] shows that the agreement between experimental data and model is poor.



**[2017ALT/YAL]**

The solubility, thermodynamics and phase stability of hydrous uranium(VI) oxides have been extensively discussed in [1992GRE/FUG] and [2003GUI/FAN]. Altmaier *et al.* give an authoritative review of previous studies that is based on their new experimental findings, information that provides clarification on a number of points that were not clear in the previous NEA reviews.

This is the first study where an in-depth phase characterisation of $UO_3{\cdot}2H_2O$(cr) and $Na_2U_2O_7{\cdot}H_2O$(cr) has been made, comprising XRD, SEM, elemental analysis, and an estimate of particle size. These phases were used in solubility experiments in the p[$H^+$]-range 4-14.5, using NaCl test solutions with molality, 0.03, 0.51, 2.64 and 5.61 m; all experiments were made at a temperature of (22 ± 2) °C. The experimental conditions and the procedures used to analyse the data are described in detail. The analysis of the experimental data requires a discussion and selection of hydrolysis constants and ion interaction parameters that are listed in Table A-10.

Table A-10: Hydrolysis constants[a] at $I$ = 0 and 25 °C considered in [2017ALT/YAL], and SIT coefficients from [2003GUI/FAN] obtained in acidic or near-neutral solutions.

| Species, $i$ | ($xy$) | $\log_{10}{}^{*}\beta^{\circ}_{(xy)}$ | $j$ | $\varepsilon(i, j)$ /kg·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2OH^+$ | (11) | – (5.25 ± 0.24) | $Cl^-$ | (0.46 ± 0.03) |
| $UO_2(OH)_2$(aq) | (12) | – (12.15 ± 0.17) | | |
| $(UO_2)_2OH^{3+}$ | (21) | – (2.7 ± 1.0) | | |
| $(UO_2)_2(OH)_2^{2+}$ | (22) | – (5.62 ± 0.04) | $Cl^-$ | (0.69 ± 0.07) |
| $(UO_2)_3(OH)_4^{2+}$ | (34) | – (11.90 ± 0.30) | $Cl^-$ | (0.50 ± 0.18) |
| $(UO_2)_3(OH)_5^{+}$ | (35) | – (15.55 ± 0.12) | $Cl^-$ | (0.81 ± 0.17) |
| $(UO_2)_3(OH)_7^{-}$ | (37) | – (32.20 ± 0.80) | | |
| $(UO_2)_4(OH)_7^{+}$ | (47) | – (21.9 ± 1.0) | | |

(a) $\log_{10}{}^{*}\beta^{\circ}_{(xy)}$ for the reactions: $x UO_2^{2+} + y H_2O(l) \rightleftharpoons (UO_2)_x(OH)_y^{2x-y} + y H^+$ .

Altmaier *et al.* have accepted the hydrolysis constants at zero ionic strength selected in [2003GUI/FAN], but not the reported ion interaction coefficients that are needed to recalculate the selected constants to conditional constants in the various test solutions. The SIT coefficients selected by NEA have been obtained by taking formation of $UO_2Cl^+$ and $UO_2Cl_2$(aq) into account and assuming that the interaction coefficients between $UO_2^{2+}$ and the various hydroxide complexes and $Cl^-$ and $ClO_4^-$ are the same. This choice can be debated (*cf.* the discussion in the App. A reviews of [2002DES/GIA]) and Altmaier *et al.* prefers not to include the chloride complexes, and instead replace them with a specific $\varepsilon(UO_2^{2+}, Cl^-)$ constant equal to (0.21 ± 0.02) kg·mol$^{-1}$; in our opinion the two methods are equivalent (but it is well established that uranyl(VI) chloride complexes *are* formed). The change of the interaction coefficient for $UO_2^{2+}$ listed in Table A-11 will of course result in significant changes in the Δε-values for the different reactions. The equilibrium constants in Table A-10 are the same as those selected in the present review (Table 9-7 in main text) and those discussed in [2002DES/GIA].

Table A-11: Ion-interaction coefficients for $UO_2^{2+}$ and uranyl hydroxide complexes from [2017ALT/YAL].

| U(VI) species | | SIT coefficients | |
|---|---|---|---|
| *I* | *j* | $\varepsilon(i, j)$ | References |
| $UO_2^{2+}$ | $Cl^-$ | $(0.21 \pm 0.02)^{(a)}$ | [1980CIA] |
| $UO_2OH^+$ | $Cl^-$ | $(0.10 \pm 0.10)^{(b)}$ | [2017ALT/YAL] |
| $(UO_2)_2(OH)_2^{2+}$ | $Cl^-$ | $(0.30 \pm 0.06)^{(c)}$ | [2017ALT/YAL] |
| $(UO_2)_3(OH)_4^{2+}$ | $Cl^-$ | $-(0.07 \pm 0.17)^{(c)}$ | [2017ALT/YAL] |
| $(UO_2)_3(OH)_5^+$ | $Cl^-$ | $(0.24 \pm 0.15)^{(c)}$ | [2017ALT/YAL] |
| $(UO_2)_4(OH)_7^+$ | $Cl^-$ | $(0.17 \pm 0.18)^{(c)}$ | [2017ALT/YAL] |
| $UO_2(OH)_3^-$ | $Na^+$ | $-(0.24 \pm 0.09)$ | [2017ALT/YAL] |
| $UO_2(OH)_4^{2-}$ | $Na^+$ | $(0.01 \pm 0.04)$ | [2017ALT/YAL] |
| $(UO_2)_3(OH)_7^-$ | $Na^+$ | $-(0.24 \pm 0.09)^{(d)}$ | [2017ALT/YAL] |
| $UO_2(OH)_2(aq)$ | $Na^+$, $Cl^-$ | 0 | (e) |

(a) This value given in [1980CIA] includes chloride complexation treated as strong ion-ion interaction;
(b) Estimated using the approach in [1997GRE/PLY2] or from typical values for the corresponding valence type;
(c) Determined in [2017ALT/YAL] from potentiometric data reported elsewhere ([2002DES/GIA], [1962RUS/JOH], [1963DUS/SIL], [1963DUS/SIL2]) considering chloride complexation as strong ion-ion interaction;
(d) set equal to $\varepsilon(UO_2(OH)_3^-, Na^+)$;
(e) by definition in SIT.

Based on the experimental solubilities, selected equilibrium model and ion-interaction coefficients, Altmaier *et al.* have obtained the solubility and hydrolysis constants listed in Table A-12.

Table A-12: Solubility and hydrolysis constants at $I = 0$ and 25 °C for the $U^{VI} - Na^+$-$H^+$-$Cl^-$-$OH^-$ – $H_2O$(l) system. Only the new equilibrium constants from [2017ALT/YAL] are listed. The remaining ones from acidic to near neutral solutions are given in Table A-10.

| Solid phase | $\log_{10} K_s^o$ | $\log_{10}{}^* K_s^o$ |
|---|---|---|
| $UO_3 \cdot 2H_2O$(cr) | $-(22.65 \pm 0.13)$ | $(5.35 \pm 0.13)$ |
| $1/2Na_2U_2O_7 \cdot H_2O$(cr) | $-(29.80 \pm 0.20)$ | $(12.20 \pm 0.20)$ |
| Hydrolysis species | $\log_{10} \beta_{p,q}^o$ | $\log_{10}{}^* \beta_{p,q}^o$ |
| $UO_2(OH)_3^-$ | $(21.3 \pm 0.4)$ | $-(20.7 \pm 0.4)$ |
| $UO_2(OH)_4^{2-}$ | $(24.1 \pm 0.2)$ | $-(31.9 \pm 0.2)$ |

The accuracy of the reported equilibrium data is strongly dependent on the measured $p[H^+]$ for which the authors report an uncertainty of ± 0.05, except in the region where two phases are present.

The present review considers the solubility constant for $UO_3 \cdot 2H_2O$(cr) more reliable than the ones from previous studies, but we note that most of the solubility constants discussed in [2003GUI/FAN] are in good agreement with $\log_{10}{}^* K_s^o = (5.35 \pm 0.13)$ from [2017ALT/YAL]. It should be noted that the solid phase characterisation conducted in this study is by far the most comprehensive one. The

minimum particle size of the schoepite phase used by Altmaier *et al.* is about 100 nm and this indicates that the particle size will only have a small effect on the measured solubility (*cf.* [2008RAN/FUG], section VII.4.2.3, pp. 194-197). The value from Altmaier *et al.* is consistent with the value obtained by calorimetry, $\log_{10}{}^{*}K_{s}^{o} = (4.81 \pm 0.43)$, within the rather large uncertainty of the latter. The Gibbs energy of formation calculated from calorimetry and the solubility constant are $\Delta_f G_m^o(UO_3{\cdot}2H_2O, cr) = -(1636.506 \pm 1.705)$ kJ·mol$^{-1}$ and $\Delta_f G_m^o(UO_3{\cdot}2H_2O, cr) = -(1633.43 \pm 1.86)$ kJ·mol$^{-1}$, respectively. The molar entropy $S_m^o(UO_3{\cdot}2H_2O, cr, 298.15\ K) = (188.54 \pm 0.38)$ J·K$^{-1}$·mol$^{-1}$ is more accurate than both the enthalpy and Gibbs energy of formation and should be used in the Gibbs-Helmholtz equation. In the present review we have preferred to use the enthalpy of formation and molar entropy to calculate the Gibbs energy of formation.

The solubility constant reported in [2017ALT/YAL] for $Na_2U_2O_7{\cdot}H_2O(cr)$ has been calculated from the solubility constant of $UO_3{\cdot}2H_2O(cr)$, $\log_{10}{}^{*}K_{s}^{o} = (5.35 \pm 0.13)$ and the p[H$^+$] value where the two solids are in equilibrium. The variation in p[H$^+$] in the cross-over region between the solubility curves for the two phases suggests that equilibrium between them is not complete, but an average value of the p[H$^+$] in this region can nevertheless be used for a reliable location. Based on this, Altmaier *et al.* obtain the conditional equilibrium constants for Reaction (A.7), which recalculated to zero ionic strength is $\log_{10}{}^{*}K_{s}^{o} = (12.20 \pm 0.20)$.

$$1/2Na_2U_2O_7{\cdot}H_2O(cr) + 3H^+ \rightleftharpoons Na^+ + UO_2^{2+} + 2H_2O(l) \qquad (A.7)$$

Based on their solubility data in the alkaline pH region and slope analysis, Altmaier *et al.* propose that Reactions (A.8) and (A.9) control the solubility of U(VI) within $8 \le p[H^+] \le 14.5$ and report the corresponding solubility constants, $\log_{10} K_{s,(3,1)}^{o}$ and $\log_{10} K_{s,(4,1)}^{o}$:

$$0.5Na_2U_2O_7 \cdot H_2O(cr) + H_2O(l) \rightleftharpoons UO_2(OH)_3^- + Na^+ \qquad (A.8)$$

$$0.5Na_2U_2O_7 \cdot H_2O(cr) + H_2O(l) + OH^- \rightleftharpoons UO_2(OH)_4^{2-} + Na^+ \qquad (A.9)$$

Using these solubility constants and the solubility product $\log_{10} K_s^o(0.5\ Na_2U_2O_7{\cdot}H_2O, cr)$, the authors determined the hydrolysis constants for the (3,1) and (4,1) complexes, as summarised in Table A-12.

We have compared the equilibrium constants for formation of $UO_2(OH)_3^-$ in [2017ALT/YAL] with the ones from the TRLFS study in [2016DRO/BAU] and the selected values in [2003GUI/FAN], we have made the same comparison for the $UO_2(OH)_4^{2-}$ complex:

Table A-13: Equilibrium constants, $\log_{10}{}^{*}\beta^{o}_{3,1}$ and $\log_{10}{}^{*}\beta^{o}_{4,1}$ for the formation of the hydrolisis species $UO_2(OH)_3^-$ and $UO_2(OH)_4^{2-}$.

| $\log_{10}{}^{*}\beta^{o}_{3,1}$ | $\log_{10}{}^{*}\beta^{o}_{4,1}$ | Reference |
|---|---|---|
| – (21.1 ± 0.9) | – | [2016DRO/BAU] |
| – (20.4 ± 0.4) | – (31.9 ± 0.2) | [2017ALT/YAL] |
| – (20.25 ± 0.42) | – (32.4 ± 0.68) | [2003GUI/FAN] |

The equilibrium constants are in fairly good agreement in all studies, but in our review of [2016DRO/BAU] we noted a large difference between their equilibrium constants for the (1,1) and (2,1) complexes and the selected values in [2003GUI/FAN] and we cannot exclude that the agreement in $\log_{10}{}^{*}\beta^{o}_{3,1}$ noted in Table A-13 is accidental.

## A-1.3 Uranium halides; solids, complexes and gases

**[2002HUN/BOO]**

This paper describes an extensive thermodynamic study of UNCl(cr). The sample was synthesised by reacting powdered uranium sesquinitride ($U_2N_3$) and uranium trichloride ($UCl_3$). The enthalpy of formation has been measured using solution calorimetry measurements in (0.76 mol·dm$^{-3}$ HCl + 0.03 mol·dm$^{-3}$ $FeCl_3$). The standard entropy has been derived from adiabatic calorimetry measurements from 5 to 430 K. The measurements showed a λ-type anomaly, observed with a maximum at 30.8 K, which has been found to be of antiferro-magnetic nature using magnetisation measurements [2005NAK/AKA]. A detailed analysis of the transition entropy has not been reported, and in absence of experimental data, it is difficult to judge whether the value is close to the theoretical value expected for the $U^{4+}$ ion. The high-temperature heat capacity has been measured by DSC (300-1100 K) and drop calorimetry (399-933 K), the results being in good agreement.

**[2002PRI/SCH]**

*Ab initio* quantum chemical methods were used to calculate the electronic energy, the molar entropy and heat capacity of gaseous $UO_2F_2$, $UO_2(OH)_2$, $UF_6$ and $UO_3$ as shown in Table A-14, where the values selected in [2003GUI/FAN] are given in parenthesis.

Table A-14: Molar entropies and isobaric heat capacities at 298.15 K.

| Compound | $UO_2F_2$(g) | $UF_6$(g) | $UO_3$(g) | $UO_2(OH)_2$(g) |
|---|---|---|---|---|
| $S^o_m$ /J·K$^{-1}$·mol$^{-1}$ | 334 | 377 | 301 | 349 |
| | (342.7 ± 6.0) | (376.3 ± 1.0) | (309.5 ± 2.0) | – |
| $C^o_{p,m}$ /J·K$^{-1}$·mol$^{-1}$ | 82 | 127 | 61 | 102.5 |
| | (86.4 ± 3.0) | (129.4 ± 0.5) | (64.5 ± 2.0) | – |

For $UF_6$(g) the calculated frequencies from Hay *et al.* [1998HAY/MAR] at the B3LYP level are in good agreement with the experimental data from [1985ALD/BRO]; these are the data used in [2003GUI/FAN]. The frequencies used for $UO_2F_2$ in [2003GUI/FAN] are from [1995EBB], and they differ from the ones calculated in [2003PRI/SCH], which is reflected in the somewhat different entropy and enthalpy values. There are significant differences between experimental and calculated high energy vibration frequencies in $UO_2F_2$, but the corresponding energy levels are sparsely populated at room temperature and do therefore not affect the calculated entropy and heat capacity very much, however, at higher temperature one can expect significant differences. Bond distances and calculated frequencies in $UF_6$ are in very good agreement with experimental data.

The agreement with the data selected in [2003GUI/FAN] is excellent and the values selected there have been retained. There is no experimental information on $UO_2(OH)_2$(g) and $UO_3$(g) and accordingly we have not selected the values from Table 12 in [2002PRI/SCH]. The calculated values of Gibbs energy of reaction in [2002PRI/SCH] are given for information only.

Privalov *et al.* have also calculated the enthalpy of reaction at different level of theory, where the most reliable ones are taken from their Table 3 and given in the Table A-15.

Table A-15: Enthalpies of reaction at 298.15 K for gas phase reactions in the U(VI)-fluoride-oxide-water system.

| Reaction | Corrected enthalpy of reaction /kJ·mol$^{-1}$ | Selected from [2003GUI/FAN] |
|---|---|---|
| $2UO_3 + UF_6 \rightleftharpoons 3UO_2F_2$ | – 329 | – 310.5 |
| $UO_2F_2 + 2H_2O \rightleftharpoons UO_2(OH)_2 + 2HF$ | 72 | 64 |
| $UF_6 + 2H_2O \rightleftharpoons UO_2F_2 + 4HF$ | 187 | 187 |
| $UO_3 + H_2O \rightleftharpoons UO_2(OH)_2$ | – 166 | – |
| $UF_6 + 3H_2O \rightleftharpoons UO_3 + 6HF$ | 411 | 435 |

**[2002VAL/WAH]**

This is an *ab initio* study of the mechanism of fluoride and water exchange in $UO_2F_5^{3-}$ and $UO_2F_4(OH_2)^{2-}$. There are no thermodynamic data in this study, but it supports the experimental evidence for the formation of $UO_2F_5^{3-}$ at high total concentrations of fluoride discussed in [2002VAL/WAH].

**[2003FIS]**

This is an important single-crystal X-ray study of the structures of three uranyl perchlorate hydrates that demonstrates the relative affinity of water and perchlorate to

the uranyl-ion. The following structures were identified, $[UO_2(ClO_4)_2(OH_2)_3](cr)$, $[UO_2(OH_2)_5](ClO_4)_2(cr)$ and $[UO_2(OH_2)_5](ClO_4)_2{\cdot}2H_2O(cr)$. The structure and bond distances are in excellent agreement with both EXAFS data and quantum chemical calculations. The observations by Fischer provide strong support to the predominance of the inner-sphere complex $UO_2(OH_2)_5^{2+}$.

**[2003KAR/FOU]**

In this experimental study the authors have studied complex formation in the uranyl(VI)-iodate system using three different experimental methods, time-resolved fluorescence spectroscopy, UV/VIS spectrophotometry and capillary zone electrophoresis. The experiments have been made in 0.05 M $HClO_4$ and a constant pH of 2.6. Capillary zone electrophoresis involves measurement of the mobility of complexes in an applied electric field, in this case using creatinine as an uncharged reference. As the rate of equilibration between the various complexes is much larger than the mobility in the electric field, one only observes a single mobile peak that is a weighted average of the concentration and individual mobility of the two species, $UO_2^{2+}$ and $UO_2IO_3^+$. The mobility of $UO_2^{2+}$ can be determined in the absence of iodate and the analysis of the experimental data thus requires three parameters, two equilibrium constants and the mobility of $UO_2IO_3^+$; the resulting equilibrium constants are $\log_{10}\beta_1 = (1.62 \pm 0.1)$ and $\log_{10}\beta_2 = (3.05 \pm 0.1)$, at a temperature around 25 °C; a check of experimental data at higher total concentration of uranium, $5 \times 10^{-4}$, confirmed these values. The TRLFS data have been recorded at 20 °C, in addition to equilibrium constants there is detailed information about fluorescence spectra and fluorescence lifetimes for the different complexes. The authors report $\log_{10}\beta_1 = (1.5 \pm 0.2)$ and $\log_{10}\beta_2 = (3.6 \pm 0.2)$ from the TRLFS experiments at the experimental ionic strength 0.05 M. The values of $\log_{10}\beta_1$ from the two experimental methods are in good agreement with the NEA selected value after recalculation to zero ionic strength, $\log_{10}\beta_1^o = (1.9 \pm 0.2)$. However, the experimental values of $\log_{10}\beta_2$ differ significantly, where only the one from electrophoresis, recalculated to zero ionic strength, $\log_{10}\beta_2^o = (3.67 \pm 0.20)$ is in good agreement with the value selected in [1992GRE/FUG] $\log_{10}\beta_2^o = (3.59 \pm 0.15)$. The authors point out that the value from TRLFS might be affected by systematic errors in their data analysis and this value has therefore not been considered by the present review. The spectra from the TRLFS measurements have been deconvoluted into their principal components using the NEA selected values for the equilibrium constants. The fit was excellent, which is an indirect confirmation of the numerical values of the equilibrium constants selected in [1992GRE/FUG] and [2003GUI/FAN].

**[2003TOR/PRI]**

Toraishi *et al.* have compared the experimental and quantum chemistry equilibrium constants/Gibbs energies of Reactions (A.10) and (A.11), where the latter is the chemical model used in the quantum chemistry calculation. It involves the transfer of fluoride from the second to the first coordination sphere of the uranyl ion and the formation of $H_3O^+$ in the second sphere.

$$UO_2^{2+}(aq) + HF(aq) \rightleftharpoons UO_2F^+(aq) + H^+(aq) \quad (A.10)$$

$$[UO_2(OH_2)_5^{2+}]HF(H_2O)_n \rightleftharpoons [UO_2F(OH_2)_4^+](H_3O^+)(H_2O)_n;\ n = 1, 2 \quad (A.11)$$

Toraishi *et al.* report $\Delta_r G_m^o$ (A.11) = – 25 kJ·mol$^{-1}$ after correction for a known systematic error in the electronic energy of hydrogen fluoride, HF, and estimates of the equilibrium constants for the formation of outer-sphere complexes between the reactant and product, using the Fuoss equation. Considering the expected errors in quantum chemistry calculations of this type, this reaction energy is in fair agreement with the experimental value from [1992GRE/FUG], – 11 kJ·mol$^{-1}$, which is of interest for testing of quantum chemistry models, but not for the selection of thermodynamic data for the present review. Toraishi *et al.* have also studied the mechanism for Reaction (A.10) using quantum chemistry modeling; their multi-step mechanism has an activation energy that is in good agreement with experiment but these data are of minor interest for the current review.

**[2004KAR/HUB]**

This study of the uranyl(VI)-periodate system has been made by using capillary electrophoresis and TRLFS, the same methodology as in [2003KAR/FOU]. The TRLFS experiments have been made at pH = 2.6, using test solutions at a uranyl concentration of $1 \times 10^{-4}$ M where the periodate concentration was varied between 1 and 90 mM, at an ionic strength of 0.10 M; the capillary electrophoresis experiments were made in test solutions with $I$ = 0.05 M. Only one complex, $UO_2IO_4^+$, is formed in the concentration range studied and the equilibrium constant obtained by the TRLFS and capillary electrophoresis, $\log_{10}\beta_1$ (TRLFS) = (1.8 ± 0.2) and $\log_{10}\beta_1$ (CE) = (2.0 ± 0.2), are in good agreement. The corresponding values at zero ionic strength using SIT are $\log_{10}\beta_1^o$ = (2.4 ± 0.2) and $\log_{10}\beta_1^o$ = (2.3 ± 0.2), respectively. Both these constants are judged as reliable by the careful experiments and the following data analysis. The formation of periodate complexes was discussed in [1992GRE/FUG] based on the data of Hutin [1975HUT] that claimed the formation of $[(UO_2)_2(HIO_6)](aq)$ and $H_3[UO_2(IO_5)]$, but these equilibrium constants were not accepted. The equilibrium constant from [2003KAR/FOU] at zero ionic strength $\log_{10}\beta_1^o$ = (2.35 ± 0.20) is accepted by the present review.

**[2004KIR/KIM2]**

This is an experimental study of complex formation in the uranyl(VI)-phosphate and fluoride systems at high temperatures (20-150 °C) and high pressure (0.1-40 MPa) using time-resolved fluorescence spectroscopy (TRLFS). The test solutions had a uranyl concentration of $5 \times 10^{-5}$ M in 0.50 M $NaClO_4$ and were studied in the pH range 0-3. The focus of the study is on the lifetime of the excited states, but in order to obtain this information the authors need information on the speciation. To obtain this they have used equilibrium constants from the literature, [1992GRE/FUG], [1991MAT] on hydroxide, phosphate and fluoride complexes. The temperature dependence of these constants were estimated using the DQUANT equation [1997GRE/PLY]; in order to obtain data at zero ionic strength, the activity coefficients were estimated using the HKF model [1981HEL/KIR]. The authors have identified the fluorescence components of $UO_2^{2+}$, $UO_2F^+$, $UO_2F_2(aq)$, $UO_2H_2PO_4^+$ and $UO_2(H_2PO_4)_2(aq)$, information that is useful for speciation studies. This is an interesting study but it relies on published equilibrium constants. The reported data at higher temperature and pressure relies on the DQUANT equation and activity factor models. The paper includes figures of speciation at 25, 100 and 150 °C, which are useful for estimates.

**[2004SUL/JEN]**

The paper describes cation-cation interactions between uranyl(VI) units in an open framework structure of uranyl periodate with the composition $M[(UO_2)_3(HIO_6)(OH)(O)(H_2O)]\cdot 1.5H_2O(cr)$, M = Na-Cs. Details of coordination geometry and inter-atomic distances are based on an X-ray structure; there are no thermodynamic data.

**[2005CRA/MAY]**

The structure of $(Ph_4P)_2UO_2I_4\cdot 2NCCH_3(cr)$ has been determined by X-ray diffraction, where $Ph_4P$ denotes the tetra-phenyl-phosphonium ion. The structure contains isolated units of the complex $UO_2I_4^{2-}$ with four coordinated iodides in the equatorial plane of the uranyl ion, which is the same coordination geometry as in the corresponding $Cl^-$, and $Br^-$ complexes. The authors have also made a quantum chemistry study of possible cis- and trans-isomers in the gas phase—this is a rather speculative study with no bearing on the known chemistry in uranyl(VI) systems. The authors report Raman data but no thermodynamic information. It should also be pointed out that it is unlikely that $UO_2I_4^{2-}$ can form in aqueous solution.

**[2005HEN/TUT]**

Hennig *et al.* have studied chloride complex formation in the uranyl(VI) and uranium(IV) systems in 3, 6 and 9 M chloride solutions using EXAFS, which allowed them to determine the number of coordinated water and chloride ligands and the corresponding U-O and U-Cl distances in the complexes formed. As noted in previous issues of the NEA *Chemical Thermodynamics* series, it is difficult to distinguish between complex formation and activity variations caused by the often large changes in ligand concentration, in systems where weak complex formation is expected. Even if this study does not contain thermodynamic information, it is important because it clearly demonstrates that chloride complexes *are* formed in the systems investigated. The complexes are identified by a second shell outside the uranium atoms, providing information on the U-Cl distance and the number of these, *N*. The first quantity is defined within an accuracy of 0.01-0.02 Å, while the uncertainty in the latter is no better than 10 %. Table A-16 summarises the results, where $N_{H2O}$ and $N_{Cl}$ denote the number of coordinated water and chloride, respectively.

Table A-16: Results of the analysis of EXAFS-data in the U(VI) and U(IV) chloride systems by Hennig *et al.*

| $[Cl^-]$ in M/L | U – $OH_2$ /Å | $N_{H2O}$ | U-$Cl^-$ /Å | $N_{Cl}$ |
|---|---|---|---|---|
| U(VI) – chloride system | | | | |
| 0 | 2.41 [a] | 5.2 | – | – |
| 3 | 2.41 [a] | 3.9 | 2.71 | 1.1 |
| 6 | 2.41 [a] | 1.7 | 2.71 | 2.3 |
| 9 | 2.41 [a] | 0.7 | 2.71 | 3.1 |
| U(IV) – chloride system | | | | |
| 0 | 2.41 | 8.7 | – | – |
| 3 | 2.41 | 8.5 | 2.71 | 0.3 |
| 6 | 2.41 | 6.7 | 2.71 | 1.4 |
| 9 | 2.41 | 5.2 | 2.71 | 2.7 |

a) Distances U-$O_{ax}$ reported in the original publication are not included in the table

This review prefers the second analysis model used by Hennig *et al.* as it contains a smaller number of adjustable parameters and it is these values that are reported in Table A-16. The U-$O_{yl}$ distance is constant at 1.76 Å in the uranyl(VI) system.

**[2006BRA/BEI]**

This is a single-crystal X-ray structure determination of the solid $Na_2[UO_2(IO_3)_4(OH_2)](cr)$ that contains isolated units of the anion $[UO_2(IO_3)_4(OH_2)]^{2-}$. The coordination of iodate has been studied in solution in [2003KAR/FOU] but not at sufficiently high iodate concentration to identify the complex $[UO_2(IO_3)_4(OH_2)]^{2-}$.

Even if it is feasible that the anionic complex might be formed at high iodate concentrations, there are no thermodynamic experimental data.

**[2006GAR/WIL]**

This is a quantum chemistry study of structures, chemical bonding and reaction energies in uranium and neptunium(VI) complexes, $[AnO_2L_4]$ with the ligands, L = $H_2O$, $F^-$, $Cl^-$ and $OH^-$, in gas phase and in water using a COSMO model. The paper provides details about structures, bond distances and energy differences between isomers but also the average electronic bonding energy for reactions such as:

$$UO_2(OH_2)_4^{2+}(aq) \rightleftharpoons UO_2^{2+}(aq) + 4H_2O\ ;\ \Delta E = 104\ \text{kcal}\cdot\text{mol}^{-1} \quad (A.12)$$

$$UO_2F_4^{2-}(aq) \rightleftharpoons UO_2^{2+}(aq) + 4F^-(aq)\ ;\ \Delta E = 284\ \text{kcal}\cdot\text{mol}^{-1} \quad (A.13)$$

Using these electronic energies one can calculate the electronic energy of Reaction (A.14) to – 180 kcal·mol$^{-1}$, which differs at least 100 kcal from the experimental value.

$$UO_2(OH_2)_4^{2+}(aq) + 4F^-(aq) \rightleftharpoons UO_2F_4^{2-}(aq) + 4H_2O \quad (A.14)$$

This result is not surprising in view of the difficulty to estimate solvent effects for charged species.

**[2006GOR/DUB]**

The paper discusses a simulation of the reduction of $UF_6$(g) by H and F atoms. Enthalpies of reaction are given for a number of possible reactions based on literature information. However, the reactions discussed are outside the scope of the present review.

**[2007CHI]**

A MSc thesis, where the use of electro-spray mass-spectroscopy for the analysis of equilibria in solution is discussed. The method allows the determination of the mol weight of different species formed in the experiment, but a critical issue is if these correspond to species present in solution, or not. The reactions studied take place in gas-phase and the method allows identification of complexes with different number of coordinated water, *e.g.* $UO_2Cl(OH_2)^+$, $UO_2Cl(OH_2)_2^+$ and $UO_2Cl(OH_2)_3^+$. In aqueous solution one expects that coordinated water occupies the coordination sites that are not used by chloride, which rules out the formation of the first two complexes. In addition, the EXAFS study by Hennig *et al.* [2005HEN/TUT] indicates that $UO_2Cl(OH_2)_4^+$ is a more likely composition than $UO_2Cl(OH_2)_3^+$. This review finds no compelling evidence that mass-spectroscopy in this case provides useful information on the constitution of

complexes in solution with ligands like $Cl^-$, $NO_3^-$, $Br^-$, $ClO_4^-$ and acetate. There are no thermodynamic data reported.

**[2007DEN]**

An important review article dealing with the electronic structure and bonding in actinyl ions and their analogs. In the article both experimental data and theoretical approaches are discussed by one of the leading experts in the field. The article does not provide information on thermodynamics and is in this respect of minor interest for the present review.

**[2007LUC/BOR]**

See entry for the same reference in Section *A-1.2. Compounds and complexes in the uranium hydroxide, oxide and peroxide systems*.

**[2007SHA/SCH]**

This is an important study using different quantum chemical methods, where the authors have studied structure, chemical bonding and reaction energies for the gas-phase compounds $UF_6$, $UOF_4$, $UO_2F_2$, $UO_3$, $UF_5$, $UOF_3$, $UO_2F$, $UF_4$, UOF and $UO_2$, testing different basis sets, approximations for relativistic effects and different functionals. In some cases the different methods result in different structures, *e.g.* for $UOF_4$. The authors have also studied how the U-$O_{yl}$ stretch frequency depends on the approximation method used, useful information for comparisons with experimental data. A number of gas-phase reactions have been studied by calculation of reaction enthalpies in kcal·mol$^{-1}$ (Table A-17) followed by comparison with experimental data based on studies by Lau and Hildenbrand ([1985LAU/HIL], [1987LAU/HIL], [1991HIL/LAU], [1992HIL/LAU], [1995EBB]); the latter are included in the table and reviewed in [2003GUI/FAN].

$$UF_6 + 2UO_3 \rightleftharpoons 3UO_2F_2 \quad \text{(A.15)}$$

$$UF_6 + UO_2F_2 \rightleftharpoons 2UOF_4 \quad \text{(A.16)}$$

$$UOF_4 + UO_3 \rightleftharpoons 2UO_2F_2 \quad \text{(A.17)}$$

$$UF_6 \rightleftharpoons UF_5 + F \quad \text{(A.18)}$$

$$UF_5 \rightleftharpoons UF_4 + F \quad \text{(A.19)}$$

$$UOF_4 \rightleftharpoons UOF_3 + F \quad \text{(A.20)}$$

$$UOF_4 \rightleftharpoons UOF_2 + 2F \quad \text{(A.21)}$$

$$UOF_4 \rightleftharpoons UF_4 + O \quad \text{(A.22)}$$

$$UO_2F_2 \rightleftharpoons UO_2F + F \quad \text{(A.23)}$$

$$UO_2F_2 \rightleftharpoons UO_2 + 2F \quad \text{(A.24)}$$

$$UO_2F_2 \rightleftharpoons UOF_2 + O \quad \text{(A.25)}$$

$$UO_3 \rightleftharpoons UO_2 + O \quad \text{(A.26)}$$

$$UF_6 + H_2O \rightleftharpoons UOF_4 + 2HF \quad \text{(A.27)}$$

$$UF_6 + 2H_2O \rightleftharpoons UO_2F_2 + 4HF \quad \text{(A.28)}$$

$$UF_6 + 3H_2O \rightleftharpoons UO_3 + 6HF \quad \text{(A.29)}$$

The comparison of reaction enthalpies obtained at different levels of theory and with experiments provides useful insights into the errors one can expect by using different functional and basis sets in the quantum chemistry calculations. Even if the agreement between theory and experiment sometimes is satisfactory, the experimental data are preferred by the present review.

**[2007ZHE/USO]**

This is a study of phase equilibria in the $UF_6$-$IF_5$-$BrF_3$ system that is not relevant for the NEA database project.

**[2008BUH/SIE]**

Bühl *et al.* have studied structures, isomers and reaction energies of uranyl(VI) chloride complexes using static (at DFT level in gas phase and a PCM model for the solvent) and dynamic (Car-Parrinello molecular dynamics simulations) quantum chemistry methods. The accuracy of bond distances is in good agreement with experimental EXAFS data. The authors have also calculated reaction energies, where the following are of interest for this review:

$$UO_2(OH_2)_5^{2+} + nCl^- \rightleftharpoons [UO_2(OH_2)_{5-n}Cl_n]^{2-n} + nH_2O\,.$$

Table A-17: Calculation and experimental reaction enthalpies at 298.15 K (in kcal·mol$^{-1}$) as reported in [2007SHA/SCH].

| Reaction number | AE | | | | | G03, SC-RECPs | | ADF ZORA | Expt. |
|---|---|---|---|---|---|---|---|---|---|
| | PBE/L1 | PBE0/L1 | MP2/L1 | PBE/B1 | PBE/B2 | PBE0/B1 | PBE0/B2 | PBE/TZP | |
| A.15 | – 44.7 | – 70.1 | – 67.0 | – 43.1 | – 47.5 | – 68.1 | – 72.5 | – 47.2 | – 74.6 |
| A.16 | 5.9 | 5.0 | – 5.5 | 6 | 5.4 | 4.3 | 4.0 | 5.3 | 7.2 |
| A.17 | – 25.3 | – 37.5 | – 30.8 | – 24.6 | – 26.4 | – 36.2 | – 38.3 | – 26.2 | – 40.9 |
| A.18 | 100.5 | 73.6 | 84.0 | 107.07 | 100.8 | 80.65 | 76.3 | 101.5 | 71.0 |
| A.19 | 120.8 | 97.8 | 97.8 | 127.38 | 120.9 | 105.14 | 99.8 | 126.6 | 98.0 |
| A.20 | 111.2 | 89.9 | 106.0 | 118.4 | 112.6 | 97.5 | 93.4 | 112.8 | |
| A.21 | 248.5 | 211.6 | 234.6 | 261.4 | 251.1 | 225.6 | 217.3 | 252.5 | |
| A.22 | 132.6 | 95.3 | 120.9 | 134.9 | 131.8 | 97.8 | 97.4 | 137.7 | 91.3 |
| A.23 | 126.2 | 110.4 | 125.1 | 132.8 | 127.3 | 117.1 | 114.4 | | |
| A.24 | 266.2 | 241.9 | 249.9 | | | 254.6 | 248.6 | | 248.6 |
| A.25 | 165.7 | 140.5 | 168.2 | 167.9 | 166.6 | 153.3 | 142.5 | 167.5 | |
| A.26 | 158.0 | 133.3 | 152.7 | | | 134.8 | 135.6 | | 138.0 |
| A.27 | 43.2 | 33.2 | 11.8 | 59.6 | 53.9 | 49.1 | 45.7 | 38.3 | 25.9 |
| A.28 | 80.5 | 61.5 | 29.1 | 113.2 | 75.4 | 93.8 | 60.0 | 71.4 | 44.6 |
| A.29 | 143.1 | 127.3 | 77.2 | 191.3 | 136.9 | 174.7 | 126.2 | 130.6 | 104.1 |
| mean error[(a)] | 24.3 | 4.4 | 0.6 | 38.4 | 25.0 | 16.1 | 6.3 | 23.5 | |
| M.A.E.[(a)] | 24.6 | 6.9 | 13.2 | 38.6 | 25.4 | 17.2 | 7.3 | 23.9 | |

(a) Taking only those reactions into account where experimental data exists; M.A.E. = mean absolute error.

The cumulative Gibbs energies of reaction at the B3LYP level in the PCM model turns out to be – 18.4, – 27.8, – 27.8 and – 6.3 kcal·mol$^{-1}$, respectively, for $n$ = 1-4. These values are very different from the experimental data calculated from equilibrium constants. The paper is of interest from a methodological point of view but does not provide thermodynamic data that are accurate enough for the present review. Bühl *et al.* have also calculated the Gibbs energy of water dissociation from the various chloride complexes that turn out to be positive for all complexes except $UO_2Cl_4(OH_2)^{2-}$, where it is negative. This finding supports overall coordination number of five in the equatorial plane for all chloride complexes except $UO_2Cl_4^{2-}$, where it is four. The Car-Parinello simulation of the reaction $UO_2(OH_2)_5^{2+} + Cl^- \rightleftharpoons UO_2Cl(OH_2)_4^+ + H_2O$, results in an Helmholtz free energy of 9.6 kcal·mol$^{-1}$, very different from the experimental value.

**[2008GAR/BEC]**

This is a quantum chemistry study that identifies a possible transition state and an intermediate in the gas-phase hydrolysis of $UF_6$ with water, leading to the formation of $UOF_4$(g) and $UO_2F_2$(g). The reactions studied are:

$$UF_6 + H_2O \rightleftharpoons UOF_4 + 2HF \quad \text{(A.30)}$$

$$UF_6 + 2H_2O \rightleftharpoons UO_2F_2 + 4HF \quad \text{(A.31)}$$

The transition state and the intermediate have both the structure $UO_2F_5OH$; the activation enthalpy at the MP2 level is $\Delta H^{\ddagger}$ = 62 kcal·mol$^{-1}$ and the intermediate $\Delta H$ = 31 kJ·mol$^{-1}$ but these data are not relevant for the present review.

**[2008HU/WAN]**

This is a more detailed quantum chemistry study of the hydrolysis of $UF_6$(g) than the one in [2008GAR/BEC] and results in about same enthalpy of reaction for the formation of the intermediate $UF_5OH$. The thermodynamic information, however, is not relevant for the current review.

**[2008ZHA/LI]**

In this quantum chemistry study the authors have used a number of different theory approaches to study the structure and vibrational frequencies of $UX_4$, X = F, Cl, Br, I, in the gas phase and compared the result with experimental observations. The agreement between experimental and calculated frequencies is excellent with average deviations of 4.9, 2.8, 3.1 and 7.4 cm$^{-1}$, respectively, for $UF_4$, $UCl_4$, $UBr_4$ and $UI_4$. Accordingly, the

agreement between calculated and experimental entropies is very good as seen in Table A-18.

Table A-18: Molar entropies for $UF_4$(g), $UCl_4$(g), and $UBr_4$(g) at different temperatures.

| *T* /K | *S* /cal·K$^{-1}$·mol$^{-1}$ for $UF_4$ | | *S* /cal·K$^{-1}$·mol$^{-1}$ for $UCl_4$ | | *S* /cal·K$^{-1}$·mol$^{-1}$ $UBr_4$ | |
|---|---|---|---|---|---|---|
| | calc | exptl. | calc | exptl. | calc | exptl. |
| 1050 | 117.2 | (119.3 ± 1.0)[a]<br>(117.8 ± 0.7)[a]<br>(120.5 ± 0.5)[b] | – | – | – | – |
| 650 | – | – | 118.7 | (117.8 ± 0.3)[a] | 133.6 | (130.7 ± 1.5)[a]<br>(130.7 ± 1.9)[a] |
| 700 | – | – | 120.6 | (120.0 ± 0.5)[a] | – | – |

(a) The experimental data are from [1988HIL2], and [1991HIL/LAU].
(b) [1996KON/BOO].

**[2009BUH/SCH]**

In order to make molecular dynamics simulations more similar to experimental conditions, Bühl *et al.* have made simulations of the reaction $UO_2X_5^{3-} \rightleftharpoons UO_2X_4^{2-} + X^-$, in the presence of ammonium ions, X = $F^-$ and $OH^-$. The result suggests that the fifth fluoride is bound much stronger than hydroxide, which is consistent with experimental observations. They also studied the reaction $[UO_2F_4(OH_2)]^{2-} \rightleftharpoons [UO_2F_4]^{2-} + H_2O$ and noted that the presence of ammonium ions strengthened the U-water bond by about 10 kJ·mol$^{-1}$, which resulted in a Helmholtz energy of reaction in better agreement with experiment; EXAFS studies in [2001VAL/WAH] demonstrates that $[UO_2F_4(OH_2)]^{2-}$ is formed at fluoride concentrations above 0.2 M.

**[2009BUH/SIE]**

This is a quantum chemistry study that uses two different computation methods, a "static" calculation where the aqueous solvent is described as a dielectric continuum and a Car-Parrinello Molecular dynamics simulation (MD) using discrete water molecules as the solvent. The two methods have been compared using a calculation of the Gibbs energy of Reaction (A.32).

$$UO_2(OH_2)_5^{2+} + F^- \rightleftharpoons [UO_2F(OH_2)_4]^+ + H_2O \qquad \text{(A.32)}$$

$$UO_2(OH_2)_5^{2+} + nF^- \rightleftharpoons [UO_2F_n(OH_2)_{5-n}]^{2-n} + nH_2O \qquad \text{(A.33)}$$

$\Delta_r G_m^o$((A.32), aq, 298.15 K) using the Car-Parrinello MD is – (23.8 ± 10) kJ·mol$^{-1}$, which is in good agreement with the experimental value from [2003GUI/FAN], – 29.5 kJ·mol$^{-1}$, considering the estimated uncertainty; the corresponding energy of reaction using the "static" approach is – 95 kJ·mol$^{-1}$, very far from the experimental value. Bühl *et al.* have also calculated the Gibbs energies for the Reactions (A.33) using the "static"

method but these also deviate very much, up to 100 kJ·mol$^{-1}$ from the experimental values as seen from the following table (Table A-19):

Table A-19: Comparison of static and experimental Gibbs energies for the reaction $UO_2(OH_2)_5^{2+} + nF^- \rightleftharpoons [UO_2F_n(OH_2)_{5-n}]^{2-n} + nH_2O$.

| Reaction(A.33) with value *n* | $-\Delta_r G_m^o$ stat. /kJ·mol$^{-1}$ from quantum chemistry | $-\Delta_r G_m^o$ exp /kJ·mol$^{-1}$ |
|---|---|---|
| 1 | 95 | 28.9 |
| 2 | 167 | 49.0 |
| 3 | 220 | 62 |
| 4 | 257 | 67 |

In addition, Bühl *et al.*, provide molecular insights on structures, both in the ground and intermediate states and along the reaction coordinate used in the MD simulation. Most importantly, the study illustrates the difficulties that one may encounter using a dielectric continuum to describe the water solvent.

**[2009MCN/SCH]**

This study demonstrates that $NF_3$ gas can fluorinate elemental uranium and the solid compounds $UO_2$, $U_3O_8$ and $UO_2F_2$ with formation of $UF_6$(g) in the temperature range 100-550 °C. The enthalpy and Gibbs energy of reaction are listed in the following table, where the Gibbs energy of formation and the enthalpy of formation differ significantly from the values selected in the NEA reviews. For this reason the reported thermodynamic data have not been included among the selected values.

Table A-20: Enthalpies and free energies per mol uranium for the reaction of $NF_3$ with elemental uranium, uranium oxides, $UF_4$ and $UO_2F_2$ to produce $UF_6$.

| Equation | Overall reaction to $UF_6$ | $\Delta H$ /kJ·mol$^{-1}$ U | $\Delta G$ /kJ·mol$^{-1}$ U |
|---|---|---|---|
| 1 | $UO_2 + 2NF_3(g) \rightleftharpoons UF_6(g) + N_2(g) + O_2(g)$ | – 799.9 | – 901.1 |
| 2 | $UO_2F_2 + NF_3(g) \rightleftharpoons UF_6(g) + N_2(g) + O_2(g)$ | – 321.2 | – 448.8 |
| 3 | $UO_3 + 2NF_3(g) \rightleftharpoons UF_6(g) + N_2(g) + O_2(g)$ | – 661.9 | – 809.8 |
| 4 | $U_3O_8 + 6NF_3(g) \rightleftharpoons 3UF_6(g) + 3N_2(g) + 4O_2(g)$ | – 695.2 | – 823.2 |
| 5 | $UF_4 + NF_3(g) \rightleftharpoons UF_6(g) + N_2(g)$ | – 144.1 | – 204.9 |
| 6 | $U + 2NF_3(g) \rightleftharpoons UF_6(g) + N_2(g)$ | – 1881.9 | – 1884.8 |

**[2009TIA/RAO]**

This is a careful experimental study of fluoride complex formation in the $UO_2^{2+}$-$F^-$ system over the temperature range 25-70 °C in 1.00 M $NaClO_4$. The equilibrium constants have been measured by using spectrophotometry and the corresponding

enthalpies of reaction by using microcalorimetry. In addition the authors have used EXAFS to determine the number of coordinated fluoride and water ligands in selected test solutions. These results suggest that there are five coordinated ligands in the equatorial plane of the uranyl ion and also that there is one coordinated water in $UO_2F_4^{2-}$, which is in agreement with [2002VAL/WAH], but not with the results in [2009BUH/SIE] that suggest that this complex does not contain coordinated water. This review finds the arguments for the presence of coordinated water strong, based on the experimental evidence. The thermodynamic quantities reported in this study are shown in Table A-21, where the enthalpies of reaction are the weighted average of those reported. In the last column we report the enthalpies of reaction at zero ionic strength obtained using the Debye-Hückel term only. There is a surprisingly large difference between the reported enthalpies of reaction between this study and the one by Ahrland *et al.* [1971AHR/KUL] given in cursive in Table A-21; the equilibrium constant are in good agreement. The reported enthalpies of reaction in both studies refer to 1.00 M $NaClO_4$ ionic medium and these data have been extrapolated to zero ionic strength as described in [1997GRE/PLY2]. We have no basis for selection between these two studies and have therefore used the weighted averages of the reported enthalpies of reaction.

Table A-21: Experimental values of equilibrium constants and enthalpies of reaction, and corresponding values extrapolated to zero ionic strength using SIT; the values in cursive are those selected in [1992GRE/FUG] and [2003GUI/FAN] based on the data from Ahrland and Kullbrg [1971AHR/KUL2].

| Reaction | t /°C | $\log \beta_n$ $I$ = 1.0 M | $\log \beta_n$ $I$ = 0 M | $\Delta_r H_m$(298.15 K) /kJ·mol$^{-1}$ | $\Delta H_{av}$(298.15 K) /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ (298.15 K) /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| $UO_2^{2+} + F^- \rightleftharpoons UO_2F^+$ | 25 | (4.60 ± 0.02) | (5.20 ± 0.07) | (2.8 ± 0.4) | (1.87 ± 0.26) | – (0.54 ± 0.26) |
| | | | *(5.16 ± 0.06)* | *(1.70 ± 0.08)* | | |
| | 40 | (4.62 ± 0.02) | (5.25 ± 0.07) | | | |
| | 55 | (4.67 ± 0.04) | (5.32 ± 0.07) | | | |
| | 70 | (4.80 ± 0.02) | (5.92 ± 0.07) | | | |
| $UO_2^{2+} + 2F^- \rightleftharpoons UO_2F_2(aq)$ | 25 | (8.07 ± 0.04) | (8.74 ± 0.07) | (5.2 ± 0.8) | (2.27 ± 0.18) | – (1.34 ± 0.18) |
| | | | *(8.83 ± 0.08)* | *(2.10 ± 0.19)* | | |
| | 40 | (8.21 ± 0.04) | (8.91 ± 0.07) | | | |
| | 55 | (8.32 ± 0.06) | (9.06 ± 0.08) | | | |
| | 70 | (8.52 ± 0.02) | (9.31 ± 0.06) | | | |
| $UO_2^{2+} + 3F^- \rightleftharpoons UO_2F_3^-$ | 25 | (10.62 ± 0.04) | (11.25 ± 0.02) | (3.4 ± 1.1) | (2.43 ± 0.31) | – (1.18 ± 0.30) |
| | | | *(10.9 ± 0.1)* | *(2.35 ± 0.31)* | | |
| | 40 | (10.78 ± 0.04) | (11.44 ± 0.09) | | | |
| | 55 | (11.21 ± 0.06) | (11.91 ± 0.10) | | | |
| | 70 | (11.55 ± 0.02) | (12.29 ± 0.09) | | | |
| $UO_2^{2+} + 4F^- \rightleftharpoons UO_2F_4^{2-}$ | 25 | (11.92 ± 0.14) | (12.01 ± 0.18) | (0.2 ± 3.3) | (0.29 ± 0.47) | – (2.12 ± 0.47) |
| | | | *(11.84 ± 0.11)* | *(0.29 ± 0.47)* | | |
| | 40 | (12.27 ± 0.02) | (12.38 ± 0.11) | | | |
| | 55 | (12.59 ± 0.06) | (11.73 ± 0.12) | | | |
| | 70 | (12.95 ± 0.04) | (13.12 ± 0.11) | | | |

The values in cursive have been obtained from the calorimetric titrations by Ahrland and Kullberg, [1971AHR/KUL2] and the equilibrium constants at zero ionic strength by using the SIT and the interaction coefficients in Appendix B. The accuracy of the enthalpies of reaction calculated from the temperature dependence of the equilibrium constants is low and we have used the calorimetric data in the comparison with the selected data in [2003GUI/FAN]. The enthalpies of reaction have been recalculated to zero ionic strength as described below, where the relative partial enthalpy of the water solvent is small and can be neglected. The same is true for the term $RT^2m\,\Delta\varepsilon_L$ because of the value of $\Delta\varepsilon_L \approx 10^{-3}$, accordingly the enthalpy correction has been made using the Debye-Hückel term only:

$$\Delta_r H_m = \Delta_r H_m^o + \frac{3}{4} \times \frac{A_L \Delta z^2 \sqrt{I_m}}{(1+1.5\sqrt{I_m})}$$

**[2010GRI/KRO]**

This X-ray diffraction study was performed at 100 K and confirms the X-ray study of $UO_2(OH_2)_5 \cdot (ClO_4)_2$(cr) from Fischer. However, because of the low temperature Grigor'ev and Krot could also locate the positions of the hydrogen atoms and the hydrogen bond network in these structures, all of which are isostructural.

**[2011BEN/GRI]**

This paper describes low temperature heat capacity data for $UF_3$(cr) using two different calorimetric techniques, adiabatic low temperature calorimetry in the temperature range from 10 to 350 K and thermal relaxation calorimetry in the temperature region from 0.5 to 20 K. A λ-type anomaly has been observed with a maximum at 1.59 K, which has been found to be of ferro-magnetic nature using additional SQUID measurements. The entropy of the transition is very close to the theoretical value $R\ln(2)$ or 5.68 $J \cdot K^{-1} \cdot mol^{-1}$ expected for the $U^{3+}$ ion. This transition has not been been observed in the unpublished work of Westrum, as cited in [1989COR/KON]. As a result the standard entropy in [2011BEN/GRI], (126.8 ± 2.5) $J \cdot K^{-1} \cdot mol^{-1}$, is slightly higher than the value from [1989COR/KON], (123.46 ± 0.50) $J \cdot K^{-1} \cdot mol^{-1}$.

**[2011ODO/WAL]**

The structure and electronic properties of $[UO_2F_n(OH_2)_{5-n}]^{2-n}$ complexes in gas-phase and a COSMO water model have been investigated using a number of different quantum chemistry approaches. The authors have tested models where water has been added in a second coordination sphere and note that this results in better agreement between calculated and experimental (EXAFS) bond distances. There is a large

difference between calculated and experimental reaction energies, which is typical for calculations based on the DFT method. The reaction energy for the formation of $[UO_2F(OH_2)_4]^+$ from $[UO_2(OH_2)_5]^{2+}$ is – 182.8 kJ·mol$^{-1}$, which corresponds to an equilibrium constant, $\log_{10} K$= 32 as compared to the experimental value, $\log_{10} K$ = 5.16, selected in [2003GUI/FAN]. The study is of some methodological interest but does not provide any thermodynamic data of relevance for the present review.

**[2011SOD/SKA]**

Soderholm *et al.* have developed a new method for measuring the structure of complexes in solution that allows them to determine the number of coordinated ligands with a much higher accuracy than in the EXAFS method. The method is based on the use of a high intensity X-ray beam from a synchrotron that allows precise measurement of X-ray diffraction also at high scattering angles, which in turn results in more precise pair-correlation functions. In the present study the authors have investigated complex formation in the uranyl(VI)-chloride system and determined the stoichiometry of the complexes formed, that is the number of coordinated water and chloride ligands and also the equilibrium constants for the reactions:

$$UO_2^{2+}(aq) + nCl^-(aq) \rightleftharpoons [UO_2Cl_n]^{2-n}(aq)$$

The latter study has been made at constant ionic strength of 5.0 m and chloride concentrations varying from 0 to 4.8 m. Analysis of the data resulted in the following equilibrium constants for the complexes $[UO_2Cl(OH_2)_4]^+$, $[UO_2Cl_2(OH_2)_{2/3}]$ and $[UO_2Cl_3(OH_2)]^-$, $\beta_1$ = (1.5 ± 1.0); $\beta_2$ = (0.8 ± 0.4); $\beta_3$ = (0.4 ± 0.1). This study confirms that weak chloride complexes are formed and also their stoichiometry; it is important to notice that the accuracy of the number of coordinated ligands is quite high, 0.1 at the 3σ level. The first equilibrium constants are in fair agreement with those selected in [1992GRE/FUG] and [2003GUI/FAN], $\beta_1$ = (1.5 ± 0.06) and $\beta_2$ = (0.08 ± 0.02).

**[2011UEH/FUJ]**

This is an EXAFS study of U(IV) and Th(IV) complexes in $CaCl_2$ solutions where the concentration of $CaCl_2$ varies from 4 to 6.9 M. The data analysis shows that the number of coordinated chlorides increases from (1.3 ± 0.2) to (3.4 ± 0.5), while the number of coordinated water decreases from (6.7 ± 1.0) to (4.5 ± 0.7), suggesting a constant coordination number of eight around both uranium and thorium. This review has the following remarks—the main part of the experiments are made without control of pH and addition of HCl results in a significant change in the number of coordinated $Cl^-$. The chloride complexes are fairly weak, $\log_{10} \beta_1^o$ = 1.72 and the stepwise constants for formation of higher complexes should therefore be smaller. Predominance of the complex $UCl^{3+}$ in 4 M $CaCl_2$ is not unreasonable, but the suggestion that complexes

with at least three coordinated $Cl^-$ is formed for the moderate increase in chloride concentration to 6.7 M $CaCl_2$ is not plausible as it would require large stepwise equilibrium constants for the formation of $UCl_2^{2+}$ and $UCl_3^+$. The uncertainty in the number of coordinated chloride ions is large, but even so, this review concludes that the findings in [2011UEH/FUJ] are not consistent with the known solution chemistry of U(IV) and Th(IV) in chloride systems.

**[2011WIL/SKA]**

In this high-energy X-ray scattering study the authors have compared the coordination of $Br^-$ in a number of solid uranyl bromide phases that contain "$UO_2Br_4$" as a structural unit with uranyl(VI) bromide complexes in solution. The solution data were obtained from a test solution with 1 m U(VI) and 11 m HBr and analysis of the scattering data and the deduced pair-correlation functions showed that the uranyl unit was surrounded by (1.9 ± 0.2) bromide and (2.0 ± 0.5) coordinated water, suggesting a slightly smaller number of coordinated water than in the corresponding chloride complex [2011SOD/SKA] and also weaker coordination.

**[2012CHE/WAN]**

This is a methodological quantum chemistry study of structures and vibrational frequencies of $ThF_4$, $UF_4$ and $UF_6$ in gas phase, where the structure data are in good agreement with experiments. There is no thermodynamic information of interest for the present review.

**[2012KOV/RYZ]**

The speciation of U(IV) in HF solutions has been determined by solubility experiments using $UO_2$(cr) as the solid phase. The experiments refer to 500 °C and a pressure of 1000 bar. This is a technically difficult experiment to perform as shown by the very detailed description of the experimental methods used. There is significant scatter in the measured solubility which makes it difficult to test how appropriate the chemical model is. The analysis of the experimental data is based on the assumption that only the uncharged complexes $U(OH)_4$, $U(OH)_3F$, $U(OH)_2F_2$ and $UF_4$ are formed. The solubility data in Fig.1 of the publication is consistent with this model because the solubility increases with increasing total concentration of HF. The fact that the solubility remains nearly constant in the range 0.7 M HF to 1 M HF suggests that the solid phase has been transformed to $UF_4$(s). In order to test if the proposed model is consistent with the experimental measurement one should calculate the solubility using the proposed constants and this has not been made in [2012KOV/RYZ] that report the following equilibrium constants:

$$UO_2(cr) + 2H_2O \rightleftharpoons U(OH)_4 \;;\; \log_{10} K = -6.04 \quad \text{(A.34)}$$

$$UO_2(cr) + HF + H_2O \rightleftharpoons U(OH)_3F \;;\; \log_{10} K = -1.29 \quad \text{(A.35)}$$

$$UO_2(cr) + 2HF \rightleftharpoons U(OH)_2F_2 \;;\; \log_{10} K = -3.15 \quad \text{(A.36)}$$

$$UO_2(cr) + 3HF \rightleftharpoons U(OH)F_3 + H_2O \;;\; \log_{10} K = -2.24 \quad \text{(A.37)}$$

$$UO_2(cr) + 4HF \rightleftharpoons UF_4 + 2H_2O \;;\; \log_{10} K = -1.17 \quad \text{(A.38)}$$

For comparison the authors also report the following constant from a similar study in HCl:

$$UO_2(cr) + HCl + H_2O \rightleftharpoons U(OH)_3Cl \;;\; \log_{10} K = -5.0 \quad \text{(A.39)}$$

$$UO_2(cr) + 2HCl \rightleftharpoons U(OH)_2Cl_2 \;;\; \log_{10} K = -3.56 \quad \text{(A.40)}$$

In view of the well-established fact that fluoride complexes are much stronger than chloride complexes, as shown by the selected values of $\log_{10}K$ for formation of $UF^{3+}$ and $UCl^{3+}$ in [2003GUI/FAN], 9.42 and 1.72, respectively, there is a surprisingly small difference between the equilibrium constants in Reactions (A.35) and (A.39) and between Reactions (A.36) and (A.40). This suggests that the chemical model used in [2012KOV/RYZ] is not correct but this review has not made a further analysis of their data and the equilibrium constants are not included among the selected values.

**[2013DAR/DUB]**

These are two Raman spectroscopic studies ([1992NGU/BEG], [2013DAR/DUB]) that use the same technique and data analysis. In both of them the authors observe changes in the position and line width of the uranyl stretch vibration when the ligand concentration in solution changes. In [1992NGU/BEG] they use known equilibrium constants from the literature for $Cl^-$, $Br^-$, $NO_3^-$, $SO_4^{2-}$ and $CO_3^{2-}$ to calculate the speciation in the test solutions and this information to deconvolute the line broadened Raman peak in up to three components, one for each complex, by using a linear combination of Gaussian and Lorentzian functions. As the average shift between the peaks is only about 12 $cm^{-1}$, this procedure relies on the assumption that the composition of the test solutions is known and the Raman data can therefore not be used for validation of these. The authors also point out that spectrophotometric data from the uranyl(VI) chloride system is not consistent with the Raman model. This is not surprising as other studies [2005HEN/TUT], [2011SOD/SKA] show that the highest complex formed even in 9 M chloride is $UO_2Cl_3^-$. To conclude, the information in [1992NGU/BEG] does not provide new equilibrium data. In [2013DAR/DUB] the same Raman method has been used to study uranyl(VI) chloride complex formation in aqueous solutions of LiCl in the temperature range 21-350 °C at saturation pressure. It is quite clear from this study that the speciation changes significantly with increasing temperature. At room temperature there is only a single Raman peak in solutions with

concentrations of LiCl equal to 0.3, 1,3 and 8 M and this peak has been deconvoluted into 4, 5 and 7 components assuming that complexes $UO_2Cl_n^{2-n}$, $n$ = 1-5 are formed. This assumption is not consistent with the information from [2005HEN/TUT], [2011SOD/SKA] and for this reason the present review has not used these data.

**[2013JOH/BHA]**

This is an accurate quantum chemistry study of the Gibbs energy of formation of Th(IV) and U(IV) fluoride, chloride and hydroxide complexes, $ML_4(g)$, L = F, Cl, OH, in gas phase. The computation method used, coupled cluster, CCSD(T) is considered as the "gold-standard" in this type of work. The same method was also tested in the structure optimisations, providing accurate structure parameters. We will only discuss the uranium data that are given in the following table, where all energies are given in kcal·mol$^{-1}$. The use of different approximation methods and different basis sets is one example of the accuracy that can be expected from this type of calculations, in the present case around 10 kcal·mol$^{-1}$ for the most accurate CCSD(T) model; the error between this and models using different DFT functionals is often significantly larger.

Table A-22: Enthalpy and Gibbs energy of formation of $UF_4(g)$, $UCl_4(g)$ and $U(OH)_4(g)$ from [2013JOH/BHA] ], and comparison with selected values in [2003GUI/FAN].

| Compound | PBEO | CCSD(T) | CCSD(T)[(a)] | Selected data in [2003GUI/FAN] |
|---|---|---|---|---|
| Enthalpy of formation $\Delta_f H_m^o$ in kcal·mol$^{-1}$ | | | | |
| $UF_4(g)$ | – 379.8 | – 379.9 | – 388.9 | – (383.7 ± 1.6) |
| $UCl_4(g)$ | – 194.9 | – 184.2 | – 194.9 | – (194.9 ± 1.6) |
| $U(OH)_4(g)$ | – 298.0 | – 303.1 | – 309.5 | – |
| Gibbs energy of formation $\Delta_f G_m^o$ in kcal·mol$^{-1}$ | | | | |
| $UF_4(g)$ | – 378.6 | – 372.7 | – 381.7 | – (376.9 ± 1.6) |
| $UCl_4(g)$ | – 189.2 | – 178.5 | – 189.2 | – (188.7 ± 1.1) |
| $U(OH)_4(g)$ | – 274.8 | – 279.9 | – 286.3 | – |

(a) These calculations have been made using a different basis set from [1970BOY/BER].

The calculated vibrational frequencies are in excellent agreement with the values in Table 9-9 of [2003GUI/FAN], with differences for $UF_4$ of at most 5 cm$^{-1}$ and slightly larger, 8 cm$^{-1}$ for $UCl_4$. The quantum chemistry molar entropy at room temperature are 84.635 and 99.336 J·K$^{-1}$·mol$^{-1}$ for $UF_4(g)$ and $UCl_4(g)$, respectively in fair agreement with the selected values (95.10 ± 3.0) and (103.5 ± 3.0) J·K$^{-1}$·mol$^{-1}$ in [2003GUI/FAN].

The authors have also calculated the enthalpy and Gibbs energy of formation of the compounds in water shown in Table A-23 together with the selected experimental data from [2003GUI/FAN]:

Table A-23: Gibbs energy of formation, $\Delta_f G_m^o$ (298.15 K) for the formation of $UF_4$(aq), $UCl_4$(aq) and $U(OH)_4$(aq) from [2013JOH/BHA], and comparison with selected values in [2003GUI/FAN].

| Compound | PBEO | CCSD(T) | CCSD(T)[(a)] | Selected values in [2003GUI/FAN] |
|---|---|---|---|---|
| $UF_4$(aq) | – 426.6 | – 426.7 | – 435.7 | – (431.7 ± 1.5) |
| $UCl_4$(aq) | – 269.5 | – 258.8 | – 269.5 | – |
| $U(OH)_4$(aq) | – 307.2 | – 312.3 | – 318.7 | – (339.7 ± 1.9) |

(a) Large aug-cc-pVQZ and expanded U/Th basis sets.

It is difficult to assess the accuracy of the quantum chemistry data, one method might be to use the difference between DFT and *ab initio* results, and based on this criterion the present review suggests an uncertainty of at least 15 to 20 kJ·mol$^{-1}$ (4-5 kcal·mol$^{-1}$), concluding that thermodynamic data from even very accurate quantum chemistry calculations do not reach the accuracy of careful experimental studies; an exception may be the calculated entropy and heat capacity of small molecules in gas phase.

## A-1.4 Uranium compounds and complexes with group 16 elements

**[2003KAR/KNY]**

Karyakin *et al.* determined the standard enthalpy, entropy and Gibbs energy of formation of $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr), M = Ni, Cu, Zn, using reaction calorimetry and measurements of the isobaric heat capacity using adiabatic vacuum calorimetry in the temperature range 7-300 K. The enthalpy of formation was obtained by calorimetry using the following thermodynamic cycle:

$$UO_2(SO_4)\cdot 3H_2O(cr) + HCl\ (2M) \rightarrow \text{soln. } 1 \qquad (A.41)$$

$$M(SO_4)\cdot nH_2O(cr) + \text{soln. } 1 \rightarrow \text{soln. } 2 \qquad (A.42)$$

$$M[UO_2(SO_4)_2]\cdot 5H_2O(cr) + HCl(2M) \rightarrow \text{soln. } 3 \qquad (A.43)$$

$$(n-2)H_2O + \text{soln. } 3 \rightarrow \text{soln. } 4 \qquad (A.44)$$

Combination of Reactions (A.41)-(A.44) gives:

$$UO_2(SO_4)\cdot 3H_2O(cr) + M(SO_4)\cdot nH_2O(cr) \rightleftharpoons M[UO_2(SO_4)_2]\cdot 5H_2O(cr) + (n-2)H_2O \qquad (A.45)$$

The enthalpy of Reaction (A.41) is $-(4.04 \pm 0.03)$; the corresponding enthalpies of Reactions (A.42) and (A.43) are given in Table A-24. By combining the enthalpies of reaction with the auxiliary data in Table A-25 taken from V.P. Glushko,

Thermal constants of elements, issue 8, part (1978) and issue 6, Part 1 (1970), Karyakin *et al.* obtain the enthalpies of formation and the estimated uncertainty reported in Table A-26, where they have used the enthalpy of formation of pure water. The enthalpy of formation of water in 2 M HCl (~ 2.09 m), $\Delta_f H^\circ_m$ ($H_2O$, 2 M HCl) = – 285.90 kJ·mol$^{-1}$, differs from the value in pure water and can be evaluated from the relative partial molar enthalpy $L_1 \approx$ – 0.07 kJ·mol$^{-1}$, see Table IX.14 in [1997GRE/PLY2].

Table A-24: Standard enthalpies of solution (kJ·mol$^{-1}$) of compounds in 2 M HCl, $T$ = 298.15 K. Mean values of five replicate measurements are given.

| $A^{II}[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | $\Delta_r H_3^\circ$ /kJ·mol$^{-1}$ | $A^{II}SO_4\cdot n H_2O$(cr) | $\Delta_r H_2^\circ$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Ni[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (10.39 ± 0.14) | $NiSO_4\cdot 6H_2O$(cr) | (32.31 ± 0.18) |
| $Cu[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (23.32 ± 0.23) | $CuSO_4\cdot 5H_2O$(cr) | (35.79 ± 0.09) |
| $Zn[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (21.47 ± 0.66) | $ZnSO_4\cdot 7H_2O$(cr) | (49.16 ± 0.59) |

Table A-25: Auxiliary data used for calculation of thermodynamic data in the thermodynamic cycles (A.41)-(A.45). These data are from the Glushko and NEA tables. The selected values are new.

| Species | $\Delta_f H^\circ_m$ /kJ·mol$^{-1}$ | Reference |
|---|---|---|
| $UO_2SO_4\cdot 3H_2O$(cr) | – (2747.2 ± 4.2) | Glushko[(a)] |
| | **– (2751.500 ± 4.600 )** | NEA |
| $NiSO_4\cdot 6H_2O$(cr) | – (2683.9 ± 2.6) | Glushko[(a)] |
| | **– (2683.817 ± 1.014)** | NEA [2005GAM/BUG] |
| $CuSO_4\cdot 5H_2O$(cr) | – (2279.4 ± 1.1) | Glushko[(a)] |
| | **– (2280.380 ± 1.290)** | This review, see Table 14-3 |
| $ZnSO_4\cdot 7H_2O$(cr) | – (3078.5 ± 1.5) | Glushko[(a)] |
| | **– (3076.850 ± 0.670)** | This review, see Table 14-3 |

(a) Glushko, V. P. Thermal Constants of Substances, 1970, issue 6, part 1.

The present review has recalculated the thermodynamic data from [2003KAR/KNY] using the selected data from [2003GUI/FAN] and [2005GAM/BUG] (Table A-25), and these data are reported in Table A-26. This table also contains the selected values of the molar heat capacity, molar entropy and the entropy and Gibbs energy of formation for the Ni, Cu and Zn phases.

The molar isobaric heat capacity and the molar entropy were determined by low-temperature calorimetry in the range 130-300 K, with extrapolation to 0 K using the following functions:

$$C_p = 1.97 \times 10^{-1} T^{1.53} \text{ for } Ni[UO_2(SO_4)_2]\cdot 5H_2O\text{(cr)}$$

$$C_p = 5.66 \times 10^{-3} T^{2.73} \text{ for } Cu[UO_2(SO_4)_2]\cdot 5H_2O\text{(cr)}$$

$$C_p = 7.37 \times 10^{-3} T^{2.58} \text{ for } Zn[UO_2(SO_4)_2]\cdot 5H_2O\text{(cr)}$$

Because of the long temperature extrapolation the uncertainty in the reported entropies are probably underestimated. Nevertheless, this review considers these as the best values available and they have been accepted as selected data.

The heat capacities and their temperature dependence in the range where no anomalities appear can, within the experimental errors, be described as:

$$C_p(\mathrm{Ni[UO_2(SO_4)_2]\cdot 5H_2O, cr}) = -28.886 + 2.9064T - 0.0034T^2,$$

valid in the temperature range 130-240 K,

$$C_p(\mathrm{Zn[UO_2(SO_4)_2]\cdot 5H_2O, cr}) = 34.664 + 1.8600T - 0.0016T^2,$$

valid in the temperature range 130-260 K.

Above the upper temperature ranges there is an anomalous increase in the isobaric heat capacity for the Ni and Zn compounds. The authors do not report the $C_p$ function for $Cu[UO_2(SO_4)_2]\cdot 5H_2O$(cr).

Above 150 K, Karyakin *et al.* [2005KAR/KNY], report anomalous increase in the isobaric heat capacity as a result of phase transitions in $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr), M = Mn, Fe, Co.

Table A-26: Absolute entropies, isobaric heat capacities, enthalpies, entropies and Gibbs energies of formation of nickel, copper and zinc uranyl sulfates $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) at 298.15 K. The values in bold have been recalculated from those reported by Karyakin *et al.* and selected by the present review. The uncertainty in $C_p^o$ is estimated to ± 1.5 $J\cdot K^{-1}\cdot mol^{-1}$ by the present review. The enthalpies of formation have been corrected using the relative partial molar entropy of water in 2 M (2.09 m) HCl. All selected values are new.

| M | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $S_m^o$ (298.15K) /J·K$^{-1}$ mol$^{-1}$ | $\Delta_f S_m^o$ /J·K$^{-1}$ mol$^{-1}$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $C_p^o$ /J·K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| Ni | – (4249.0 ± 5.0)[a] | (581.4 ± 2.1)[a] | – (1753.1 ± 2.2)[a] | – (3726.5 ± 5.5)[a] | (535.4 ± 2.7) [a] |
| | **– (4253.057 ± 4.719)** | **(581.400 ± 2.100)** | **– (1754.818 ± 2.122)** | **– (3729.858 ± 4.761)** | **(535.400 ± 1.500)** |
| Cu | – (4114.0 ± 6.0)[a] | (514.2 ± 2.1)[a] | – (1823.8 ± 2.2)[a] | – (3570.0 ± 6.5)[a] | (483.3 ± 2.4) [a] |
| | **– (4119.110 ± 4.785)** | **(514.200 ± 2.100)** | **– (1825.298 ± 2.114)** | **– (3574.897 ± 4.826)** | **(483.300 ± 1.500)** |
| Zn | – (4330.0 ± 4.5)[a] | (477.1 ± 2.1)[a] | – (1869.200 ± 2.200)[a] | – (3772.5 ± 5.0)[a] | (447.5 ± 2.2) [a] |
| | **– (4332.260 ± 4.736)** | **(477.100 ± 2.100)** | **– (1870.878 ± 2.118)** | **– (3774.458 ± 4.778)** | **(447.500 ± 1.500)** |

(a) Reported by Karyakin *et al.*

**[2004KAR/KNY]**

Karyakin *et al.* have used the same experimental method as in their previous study [2003KAR/KNY] to calculate the enthalpy of formation for $M[UO_2(SO_4)_2]\cdot nH_2O$(cr) and corresponding anhydrous amorphous phases, M = Mn, Fe, Co, Ni, Cu, Zn. Only crystalline phases are considered in this review. The experimental method is the same as

in [2003KAR/KNY], as a matter of fact the data for Ni, Cu and Zn are identical with those from this paper. In order to calculate the enthalpy of formation from the enthalpies of solution determined by calorimetry (Table A-27) , the authors used auxiliary data (Table A-28) taken from the Glushko tables (1978, issue 8, part 1 and 1987, issue 6, part 1).

Table A-27: Standard enthalpies of solution ($kJ \cdot mol^{-1}$) of crystalline compounds in 2 M (~2.09 m) HCl, $T$ = 298.15 K. Mean results of several replicate measurements are given.

| $A^{II}[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | $\Delta_r H_3^o$ / $kJ \cdot mol^{-1}$ | $A^{II}SO_4 \cdot nH_2O$ | $\Delta_r H_2^o$ / $kJ \cdot mol^{-1}$ |
|---|---|---|---|
| $Mn[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (15.23 ± 0.03) | $MnSO_4 \cdot H_2O$(cr) | – (12.55 ± 0.09) |
| $Fe[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (11.66 ± 0.10) | $FeSO_4 \cdot 7H_2O$(cr) | (41.33 ± 0.20) |
| $Co[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (28.92 ± 0.25) | $CoSO_4 \cdot 7H_2O$(cr) | (35.58 ± 0.26) |
| $Ni[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (10.39 ± 0.14) | $NiSO_4 \cdot 6H_2O$(cr) | (32.31 ± 0.18) |
| $Cu[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (23.32 ± 0.23) | $CuSO_4 \cdot 5H_2O$(cr) | (35.79 ± 0.09) |
| $Zn[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | – (21.47 ± 0.66) | $ZnSO_4 \cdot 7H_2O$(cr) | (49.16 ± 0.59) |

Table A-28: Standard enthalpies of formation of $MSO_4 \cdot nH_2O$(cr) and $UO_2SO_4 \cdot 3H_2O$(cr) in $kJ \cdot mol^{-1}$. The data in bold are the NEA selected values and from Table 14-3 in this review; the other ones from the Glushko tables, Thermal Constants of Substances, Vols. 1, 6, 7, 8, Moscow, 1968-1978. The selected values are all new.

| Compound | $\Delta_f H_m^o$ /$kJ \cdot mol^{-1}$ | Compound | $\Delta_f H_m^o$ /$kJ \cdot mol^{-1}$ |
|---|---|---|---|
| $UO_2SO_4 \cdot 3H_2O$(cr) | – (2247.2 ± 4.2) | $NiSO_4 \cdot 6H_2O$(cr) | – (2683.9 ± 2.5) |
| | **– (2751.500 ± 4.600)** | | **– (2683.817 ± 1.014)** |
| $MnSO_4 \cdot H_2O$(cr, monocl) | – (1387.4 ± 2.1) | $CuSO_4 \cdot 5H_2O$(cr) | – (2279.4 ± 1.0) |
| | | | **– (2280.380 ± 1.290)** |
| $FeSO_4 \cdot 7H_2O$(cr, monocl) | – (3015.8.2 ± 0.8) | $ZnSO_4 \cdot 7H_2O$(cr) | – (3078.5 ± 1.5) |
| | **– (3012.512 ± 0.602)** | | **– (3076.850 ± 0.670)** |
| $CoSO_4 \cdot 7H_2O$(cr) | – (2981.6 ± 2.0) | | |

Using the auxiliary data in Table A-28, this review has calculated the enthalpies of formation listed in Table A-29.

Karyakin *et al.* have also determined the enthalpy of dehydration of $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) with the formation of amorphous phases at 298.15 K. The total enthalpy of dehydration and the average enthalpy of dehydration per water are listed in Table A-30.

Table A-29: Standard enthalpies of formation, $\Delta_f H_m^o$, of 3d transition metal uranyl sulfates, $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr), at 298.15 K as reported in [2004KAR/KNY] and recalculated by this review (in bold). The Gibbs energy of formation for the $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) compounds have been obtained from the entropies of formation in [2005KAR/KNY] and entropies of elements from the NEA database. The selected values are all new.

| M | $\Delta_f H_m^o$ ($M[UO_2(SO_4)_2]\cdot 5H_2O$, am) /kJ·mol$^{-1}$ | $S_m^o$ ($M[UO_2(SO_4)_2]\cdot 5H_2O$, cr) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S_m^o$ ($M[UO_2(SO_4)_2]\cdot 5H_2O$, cr) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G_m^o$ ($M[UO_2(SO_4)_2]\cdot 5H_2O$, cr) /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| Mn | – (4422.0 ± 4.5) | | | |
| | **– (4426.160 ± 5.058)** | **(607.3 ± 2.1)** | **– (1731.058 ± 2.116)** [(a)] | **– (3910.045 ± 5.097)** |
| Fe | – (4285.0 ± 4.5) | | | |
| | **– (4285.562 ± 4.649)** | **(574.6 ± 2.1)** | **– (1758.833 ± 2.118)** | **– (3761.166 ± 4.692)** |
| Co | – (4239.0 ± 4.5) | | | |
| | **– (4243.140 ± 5.033)** | **(600.7 ± 2.1)** | **– (1735.688 ± 2.119)**[(a)] | **– (3725.645 ± 5.072)** |
| Ni | – (4249.0 ± 5.0) | | | |
| | **– (4253.057 ± 4.719)** | **(581.4 ± 2.1)** | **– (1754.818 ± 2.122)** | **– (3729.858 ± 4.761)** |
| Cu | – (4114.0 ± 4.5) | | | |
| | **– (4119.110 ± 4.785)** | **(514.2 ± 2.1)** | **– (1825.298 ± 2.114)** | **– (3574.897 ± 4.827)** |
| Zn | – (4330.3 ± 4.5) | | | |
| | **– (4332.260 ± 4.736)** | **(477.1 ± 2.1)** | **– (1870.878 ± 2.118)** | **– (3774.458 ± 4.778)** |

(a) For Mn(cr) $S_m^o$ = (32.01 ± 0.13) J·K$^{-1}$·mol$^{-1}$ and for Co(cr) $S_m^o$ = (30.04 ± 0.17) J·K$^{-1}$·mol$^{-1}$ [1972GLU/MED].

Table A-30: The total enthalpy of dehydration and the average enthalpy of dehydration per water in kJ·mol$^{-1}$ for $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) at 298.15 K.

| M | $\Delta_{dehyd} H_m^o$ /kJ·mol$^{-1}$ | $\Delta_{dehyd} H_m^o$ /kJ·mol$^{-1}$ (average per water) |
|---|---|---|
| Mn | (82.35 ± 0.64) | 16.5 |
| Fe | (101.4 ± 0.3) | 20.5 |
| Co | (113.0 ± 0.8) | 22.5 |
| Ni | (105.6 ± 0.5) | 21.0 |
| Cu | (90.49 ± 0.31) | 18.0 |
| Zn | (84.74 ± 0.33) | 17.0 |

**[2004NEU/SKA]**

Neuefeind *et al.* have used high-energy X-ray scattering to determine the structure of the $UO_2SO_4$(aq) ion pair in a 0.5 m $UO_2SO_4$ solution. The structure analysis demonstrates that the sulfate ion is mono-dentate coordinated, with a U-S distance of 3.67 Å; there are no thermodynamic data in this study. The structure information is consistent with the EXAFS information obtained by Hennig *et al.* [2007HEN/SCH], [2007HEN/SCH2].

**[2005KAR/KNY]**

Karyakin *et al.* have used low-temperature calorimetry in the temperature range 5-300 K, to determine the isobaric molar heat capacity, $C_p^o$ (298.15 K) and the molar entropy $S^o$ (298.15 K) of $M[UO_2(SO_4)_2]\cdot nH_2O$(cr) phases and combined these data with their previous ([2003KAR/KNY], [2004KAR/KNY]) determinations of the corresponding enthalpies of formation in order to determine the Gibbs energy and entropy of formation. The values of $C_p^o$ and entropy $S^o$ of $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) phases and the corresponding entropy of formation, $\Delta_f S^o$ ($M[UO_2(SO_4)_2]\cdot 5H_2O$, cr), listed in Table A-31 have been included among the selected values. The entropy of formation was obtained using entropies of the elements that agree with the NEA selected values. Only data reported in [2005KAR/KNY] for crystalline phases are considered in this review.

Table A-31: Selected molar heat capacity $C_{p,m}^o$ (298.15 K), molar entropy $S_m^o$ (298.15 K) and entropies of formation, $\Delta_f S_m^o$, for the $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) phases from [2005KAR/KNY]. The uncertainties in $C_{p,m}^o$ (298.15 K) and $S_m^o$ (298.15 K) are estimated to ± 1.5 $J\cdot K^{-1}\cdot mol^{-1}$ and 2.1 $J\cdot K^{-1}\cdot mol^{-1}$, respectively. The selected values are all new.

| Compound | $C_{p,m}^o$ (298.15 K) /$J\cdot K^{-1}\cdot mol^{-1}$ | $S_m^o$ (298.15 K) /$J\cdot K^{-1}\cdot mol^{-1}$ | $\Delta_f S_m^o$ ($M[UO_2(SO_4)_2]\cdot 5H_2O$,cr) /$J\cdot K^{-1}\cdot mol^{-1}$ |
|---|---|---|---|
| $Cu[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | **(483.3 ± 1.5)** | **(514.2 ± 2.1)** | **– (1825.298 ± 2.114)** |
| $Mn[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | **(591.9 ± 1.5)** | **(607.3 ± 2.1)** | **– (1731.058 ± 2.116)** |
| $Fe[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | **(548.2 ± 1.5)** | **(574.6 ± 2.1)** | **– (1758.833 ± 2.118)** |
| $Co[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | **(590.6 ± 1.5)** | **(600.7 ± 2.1)** | **– (1735.688 ± 2.119)** |
| $Ni[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | **(535.4 ± 1.5)** | **(581.4 ± 2.1)** | **– (1754.818 ± 2.122)** |
| $Zn[UO_2(SO_4)_2]\cdot 5H_2O$(cr) | **(447.5 ± 1.5)** | **(477.1 ± 2.1)** | **– (1870.878 ± 2.118)** |

Two phase transitions were observed for $Mn[UO_2(SO_4)_2]\cdot 5H_2O$(cr), one for $Fe[UO_2(SO_4)_2]\cdot 5H_2O$(cr) and one for $Co[UO_2(SO_4)_2]\cdot 5H_2O$(cr). The corresponding transition temperatures, enthalpy and entropy for the phase transitions are listed in Table A-32.

Table A-32: Thermodynamic characteristics of the phase transitions in manganese, iron and cobalt uranyl sulfate pentahydrates, $M[UO_2(SO_4)_2]\cdot 5H_2O$(cr) where the high-temperature phase is rhombic; there is no information on the low-temperature structures.

| M | $T_{tr}$ /K | $\Delta_{tr}H$ /$J\cdot mol^{-1}$ | $\Delta_{tr}S$ /$J\cdot K^{-1}\cdot mol^{-1}$ | $T_{tr}$ /K | $\Delta_{tr}H$ /$J\cdot mol^{-1}$ | $\Delta_{tr}S$ /$J\cdot K^{-1}\cdot mol^{-1}$ |
|---|---|---|---|---|---|---|
| Mn | 176 | (510 ± 3) | (2.90 ± 0.02) | 238 | (190 ± 3) | (0.80 ± 0.02) |
| Fe | 182 | (200 ± 3) | (1.10 ± 0.02) | – | – | – |
| Co | – | – | – | 237 | (1920 ± 3) | (8.10 ± 0.02) |

**[2006MEI/LIS]**

The analysis by Meinrath *et al.* of their experimental data on UV/VIS spectra in uranyl(VI) sulfate systems at different pH is of general interest for this review. By using chemometric methods they have deconvoluted their experimental spectra into components for each complex; in this way they also obtain information on the corresponding equilibrium constants. The authors note that several chemical models can be used to fit the experimental spectra, resulting in different values of the equilibrium constants and molar absorptivity of the complexes (the same complexes are used in the different models). This is not surprising and a result of the strong correlation between equilibrium constants and their corresponding molar absorptivity; equilibrium constants should when possible be determined in separate experiments—a method in general used by the early experimental studies (Meinrath *et al.* indicate that these are less reliable because modern instruments and computer methods were not available at the time—the present review disagrees with this statement). The study by Meinrath *et al.* does not provide new and more reliable information on the equilibria in the uranyl(VI) sulfate system.

**[2007HEN/SCH]**

Hennig *et al.* have studied sulfate complexes of U(VI), U(IV) and Th(IV) using EXAFS in acid solutions at high total concentrations of sulfate. The the U(VI) system has been studied at substantially higher sulfate concentrations than in [2007HEN/SCH2], which means that higher concentrations of $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$ are present in the test solutions. Using the equilibrium constants for the formation of U(VI) sulfate complexes one expects that $UO_2(SO_4)_2^{2-}$ is the predominant complex, which is also supported by the EXAFS analysis. The EXAFS data also indicate that sulfate is bidentate coordinated with a U-S distance of 3.11 Å. In test solutions with an equimolar concentration of $UO_2SO_4(aq)$ one finds two isomers with mono- and bi-dentate coordination in approximately equal amounts, suggesting a difference in Gibbs free energy around zero kJ·mol$^{-1}$. A quantum chemistry calculation results in a free energy difference of 14.9 kJ·mol$^{-1}$, with bidentate coordination most stable. This energy difference is not significantly different from zero, considering the accuracy of at least ± 10 kJ·mol$^{-1}$ in this type of calculations.

Hennig *et al.* have also studied the U(IV) and Th(IV) sulfate systems in acid solutions at high total concentrations of sulfate. The EXAFS analysis indicates four U-S distances, corresponding to a stoichiometry, $U(SO_4)_4^{4-}$ with mono and bidentate coordination, where the ratio mono:bi decreases with increasing total concentration of sulfate. The EXAFS analysis suggests nine oxygen donors in the coordination shell which is consistent with the structure $U(SO_{4,bid})_x(SO_{4,mono})_y(OH_2)_3^{4-}$, where (x + y) ≈ 4. There is no thermodynamic information in this study, but the observation of the

formation of anionic U(IV) sulfate complexes at high total concentrations of sulfate is important.

**[2007HEN/SCH2]**

Hennig *et al.* have studied sulfate coordination in $UO_2SO_4$(aq) and $UO_2(SO_4)_2^{2-}$ complexes using EXAFS. Based on the U-S distance they suggest that sulfate is predominantly mono-dentate in the first complex and bidentate in the second one. There is, however, one bidentate and three monodentate coordinated sulfate ion in $Na_{10}[UO_2(SO_4)_4]\cdot(SO_4)_2\cdot 3H_2O$(cr) [2002BUR/HAY]. There are no thermodynamic data reported in this study.

**[2007VAL/GRE]**

Vallet and Grenthe have studied the coordination of sulfate in $UO_2SO_4$(aq) and $UO_2(SO_4)_2^{2-}$ complexes using quantum chemical methods and a CPCM model of the aqueous solvent. The structure at the DFT level and the energy difference at the MP2 level between different isomers is reported. The difference in Gibbs energy between the most stable isomer with bidentate sulfate and the one with mono-dentate coordination is 17 $kJ\cdot mol^{-1}$ in $UO_2SO_4$(aq); in the complex $UO_2(SO_4)_2^{2-}$ this difference is 17.7 $kJ\cdot mol^{-1}$. The calculated bond distances are in both cases consistent with EXAFS results. This study does not provide new thermodynamic data relevant for the present review, but the small difference in energy between the coordination isomers is of chemical interest.

**[2007VIT/PHR]**

Vitorge *et al.* discuss correlations between equilibrium constants and atomic charge for a number of actinide complexes with ligands containing O-donors. Correlations can be used for estimates of unknown constants but these are not accepted in the NEA reviews.

**[2008HEN/IKE]**

Hennig *et al.* have continued their exploration of sulfate coordination in uranyl complexes by including UV/VIS spectrophotometric data and a theoretical analysis of these, from which they can exclude the formation of $[UO_2(SO_4)_3]^{4-}$ in test solutions with the ratio sulfate/uranium less than 59. The EXAFS data provide little new information but the identification of mono- and bi-dentate sulfate coordination is supported by high intensity X-ray scattering (HEXS) experiments from the Argonne advanced photon source.

**[2008HEN/KRA]**

Hennig *et al.* have studied the mode of coordination of sulfate in aqueous solutions of U(IV) and in $Na_{1.5}(NH_4)_{4.5}[U(SO_4)_5(OH_2)]\cdot H_2O$(cr), this study is a follow-up of [2007HEN/SCH]. The EXAFS data were collected at pH = 1, a uranyl concentration of 0.05 M and a total sulfate concentration of 2 M, which at the given pH consists mainly of $HSO_4^-$. Under these conditions the constitution of the sulfate complex suggests 2.3 mono-dentate and 2.4 bidentate coordinated sulfate ions, in good agreement with the three bidentate and two monodentate coordinated sulfates in the solid compound. In the solution chemical experiments reported in previous reviews there was only evidence for two coordinated sulfate ligands, but these experiments were made at much lower sulfate concentrations so there is no contradiction between the two sets of data.

**[2008HEN/TSU]**

This is a summary of previous studies from the group of Hennig *et al.* on sulfate coordination in U(VI) and U(IV) sulfate complexes and does not provide any new information.

**[2008KRI]**

Krivovichev reports the X-ray structure of $(H_3O)_2[UO_2(SeO_4)_2(OH_2)]\cdot(H_2O)_2$(cr) and $(H_3O)_2[UO_2(SeO_4)_2(OH_2)]\cdot(H_2O)$(cr), and finds that the uranyl-ion is coordinated by four monodentate selenate ions and one water ligand which is the same coordination as in $K_2[UO_2(SO_4)_2(OH_2)]\cdot(H_2O)_2$(cr) from Niinistö *et al.* [1979NII/TOI].

**[2008RAO/TIA]**

This conference paper presents spectroscopic data on the system uranium(VI)-sulfate, and reports equilibrium constants for the complexes $UO_2SO_4$(aq) and $UO_2(SO_4)_2^{2-}$ at $t$ = 25, 40, 55 and 70 °C. The same data is discussed in more detail in [2009TIA/RAO2], in combination with calorimetric data.

**[2008VER/VIT]**

Vercouter *et al.* have made a careful study of complex formation in the uranyl(VI)-sulfate system using fluorescence spectroscopy. They have studied the equilibria at different temperatures in the range 10-75 °C in an ionic medium with $[Na^+]$ = 0.10 M and have in this way also obtained information on the different enthalpies of reaction. The study also contains a detailed discussion of previous data that this review found of great value. The experimental data at 25 °C and 0.1 M $Na^+$ ($NaClO_4$ – $Na_2SO_4$)

reported by Vercouter *et al.* are given in the following table including the corresponding extrapolation to $I = 0$. The data for the formation of $[UO_2(SO_4)_3]^{4-}$ in 3 M $Na^+$ ($NaClO_4$ – $Na_2SO_4$) are also reported, but these have not been extrapolated to zero ionic strength by Vercouter *et al.*

Table A-33: Equilibrium constants, Gibbs energies, enthalpies and entropies of reaction for the formation of of uranyl(VI) sulfate complexes from Vercouter *et al.*

| Reaction | $\log_{10} K_n$ | $\log_{10} K_n^o$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| $UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4(aq)$ | 2.45 ± 0.05 | 3.29 ± 0.10 | 29.1 ± 4.0 | 145 ± 13 | – (18.78 ± 0.29) |
| $UO_2SO_4 + SO_4^{2-} \rightleftharpoons [UO_2(SO_4)_2]^{2-}$ | 1.03 ± 0.04 | 1.04 ± 0.10 | 16.6 ± 4.5 | 77 ± 15 | – (5.94 ± 0.57) |
| $[UO_2(SO_4)_2]^{2-} + SO_4^{2-} \rightleftharpoons [UO_2(SO_4)_3]^{4-}$ | 0.76 ± 0.20 | – | 11 ± 8 | 25 ± 27 | 4.34 ± 1.14 |

Grenthe *et al.* [1992GRE/FUG] report the equilibrium constant, $\log_{10} \beta_3$ = 3.4, for the reaction $UO_2^{2+} + 3SO_4^{2-} \rightleftharpoons [UO_2(SO_4)_3]^{4-}$ in 1 M $NaClO_4$, but no value was selected because of the difficulty to extrapolate this constant to zero ionic strength. Geipel *et al.* has obtained a similar value, $\log_{10} \beta_3$ = (3.20 ± 0.25) that was reported in [2003GUI/FAN] and extrapolated from 1.00 M ($NaClO_4$ + $HClO_4$) to zero ionic strength resulting in $\log_{10} \beta_3^o$ = (3.02 ± 0.38). The present review agrees with Vercouter *et al.* that extrapolation from their data in 3.0 M $Na^+$ ($NaClO_4$ + $Na_2SO_4$) does not result in a reliable value at zero ionic strength.

The equilibrium constants proposed by Vercouter *et al.* are in good agreement with those selected in previous reviews; $\log_{10} K_1^o$ is a borderline case because the TRLFS measurements have been made under conditions where a small amount of hydrolysis takes place; the deconvolution of the measured spectra used in this experimental method is complicated because of correlation between equilibrium constants and the molar emissivity of the complexes.

Vercouter *et al.* have an extensive discussion of the measured enthalpies of reaction using the temperature dependence of equilibrium constants as compared with data obtained by calorimetry. Accurate calorimetric data are always more precise than those obtained by the temperature dependence of equilibrium constants, but the significant difference in $\Delta_r H_1$ for the formation of $UO_2SO_4$(aq) from [2008VER/VIT] and [2009TIA/RAO] and the value selected in [1992GRE/FUG] can hardly be explained in this way. The present review notes that the data from Vercouter *et al.* requires information on the temperature dependence of the various ion interaction coefficients but as this information is not available, Vercouter *et al.* have used the tabulated values at 25 °C, which may result in a systematic error. They have also discussed the data used in [1992GRE/FUG] and point out that when the enthalpy of reaction for formation of $UO_2SO_4$(aq) reported by Bailey and Larson [1971BAI/LAR] is recalculated using the selected equilibrium in [1992GRE/FUG] one obtains a value that

is close to the one reported by them. They also discuss calorimetric data obtained by Ullman and Schreiner [1988ULL/SCH] and note that these might be affected by systematic errors due to side reactions, *cf.* Appendix A review of this paper in [1992GRE/FUG]. This review is faced with a dilemma—there are two calorimetric studies, [1971AHR/KUL3] and [2009TIA/RAO] that report values of $\Delta_r H^o$ ($UO_2SO_4$, aq) in good agreement but which deviate strongly from the value in [2008VER/VIT] based on the temperature variation of the equilibrium constant. The latter is known to be less precise than the calorimetric method, but it seems unlikely that this is an explanation for the discrepancy, because in [2009RAO/TIA] the enthalpies of reaction obtained by calorimetry and from the equilibrium constants are in good agreement. The details of the recalculation of the data in [1971BAI/LAR] by Vitorge *et al.* are not clear and no account is taken for the protonation of sulfate (which as judged by the enthalpy of protonation of $SeO_4^{2-}$ is not negligible).

The enthalpy of reaction for the formation of $[UO_2(SO_4)_3]^{4-}$ is reported for information, but has not been included among the selected values.

**[2009SLA/FOU]**

Sladkov *et al.* have studied complex formation in the $UO_2^{2+}$ - $HSeO_3^-$ system using TRLFS and UV/VIS spectrophotometry. They present equilibrium constants at pH = 1 and 2, ionic strength = 0.035, 0.05 and 0.2 M, all at a temperature of 20 °C. The equilibrium constant for the reaction $UO_2^{2+} + HSeO_3^- \rightleftharpoons UO_2HSeO_3^+$ at different ionic strengths is given in Table A-34.

Table A-34: Equilibrium constant for the formation of uranyl(VI)-selenite complexes from [2009SLA/FOU] and [2010SLA]. The value at zero ionic strength has been calculated using SIT.

| Reaction | $\log_{10}\beta_n$ $I = 0.20$ M | $\log_{10}\beta_n$ $I = 0.05$ M | $\log_{10}\beta_n$ $I = 0.035$ M | $\log_{10}\beta_n^o$ $I = 0$ | Reference |
|---|---|---|---|---|---|
| $UO_2^{2+} + HSeO_3^- \rightleftharpoons UO_2HSeO_3^+$ | 3.32 ± 0.15 | 3.35 ± 0.12 | 3.35 ± 0.17[(a)] | 3.62 ± 0.15 | [2009SLA/FOU] |
| | | 2.93 ± 0.13 | | 3.27 ± 0.15 | [2010SLA] |
| $UO_2^{2+} + 2HSeO_3^- \rightleftharpoons UO_2(HSeO_3)_2$(aq) | | 5.04 ± 0.15 | | 5.51 ± 0.11 | [2010SLA] |

(a) UV/VIS determination.

The equilibrium constants are independent of pH which means that the coordinated ligand is $HSeO_3^-$. The authors have taken the first dissociation constant from $H_2SeO_3$(aq) into account by using the value selected in [2005OLI/NOL].

**[2009TIA/RAO2]**

Tian and Rao have studied complex formation between $UO_2^{2+}$ and $SO_4^{2-}$ at 25, 40, 55 and 70 °C using spectrophotometry and reaction calorimetry. The enthalpy of reaction was determined using both these methods. The measurements were made in a 1.00 M $Na^+$ ($NaClO_4$ – $Na_2SO_4$) ionic medium and the equilibrium data were extrapolated to zero ionic strength using SIT with interaction coefficients selected in Appendix B. The results are listed below, where the enthalpy of reaction obtained by the temperature dependence of the equilibrium constant is marked with (a).

Table A-35: Experimental equilibrium constants, Gibbs energies and enthalpies of reaction for the formation of $UO_2SO_4$(aq) and $UO_2(SO_4)_2^{2-}$ in a 1.00 M $Na^+$ ($NaClO_4$ – $Na_2SO_4$) ionic medium and SIT extrapolated values at $I = 0$.

| Reaction | $\log_{10}\beta$ 1.00 M $Na^+$ | $\log_{10}\beta^\circ$ $I = 0$ | $\Delta_r G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta_r H_m^\circ$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2^{2+} + SO_4^{2-} \rightleftharpoons UO_2SO_4(aq)$ | 1.96 ± 0.06 | 3.23 ± 0.08 | – (18.44 ± 0.46) | 17.7 ± 0.3 |
| | | | | 16.1 ±1.7[(a)] |
| $UO_2^{2+} + 2SO_4^{2-} \rightleftharpoons UO_2(SO_4)_2^{2-}$ | 2.97 ± 0.03 | 4.22 ± 0.15 | – (24.09 ± 0.86) | 43.2 ± 0.9 |
| | | | | 43.0 ± 2.1[(a)] |

(a) Data from the temperature dependence of the equilibrium constant.

The equilibrium constants are in excellent agreement with those selected in previous reviews $\log_{10}\beta_1^\circ = (3.15 \pm 0.02)$ and $\log_{10}\beta_2^\circ = (4.14 \pm 0.07)$; the corresponding enthalpies of reaction differ somewhat from the selected values (19.50 ± 1.60) and (35.10 ± 1.00) kJ·mol$^{-1}$.

**[2010SLA]**

Sladkov studied the complex formation in the uranyl(VI)- $SeO_3^{2-}$ and uranyl(VI)- $SeO_4^{2-}$ systems using affinity capillary electrophoresis, a method that has been validated against other solution chemical methods such as UV/VIS spectrophotometry or TRLFS spectroscopy. The present study has been performed in $Na^+(ClO_4^-)$ ionic media with concentrations varying from 0.02 to 0.20 M and at a temperature of 25 °C. The author reports the equilibrium constants for the Reactions (A.46) and (A.47) and their values extrapolated to zero ionic strength using SIT.

$$UO_2^{2+} + n SeO_4^{2-} \rightleftharpoons UO_2(SeO_4)_n^{2-2n},\ n = 1, 2; \quad \text{(A.46)}$$

$$UO_2^{2+} + n HSeO_3^- \rightleftharpoons UO_2(HSeO_3)_n^{2-n},\ n = 1, 2; \quad \text{(A.47)}$$

Table A-36: Equilibrium constants for the formation of selenate and hydrogen selenite complexes of uranyl(VI) and the corresponding data extrapolated to zero ionic strength using SIT, with interaction coefficients from Appendix B. The interaction coefficient for $SeO_4^{2-}$ is assumed to be the same as for $SO_4^{2-}$ and the one for $HSeO_3^{2-}$ the same as for $HSO_4^-$. Values of $\log_{10}\beta_n$ are the average of determinations at different pH.

| Reaction | $\log_{10}\beta_n$ $I = 0.05$ M | $\log_{10}\beta_n^o$ | Interaction coefficients | Reference |
|---|---|---|---|---|
| $UO_2SeO_4(aq)$ | (2.29 ± 0.06) | (2.93 ± 0.06) | $\varepsilon(SeO_4^{2-}) = -0.12$ | [2010SLA] |
| $UO_2(SeO_4)_2^{2-}$ | (3.24 ± 0.10 ) | (4.03 ± 0.18) | – | [2010SLA] |
| $UO_2HSeO_3^+$ | (3.35 ± 0.12)<br>(2.93 ± 0.13) | (3.62 ± 0.15)<br>(3.27 ± 0.15) | $\varepsilon(HSeO_3^-) = -0.01$ | [2009SLA/FOU]<br>[2010SLA] |
| $UO_2(HSeO_3)_2(aq)$ | (5.04 ± 0.15) | (5.51 ± 0.11) | | [2010SLA] |

Sladkov have tested different models and this review has selected the one with two complexes, noting that they are independent of the pH in the range 1.5 to 2.5 for both ligands. This is a careful study and the data have been used in the final selection.

**[2010VOP/STA]**

An abstract of UV/VIS spectrophotometric studies of complex formation in the uranyl(VI) nitrate and sulfate systems; no equilibrium constants reported but the authors claim that their results are in agreement with published data.

**[2012SLA]**

Sladkov studied the uranyl(VI) selenate system using the same method as in his previous studies [2009SLA/FOU] and [2010SLA]. In this study he determined the equilibrium constants for the formation of $UO_2SeO_4(aq)$ and $UO_2(SeO_4)_2^{2-}$ at different temperatures between 15 and 55 °C. These data have been used in a following publication, [2013SLA], to calculate the enthalpies of reaction by using the van't Hoff equation.

Table A-37: Experimental equilibrium constants at $I = 0.05$ M for the formation of uranyl selenate complexes from [2012SLA].

| t /°C | $\log_{10} \beta_1$ | $\log_{10} \beta_2$ |
|---|---|---|
| 15 | (2.19 ± 0.03) | (2.97 ± 0.07) |
| 25 | (2.24 ± 0.02) | (3.24 ± 0.06) |
| 35 | (2.32 ± 0.02) | (3.32 ± 0.08) |
| 45 | (2.41 ± 0.03) | (3.42 ± 0.10) |
| 55 | (2.48 ± 0.03) | (3.69 ± 0.11) |

**[2012VIS/VET]**

This is an abstract of a study of the uranyl-sulfate system but there are no new thermodynamic data reported.

**[2012SCH/WIL]**

An X-ray crystallographic study where structural comparison among solids with the composition $[An(IV)(SO_4)_2 \cdot (OH_2)_7] \cdot 2H_2O(cr)$ are presented. There are no thermodynamic data reported.

**[2013SLA]**

Sladkov has studied the temperature dependence of the equilibrium constants for formation of $UO_2SeO_4(aq)$ and $UO_2(SeO_4)_2^{2-}$ using the same method as in [2010SLA] and [2012SLA]. The temperature and ionic strength ranges were the same as in these studies. The enthalpy of reaction was calculated from the van't Hoff equation. The experimental results for the formation of $UO_2SeO_4(aq)$ and $UO_2(SeO_4)_2^{2-}$ are shown in the following table.

Table A-38: Values of $\log_{10} \beta_n^o$, $\Delta_r G_m^o$, $\Delta_r H_m^o$ and $\Delta_r S_m^o$ as reported in [2013SLA].

| Reaction | $\log_{10} \beta_n^o$ | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol | $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $UO_2SeO_4(aq)$ | (2.93 ± 0.06)[(a)] | – (16.7 ± 0.3) | (20 ± 2) | (123 ± 6) |
| $UO_2(SeO_4)_2^{2-}$ | (4.03 ± 0.18)[(a)] | – (23.0 ± 1.0) | (31 ± 4) | (180 ± 15) |

(a) Values originally reported in [2010SLA].

Sladkov has also a discussion where he compares the thermodynamic data for sulfate and selenate complexes noting that they are very similar as one can expect for chemical reasons. The experimental enthalpies of reaction from Sladkov are in good agreement with the ones selected in [2003GUI/FAN] for the analogous sulfate complexes, $\Delta_r H_m^o(UO_2SO_4, aq) = (19.5 \pm 1.6)$ kJ·mol$^{-1}$ and $\Delta_r H_m^o(UO_2(SO_4)_2^{2-}) = (35.1 \pm 1.0)$ kJ·mol$^{-1}$.

# A-1.5 Compounds and complexes of uranium with group 15 elements

## A-1.5.1 Nitrogen compounds and complexes

**[1980MAR/DES]**

The study is focused on the photo-physics of $UO_2NO_3^+$ and $UO_2^{2+}$, but with information on the thermodynamics for Reaction (A.48) that was studied at different temperatures at pH = 1.66 and nitrate concentrations between 0.5 and 2 M.

$$UO_2^{2+} + NO_3^- \rightleftharpoons UO_2NO_3^+ \quad \text{(A.48)}$$

The authors report $\beta_1 = 0.25$ and $\Delta_r H_m^o$ ((A.48), 298.15 K) = 3 kJ·mol$^{-1}$ and $\Delta_r S_m^o$ ((A.48), 298.15 K) = 41 J·K$^{-1}$·mol$^{-1}$. There is a lack of experimental detail in the paper that only allows a recalculation to zero ionic strength from the data at constant ionic strength, $I$ = 2.0 M, which results in $\log_{10} \beta_1^o = -0.09$. The enthalpy and entropy of reaction have been estimated from the temperature dependence of the equilibrium constant between 274 and 298 K but this temperature interval is too small to allow even an approximate determination of these values. The data in this study have not been accepted.

**[2005KUR/ADA]**

[2005KUR/ADA] reported a molecular dynamics (MD) study of the thermophysical properties of the actinide nitrides ThN, UN, NpN and PuN in the temperature range 300-2500 K and pressure range 0.1MPa-1.5GPa. The authors used a Morse-type potential function added to the Busing-Ida type potential for the description of the ionic interactions. The calculations were performed for a system of 512 ions, and the interatomic potential parameters were derived by fitting the lattice parameters. The linear thermal expansion coefficient ($\alpha_{lin}$), compressibility ($\beta$) and heat capacity $C_p$ were subsequently calculated. The lattice heat capacity contribution was evaluated as the sum of the heat capacity at constant volume $C_V$ (calculated in the NVT MD simulations from the variation of the internal energy of the system) and lattice dilatation term $C_d$ (calculated in the NPT MD simulations from the relation $C_d = (3\alpha_{lin})^2 VT/\beta$, V being the molar volume). The calculated ($C_V + C_d$) values were found lower than the literature data, the difference being of the order of 7 J·K$^{-1}$·mol$^{-1}$ at 1600 K for ThN, 11 J·K$^{-1}$·mol$^{-1}$ at 1800 K for UN, 3 J·K$^{-1}$·mol$^{-1}$ at 1000 K for NpN, 4 J·K$^{-1}$·mol$^{-1}$ at 1400 K for PuN. The authors reported that this difference may be caused by the neglect of electronic contributions.

**[2005SED/KON]**

[2005SED/KON] reported *ab initio* calculations of the enthalpies of formation of the actinide mononitrides AnN(cr) (An = Ac, Th, Pa, U, Np, Pu, Am) using the full potential linearised augmented plane wave technique modified for local orbitals (APW + lo), yielding the difference in cohesive energies between the actinide mononitrides and the actinide metals An(cr) plus $1/2N_2$(g). The difference in magnetic states were neglected, and all spin-polarised structures considered as ferromagnetic. The contribution of the lattice and electronic excitation energies to the enthalpies of formation were estimated for ThN(cr), UN(cr) and PuN(cr) only as low temperature experimental heat capacity data were not available for the other compounds. However, these contributions represent not more than 0.5-2.0 % of the enthalpy value at room temperature. The calculated cohesive energies showed a steep decrease from Ac towards Th-Pa and a progressive increase from Pa towards Am, which was related to the covalent/ionic character of the An-5f chemical bonds. The minimum around ThN and PaN was interpreted in terms of increased hybridisation with 5f and 6d states due to covalent mixing, hence stabilising the bonding states of the valence band. The calculated enthalpies of formation showed a linear decrease from UN towards AmN, which can be extrapolated to AcN. This decreasing trend was related to the stabilising effect of the Madelung term when the bonding becomes more ionic. The values calculated for ThN and PaN were found much lower due to covalent stabilisation. The obtained enthalpies of formation are compared in Table A-39 with the experimental data recommended by [2001LEM/FUG], [2003GUI/FAN]. The uncertainty on the calculated values is estimated to be around 15 $kJ \cdot mol^{-1}$ by the present review. The agreement is very good for UN(cr) and NpN(cr), but large deviations are found for ThN(cr) and PuN(cr). The experimental value selected for ThN(cr) was derived from oxidation calorimetry data on $Th_3N_4$ and needs further experimental investigations. Nevertheless, the enthalpy of formation of ThN(cr) calculated by [2005SED/KON] is too large, and not compatible with the measured decomposition pressure of $N_2$(g) [2008RAN/FUG]. The discrepancy for PuN(cr) was attributed to correlation effects not taken into account in the (APW+lo) method, as Pu is found at the limit between itinerant and localised character of the 5f electrons. This review retains the enthalpies of formation as previously selected by [2001LEM/FUG], [2003GUI/FAN].

Table A-39: Enthalpies of formation of the actinide mononitrides as calculated by [2005SED/KON] and comparison with the experimental data selected by [2003GUI/FAN].

| Compound | AcN(cr) | ThN(cr) | PaN(cr) | UN(cr) | NpN(cr) | PuN(cr) | AmN(cr) |
|---|---|---|---|---|---|---|---|
| $\Delta_f H_m^\circ(298.15)$ /kJ·mol$^{-1}$ [2005SED/KON] calculated | – 256.8 | – 347.9 | – 365.3 | – 291.0 | – 301.3 | – 311.9 | – 324.6 |
| $\Delta_f H_m^\circ(298.15)$ /kJ·mol$^{-1}$ [2003GUI/FAN], [2008RAN/FUG] experimental | | – 381.2 | | – 290.0 | – 305.0 | – 299.2 | |
| Deviation | | 33.3 | | – 1.0 | 3.7 | – 12.7 | |

**[2007BUH/DIS]**

The structure and mode of coordination of nitrate in the complexes $[UO_2(OH_2)_4(NO_3)]^+$, $[UO_2(OH_2)_4(NO_3)_2]$, $[UO_2(NO_3)_3]^-$ and $[UO_2(NO_3)_4]^{2-}$ in gas-phase and water have been investigated using Car-Parrinello molecular dynamic simulations. The gas-phase simulations show that nitrate is preferentially coordinated in $\eta^2$ configuration, resulting in six-coordination in the equatorial plane of the uranyl-ion. More surprising is that the $\eta^1$ configuration in $[UO_2(OH_2)_4(NO_3)]^+$ is more stable by 12.6 kJ·mol$^{-1}$ than the $\eta^2$ one. $\eta^1$ configuration is also preferred in $[UO_2(OH_2)_4(NO_3)_2]$, but now the energy difference between the two modes of coordination is smaller, 4.2 kJ·mol$^{-1}$. Experimental EXAFS studies by Ikeda *et al.* [2009IKE/HEN] have demonstrated that nitrate is $\eta^2$-coordinated in aqueous solution and this mode of coordination is accepted by the present review.

**[2007BUH/GOL]**

Bühl *et al.* have used Car-Parrinello MD simulations to study the relative stability of uranyl(VI) nitrate and pertechnate complexes using the following sequence of reactions

$$[(UO_2)(OH_2)_4(NO_3)]^+ \rightleftharpoons [(UO_2)(OH_2)_4]^{2+}\ NO_3^- \quad \text{(A.49)}$$

$\Delta A$(A.49) = (32.2 ± 2.1) kJ·mol$^{-1}$

$$[(UO_2)(OH_2)_4]^{2+}\ NO_3^- \rightleftharpoons [(UO_2)(OH_2)_4]^{2+} + NO_3^- \quad \text{(A.50)}$$

$\Delta A$(A.50) ≈ (0 ± 2) kJ·mol$^{-1}$

$$[(UO_2)(OH_2)_5]^{2+} \rightleftharpoons [(UO_2)(OH_2)_4]^{2+} + H_2O \quad \text{(A.51)}$$

$\Delta A$(A.51) = 36.4 kJ·mol$^{-1}$

$$[(UO_2)(OH_2)_5]^{2+} + NO_3^- \rightleftharpoons [(UO_2)(OH_2)_4(NO_3)]^+ + H_2O \quad \text{(A.52)}$$

The computed Helmholtz free energies of reaction $\Delta A$(A.49) = (32.2 ± 2.1) kJ·mol$^{-1}$ indicates that the inner-sphere complex is much more stable than the corresponding outer-sphere one. The energy of dissociation of the outer-sphere complex is probably underestimated, but should fall within the estimated uncertainty range. Combination of the reactions leads for Reaction (A.52) to an estimated Helmholtz energy of reaction, $\Delta A^{o}$(A.52) = (4.2 ± 4.2) kJ·mol$^{-1}$, and equilibrium constant, $\log_{10} K$(A.52) = – (0.74 ± 0.74). Using $\Delta A$(A.50) = – 2 kJ·mol$^{-1}$ results in $\log_{10} K^{o}$ = 0.39, which is consistent with the experimental value $\log_{10} K^{o}$ = (0.30 ± 0.15) selected in [2003GUI/FAN] but not with $\log_{10} K^{o}$ = – (0.190 ± 0.150) selected in this review. One should note that the model is based on a coordination geometry that is not consistent with the experimental structure, *cf.* comments to [2007BUH/DIS].

A corresponding model is used to estimate the free energy of reaction with pertechnate $TcO_4^-$.

$$[(UO_2)(OH_2)_4(TcO_4)]^+ \rightleftharpoons [(UO_2)(OH_2)_4]^{2+} TcO_4^- ; \quad \text{(A.53)}$$

$\Delta A$(A.53) = (25.1 ± 2.1) kJ·mol$^{-1}$

$$[(UO_2)(OH_2)_4]^{2+} TcO_4^- \rightleftharpoons [(UO_2)(OH_2)_4]^{2+} + TcO_4^- ; \quad \text{(A.54)}$$

$\Delta A$(A.54) ≈ (0 ± 2) kJ·mol$^{-1}$

$$[(UO_2)(OH_2)_5]^{2+} \rightleftharpoons [(UO_2)(OH_2)_4]^{2+} + H_2O ; \quad \text{(A.55)}$$

$\Delta A$(A.55) = 36.4 kJ·mol$^{-1}$

$$[(UO_2)(OH_2)_5]^{2+} + TcO_4^- \rightleftharpoons [(UO_2)(OH_2)_4(TcO_4)]^+ + H_2O ; \quad \text{(A.56)}$$

The resulting Helmholtz energy of reaction for formation of $[(UO_2)(OH_2)_4(TcO_4)]^+$, $\Delta A_r^{o}$(A.56) = (11.3 ± 4.2) kJ·mol$^{-1}$, and $\log_{10} K$(A.56) = – (1.98 ± 0.74), demonstrating that the pertechnate complex is significantly weaker than the corresponding nitrate one, as is also the case for the perchlorate complexes. The present review does not include this value among the selected ones and it is reported for information only.

**[2007SUL/SEW]**

Suleimenov *et al.* have studied Reaction (A.57) from 298 to 423 K using spectrophotometry and from these data deduced the enthalpy of reaction. The concentration of U(VI) in the test solutions was approximately constant at 0.008 *m*, while the nitrate concentration varied between 0.05 and 3.14 *m* using nitric acid; the pressure varied between 1 and 4 bar. The ionic strength in the test solutions was determined by the nitric acid concentration. The experimental method to collect and analyse data is described in detail and is similar to the one used in [2010SMI] and [2013SMI/CZE], where the methodological problems with the spectrophotometric

method are discussed. Suleimenov *et al.* have corrected the conditional equilibrium constants to zero ionic strength using SIT. The experimental information is given in Table A-40. The enthalpy of reaction based on these data was extrapolated to zero ionic strength by the present review as described in Appendix B. The data in Table A-40 demonstrates that the interaction coefficients vary significantly with temperature as is the case for the formation of U(VI) carbonate complexes, *cf.* [1983DEV/YEF].

$$UO_2^{2+} + NO_3^- \rightleftharpoons UO_2NO_3^+ \qquad \text{(A.57)}$$

Table A-40: Experimental equilibrium constants and ion interaction coefficient $b = \Delta\varepsilon$ for the reaction $UO_2^{2+} + NO_3^- \rightleftharpoons UO_2NO_3^+$, as reported in [2007SUL/SEW].

| $t$/°C | $\log_{10}\beta_1^o$ | $\Delta\varepsilon$ | $\beta_1$ at $I$ = 1 M | $\beta_1$ at $I$ = 3 M |
|---|---|---|---|---|
| 25 | – (0.19 ± 0.02) | (0.05 ± 0.01) | 0.11 | 0.09 |
| 40 | – (0.02 ± 0.02) | (0.09 ± 0.02) | 0.17 | 0.17 |
| 55 | (0.16 ± 0.03) | (0.12 ± 0.03) | 0.26 | 0.30 |
| 70 | (0.26 ± 0.04) | (0.17 ± 0.03) | 0.34 | 0.49 |
| 100 | (0.49 ± 0.04) | (0.20 ± 0.04) | 0.53 | 0.85 |
| 150 | (0.78 ± 0.04) | (0.24 ± 0.04) | 0.81 | 1.47 |

The authors have not reported the uncertainty in the experimental values of $\log_{10}\beta_1$. The recalculated value of $\log_{10}\beta_1^o$ is significantly different from the one selected in [1992GRE/FUG] and [2003GUI/FAN] but in fair agreement with data from other experiments (Table 9-33 in the main text).

Suleimenov *et al.* report the enthalpy and entropy of reaction obtained from the temperature dependence of the equilibrium constants at $I$ = 1 and 3 M (data in Table A-40), $\Delta_r H_m$((A.57), 298.15 K) = 18.5 kJ·mol$^{-1}$ and $\Delta_r S_m$((A.57), 298.15 K) = 59 J·K$^{-1}$·mol$^{-1}$, respectively. The van't Hoff plot is close to linear in the evaluated temperature range and the present review has estimated the uncertainty in the enthalpy and entropy of reaction to 3.5 kJ·mol$^{-1}$ and 16 J·K$^{-1}$·mol$^{-1}$, respectively. The enthalpy of reaction extrapolated to zero ionic strength using only the Debye-Hückel term (Appendix B) is $\Delta_r H_m^o$ ((A.57), 298.15 K) = (20.9 ± 3.5) kJ·mol$^{-1}$, and $\Delta_r S_m^o$ ((A.57), 298.15 K) = (62 ± 16) J·K$^{-1}$·mol$^{-1}$, respectively. These values are very different from the ones reported by Day and Powers [1954DAY/POW] and [1980MAR/DES] but the data from [2007SUL/SEW] have been obtained over a larger temperature interval and should therefore be more reliable and for this reason the present review has accepted the corresponding enthalpy and entropy of reaction.

**[2007WEC/KIM]**

The authors reported first-principles all-electron relativistic calculations of the total energies, optimised geometries, electronic and thermodynamic properties of

stoichiometric UN(cr) and $UN_2$(cr) single crystals using the spin-polarised density functional theory (DFT). The calculated lattice parameters were found to reproduce experimental values within 0.03 Å. The calculated interatomic distances were also in good agreement with the EXAFS and XRD literature data [2012POI/YEA]. The density of states calculations revealed a marked f-orbital character in the conduction band for both compounds, as well as d-f hybridisation and 2p-orbital contributions in the valence bands of UN(cr) and $UN_2$(cr), respectively. From the calculated vibrational frequencies of the normal modes, the authors derived the lattice contribution to the isobaric heat capacity. The calculated data were found in close agreement with that of Counsell *et al.* [1966COU/DEL] up to 200 K. At higher temperatures, the calculated lattice contribution was found lower than the experimental data of Oetting and Leitnaker [1972OET/LEI] and Matsui and Ohse [1987MAT/OHS], however, the difference being about 7.3 $J \cdot K^{-1} \cdot mol^{-1}$ and 8.4 $J \cdot K^{-1} \cdot mol^{-1}$ at 1000 K, respectively. When adding the contribution for the conduction electrons, the calculated data were found much closer to the experiment, the difference being of the order of 3-4 %, hence showing the importance played by itinerant 5f-electrons.

**[2009IKE/HEN]**

Ikeda-Ohno *et al.* have studied the coordination of perchlorate, and nitrate to $UO_2^{2+}$ and $U^{4+}$ using EXAFS in test solutions of nitric and perchloric acid, where the former varied between 2.9 and 14.5 M $HNO_3$. The data from 1.0 M perchloric acid confirms many previous experimental observations that the aqua-ions $UO_2^{2+}(aq)$ and $U^{4+}(aq)$ have the constitution $[UO_2(OH_2)_5]^{2+}$ and $[U(OH_2)_{9\text{-}10}]^{4+}$, respectively. The EXAFS experiments in the uranyl(VI) systems revealed very clearly that at most two nitrate ligands were coordinated in $\eta^2$ fashion, an observation that is not consistent with the modelling in [2007BUH/GOL] and [2007BUH/DIS]. The number of coordinated nitrate in the uranyl(VI) system varies from 1.1 in 2.9 M $HNO_3$, 1.7 in 5.8 M $HNO_3$, 2.1 in 8.7 M $HNO_3$, to reach a limiting value of 2.5 in 14.5 M $HNO_3$.

In the U(IV)-nitrate system the coordination of nitrate is stronger and bidentate coordination is observed in 1.3 M $HNO_3$; the coordination number increases to about four between 4 M and 9 M $HNO_3$. These observations are important as they provide independent information on the chemical models that can be used in the analysis of equilibrium data in aqueous solutions. Ikeda-Ohno *et al.* have also made a spectrophotometric study of the U(VI)- $NO_3^-$ system in order to determine the number of principal components in the spectra, which in turn could be used as support for their EXAFS analysis. Unfortunately, they have not published the deconvoluted spectra, the intensities of which might have provided information on the symmetry at the uranium site. The quantum chemical data in [2009IKE/HEN] provides useful information on structures but not on reaction energies.

**[2009TSI/ROI]**

Electrospray ionisation mass spectroscopy has been used to explore the composition in gas-phase from uranyl nitrate solutions of different total concentration $1 \times 10^{-8}$ M < $[UO_2(NO_3)_2]$ < $1.2 \times 10^{-2}$ M. At a total concentration of $10^{-8}$ M, the predominant gas-phase species is $[UO_2(OH)(OH_2)_3]^+$ together with a smaller amount of $[UO_2(NO_3)(OH_2)_3]^+$; with increasing total concentration of uranium, the latter concentration increases and the former decreases. The general trends in these observations are consistent with the known chemistry in aqueous solution but this review does not find it possible to quantify the information into useful thermodynamic data for aqueous solutions. The composition of gas-phase complexes, suggests that there are four coordinated oxygen donors in the equatorial plane of the uranyl(VI) hydroxide complexes, while it may be four or five in the nitrate complex. These results are not consistent with observations in aqueous solution and have not been considered in the present review that has the focus on aqueous systems.

**[2010LU/WAN]**

The authors reported first-principles calculations of the lattice parameter, thermal expansion, electronic structure, bonding properties, phonon dispersion, and heat capacity at constant pressure of UN(cr) using the LDA/GGA + *U* method. Using the Hubbard *U* coefficient around 2 eV, the ground state antiferromagnetic nature of UN could be successfully reproduced. The calculated lattice parameter, *i.e.*, $a$ = 4.896-4.926 Å, for $U$ = 1-2 eV was found in good agreement with the literature data (4.886 Å) [2010KON/GRI]. A large degree of d-f hybridisation was obtained near the Fermi level in the total electronic density of states (DOS) calculations as in the work of [2007WEC/KIM], while the f orbitals were found to contribute to the conduction band with an occupancy of ~ 2.44 electrons, in good agreement with the photoelectron-spectroscopic results of [1980NOR/TAP] (2.2 ± 0.5 electrons). The results showed that the bonding in UN(cr) was covalent in nature. Using the quasi-harmonic approximation (QHA), the specific heat at constant pressure was derived from the phonon DOS. The lattice contribution to the heat capacity was found lower than the literature data as in the work of Weck *et al.* [2007WEC/KIM] based on all-electron calculations. When considering the contribution from the conduction electrons, the calculated data were found much closer to the experimental results of [1966COU/DEL] and [1987MAT/OHS] selected in the present review. The authors report that the agreement with the experiment should be further improved by considering electron-phonon interactions and many-body effects.

**[2010SMI], [2013SMI/CZE]**

[2010SMI] is the Ph. D. thesis of Smith that contains extensive information on the chemistry of uranium and plutonium in nitrate systems and their importance for analysing process streams in nuclear reprocessing systems. An impressive repertoire of experimental methods is described in detail, together with methods for analysis of experimental data. The accuracy of the measured absorptivities is satisfactory and this review was given access by the author to the primary data for the uranyl(VI) system that were not retrievable from the publications. The analysis of the spectrophotometric data is not satisfactory as will be discussed in the following. Smith and Czerwinski obtained spectrophotometric data at ambient temperatures, 18-22 °C and used these to determine the equilibrium constant(s) based on factor analysis combined with a least-squares refinement. The factor analysis indicates very clearly that the test solutions contain two coloured species and Smith and Czerwinski suggest that these are $UO_2^{2+}$ and $UO_2(NO_3)_2$(aq).This speciation is radically different from the one observed in a very large number of other studies, and results in a predominance of $UO_2(NO_3)_2$(aq) over a large part of the investigated nitrate concentration range; the authors report an equilibrium constant $\log_{10} K$ ($UO_2(NO_3)_2$, aq) ≈ 2.7 at an ionic strength of 1 *m*. This is neither consistent with the analysis in [2007SUL/SEW] that was made using the same experimental method and data analysis, nor with the EXAFS structure in [2009IKE/HEN] where the number of coordinated nitrate ions in 2.9 M $HNO_3$ is 1.1, with an uncertainty of about 10 %. This review has looked in more detail into the analysis made by Smith and Czerwinski. The factor analysis presents no problem, but this is not the case for the least-squares analysis. This method can present problems, in particular when the changes in molar absorptivity are small (as is the case here) and if there are correlations between the molar absorptivity and the equilibrium constant(s). We note that Ahrland [1951AHR] commented on the use of his spectrophotometric data on the uranyl(VI) nitrate system and concluded that they could not be used to determine equilibrium constants, and for this reason he based his data on a potentiometric study. In the following we will illustrate the difficulty to analyse the spectrophotometric data by using Smith's experimental absorptivities at an ionic strength of 1 *m*. We have used the selected value from [1992GRE/FUG] as the starting point together with Equation (A.58) that is valid if the two absorbing species are $UO_2^{2+}$ and $UO_2NO_3^+$.

$$E_j = \frac{\varepsilon_o + \varepsilon_1 \beta_1 [NO_3^-]}{1 + \beta_1 [NO_3^-]} \tag{A.58}$$

$E_j$ is the measured molar absorptivity at the experimental point $j$ and $[NO_3^-]$ the corresponding free concentration of nitrate; $\beta_1$ is the equilibrium constant and $\varepsilon_o$ and $\varepsilon_1$ are the molar absorptivities of $UO_2^{2+}$ and $UO_2NO_3^+$, respectively. The value of $\varepsilon_o$ is known from the experiment at zero concentration of nitrate, while the values of $\beta_1$ and $\varepsilon_1$ must be fitted from the experimental values at different nitrate concentrations. We were not able to make a direct least-squares fit using the experimental data and have

Table A-41: Test of model with $UO_2^{2+}$ and $UO_2NO_3^+$ and different equilibrium constants from $\beta_1 = 0.5$ $M^{-1}$ to $\beta_1 = 50$ $M^{-1}$.

| $E_j$ | $[NO_3^-]$ / M | $1+\beta_1 [NO_3^-]$ $\beta_1 = 0.5$ | $E_j(1+\beta_1 [NO_3^-])$ - $\varepsilon_o$ | $\varepsilon_1 \beta_1$ | $1+\beta_1 [NO_3^-]$ $\beta_1 = 5$ | $E_j(1+\beta_1 [NO_3^-])$ - $\varepsilon_o$ | $\varepsilon_1 \beta_1$ | $1+\beta_1 [NO_3^-]$ $\beta_1 = 50$ | $E_j(1+\beta_1 [NO_3^-])$ - $\varepsilon_o$ | $\varepsilon_1 \beta_1$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 5.825 | 0 | 1 | 0 | | 1 | 0 | | 1 | 0 | |
| 6.307 | 0.349 | 1.175 | 1.586 | 4.54 | 2.75 | 11.5 | 32.2 | 18.45 | 110.5 | 317 |
| 6.529 | 0.530 | 1.265 | 2.434 | 4.59 | 3.65 | 18.0 | 34.0 | 27.50 | 173.7 | 328 |
| 6.638 | 0.614 | 1.307 | 2.850 | 4.64 | 4.07 | 21.2 | 34.5 | 31.70 | 204.6 | 333 |
| 6.711 | 0.678 | 1.339 | 3.161 | 4.66 | 4.39 | 23.6 | 34.9 | 34.90 | 228.4 | 337 |
| 6.724 | 0.714 | 1.357 | 3.300 | 4.62 | 4.57 | 24.9 | 34.9 | 36.70 | 240.9 | 337 |
| 6.855 | 0.850 | 1.425 | 3.943 | 4.64 | 5.25 | 30.2 | 35.5 | 43.50 | 292.4 | 344 |

Table A-42**:** Test of model with $UO_2^{2+}$ and $UO_2(NO_3)_2$(aq) and $\beta_2 = 100$ $M^{-2}$.

| $E_j$ | $[NO_3^-]$ /M | $1+\beta_2 [NO_3^-]^2$ $\beta_1 = 100$ | $E_j(1+\beta_2 [NO_3^-]^2)$ - $\varepsilon_o$ | $\varepsilon_2 \beta_2$ |
|---|---|---|---|---|
| 6.307 | 0.349 | 13.18 | 77.3 | 635 |
| 6.529 | 0.530 | 29.09 | 184.1 | 655 |
| 6.638 | 0.614 | 38.70 | 251 | 666 |
| 6.711 | 0.678 | 46.97 | 309 | 672 |
| 6.724 | 0.714 | 51.98 | 344 | 675 |
| 6.855 | 0.850 | 73.25 | 496 | 686 |

therefore demonstrated that these data in Table A-41, can be described equally well using different sets of $\beta_1$ and $\varepsilon_1$ values. We found that the values of $\varepsilon_1\beta_1$ are very near constant throughout the nitrate concentration range for each set of equilibrium constants ranging from $\beta_1 = 0.5$ to $\beta_1 = 50$ $M^{-1}$, hence it is not possible to determine a unique value of the equilibrium constant. The data in Table A-42 illustrates that also a model with the complex $UO_2(NO_3)_2(aq)$ results in a near constant value of $\varepsilon_2\beta_2$, which means that it is impossible to determine the stoichiometry of the light absorbing complex. A least-squares program cannot resolve this inherent ambiguity and this review has therefore not accepted the chemical model and the equilibrium constant(s) proposed by Smith and Czerwinski, but we note that their experimental data can be described quite well using the selected equilibrium constant from [1992GRE/FUG].

**[2010YE/SMI]**

Molecular Dynamics simulations based on force-fields are used to describe the interactions between the components $H_3O^+$, $NO_3^-$ and $UO_2^{2+}$ in a box with 3490 water molecules. Three simulations with different concentrations of nitrate and $H_3O^+$ and a constant concentration of $UO_2^{2+}$ = 0.27 M were studied:

Model 1, [ $NO_3^-$ ] = 1.60 M; [ $H_3O^+$ ] = 1.06 M; Model 2, [ $NO_3^-$ ] = 1.09 M; [ $H_3O^+$ ] = 0.54 M; Model 3, [ $NO_3^-$ ] = 0.84 M; [ $H_3O^+$ ] = 0.28 M;

The simulations result in the following composition of the complexes $[UO_2(OH_2)_5]^{2+}$, $[UO_2(NO_3)(OH_2)_4]^+$, $[UO_2(NO_3)_2(OH_2)_3]$ and $[UO_2(NO_3)_3(OH_2)]^-$, with nitrate $\eta^1$-coordinated, which is not in agreement with experimental EXAFS information. In addition, the modelling results in a predominance of $[UO_2(OH_2)_5]^{2+}$ in model 3, which also is not in agreement with experimental observations. The modelling is very sensitive to the quality of the interaction potentials and this is presumably one reason for the discrepancy with experimental data. The information in [2010YE/SMI] is not useful for the purposes of the present review.

## A-1.5.2 Phosphorous compounds and complexes

**[1961KLY/ZAV]**

Klygin *et al.* synthesised $NH_4[(UO_2)(PO_4)]\cdot 3H_2O$(cr) by precipitation from aqueous solutions. The phase was characterised by standard chemical analysis methods, including the Karl Fisher method to determine the water content; the exact stoichiometry calculated in this review from chemical analysis data is $(NH_4)_{0.946}(UO_2)(PO_4)_{0.977}\cdot 3.005H_2O$(cr). The calcination of the synthesised phase resulted in the formation of $U_2O_3P_2O_7$. Additionally, what it is of primary interest for this review, the authors reported the solubility product of ammonium uranyl phosphate hydrate at (25 ± 0.2) °C from solubility measurements in dilute (0.007943-0.2344 M) HCl solutions by a shake-flask method from both the dissolution and precipitation

experiments of 72-hour duration. Some solutions contained diammonium hydrogen phosphate. Filtered equilibrium solutions were analysed for uranium, phosphorus and ammonium content. In all there are 20 data points, although results of only odd number runs are tabulated in the paper. The authors reported concentration solubility products corresponding to the Reaction (A.59):

$$NH_4[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons UO_2^{2+} + NH_4^+ + PO_4^{3-} + 3H_2O(l) \qquad (A.59)$$

after correction of data for (slight) hydrolysis of the uranyl ion and dissociation of phosphoric acid. The average value of $\log_{10} K_s$ is – 25.44. This review attempted to extrapolate ten reported $\log_{10} K_s$ values to $I = 0$, although due to the lack of exact starting compositions of the solutions the results are only approximate: the obtained value is $\log_{10} K_s^{\circ} = -(27.1 \pm 0.9)$.

**[1968PEK/VES]**

Pekárek *et al.* studied the solubility of synthetic samples of Ca-, Sr-, Ba-, Cu-, Zn-, Co-, and Ni-uranophosphates of the general formula $M^{II}[(UO_2)(PO_4)]_2{\cdot}nH_2O$(cr), the stoichiometry is shown in the second column of Table A-43. The phases were characterised by X-ray diffraction and IR-spectroscopy. Solubility studies were conducted at 25 ºC in $HNO_3$ + $M^{II}(NO_3)_2$ solutions of the ionic strength 0.2 M by a shake-flask method. Concentrations of U, P, and $M^{II}$ were measured by unspecified methods (presumably the same as in [1965VES/PEK]), as well as pH (the activity scale), however, no primary solubility data are reported. The authors tabulated solubility products (the third column of Table A-43) without providing any details of calculations (judging by the previous work of this group [1965VES/PEK], at least the complexation of uranyl with phosphates was taken into account). This review used the SIT model (only the electrostatic term) to extrapolate solubility products to infinite dilution, see the last column of Table A-43.

Table A-43: Values of solubility products of uranyl phosphates based on data [1968PEK/VES].

| Compound | Molar ratio of $M^{II}$: $UO_2$: P | $-\log_{10} K_s$ (a) ($I$ = 0.2 M) | $-\log_{10} K_s^{\circ}$ (a) ($I$ = 0) |
|---|---|---|---|
| $Ca[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) | 1 : 2.00 : 2.06 | (47.28 ± 0.20) | 50.83 |
| $Sr[(UO_2)(PO_4)]_2{\cdot}7.5H_2O$(cr) | 1 : 2.02 : 2.02 | (48.36 ± 0.15) | 51.91 |
| $Ba[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) | 1 : 2.00 : 2.01 | (49.62 ± 0.15) | 53.17 |
| $Cu[(UO_2)(PO_4)]_2{\cdot}9H_2O$(cr) | 1 : 2.09 : 2.09 | (52.10 ± 0.15) | 55.65 |
| $Zn[(UO_2)(PO_4)]_2{\cdot}7.5H_2O$(cr) | 1 : 1.96 : 2.04 | (46.77 ± 0.35) | 50.32 |
| $Co[(UO_2)(PO_4)]_2{\cdot}7H_2O$(cr) | 1 : 1.97 : 2.03 | (46.80 ± 0.20) | 50.35 |
| $Ni[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | 1 : 1.95 : 2.09 | (46.86 ± 0.25) | 50.41 |

(a) For the reaction $M^{II}[(UO_2)(PO_4)]_2{\cdot}nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2PO_4^{3-} + nH_2O(l)$

**[1981VOC/PIR]**

Vochten *et al.* have synthesised and characterised $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$, $Ni[(UO_2)(PO_4)]_2 \cdot 7H_2O(cr)$ and $Co[(UO_2)(PO_4)]_2 \cdot 7H_2O(cr)$ by X-ray diffraction, elemental and water analyses, thermogravimetry and differential thermal analysis (DTA). The solubility of the solids were investigated in the pH range 1-3.5 and these data were used to determine the solubility product, $pK_s$(A.60) for Reaction (A.60):

$$M[(UO_2)(PO_4)]_2 \cdot nH_2O(cr) + 4H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2H_2PO_4^- + nH_2O(l) \; ; \qquad (A.60)$$

where M = Cu, Ni, Co.

Vochten *et al.* make a strong case for congruent dissolution with no phase transformation in their experiments (a more direct method had been to use an X-ray analysis), by using published solubility products for the $M_3(PO_4)_2$, $CoHPO_4$, $(UO_2)_3(PO_4)_2$ and $UO_2HPO_4$ phases from [1964SIL/MAR]. From the measured total concentration of M and phosphate and equilibrium constants for protonation of phosphate, formation of hydroxide and phosphate complexes (all from [1964SIL/MAR]) they have calculated the free concentrations of $M^{2+}$, $UO_2^{2+}$ and $H_2PO_4^-$ and the resulting solubility product. They note that the equilibrium constants used refer to different ionic media, but their values do not differ much from the ones selected by the NEA TDB. Vochten *et al.* report the following solubility products $-\log_{10} K_s$ (A.60) = (12.8 ± 0.3), (9.5 ± 0.1) and (9.9 ± 0.4), for $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$, $Ni[(UO_2)(PO_4)]_2 \cdot 7H_2O(cr)$ and $Co[(UO_2)(PO_4)]_2 \cdot 7H_2O(cr)$, respectively. However, these are conditional equilibrium constants, representing an average value in test solution with varying ionic strength from $10^{-1}$ to $10^{-3.5}$ M. In view of the present review; they should be sufficiently accurate to allow scoping calculations. The data from the thermogravimetric and DTA analyses and the electrokinetic data are of less interest for the present review and are therefore not evaluated.

This review extrapolated $-\log_{10} K_s$ for the Reaction (A.60) from Vochten *et al.* (all six points for each studied compound) to $I = 0$ with the SIT (using only the Debye-Hückel term) and then recalculated these results to the values of $\log_{10} K_s^o$ for the following reaction:

$$M[(UO_2)(PO_4)]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2PO_4^{3-} + nH_2O(l) \; ; \qquad (A.61)$$

see Table A-44.

Table A-44: Values of $\log_{10} K^o$ of uranyl phosphates of Cu, Ni, Co calculated from data [1981VOC/PIR].

| Compound | Ionic strength | Number of points | $\log_{10}{}^*K^o$ |
|---|---|---|---|
| $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$ | $I < 0.09$ M | 6 | $-(52.4 \pm 1.1)^{(a)}$ |
| $Ni[(UO_2)(PO_4)]_2 \cdot 7H_2O(cr)$ | $I < 0.02$ M | 6 | $-(48.96 \pm 0.25)^{(a)}$ |
| $Co[(UO_2)(PO_4)]_2 \cdot 7H_2O(cr)$ | $I < 0.02$ M | 6 | $-(49.36 \pm 0.33)^{(a)}$ |

(a) Recalculated in this review, uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10}{}^*K^o$, see Appendix C.

**[1983VOC/PEL]**

Vochten *et al.* have synthesised and characterised $HAl[(UO_2)(PO_4)]_4 \cdot 16H_2O$(cr), which is known as the mineral sabugalite, by X-ray diffraction, elemental and water analyses, thermogravimetry and differential thermal analysis (DTA), and by IR spectroscopy. The authors also studies the electrokinetic properties and solubility of the synthetic phase. Solubility was determined in the pH range 2-5 in HCl or $H_3PO_4$ media, in runs of one week duration. The U(VI) concentrations and pH values were measured in solutions. Solubility data are presented only on a plot in the paper (Fig. 7). No solubility products were evaluated by the authors. Preparing this review, we read from the plot the following values for the solubility in HCl medium in the most acid solutions, between pH 2 and 3.5 (see Table A-45).

Table A-45: Values of solubility product of $HAl[(UO_2)(PO_4)]_4 \cdot 16H_2O$(cr) calculated from data of Vochten *et al.* [1983VOC/PEL].

| pH | $\log_{10} S$ | $\log_{10} {}^*K^{\circ}$ (A.62) | $\log_{10} {}^*K^{\circ}_{corr}$ (A.62)[(a)] |
|---|---|---|---|
| 2.05 | – 2.85 | – 12.8 | – 13.1 |
| 2.25 | – 3.10 | – 12.6 | – 12.9 |
| 2.73 | – 3.68 | – 12.5 | – 12.7 |
| 3.03 | – 4.00 | – 12.5 | – 12.6 |
| 3.25 | – 4.32 | – 13.2 | – 13.3 |
| 3.42 | – 4.60 | – 14.2 | – 14.2 |

(a) Corrected value, see text

These solubility values were used to calculate the equilibrium constants for the following dissolution reaction:

$$HAl[(UO_2)(PO_4)]_4 \cdot 16H_2O(cr) + 7H^+ \rightleftharpoons Al^{3+} + 4UO_2^{2+} + 4H_2PO_4^- + 16H_2O(l) \qquad (A.62)$$

taking into account the complex formation of uranyl ion with the formation of hydroxyl and phosphate complexes. The calculated values of $\log_{10} {}^*K^{\circ}$(A.62) are given in the third column of Table A-45. As the $pK^{\circ}$ of the first hydrolysis constant of $Al^{3+}$ is around 5, see for example, the book, referenced below, then the hydrolysis of $Al^{3+}$ is not important. A more complicated issue is the formation of complexes between aluminum and phosphates. The book "The Environmental Chemistry of Aluminum", edited by G. Sposito, Second Ed., 1996, CRC Press, estimates the following stability constants of aluminum phosphate complexes,

$$Al^{3+} + H_2PO_4^- \rightleftharpoons AlH_2PO_4^{2+} \qquad (A.63)$$

$$\log_{10} K\,(A.63) \sim 3$$

and

$$Al^{3+} + HPO_4^{2-} \rightleftharpoons AlHPO_4^+ \qquad (A.64)$$

$$\log_{10} K\,(A.64) \sim 7,$$

quoting the papers [1931BJE/DAH] and [1969BOH/PEE]. These values allow an approximate correction of the calculated $\log_{10}{}^{*}K^{\circ}$ (A.62) for the effect of formation of aluminum phosphate complexes, see the last column of the Table. Finally, the average value is of $\log_{10}{}^{*}K^{\circ}$ (A.62) = – (13.1 ± 1.2). This value can be used for scoping calculations only.

**[1984VOC/GRA]**

Vochten *et al.* have studied the mineral bassetite, $Fe^{II}_{1-x}Fe^{III}_{x}[(UO_2)(PO_4)]_2(OH)_x \cdot (7-x)H_2O(cr)$, $0 \le x \le 1$, using a number of methods (X-ray diffraction, Mössbauer and IR-spectroscopy, zeta potential measurements and thermal analysis). There are no thermodynamic data in this study, but the observation that the solubility decreases strongly (by two orders of magnitude) at pH ≈ 6 when the fully oxidised bassetite is formed might be of interest for modeling of aqueous solutions.

**[1985MAG/JES]**

Magalhães *et al.* studied the solubility of synthetic samples of H-autunite (chernikovite), $H[(UO_2)(PO_4)]\cdot 4.16H_2O(cr)$; lithium autunite, $Li[(UO_2)(PO_4)]\cdot 4.13H_2O(cr)$; sodium autunite, $Na[(UO_2)(PO_4)]\cdot 3.45H_2O(cr)$; potassium autunite, $K[(UO_2)(PO_4)]\cdot 2.77H_2O(cr)$; autunite, $Ca[(UO_2)_2(PO_4)]_2\cdot 6.96H_2O(cr)$; saléeite, $Mg[(UO_2)(PO_4)]_2\cdot 10.25H_2O(cr)$; torbernite, $Cu[(UO_2)_2(PO_4)]_2\cdot 8.96H_2O(cr)$; and Ni-autunite, $Ni[(UO_2)(PO_4)]_2\cdot 9.16H_2O(cr)$ in 0.0931 M solutions of $HClO_4$ (H-, Ca-, Cu-phases) or in $H_2O$ (other phases) at (25.0 ± 0.2) °C. No details of measurements are given, only a reference to a previous study. It is indicated that $[U_{tot}]$ and pH (the activity scale) were measured, and in the case of autunite and torbernite it was verified that the Ca and Cu concentrations were one half of the uranium concentration, confirming the congruent character of dissolution. The hydrolysis and complex formation between solution components were taken into account, and the extended Debye-Hückel equation was used to evaluate activity coefficients.

For the chernikovite dissolution reaction:

$$H[(UO_2)(PO_4)]\cdot nH_2O(cr) \rightleftharpoons UO_2^{2+} + HPO_4^{2-} + nH_2O(l) \quad \log_{10} K^{\circ} = -(12.22 \pm 0.03).$$

For the monovalent cation minerals, M = Li, Na, K, the dissolution Reaction (A.65) gives

$$M[(UO_2)(PO_4)]\cdot nH_2O(cr) + H^{+} \rightleftharpoons M^{+} + UO_2^{2+} + HPO_4^{2-} + nH_2O(l) \qquad (A.65)$$

$\log_{10} K^{\circ} = -(12.6 \pm 0.1)$ for $Li[(UO_2)(PO_4)]\cdot 4.13H_2O(cr)$;

$\log_{10} K^{\circ} = -(12.5 \pm 0.1)$ for $Na[(UO_2)(PO_4)]\cdot 3.45H_2O(cr)$;

$\log_{10} K^{o} = -(13.2 \pm 0.1)$ for $K[(UO_2)(PO_4)]\cdot 2.77H_2O$(cr).

For the divalent cation minerals, M = Ca, Mg, Cu, Ni, the dissolution Reaction (A.66) gives

$$M[(UO_2)(PO_4)]_2 \cdot nH_2O(cr) + 2H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2HPO_4^{2-} + nH_2O(l) \qquad (A.66)$$

$\log_{10} K^{o} = -(26.7 \pm 0.1)$ for $Ca[(UO_2)(PO_4)]_2\cdot 6.96H_2O$(cr);

$\log_{10} K^{o} = -(22.3 \pm 0.1)$ for $Mg[(UO_2)(PO_4)]_2\cdot 10.25H_2O$(cr);

$\log_{10} K^{o} = -(30.0 \pm 0.1)$ for $Cu[(UO_2)(PO_4)]_2\cdot 8.96H_2O$(cr);

$\log_{10} K^{o} = -(26.2 \pm 0.1)$ for $Ni[(UO_2)(PO_4)]_2\cdot 9.16H_2O$(cr).

These results are based on a single solubility value for each phase, and the current review considers the uncertainty of $\log_{10} K^{o}$ for monovalent cation minerals dissolution to be ± 0.3, and for divalent cation minerals ± 1.0.

**[1985ZHI/POL]**

Zhiltsova *et al.* studied the solubility of synthetic samples of uranyl phosphates: chernikovite of the stoichiometry $(H_3O)_2[(UO_2)_{2.00}(PO_4)_{2.00}]\cdot 6.74H_2O$(cr); autunite, $Ca_{1.08}[(UO_2)_{2.04}(PO_4)_2]\cdot 8.5H_2O$(cr); and torbernite, $Cu_{0.94}[(UO_2)_{1.96}(PO_4)_2]\cdot 7.73H_2O$(cr). The phases were characterised by X-ray diffraction and chemical analysis. Solubility studies were conducted at 25 °C in HCl solutions of pH 1.0-1.7 (two solutions for each phase) in polyethylene flasks with periodic manual shaking. Concentrations of U, P, Ca, and Cu were measured: U by vanadatometric titration, Ca and Cu by Atomic absorption spectroscopy (AAS), P-photometrically using molybdophosphoric heteropoly acid. Values of pH (the activity scale) were also reported. The steady-state concentrations were reached in 15-20 days. Dissolution of all phases was congruent.

The experimental data were used to evaluate solubility products of the various uranyl phosphates. Activity coefficients were calculated using the extended Debye-Hückel equation. Hydrolysis and formation of the chloride complex of uranyl ion (but not U(VI) phosphate complexes) were taken into account. Results are listed in Table A-46:

Table A-46: Values of solubility products of uranyl phosphates from [1985ZHI/POL] averaged in this review.

| Compound | Formula | $\log_{10} K^{o}$ |
|---|---|---|
| Chernikovite | $(H_3O)_2[(UO_2)_{2.00}(PO_4)_{2.00}]\cdot 6.74H_2O$(cr) | $-(48.35 \pm 0.42)^{(a)}$ |
| Autunite | $Ca_{1.08}[(UO_2)_{2.04}(PO_4)_2]\cdot 8.5H_2O$(cr) | $-(49.61 \pm 0.25)^{(a)}$ |
| Torbernite | $Cu_{0.94}[(UO_2)_{1.96}(PO_4)_2]\cdot 7.73H_2O$(cr) | $-(52.61 \pm 0.18)^{(a)}$ |

(a) Averaged from two reported values in this review, uncertainties are given as $1.96\sigma_x$, where $\sigma_x$ is the standard deviation associated with $\log_{10} K^{o}$, see Appendix C.

These values likely represent the upper boundary of $\log_{10}K^{o}$, because the complexation of metals with phosphate was neglected.

**[1991MAT]**

Mathur studied the complex formation in the uranyl(VI)-phosphoric acid system and determined the equilibrium constant for the complex $UO_2H_2PO_4^+$: the experiments were conducted using liquid-liquid extraction with test solutions where the ionic strength varied between 0.1 and 1 M $NaClO_4$. Experiments were performed at four different temperatures, 10, 25, 40 and 50 °C. In addition, Mathur determined the first dissociation constant of phosphoric acid using potentiometric determination of the hydrogen-ion concentration $-\log_{10}[H^+]$. The results, shown in Table A-47, were used to make extrapolation to the zero ionic strength using SIT.

$$H_2PO_4^- + H^+ \rightleftharpoons H_3PO_4(aq) \quad \text{(A.67)}$$

Table A-47: Experimental values of the dissociation constant for the Reaction (A.67).

| Ionic strength in molality | $\log_{10}\beta$ | 2D | $\log_{10}\beta + 2D$ |
|---|---|---|---|
| 0.100 | (2.09 ± 0.02) | 0.22 | (2.31 ± 0.02) |
| 0.305 | (2.01 ± 0.02) | 0.31 | (2.32 ± 0.02) |
| 0.513 | (1.95 ± 0.03) | 0.35 | (2.30 ± 0.03) |
| 0.726 | (1.86 ± 0.02) | 0.38 | (2.24 ± 0.02) |
| 1.051 | (1.70 ± 0.02) | 0.41 | |

The values of ( $\log_{10}\beta + 2D$ ) deviate from the expected linearity, and the value of $\log_{10}\beta^{o}$ ((A.67), 298.15 K) = (2.3 ± 0.1), is also significantly different from the selected value in [1992GRE/FUG], $\log_{10}\beta^{o}$ ((A.67), 298.15 K) = (2.14 ± 0.03). This review finds no explanation for this discrepancy. The value of Δε from the SIT plot is accordingly very uncertain and cannot be used to derive a more precise value of the interaction coefficient $\varepsilon(H_2PO_4^-, Na^+)$ than that selected in previous NEA reviews.

$$UO_2^{2+} + H_2PO_4^- \rightleftharpoons UO_2H_2PO_4^+ \quad \text{(A.68)}$$

$$UO_2^{2+} + 2H_2PO_4^- \rightleftharpoons UO_2(H_2PO_4)_2(aq) \quad \text{(A.69)}$$

This review finds $\log_{10}\beta_1^{o}$ = (3.40 ± 0.05) and Δε = – (0.00 ± 0.05) kg·mol$^{-1}$, which suggests an interaction coefficient $\varepsilon(UO_2H_2PO_4^+, ClO_4^-) \approx 0.54$ kg·mol$^{-1}$. This value seems too large for a uranyl complex with the charge +1. The equilibrium constant for Reaction (A.68) based on the selected values in previous reviews is $\log_{10}\beta_1^{o}$ = (3.26 ± 0.07), consistent with the value from Mathur. $\log_{10}\beta_2^{o}$ = (5.31 ± 0.05) obtained by using the SIT extrapolation of the equilibrium constant for Reaction (A.69) is in fair agreement with the selected value in [1992GRE/FUG], $\log_{10}\beta_2^{o}$ = (5.12 ± 0.12). We noted that the experimental equilibrium constants at $I$ = 0.10 M deviated

significantly from the expected linear SIT plot both for Reactions (A.68) and (A.69). The value of $\Delta\varepsilon = -(0.05 \pm 0.05)$ kg·mol$^{-1}$ for Reaction (A.69), results in an interaction coefficient $\varepsilon(UO_2(H_2PO_4)_2, NaClO_4) \approx -0.35$ kg·mol$^{-1}$, which seems too large in magnitude for an uncharged complex.

Table A-48: Equilibrium constants for Reactions (A.68) and (A.69) from Mathur [1991MAT], together with an extrapolation to zero ionic strength made by this review using SIT; Mathur has used a different expression for his extrapolation.

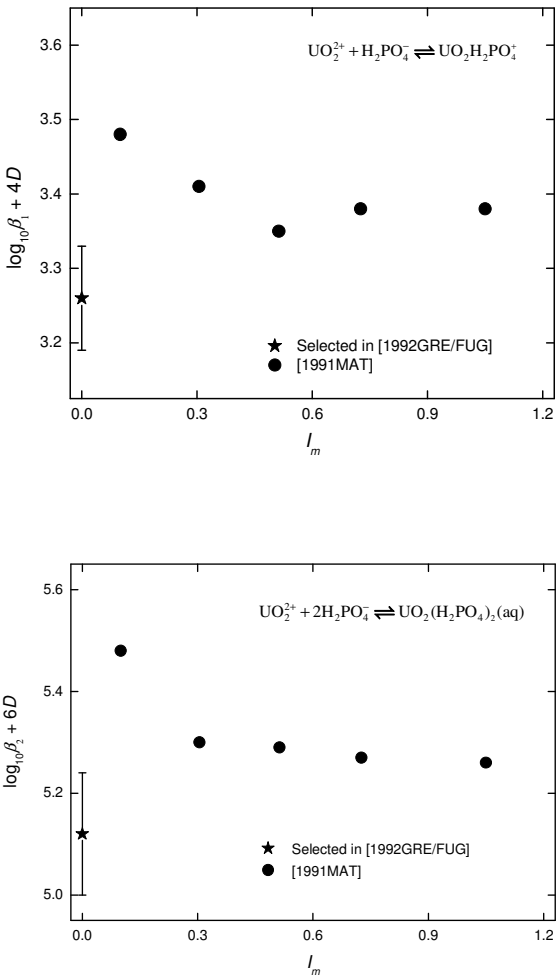
| Ionic strength in m | *D* | $\log_{10}\beta_1$ | $\log_{10}\beta_1 + 4D$ | $\log_{10}\beta_2$ | $\log_{10}\beta_2 + 6D$ |
|---|---|---|---|---|---|
| 0 | 0 | 3.47 | | 5.47 | |
| | | (3.40 ± 0.05)[(a)] | | (5.31 ± 0.05)[(a)] | |
| | | (3.26 ± 0.07)[(b)] | | (5.12 ± 0.12)[(b)] | |
| 0.100 | 0.11 | (3.04 ± 0.03) | 3.48 | (5.15 ± 0.02) | 5.48 |
| 0.305 | 0.155 | (2.97 ± 0.01) | 3.41 | (4.97 ± 0.03) | 5.30 |
| 0.513 | 0.175 | (2.91 ± 0.02) | 3.35 | (4.96 ± 0.03) | 5.29 |
| 0.726 | 0.19 | (2.94 ± 0.02) | 3.38 | (4.94 ± 0.03) | 5.27 |
| 1.051 | 0.205 | (2.94 ± 0.02) | 3.38 | (4.93 ± 0.03) | 5.26 |

(a) Recalculated in this review using SIT.
(b) Selected in [1992GRE/FUG] and [2003GUI/FAN].

When analysing the extraction data, Mathur uses a model with two complexes (his experimental data show quite clearly that a single complex cannot describe them), $UO_2H_2PO_4^+$ and $UO_2(H_2PO_4)_2$(aq). The experiments have been made at a constant hydrogen ion concentration, $-\log_{10}[H^+] = 2.5$ and under this condition it is necessary to test if the complex $UO_2H_3PO_4^{2+}$ is formed. Baes, [1956BAE] has investigated the equilibrium constant for the formation of this complex in 0.1 and 1.0 M $HClO_4$ and finds an equilibrium constant of $\log_{10} K = 0.72$, for the reaction

$$UO_2^{2+} + H_3PO_4(aq) \rightleftharpoons UO_2H_3PO_4^{2+}; \qquad (A.70)$$

Figure A-8: Deviations of [1991MAT] data from the expected linearity on the SIT plot and from the values selected in [1992GRE/FUG].




This reaction has been discussed in [1992GRE/FUG]. Using this constant and the one for Reaction (A.68) in 1 M $NaClO_4$ and pH = 2.5 from Mathur we find:

$$[\,UO_2H_3PO_4^{2+}\,]/\{[\,UO_2H_2PO_4^{+}\,]\cdot[H^+]\} = 10^{-2.75} \times 10^{2.5} = 10^{-0.25} = 0.56.$$

This means that the concentration of the complex $UO_2H_3PO_4^{2+}$ is not negligible.

This review notes the equilibrium constants in 0.10 M perchlorate deviate significantly from those at higher ionic strength, but also that the analysis of the

experimental data has not considered the influence of the complex $UO_2H_3PO_4^{2+}$. For this reason we have retained the selected equilibrium constants from [1992GRE/FUG].

Mathur has also determined the enthalpy of reaction for Reactions (A.68) and (A.69) using the temperature dependence of the equilibrium constants. He reports $\Delta_r H_m^o$ (A.68) = (7.9 ± 1.7) kJ·mol$^{-1}$ and $\Delta_r H_m^o$ (A.69) = (16.3 ± 1.7) kJ·mol$^{-1}$. As this review has not selected the equilibrium constants, we have not selected the corresponding enthalpies of reaction, but suggest that they can be used as estimates in scoping calculations.

**[1991VOC/HAV2]**

Chernikovite, $(H_3O)_2[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) was synthesised and used to prepare parsonite, $(Pb)_2(UO_2)(PO_4)_2{\cdot}0.5H_2O$(cr) by cation exchange. The phase was characterised by X-ray diffraction and chemical analysis and shown to be identical with the natural mineral. The solubility was measured and the data analysed as described in [1981VOC/PIR] to give the solubility product for Reaction (A.71)

$$(Pb)_2(UO_2)(PO_4)_2 \cdot 0.5H_2O(cr) \rightleftharpoons 2Pb^{2+} + UO_2^{2+} + 2PO_4^{3-} + 0.5H_2O \qquad (A.71)$$

The solubility varied between $307 \times 10^{-6}$ and $0.5 \times 10^{-6}$ M in the pH range 1.50-4.98 ($HNO_3$ medium). The concentration solubility products were recalculated to $I = 0$ (the SIT model with the electrostatic term only) and averaged for pH ranges indicated in Table A-49:

Table A-49: Values of solubility constants, $\log_{10}{}^*K_s^o$ of parsonite extrapolated to $I = 0$ in this review based on data of [1991VOC/HAV2].

| pH range | Number of points | $\log_{10}{}^*K_s^o$ |
|---|---|---|
| 1.5-4.98 | 7 | – (51.5 ± 2.7)[(a)] |
| 1.5-3.0 | 5 | – (52.2 ± 0.8)[(a)] |

(a) Recalculated in this review, uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10}{}^*K_s^o$, see Appendix C.

At pH > 3 the calculated $\log_{10}{}^*K^o$ values are 2-3 $\log_{10}$ units larger than the results in more acid solutions. Accepting only data over the pH range 1.5-3.0, this review obtains $\log_{10}{}^*K^o$ = – (52.2 ± 0.8). The proposed solubility product has not been accepted by the present review as we do not have sufficient information of details in the analysis of the experimental data. However, we suggest that the solubility product can be used in scoping calculations of phase-equilibria.

**[1992VOC/HAV]**

Vochten *et al.* have synthesised the mineral meta-uranocircite-II, $Ba[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) and determined the solubility product for Reaction (A.72) at $1.37 < pH < 3.79$ and $T = 25$ °C. In this range the measured solubility varies from $300 \times 10^{-6}$ to $1.5 \times 10^{-6}$ M. There is no information on experimental details, if the dissolution is congruent, or not (only the U concentration is measured), time for equilibration, etc. Data were used to calculate the concentration equilibrium constants of the reaction:

$$Ba[(UO_2)(PO_4)]_2 \cdot 6H_2O(cr) \rightleftharpoons Ba^{2+} + 2UO_2^{2+} + 2PO_4^{3-} + 6H_2O(l) \quad (A.72)$$

When analysing these data, Vochten et al. have taken protonation of $PO_4^{3-}$ and hydrolysis of U(VI) into account using the literature data (references are given, but these literature sources show a range of numerical values for the equilibrium constants and it is therefore not possible to know which ones Vochten et al. have used, but they are presumably the same as in [1981VOC/PIR]). The concentration solubility products (five data points) were recalculated in this review to I = 0 (the SIT model with the electrostatic term only) and averaged: $\log_{10}{}^{*}K^{o} = -(53.2 \pm 1.6)$, where the uncertainty is given as $1.96\sigma_X$, $\sigma_X$ is the standard deviation associated with $\log_{10}{}^{*}K^{o}$, see Appendix C.

**[1993KAR/CHE]**

This study reports the enthalpies of formation of $M[(UO_2)(PO_4)]$(cr) (M= Na, K, Rb, Cs). Samples were prepared by calcination of synthetic crystallohydrates of corresponding salts at 400 °C for ten hours. The purity of the phases was confirmed with X-ray diffractometry; however, the exact stoichiometry of studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($UO_3$(cr), $KH_2PO_4$(cr), $MNO_3$(cr) and $M[(UO_2)(PO_4)]$(cr) (M= Na, K, Rb, Cs) in concentrated HF solutions (molar ratio $HF:H_2O$ 52:160, *i.e.*, ~18 m HF). The thermochemical cycle employed resulted in the following values of $\Delta_r H_m$ for the reaction:

$$KH_2PO_4(cr) + UO_3(cr) + MNO_3(cr) \rightleftharpoons M[(UO_2)(PO_4)](cr) + KNO_3(cr) + H_2O(l) \quad (A.73)$$

Table A-50: Enthalpies of reaction $\Delta_r H_m$ (A.73) and enthalpies of formation of $M[(UO_2)(PO_4)]$(cr); M = Na-Cs.

| Compound | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$(298.15 K) /kJ·mol$^{-1}$ |
|---|---|---|
| $Na[(UO_2)(PO_4)]$(cr) | – (31.73 ± 1.71) | – (2517.2 ± 3.0) |
| $K[(UO_2)(PO_4)]$(cr) | – (31.68 ± 3.09) | – (2543.5 ± 3.9) |
| $Rb[(UO_2)(PO_4)]$(cr) | – (30.03 ± 2.00) | – (2542.6 ± 3.2) |
| $Cs[(UO_2)(PO_4)]$(cr) | – (33.53 ± 3.41) | – (2556.4 ± 4.2) |

The calculations of the enthalpies of formation of alkali metal uranyl phosphates require values of $\Delta_f H_m^o$ of the reaction participants. Of particular concern is the enthalpy of formation for $KH_2PO_4$(cr). The authors of [1993KAR/CHE] used the value from the old Glushko handbook, compiled in 1965-1981: in it $\Delta_f H_m^o(KH_2PO_4, \text{cr}, 298.15\ \text{K}) = -(1568.0 \pm 1.3)$ kJ·mol$^{-1}$ [1981GLU/MED]. However, the values of $\Delta_f H_m^o$ for all phosphate phases from that handbook have to be corrected, because they are based on the enthalpy of formation of $P_4O_{10}$(cr) equal to $\Delta_f H_m^o = -(2984.0 \pm 4.2)$ kJ·mol$^{-1}$, see [1968GLU/MED]. This value was later strongly revised by the same research group, when preparing the handbook [1978GLU/GUR]. By the analysis of relevant data for solid compounds and aqueous solutions, the authors of [1978GLU/GUR] selected two key values: for $P_4O_{10}$(cr) $\Delta_f H_m^o = -(3010.1 \pm 3.2)$ kJ·mol$^{-1}$ and for aqueous $H_3PO_4$ $\Delta_f H_m^o(H_3PO_4 \cdot 100H_2O, \text{sln}) = -(1296.2 \pm 1.0)$ kJ·mol$^{-1}$. For the aqueous solution the identical value was accepted by CODATA [1989COX/WAG], and even though the CODATA team did not endorse the $\Delta_f H_m^o$ value for $P_4O_{10}$(cr), a large difference from the value $\Delta_f H_m^o = -(3010.1 \pm 3.2)$ kJ·mol$^{-1}$ cannot be expected. The difference between the "new" and "old" values of $\Delta_f H_m^o$ for $P_4O_{10}$(cr) is about 26 kJ·mol$^{-1}$. Therefore, the values of $\Delta_f H_m^o$ for phosphate phases from the old Glushko handbook have to be made more negative by 6.5 kJ·mol$^{-1}$ per each P atom in the chemical formula of a compound. As an example, such a procedure gives for $KH_2PO_4$(cr) $\Delta_f H_m^o = -1574.5$ kJ·mol$^{-1}$ with an expected uncertainty of ± 2 kJ·mol$^{-1}$. A quick check can be made using the value of $\Delta_r H_m^o = 19.69$ kJ·mol$^{-1}$ [1966EGA/LUF] for the reaction $KH_2PO_4(\text{cr}) \rightleftharpoons K^+ + H_2PO_4^-$. Applying for $K^+$ $\Delta_f H_m^o = -(252.14 \pm 0.08)$ kJ·mol$^{-1}$ and for $H_2PO_4^-$ $\Delta_f H_m^o = -(1302.6 \pm 1.5)$ kJ·mol$^{-1}$ (both from the NEA database), one calculates for $KH_2PO_4$(cr) $\Delta_f H_m^o = -1574.43$ kJ·mol$^{-1}$, in a good agreement with the corrected, as described above, value from the old Glushko handbook [1981GLU/MED].

Auxiliary data used in the current review to calculate $\Delta_f H_m^o$ are as follows (in kJ·mol$^{-1}$): $-(1223.8 \pm 1.2)$ for $UO_3$(cr), $-(467.58 \pm 0.41)$ for $NaNO_3$(cr), from the NEA database [2003GUI/FAN]; $-(494.0 \pm 0.5)$ for $KNO_3$(cr), $-(494.7 \pm 0.5)$ for $RbNO_3$(cr), $-(505.0 \pm 0.5)$ for $CsNO_3$(cr), all from [1982GLU/GUR], and $\Delta_f H_m^o = -(1574.5 \pm 2.0)$ for $KH_2PO_4$(cr), evaluated as described above with the uncertainty estimated in this review. The following relation was used to calculate $\Delta_f H_m^o$ of M[$(UO_2)(PO_4)$](cr):

$$\Delta_f H_m^o = \Delta_r H_m - \Delta_f H_m^o(KNO_3, \text{cr}) - (\Delta_f H_m^o(H_2O(\text{l}) + \overline{L}_1) + \Delta_f H_m^o(KH_2PO_4, \text{cr}) + \Delta_f H_m^o(UO_3, \text{cr}) + \Delta_f H_m^o(MNO_3, \text{cr})$$

where the relative partial molar enthalpy of water, $\overline{L}_1$, is equal to $-0.63$ kJ·mol$^{-1}$ in 18 m HF, its calculation was discussed in the review of [2002KAR/CHE2]. The resulting values of $\Delta_f H_m^o$ (in kJ·mol$^{-1}$) are shown in the last column of Table A-50. The uncertainties are calculated using rules of propagation of errors, see Appendix C. Note that the authors gave larger uncertainties to their $\Delta_f H_m^o$ results, from 7 to 10 kJ·mol$^{-1}$.

**[1994KAR/CHE]**

Karyakin and Chernorukov determined the enthalpies of formation of $H[(UO_2)(PO_4)](cr)$, $H[(UO_2)(AsO_4)](cr)$ and their hydrates $H[(UO_2)(PO_4)]\cdot 4H_2O(cr)$ and $H[(UO_2)(AsO_4)]\cdot 4H_2O(cr)$. Hydrates were synthesised from aqueous solutions, and heated at 200-300 °C to prepare the anhydrous phases. The compounds were analysed chemically and by X-ray and IR, however, the exact stoichiometry of the studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions involving $UO_3(cr)$, $KH_2PO_4(cr)$, $KH_2AsO_4(cr)$, $KNO_3(cr)$, $H[(UO_2)(PO_4)](cr)$, $H[(UO_2)(AsO_4)](cr)$, $H[(UO_2)(PO_4)]\cdot 4H_2O(cr)$, and $H[(UO_2)(AsO_4)]\cdot 4H_2O(cr)$ in concentrated HF solutions, ~18 m HF. The thermochemical cycle employed resulted in the following values of $\Delta_r H_m$ for the reactions:

$$KH_2PO_4(cr) + UO_3(cr) + HF(sln) \rightleftharpoons H[(UO_2)(PO_4)](cr) + KF(sln) + H_2O(l) \quad (A.74)$$

$\Delta_r H_m$ (A.74) = – (17.04 ± 2.01) kJ·mol$^{-1}$;

$$KH_2AsO_4(cr) + UO_3(cr) + HF(sln) \rightleftharpoons H[(UO_2)(AsO_4)](cr) + KF(sln) + H_2O(cr) \quad (A.75)$$

$\Delta_r H_m$ (A.75) = (7.50 ± 2.55) kJ·mol$^{-1}$;

$$KH_2PO_4(cr) + UO_3(cr) + HF(sln) + 3H_2O(l) \rightleftharpoons H[(UO_2)(PO_4)]\cdot 4H_2O(cr) + KF(sln) \quad (A.76)$$

$\Delta_r H_m$ (A.76) = – (71.73 ± 2.11) kJ·mol$^{-1}$;

$$KH_2AsO_4(cr) + UO_3(cr) + HF(sln) + 3H_2O(l) \rightleftharpoons H[(UO_2)(AsO_4)]\cdot 4H_2O(cr) + KF(sln) \quad (A.77)$$

$\Delta_r H_m$ (A.77) = – (67.80 ± 1.87) kJ·mol$^{-1}$.

The authors used the auxiliary $\Delta_f H_m^o$ values (mainly from [1981GLU/MED], *i.e.* the older Glushko handbook) for solid phases and aqueous ions at infinite dilution to calculate the following $\Delta_f H_m^o$ results, in kJ·mol$^{-1}$: – (2275 ± 7) for $H[(UO_2)(PO_4)](cr)$; – (1868 ± 7) for $H[(UO_2)(AsO_4)](cr)$; – (3473 ± 8) for $H[(UO_2)(PO_4)]\cdot 4H_2O(cr)$; and – (3086 ± 7) for $H[(UO_2)(AsO_4)]\cdot 4H_2O(cr)$.

However, as discussed in the review of [2002KAR/CHE2], these results require the following corrections: a) for the relative partial molar enthalpy of water, $\overline{L}_1$, in 18 m HF aqueous solution; b) for $\overline{L}_2$ (HF(sol)), the partial molar enthalpy of HF at its 18 m aqueous solution; c) for $\overline{L}_2$ (KF(sol)), the partial molar enthalpy of KF at its trace concentration in 18 m HF aqueous solution. Contrary to the first two corrections, the

last correction cannot be evaluated in the absence of additional calorimetric data, and it may be large, up to 20 kJ·mol$^{-1}$ in magnitude. Therefore, the current review does not credit the presented values of $\Delta_f H_m^o$ of the studied compounds.

Still, the published data may be used to calculate the enthalpies of the following reactions in 18 m HF solution, in kJ·mol$^{-1}$:

$$H[(UO_2)(PO_4)]\cdot 4H_2O(cr) \rightleftharpoons H[(UO_2)(PO_4)](cr) + 4H_2O(l), \quad (A.78)$$

$$\Delta_r H_m\,(A.78) = \Delta_r H_m\,(A.74) - \Delta_r H_m\,(A.76) = (54.69 \pm 2.91);$$

$$\Delta_r H_m^o\,(A.78) = (57.2 \pm 2.9);$$

$$H[(UO_2)(AsO_4)]\cdot 4H_2O(cr) \rightleftharpoons H[(UO_2)(AsO_4)](cr) + 4H_2O(l), \quad (A.79)$$

$$\Delta_r H_m\,(A.79) = \Delta_r H_m\,(A.75) - \Delta_r H_m\,(A.77) = (75.30 \pm 3.16),$$

$$\Delta_r H_m^o\,(A.79) = (77.8 \pm 3.2).$$

These $\Delta_r H_m$ values are recalculated to the pure water standard state using the relation (for the Reaction (A.78) as an example):

$$\Delta_r H_m^o\,(A.78) = \Delta_f H_m^o(H[(UO_2)(PO_4)](cr)) + 4(\Delta_f H_m^o(H_2O(l))$$

$$-\Delta_f H_m^o([(UO_2)(PO_4)]\cdot 4H_2O(cr)) = \Delta_r H_m\,(A.74) - \Delta_r H_m\,(A.76) - 4\,\overline{L}_1$$

$$= \Delta_r H_m\,(A.78) - 4\,\overline{L}_1$$

where the relative partial molar enthalpy of water, $\overline{L}_1$, is equal to – 0.63 kJ·mol$^{-1}$ in 18 m HF, its calculation was discussed in the review of [2002KAR/CHE]. The obtained $\Delta_r H_m^o$ (A.78) and $\Delta_r H_m^o$ (A.79) values are given above.

**[1995CHE/KAR]**

This is a review of structural and thermodynamic characteristics of uranyl phosphates of H, Li, Na, K, Rb, Cs and their crystal hydrates. Both literature and authors' data are discussed, including solubility products and enthalpies of formation.

**[1996HAV/VOC]**

Haverbeke *et al.* have synthesised and characterised chernikovite, $(H_3O)[(UO_2)(PO_4)]\cdot 3H_2O(cr)$, and meta-ankoleite, $K[(UO_2)(PO_4)]\cdot 3H_2O(cr)$ by X-ray diffraction, IR and chemical analysis. The solubility of chernikovite, $(H_3O)[(UO_2)(PO_4)]\cdot 3H_2O(cr)$, was studied with a shake-flask method under a $N_2$ atmosphere at 25 °C in $HClO_4$ solutions at pH 0.98-1.38 (three data points), and of $K[(UO_2)(PO_4)]\cdot 3H_2O(cr)$ solutions at pH 2.60-5.24 (four data points, at lower pH the

phase transformed into $(UO_2)_3(PO_4)_2$(cr)). Only the U concentration was measured (spectrophotometrically, with Arsenazo III). The data were corrected for the hydrolysis of U(VI) and the formation of phosphate complexes of U(VI) to calculate for the reactions:

$$(H_3O)[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons H_3O^+ + UO_2^{2+} + PO_4^{3-} + 3H_2O(l) \qquad (A.80)$$

and

$$K[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons K^+ + UO_2^{2+} + PO_4^{3-} + 3H_2O(l) \qquad (A.81)$$

the values of $\log_{10} K$ are given in the third and fifth columns of Table A-51. This review estimated the ionic strength of solutions and used the Debye-Hückel equation (the SIT model with values of interaction coefficients set to 0) to extrapolate $\log_{10} K$ to $I = 0$.

Table A-51: Solubility products reported in [1996HAV/VOC] and their values extrapolated to $I = 0$ in this review.

| pH | ~ $I$ (M)[a] | $-\log_{10} K$ (A.80)[b] | $-\log_{10} K^\circ$ (A.80)[a] | $-\log_{10} K$ (A.81)[b] | $-\log_{10} K^\circ$ (A.81)[a] |
|---|---|---|---|---|---|
| 0.98 | 0.11 | 22.45 | 24.43 | | |
| 1.12 | 0.08 | 22.81 | 24.64 | | |
| 1.38 | 0.05 | 22.91 | 24.52 | | |
| | | Average | (24.53 ± 0.21)[c] | | |
| 2.60 | 0.03 | | | 23.20 | 24.59 |
| 4.13 | $10^{-4}$ | | | 25.07 | 25.25 |
| 4.90 | $3 \times 10^{-4}$ | | | 24.71 | 24.82 |
| 5.24 | $10^{-5}$ | | | 24.21 | 24.28 |
| | | | | Average | (24.74 ± 0.80)[c] |

(a) Evaluated in this review;
(b) Authors' value;
(c) Uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10} {}^*K^\circ$, see Appendix C.

**[1996KAR/CHE]**

This study reports the enthalpies of formation of synthetic samples of $M^{II}[(UO_2)(PO_4)]_2$(cr) (M = Ca, Sr, Ba). The phases were obtained by calcination of the corresponding synthetic crystallohydrates at 500 °C. As the compounds were highly hygroscopic, samples were prepared in a dry Ar atmosphere. The exact composition of studied samples was not reported. Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($UO_3$(cr, γ), $KH_2PO_4$(cr, tetr), $CaCO_3$(cr, hex), $K_2CO_3$(cr, monocl), $Ca(H_2PO_4)_2\cdot H_2O$(cr, tricl), $SrCO_3$(cr, rhomb), $BaCO_3$(cr, rhomb), $Ca[(UO_2)(PO_4)]_2$(cr), $Sr[(UO_2)(PO_4)]_2$(cr), $Ba[(UO_2)(PO_4)]_2$(cr)) in aqueous 4 M (~ 4.36 m) HCl medium.

The value of $\Delta_f H_m^\circ$ of $Ca[(UO_2)(PO_4)]_2$(cr) can be evaluated from two reactions:

$$2KH_2PO_4(cr) + 2UO_3(cr) + CaCO_3(cr) \rightleftharpoons Ca[(UO_2)(PO_4)]_2(cr) + K_2CO_3(cr) + 2H_2O(l) \qquad (A.82)$$

$\Delta_r H_m$ (A.82) = (21.05 ± 2.68) kJ·mol$^{-1}$;

and

$$Ca(H_2PO_4)_2 \cdot H_2O(cr) + 2UO_3(cr) \rightleftharpoons Ca[(UO_2)(PO_4)]_2(cr) + 3H_2O(l) \quad (A.83)$$

$\Delta_r H_m$ (A.83) = – (58.04 ± 2.06) kJ·mol$^{-1}$.

The values of $\Delta_f H_m^o$ of Sr[(UO$_2$)(PO$_4$)]$_2$(cr) and Ba[(UO$_2$)(PO$_4$)]$_2$(cr) were evaluated from the following general reaction:

$$2KH_2PO_4(cr) + 2UO_3(cr) + MCO_3(cr) \rightleftharpoons M[(UO_2)(PO_4)]_2(cr) + K_2CO_3(cr) + 2H_2O(l) \quad (A.84)$$

with $\Delta_r H_m$ = (11.97 ± 3.63) kJ·mol$^{-1}$ for M = Sr and with $\Delta_r H_m$ = (2.75 ± 3.01) kJ·mol$^{-1}$ for M = Ba.

For calculations of $\Delta_f H_m^o$ the authors used the auxiliary data from Glushko *et al.* (1965-1981) and Naumov *et al.* (1971). This review has recalculated the enthalpies of formation using the following auxiliary $\Delta_f H_m^o$ data (in kJ·mol$^{-1}$): – (1223.8 ± 1.2) for UO$_3$(cr) (the NEA database); – (1207.5 ± 1.2) for calcite, CaCO$_3$(cr), and – (3423.405 ± 2.295) for Ca(H$_2$PO$_4$)$_2$·H$_2$O(cr) (both are from the [NEA TDB review on Ancillary Data – to be published]); – (1226.0 ± 2.0) for SrCO$_3$(cr) [1994GUR/VEY]; – (1213.03 ± 2.0) for BaCO$_3$(cr) [1995PAR2]; – (1151.5 ± 2.0) for K$_2$CO$_3$(cr) [1982GLU/GUR]; – (285.83 ± 0.04) for H$_2$O(l) from the NEA database; – (1574.5 ± 2.0) for KH$_2$PO$_4$(cr) (see the review of [1993KAR/CHE]).

Calculation of $\Delta_f H_m^o$ for Ca[(UO$_2$)(PO$_4$)]$_2$(cr) from the Reaction (A.82) were made using the relation:

$$\Delta_f H_m^o = \Delta_r H_m(l) - \Delta_f H_m^o(K_2CO_3(cr)) - 2(\Delta_f H_m^o(H_2O(l) + \bar{L}_1)$$
$$+2\Delta_f H_m^o(KH_2PO_4(cr)) + 2\Delta_f H_m^o(UO_3(cr)) + \Delta_f H_m^o(CaCO_3(cr))$$

where $\bar{L}_1$ = – 0.34 kJ·mol$^{-1}$ is the relative partial molar enthalpy of water in 4.36 m HCl solution, see the review of [2002KAR/CHE2] for explanations. Similar calculations for other reactions resulted in the following values of $\Delta_f H_m^o$ for the uranyl phosphates:

For Ca[(UO$_2$)(PO$_4$)]$_2$(cr) $\Delta_f H_m^o$ = – (5059.2 ± 5.6) kJ·mol$^{-1}$ from Reaction (A.82) and $\Delta_f H_m^o$ = – (5070.5 ± 3.5) kJ·mol$^{-1}$ from Reaction (A.83) with an average value of $\Delta_f H_m^o$ = – (5064.9 ± 5.0) kJ·mol$^{-1}$;

For Sr[(UO$_2$)(PO$_4$)]$_2$(cr) $\Delta_f H_m^o$ = – (5086.8 ± 6.6) kJ·mol$^{-1}$;

for Ba[(UO$_2$)(PO$_4$)]$_2$(cr) $\Delta_f H_m^o$ = – (5083.0 ± 6.3) kJ·mol$^{-1}$.

The uncertainties are calculated using rules of propagation of errors, see

Appendix C. Note that the authors reported larger uncertainties, from 11 to 17 kJ·mol$^{-1}$, in their $\Delta_f H_m^o$ results.

**[1996SOW/CLA]**

This study concerns the transformation of synthetic metaschoepite $UO_3 \cdot 2H_2O$(cr) to becquerelite and other phases in the presence of silica and phosphate. The presence of silica ($10^{-3}$ M) does not lead to the formation of silicates. In the presence of 0.01 M Ca, 0.01 M of phosphate at pH 5.41 at 25 °C metaschoepite rapidly (within one day) transforms into autunite, $Ca[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr), as confirmed by XRD and the electron micrography.

**[1998KAR/CHE2]**

In this study, Karyakin *et al.* determined the low-temperature heat capacity of a synthetic sample of $K[(UO_2)(PO_4)] \cdot 3H_2O$(cr). The phase was identified with X-ray diffractometry, but its the exact composition was not given.

The heat capacity was measured at 8-300 K, data were extrapolated to 0 K and numerically integrated to evaluate at 298.15 K (in J·K$^{-1}$·mol$^{-1}$): $S_m^o$ = (342.4 ± 1) and $C_{p,m}^o$ = 304.2. This review considers the $S_m^o$ results of [1998KAR/CHE] as semi-quantitative due to lack of data on the exact composition of phases and increases its uncertainty up to ± 10 J·K$^{-1}$·mol$^{-1}$. However, the agreement of the measured entropy and one based on the method of Latimer (1951), as outlined in Appendix D, $S_m^o$ = (330 ± 22) J·K$^{-1}$·mol$^{-1}$, is satisfactory.

**[1998KAR/CHE4]**

This study reports the enthalpies of formation of synthetic samples of the $A^{II}[(UO_2)(B^{V}O_4)]_2{\cdot}nH_2O$(cr) compounds ($A^{II}$ = Mg, Ca, Sr, Ba; $B^{V}$ = P, As). The phases were obtained by precipitation from dilute solutions of alkaline-earth metal chlorides, orthophosphoric acid and uranyl nitrate; the precipitates were washed and dried; some compounds were prepared by drying higher crystal hydrates in a desiccator. Anhydrous compounds were obtained by calcination of the corresponding synthetic hydrates at 600 °C. As the compounds were highly hygroscopic, samples were prepared in a dry Ar atmosphere. The exact composition of the studied samples was not reported.

The authors measured in an adiabatic calorimeter at 298.15 K enthalpies of solution of hydrates and anhydrous compounds in 4 N (~ 4.36 m) HCl medium and calculated the following values of the enthalpies of dehydration, $\Delta_r H_m$, according to the reaction:

$$A^{II}[(UO_2)(B^{V}O_4)]_2 \cdot nH_2O(cr) \rightleftharpoons A^{II}[(UO_2)(B^{V}O_4)]_2(cr) + nH_2O(l)$$

(see Table A-52).

Table A-52: Values of enthalpies of dehydration (the second column) from [1998KAR/CHE3], and the standard enthalpies of dehydration and formation (the third and fourth columns, respectively), calculated in this review.

| $A^{II}[(UO_2)(BVO_4)]_2{\cdot}nH_2O$(cr) | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[(UO_2)(PO_4)]_2{\cdot}2H_2O$(cr) | (79.29 ± 2.88) | (80.0 ± 2.9) | |
| $Mg[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | (158.14 ± 1.26) | (161.5 ± 1.3) | |
| $Mg[(UO_2)(AsO_4)]_2{\cdot}10H_2O$(cr) | (171.69 ± 1.73) | (175.1 ± 1.7) | |
| $Ca[(UO_2)(PO_4)]_2{\cdot}5H_2O$(cr) | (66.76 ± 0.70) | (68.5 ± 0.7) | – (6562.6 ± 5.0) |
| $Ca[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) | (82.00 ± 0.70) | (84.0 ± 0.7) | – (6863.9 ± 5.0) |
| $Ca[(UO_2)(AsO_4)]_2{\cdot}6H_2O$(cr) | (92.25 ± 0.53) | (94.3 ± 0.5) | – (6052.5 ± 9.0) |
| $Ca[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | (126.70 ± 0.98) | (130.1 ± 1.0) | – (8053.30 ± 5.1) |
| $Ca[(UO_2)(AsO_4)]_2{\cdot}10H_2O$(cr) | (138.00 ± 0.60) | (141.4 ± 0.6) | – (7242.9 ± 9.0) |
| $Sr[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) | (83.99 ± 1.43) | (86.0 ± 1.4) | – (6887.8 ± 6.7) |
| $Sr[(UO_2)(PO_4)]_2{\cdot}8H_2O$(cr) | (116.39 ± 2.18) | (119.1 ± 2.2) | – (7492.5 ± 7.0) |
| $Sr[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) | (117.59 ± 1.55) | (120.3 ± 1.6) | – (6691.6 ± 9.5) |
| $Ba[(UO_2)(PO_4)]_2{\cdot}6H_2O$(cr) | (85.48 ± 2.03) | (87.5 ± 2.0) | – (6885.5 ± 6.6) |
| $Ba[(UO_2)(AsO_4)]_2{\cdot}7H_2O$(cr) | (97.97 ± 1.26) | (100.4 ± 1.3) | – (6393.5 ± 9.4) |

These $\Delta_r H_m$ values are valid in a 4 N (~ 4.36 m) HCl medium, and they are extrapolated in this review to the pure water medium ($\Delta_r H_{\underline{m}}^o$) as $\Delta_r H_m^o = \Delta_r H_m - n\overline{L}_1$ (see the Appendix A entry for [1994KAR/CHE]), where $\overline{L}_1 = -0.34$ kJ·mol$^{-1}$ is the relative partial molar enthalpy of water in a 4.36 m HCl solution. The resulting values of $\Delta_r H_m^o$ are also summarised in Table A-52.

Using the values of enthalpies of formation, $\Delta_f H_m^o$, of the anhydrous phases from [1996KAR/CHE] for phosphates and [1996KAR/CHE2] for arsenates, in

combination with measured enthalpies of hydration and $\Delta_f H_m^o$ of liquid water the authors of [1998KAR/CHE4] calculated the enthalpies of formation of uranyl phosphates and their hydrates, including those of Mg, where the source of data on $\Delta_f H_m^o$ is not clear. This review recalculated these values using the $\Delta_r H_m^o$ of the hydration reaction revised in this review, $\Delta_r H_m^o$ and the values of $\Delta_f H_m^o$ for the corresponding anhydrous compounds recalculated from [1996KAR/CHE] and [1998KAR/CHE4]. The resulting values of $\Delta_f H_m^o$ for the hydrated compounds are summarised in the last column of Table A-52.

**[1999KAR/CHE]**

This study reports the low-temperature heat capacity of synthetic samples of $A^I[(UO_2)(PO_4)](cr)$ ($A^I$ – H, Li, Na, K, Rb, Cs) at 80-320 K with an adiabatic vacuum calorimeter. First, hydrates of the corresponding uranyl phosphates were synthesised, and anhydrous phases were obtained by heating of $H[(UO_2)(PO_4)]\cdot 4H_2O(cr)$ at 450 K and other crystallohydrates at 750 K. No chemical compositions of the studied samples are presented. Data are extrapolated to 0 K and numerically integrated to evaluate the entropy at 298.15 K (in $J\cdot K^{-1}\cdot mol^{-1}$), see below:

Table A-53: Experimental (the second and fourth columns) and estimated with the Latimer method [1951LAT] values of the entropy and heat capacity of some anhydrous uranyl phosphate phases.

| Compound | $S_m^o$ (298.15)[(a)] | $S_m^o$ (298.15 K)[(b)] | $C_{p,m}^o$ (298.15)[(a)] |
|---|---|---|---|
| $H[(UO_2)(PO_4)](cr)$ | 167.2 | (158 ± 12)[(c)] | 145.9 |
| $Li[(UO_2)(PO_4)](cr)$ | 169.3 | (172 ± 12) | 157.1 |
| $Na[(UO_2)(PO_4)](cr)$ | 202.6 | (189 ± 12) | 161.0 |
| $K[(UO_2)(PO_4)](cr)$ | 194.0 | (196 ± 12) | 164.0 |
| $R[(UO_2)(PO_4)](cr)$ | 219.8 | (207 ± 12) | 162.6 |
| $Cs[(UO_2)(PO_4)](cr)$ | 230.7 | (214 ± 12) | 168.8 |

(a) Experimental value.
(b) Estimated with the Latimer method [1951LAT], see Appendix D.
(c) Assuming that contribution of H is equal to 0.

The authors did not give uncertainties of evaluated $S_m^o$ (298.15 K) results. These data differ from values reported by the same research group in [2000KAR/CHE], in some cases by 25 $J\cdot K^{-1}\cdot mol^{-1}$. The current data are in a better agreement with estimates by the Latimer method [1951LAT], as outlined in Appendix D, compared with those in the [2000KAR/CHE] study. This review estimates the uncertainty of [1999KAR/CHE] in $S_m^o$ data as ± 12 $J\cdot K^{-1}\cdot mol^{-1}$.

**[2000KAR/CHE]**

This study reports the low-temperature heat capacity of synthetic samples of

$A^I[(UO_2)(B^VO_4)]\cdot nH_2O$(cr) ($A^I$ – H, Li, Na, K, Rb, Cs; $B^V$ – P, As) at 80-300 K with an adiabatic vacuum calorimeter. No chemical compositions of the studied samples are presented. Data are extrapolated to 0 K and numerically integrated to evaluate the entropy at 298.15 K (in $J\cdot K^{-1}\cdot mol^{-1}$), see Table A-54.

Table A-54: Experimental and estimated with the Latimer method [1951LAT] values of the entropy and heat capacity of some uranyl phosphate and arsenate phases.

| Compound | $S^o_m$ (298.15 K)[(a)] | $S^o_m$ (298.15 K)[(b)] | $C^o_{p,m}$ (298.15 K)[(a)] |
|---|---|---|---|
| $H[(UO_2)(PO_4)]\cdot 4H_2O$(cr) | 327.5 | (336 ± 27)[(c)] | 317.0 |
| $Li[(UO_2)(PO_4)]\cdot 4H_2O$(cr) | 336.1 | (351 ± 25) | 332.1 |
| $Na[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | 358.5 | (323 ± 19) | 371.6 |
| $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | 343.9 | (330 ± 19) | 308.4 |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | 348.0 | (341 ± 19) | 300.3 |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O$(cr) | 337.7 | (326 ± 17) | 269.8 |
| $Li[(UO_2)(PO_4)]$(cr) | 177.9 | (172 ± 12) | 154.7 |
| $Na[(UO_2)(PO_4)]$(cr) | 216.9 | (189 ± 12) | 159.7 |
| $K[(UO_2)(PO_4)]$(cr) | 221.8 | (196 ± 12) | 163.5 |
| $Rb[(UO_2)(PO_4)]$(cr) | 247.1 | (207 ± 12) | 169.8 |
| $Cs[(UO_2)(PO_4)]$(cr) | 236.7 | (214 ± 12) | 160.5 |
| $H[(UO_2)(AsO_4)]\cdot 4H_2O$(cr) | 349.1 | (353 ± 27)[(c)] | 326.3 |
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O$(cr) | 364.8 | (367 ± 25) | 354.0 |
| $Na[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | 402.7 | (339 ± 19) | 376.5 |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | 371.9 | (346 ± 19) | 323.4 |
| $Rb[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | 383.5 | (358 ± 19) | 338.4 |
| $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O$(cr) | 372.7 | (342 ± 17) | 306.2 |
| $Li[(UO_2)(AsO_4)]$(cr) | 224.6 | (189 ± 12) | 178.9 |
| $Na[(UO_2)(AsO_4)]$(cr) | 236.8 | (206 ± 12) | 178.4 |
| $K[(UO_2)(AsO_4)]$(cr) | 245.0 | (213 ± 12) | 173.8 |
| $Rb[(UO_2)(AsO_4)]$(cr) | 254.6 | (224 ± 12) | 171.7 |
| $Cs[(UO_2)(AsO_4)]$(cr) | 292.1 | (231 ± 12) | 205.6 |

(a) Experimental value.
(b) Estimated with the Latimer method [1951LAT] as outlined in Appendix D.
(c) Assuming that contribution of H is equal to 0.

Using the Latimer [1951LAT] method as outlined in Appendix D, this review calculates the values given in the 3rd column of Table A-54. The difference for H and Li compounds is less than 20 $J\cdot K^{-1}\cdot mol^{-1}$, for other compounds it is larger. These data differ somewhat, up to 25 $J\cdot K^{-1}\cdot mol^{-1}$, from values reported by the same research group in [1999KAR/CHE]. As there are no reports of the chemical compositions of the studied samples, especially the amount of crystallisation water, the data are considered semi-quantitative.

Note that the difference between entropies of the isostructural P and As compounds is expected to be approximately constant. Experimental data show the difference within 8-55 $J\cdot K^{-1}\cdot mol^{-1}$, *i.e.* the scatter is rather high. This suggests that the uncertainty of ± 20-30 $J\cdot K^{-1}\cdot mol^{-1}$ seems more reasonable for these data.

**[2000KIR/CHE]**

This study reports the enthalpy of formation of synthetic samples of $A^{II}[(UO_2)(PO_4)]\cdot nH_2O$(cr), where $A^{II}$ – Fe, Co, Ni. Samples of the studied phases were synthesised by reaction of aqueous solutions of sulfates of Fe(II), acetates of Ni(II) and Co(II) with crystalline chernikovite $H[(UO_2)(PO_4)]\cdot 4H_2O$(cr). The elemental composition was measured with a X-ray fluorescence energy-dispersive spectrometer. The water content was determined by the weight method by heating samples at 500 °C for two hours. Calorimetric runs were made with a Calvet type calorimeter. Enthalpies of solutions of solid compounds and water were measured in HCl solutions of the concentration of 14 wt. % (~ 4.46 m HCl, where $\overline{L}_1 = -0.36$ kJ·mol$^{-1}$, see, for example, [2002KAR/CHE] for explanations). The thermochemical cycle used to calculate $\Delta_f H^o_m$ was described by the authors in detail.

For the reaction:

$$2UO_3(cr) + 2KH_2PO_4(cr) + FeSO_4\cdot 7H_2O(cr) + H_2O(l) \rightleftharpoons K_2SO_4(cr) + Fe[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$$

$\Delta_r H_m = -(134.3 \pm 1.5)$ kJ·mol$^{-1}$;

For the reaction:

$$2UO_3(cr) + 2KH_2PO_4(cr) + CoSO_4\cdot 6H_2O(cr) \rightleftharpoons K_2SO_4(cr) + Co[(UO_2)(PO_4)]_2\cdot 7H_2O(cr) + H_2O(l)$$

$\Delta_r H_m = -(112.9 \pm 1.5)$ kJ·mol$^{-1}$;

For the reaction:

$$2UO_3(cr) + 2KH_2PO_4(cr) + NiSO_4\cdot 6H_2O(cr) + 2H_2O(l) \rightleftharpoons K_2SO_4(cr) + Ni[(UO_2)(PO_4)]_2\cdot 10H_2O(cr)$$

$\Delta_r H_m = -(130.6 \pm 1.5)$ kJ·mol$^{-1}$.

The current review calculated $\Delta_f H^o_m$ of uranyl phosphates from these data as was described in the reviews of [1994KAR/CHE] and [1996KAR/CHE]. For calculations of $\Delta_f H^o_m$ the authors used the auxiliary data from the Glushko *et al.* handbook (1965-1981). This review has recalculated the enthalpies of formation using the following auxiliary $\Delta_f H^o_m$ data (in kJ·mol$^{-1}$): for $UO_3$(cr) $-(1223.8 \pm 1.2)$ (NEA TDB); for α-$NiSO_4\cdot 6H_2O$(cr), $\Delta_f H^o_m = -(2683.817 \pm 1.014)$ kJ·mol$^{-1}$ [2005GAM/BUG]; for $FeSO_4\cdot 7H_2O$(cr) $\Delta_f H^o_m = -(3012.512 \pm 0.602)$ kJ·mol$^{-1}$ [2013LEM/BER]; for $K_2SO_4$(cr) $-(1437.7 \pm 0.5)$ kJ·mol$^{-1}$ [1982GLU/GUR]; for $KH_2PO_4$(cr) $-(1574.5 \pm 2.0)$, see the corresponding discussion in the review of [1993KAR/CHE], and for $CoSO_4\cdot 6H_2O$(cr) $-(2685.2 \pm 2.1)$ from Glushko *et al.* handbook (1965-1981) [1972GLU/MED]; $\overline{L}_1 = -0.36$ kJ·mol$^{-1}$, see above. The calculated values are given in Table A-55.

Table A-55: Values of $\Delta_f H_m^o$ (298.15 K) of uranyl phosphates of Fe(II), Co(II), Ni(II) calculated in this review from data reported in [2000KIR/CHE].

| Compound | $\Delta_f H_m^o$ (298.15 K) /kJ·mol$^{-1}$ |
|---|---|
| $Fe[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr) | – (7591.9 ± 4.7) |
| $Fe[(UO_2)(PO_4)]_2$(cr) | – (4564.2 ± 4.8) |
| $Co[(UO_2)(PO_4)]_2 \cdot 7H_2O$(cr) | – (6670.8 ± 5.0) |
| $Co[(UO_2)(PO_4)]_2$(cr) | – (4514.7 ± 5.1) |
| $Ni[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr) | – (7545.7 ± 4.7) |
| $Ni[(UO_2)(PO_4)]_2$(cr) | – (4490.3 ± 4.8) |

In addition, the authors calculated from heats of solution the enthalpy changes of the following reactions:

$$Fe[(UO_2)(PO_4)]_2 \cdot 10H_2O(cr) \rightleftharpoons Fe[(UO_2)(PO_4)]_2(cr) + 10H_2O(l)$$

$\Delta_r H_m$ = (165.8 ± 1.0) kJ·mol$^{-1}$; $\Delta_r H_m^o$ = (169.4 ± 1.0) kJ·mol$^{-1}$;

$$Co[(UO_2)(PO_4)]_2 \cdot 7H_2O(cr) \rightleftharpoons Fe[(UO_2)(PO_4)]_2(cr) + 7H_2O(l)$$

$\Delta_r H_m$ = (152.8 ± 1.0) kJ·mol$^{-1}$; $\Delta_r H_m^o$ = (155.3 ± 1.0) kJ·mol$^{-1}$

$$Ni[(UO_2)(PO_4)]_2 \cdot 10H_2O(cr) \rightleftharpoons Ni[(UO_2)(PO_4)]_2(cr) + 10H_2O(l)$$

$\Delta_r H_m$ = (193.5 ± 0.9) kJ·mol$^{-1}$, $\Delta_r H_m^o$ = (197.1 ± 0.9) kJ·mol$^{-1}$.

These values were recalculated in this review to the pure water medium ($\Delta_r H_m^o$) as described in review of [1994KAR/CHE] and used to obtain the enthalpies of formation of anhydrous uranyl phosphates, see Table A-55.

**[2002CHE/KAR]**

This study reports the low-temperature heat capacity and the enthalpy of formation of synthetic samples of $Al[(UO_2)(PO_4)]_2(OH) \cdot 11H_2O$(cr) and $Al[(UO_2)(AsO_4)]_2(OH) \cdot 13H_2O$(cr). The identity of the phases was confirmed with X-ray diffractometry and the elemental composition by X-ray fluorescence energy-dispersive spectrometry. The water content was determined gravimetrically after calcinating the samples at 500 °C for ten hours. In addition, the Al:U ratio was determined, but the exact composition of studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds (including water and HCl solutions) in aqueous HCl medium (the molar ratio HCl:$H_2O$ 1:10, *i.e.* in 5.55 m HCl). Closing the thermochemical cycle, the authors obtained for the reaction:

$$2UO_3(cr) + 2KH_2PO_4(cr) + 1/2Al_2(SO_4)_3(cr) + KCl(cr) + 10H_2O(l) \rightleftharpoons$$
$$3/2K_2SO_4(cr) + Al(PO_4)_2(UO_2)_2(OH) \cdot 11H_2O(cr) + HCl(aq) \qquad (A.85)$$

$\Delta_r H_m$ (A.85) = – (235.60 ± 2.67) kJ·mol$^{-1}$;

and for the reaction:

$$2UO_3(cr) + 2KH_2AsO_4(cr) + 1/2Al_2(SO_4)_3(cr) + KCl(cr) + 12H_2O(l) \rightleftharpoons$$
$$3/2K_2SO_4(cr) + Al(AsO_4)_2(UO_2)_2(OH)\cdot 13H_2O(cr) + HCl(aq) \quad (A.86)$$

$\Delta_r H_m$ (A.86) = – (238.98 ± 2.65) kJ·mol$^{-1}$.

In order to calculate the enthalpy of formation of phases from these results, the current review used the following $\Delta_f H^o_m$ auxiliary data: for $UO_3$(cr) – (1223.8 ± 1.2) kJ·mol$^{-1}$ (NEA TDB); for $K_2SO_4$(cr) – (1437.7 ± 0.5) kJ·mol$^{-1}$ [1982GLU/GUR]—the later edition of the Glushko handbook [1982GLU/GUR]; for KCl(cr) – (436.461 ± 0.129) kJ·mol$^{-1}$, for HCl(aq) at infinite dilution in water $\Delta_f H^o_m$ = – (167.08 ± 0.10) kJ·mol$^{-1}$ (NEA TDB); for $Al_2(SO_4)_3$(cr) – (3441.8 ± 1.8) from Glushko *et al.* (1965-1981) [1972GLU/MED]; for $KH_2PO_4$(cr) – (1574.5 ± 2.0), see the synopsis of [1993KAR/CHE]; and for $KH_2AsO_4$(cr) $\Delta_f H^o_m$ = – (1181.3 ± 4.2), obtained as discussed in Section 9.6.2.2.2. This review used the following relations to calculate $\Delta_f H^o_m$:

$$\Delta_f H^o_m(Al[(PO_4)(UO_2)]_2(OH)\cdot 11H_2O, cr) =$$
$$\Delta_r H_m\ (A.85) - 3/2\Delta_f H^o_m(K_2SO_4, cr) - (\Delta_f H^o_m(HCl, aq) + \overline{L}_2) + 2\Delta_f H^o_m(UO_3, cr) +$$
$$2\Delta_f H^o_m(KH_2PO_4, cr) + 1/2\Delta_f H^o_m(Al_2(SO_4)_3, cr) + \Delta_f H^o_m(KCl, cr) + 10(\Delta_f H^o_m(H_2O, l) + \overline{L}_1)$$

and

$$\Delta_f H^o_m(Al[(AsO_4)(UO_2)]_2(OH)\cdot 13H_2O, cr) =$$
$$\Delta_r H_m\ (A.86) - 3/2\Delta_f H^o_m(K_2SO_4, cr) - (\Delta_f H^o_m(HCl, aq) + \overline{L}_2) + 2\Delta_f H^o_m(UO_3, cr) +$$
$$2\Delta_f H^o_m(KH_2AsO_4, cr) + 1/2\Delta_f H^o_m(Al_2(SO_4)_3, cr) - \Delta_f H^o_m(KCl, cr) + 12(\Delta_f H^o_m(H_2O, l) + \overline{L}_1)$$

where $\overline{L}_2$ = 11.1 kJ·mol$^{-1}$ and $\overline{L}_1$ = – 0.53 kJ·mol$^{-1}$ are the relative partial molar enthalpies of HCl and water in 5.55 m HCl solutions, calculated from the enthalpy of dilution data for HCl [1965PAR], see review of [2002KAR/CHE2] for explanations. Results are given in Table A-56. The uncertainties are calculated using rules of propagation of errors, see Appendix C.

Table A-56: Thermodynamic properties of aluminum uranyl phosphate and arsenate at 298.15 K, recalculated in this review:

| Compound | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ | $S^{o\ (a)}_m$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S^{o\ (b)}_m$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G^o_m$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $Al[(UO_2)(PO_4)]_2(OH)\cdot 11H_2O$(cr) | – (8540.7 ± 5.5) | (785.3 ± 4) | – (3390 ± 50) | – (7530 ± 16) |
| $Al[(UO_2)(AsO_4)]_2(OH)\cdot 13H_2O$(cr) | – (8330.4 ± 9.2) | (818.9 ± 4) | – (3811 ± 50) | – (7194 ± 18) |

(a) Authors' value of uncertainty.
(b) Uncertainty is estimated in the current review.

The heat capacity was measured at 80-300 K with an adiabatic vacuum calorimeter, at 298.15 K $C^{o}_{p,m}$ = 835 J·K$^{-1}$·mol$^{-1}$ for the phosphate phase and $C^{o}_{p,m}$ = 900 J·K$^{-1}$·mol$^{-1}$ for the arsenate phase. Data are extrapolated to 0 K and numerically integrated to evaluate the entropy at 298.15 K (in J·K$^{-1}$·mol$^{-1}$), see values in the Table A-56. These entropy values are only in a fair agreement with estimates based on Latimer method [1951LAT] as outlined in Appendix D (suggesting an uncertainty in the water content): (859 ± 70) and (982 ± 82) J·K$^{-1}$·mol$^{-1}$, therefore, their uncertainties are increased up to ± 50 J·K$^{-1}$·mol$^{-1}$. The values of entropies of elements were taken from the NEA TDB: U(cr) (50.20 ± 0.20); $H_2$(g) (130.680 ± 0.003); $O_2$(g) (205.152 ± 0.005); P(white) (41.09 ± 0.25); As(cr) (35.10 ± 0.60); Al(cr) (28.30 ± 0.10). The values of $\Delta_f G^{o}_{m}$ are calculated with the Gibbs-Helmholtz relation. All results in Table A-56 are given for information only.

**[2002ERM]**

This Ph. D. dissertation of Ermilov reports primary data on the water vapor pressures over monovariant phase associations of the alkali metal uranyl phosphates and arsenates. Part of these results is published in [2003SUL/KAR] and [2003SUL/CHE] and will not be reviewed again. The vapor pressures over the solid phases were determined using isopiestic and tensimetric methods. Vapor pressure results (in atm) over coexisting phases were fitted by the authors with the equation ln $P$ = A + B/$T$ (see Table A-57).

Table A-57: Dehydration reactions, their temperature ranges, and parameters of the equation ln $P$(atm) = A+ B/$T$.

| Reaction | $T$, K range/ # of points | $A$ | $-B$ |
|---|---|---|---|
| $Li[(UO_2)(PO_4)]\cdot 4H_2O(cr) \rightleftharpoons Li[(UO_2)(PO_4)]\cdot 3H_2O(cr) + H_2O(g)$ | 324-384/10 | 17.75 | 6939.4 |
| $Li[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons Li[(UO_2)(PO_4)]\cdot H_2O(cr) + 2H_2O(g)$ | 332-416/9 | 16.28 | 6889.8 |
| $Li[(UO_2)(PO_4)]\cdot H_2O(cr) \rightleftharpoons Li[(UO_2)(PO_4)](cr) + H_2O(g)$ | 366-484/10 | 13.71 | 6888.1 |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons Rb[(UO_2)(PO_4)]\cdot 0.5H_2O(cr) + 2.5H_2O(g)$ | 349-373/8 | 16.54 | 6293.6 |
| $Rb[(UO_2)(PO_4)]\cdot 0.5H_2O(cr) \rightleftharpoons Rb[(UO_2)(PO_4)](cr) + 0.5H_2O(g)$ | 361-443/10 | 17.33 | 7770.2 |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O(cr) \rightleftharpoons Cs[(UO_2)(PO_4)](cr) + 2.5H_2O(g)$ | 332-397/15 | 15.76 | 6363.5 |
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr) \rightleftharpoons Li[(UO_2)(AsO_4)]\cdot 3H_2O(cr) + H_2O(g)$ | 347-378/12 | 19.38 | 7426.3 |
| $Li[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons Li[(UO_2)(AsO_4)]\cdot H_2O(cr) + 2H_2O(g)$ | 350-426/12 | 17.69 | 7577.9 |
| $Li[(UO_2)(AsO_4)]\cdot H_2O(cr) \rightleftharpoons Li[(UO_2)(AsO_4)](cr) + H_2O(g)$ | 418-508/13 | 16.61 | 8506.8 |
| $Na[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons Na[(UO_2)(AsO_4)]\cdot 1.5H_2O(cr) + 1.5H_2O(g)$ | 347-378/13 | 17.72 | 6760.0 |
| $Na[(UO_2)(AsO_4)]\cdot 1.5H_2O(cr) \rightleftharpoons Na[(UO_2)(AsO_4)]\cdot H_2O(cr) + 0.5H_2O(g)$ | 323-381/10 | 16.23 | 7995.2 |
| $Na[(UO_2)(AsO_4)]\cdot H_2O(cr) \rightleftharpoons Na[(UO_2)(AsO_4)](cr) + H_2O(g)$ | 429-510/18 | 15.18 | 8012.1 |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons K[(UO_2)(AsO_4)]\cdot 0.5H_2O(cr) + 2.5H_2O(g)$ | 325-367/9 | 18.14 | 6982.0 |
| $K[(UO_2)(AsO_4)]\cdot 0.5H_2O(cr) \rightleftharpoons K[(UO_2)(AsO_4)](cr) + 0.5H_2O(g)$ | 429-508/15 | 18.95 | 10038.4 |

(Continued on next page)

Table A-57 (continued)

| Reaction | $T$, K range/ # of points | $A$ | $-B$ |
|---|---|---|---|
| $Rb[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons Rb[(UO_2)(AsO_4)]\cdot H_2O(cr) + 2H_2O(g)$ | 324-380/12 | 16.55 | 6400.6 |
| $Rb[(UO_2)(AsO_4)]\cdot H_2O(cr) \rightleftharpoons Rb[(UO_2)(AsO_4)]\cdot 0.5H_2O(cr) + 0.5H_2O(g)$ | 324-403/15 | 16.67 | 6774.7 |
| $Rb[(UO_2)(AsO_4)]\cdot 0.5H_2O(cr) \rightleftharpoons Rb[(UO_2)(AsO_4)](cr) + 0.5H_2O(g)$ | 393-505/22 | 15.57 | 8027.3 |
| $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr) \rightleftharpoons Cs[(UO_2)(AsO_4)]\cdot H_2O(cr) + 1.5H_2O(g)$ | 324-378/12 | 17.73 | 6775.0 |
| $Cs[(UO_2)(AsO_4)]\cdot H_2O(cr) \rightleftharpoons Cs[(UO_2)(AsO_4)]\cdot 0.5H_2O(cr) + 0.5H_2O(g)$ | 322-404/17 | 16.02 | 6588.1 |
| $Cs[(UO_2)(AsO_4)]\cdot 0.5H_2O(cr) \rightleftharpoons Cs[(UO_2)(AsO_4)](cr) + 0.5H_2O(g)$ | 367-452/17 | 16.78 | 7655.7 |

Presented results were used in this review to evaluate $\Delta_r G_m^o$ at 298.15 K for a number of dehydrations reactions, see Table A-58 below (details of calculations are discussed in the review of [2002SUL/KAR]):

Table A-58: The Gibbs energy changes at 298.15 K for some dehydration reactions.

| Reaction | $\Delta_r G_m^o$ /kJ·mol$^{-1}$ |
|---|---|
| $Li[(UO_2)(PO_4)]\cdot 4H_2O(cr) \rightleftharpoons Li[(UO_2)(PO_4)]\cdot 3H_2O(cr) + H_2O(g)$ | 71.0 |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons Rb[(UO_2)(PO_4)](cr) + 3H_2O(g)$ | 39.2 |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O(cr) \rightleftharpoons Cs[(UO_2)(PO_4)](cr) + 2.5H_2O(g)$ | 34.7 |
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr) \rightleftharpoons Li[(UO_2)(AsO_4)](cr) + 4H_2O(g)$ | 81.7 |
| $Na[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons Na[(UO_2)(AsO_4)](cr) + 3H_2O(g)$ | 60.6 |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons K[(UO_2)(AsO_4)](cr) + 3H_2O(g)$ | 51.1 |
| $Rb[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons Rb[(UO_2)(AsO_4)](cr) + 3H_2O(g)$ | 46.1 |
| $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr) \rightleftharpoons Cs[(UO_2)(AsO_4)](cr) + 2.5H_2O(g)$ | 37.2 |

The dissertation also reports the values of heats of solutions of compounds in concentrated HF solutions. Data for uranyl phosphates of Na and K were reported in [2002SUL/KAR] and data for alkali metal uranyl arsenates in [2003SUL/KAR] and will not be reviewed again. However, data for lithium uranyl phosphates appear to be reported only in the dissertation. Experimental determinations of heats of solution (in the reaction medium the molar ratio HF:$H_2O$ was equal to 289:1230, *i.e.* ~13.0 m HF) resulted in the following $\Delta_r H_m$ values for the reactions given below:

$$KH_2PO_4(cr) + UO_3(cr) + 0.5Li_2CO_3(cr) + 3H_2O(l) \rightleftharpoons Li[(UO_2)(PO_4)]\cdot 4H_2O(cr) + 0.5K_2CO_3(cr) \quad (A.87)$$

$\Delta_r H_m$ (A.87) = – (53.7 ± 3.4) kJ·mol$^{-1}$;

$$KH_2PO_4(cr) + UO_3(cr) + RbCl(cr) + 2H_2O(l) \rightleftharpoons Rb[(UO_2)(PO_4)]\cdot 3H_2O(cr) + KCl(cr) \quad (A.88)$$

$\Delta_r H_m$ (A.88) = – (81.5 ± 3.0) 1 kJ·mol$^{-1}$;

$$KH_2PO_4(cr) + UO_3(cr) + CsCl(cr) + 1.5H_2O(l) \rightleftharpoons Cs[(UO_2)(PO_4)]\cdot 2.5H_2O(cr) + KCl(cr) \quad (A.89)$$

$\Delta_r H_m$ (A.89) = – (48.0 ± 3.2) 1 kJ·mol$^{-1}$.

Using the following auxiliary data for $\Delta_f H_m^o$ (in kJ·mol$^{-1}$): – (1574.5 ± 2.0) for $KH_2PO_4$(cr), see the review of [1993KAR/CHE]; – (1223.8 ± 1.2) for $UO_3$(cr), – (285.83 ± 0.04) for $H_2O$(l), – (436.461 ± 0.129) for KCl(cr), both from the NEA database, – (1214.1 ± 1.0) for $Li_2CO_3$(cr), – (435.22 ± 0.16) for RbCl(cr), – (442.31 ± 0.16) for CsCl(cr), all from [1982GLU/GUR]; – (1151.5 ± 2.0) for $K_2CO_3$(cr) from [NEA TDB review on Ancillary Data – to be published], as well as the value of the relative partial molar enthalpy of water, $L_1$, equal to – 0.31 kJ·mol$^{-1}$ in 13.0 m HF, evaluated from [1965PAR] data as explained in the review of [2002KAR/CHE2]; this review calculated the enthalpies of formation, reported in Table A-59:

Table A-59: The enthalpies of formation at 298.15 K for some alkali metal uranyl phosphates, recalculated in this review. As discussed in the main text, these are not included among the selected values.

| Compound | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ |
|---|---|
| $Li[(UO_2)(PO_4)]\cdot 4H_2O$(cr) | – (3741.7 ± 4.3) |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | – (3450.8 ± 3.8) |
| $Cs[(UO_2)(PO_4)]\cdot 2.5H_2O$(cr) | – (3281.3 ± 4.0) |
| $Li[(UO_2)(PO_4)]$(cr) | – (2539.9 ± 4.5) |
| $Rb[(UO_2)(PO_4)]$(cr) | – (2554.8 ± 3.9) |
| $Cs[(UO_2)(PO_4)]$(cr) | – (2541.2 ± 4.1) |

Additional calorimetric measurements were made in pure water to determine that enthalpies of interaction of water with alkali metal uranyl phosphates and arsenates. The corresponding data for uranyl phosphates of Na and K were reported in [2002SUL/KAR] and for alkali metal uranyl arsenates in [2003SUL/KAR] and will not be repeated here. Other results are presented below:

$$Li[(UO_2)(PO_4)]\cdot 4H_2O(cr) \rightleftharpoons Li[(UO_2)(PO_4)] + 4H_2O(l) \quad (A.90)$$

$\Delta_r H_m^o$ (A.90) = (58.5 ± 1.2) kJ·mol$^{-1}$;

$$Rb[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons Rb[(UO_2)(PO_4)] + 3H_2O(l) \quad (A.91)$$

$\Delta_r H_m^o$ (A.91) = (38.5 ± 1.0) kJ·mol$^{-1}$;

$$Cs[(UO_2)(PO_4)]\cdot 2.5H_2O(cr) \rightleftharpoons Cs[(UO_2)(PO_4)] + 2.5H_2O(l) \quad (A.92)$$

$\Delta_r H_m^o$ (A.92) = (25.5 ± 1.0) kJ·mol$^{-1}$.

These results were used to calculate the enthalpies of formation of anhydrous compounds, see Table A-59.

**[2002KAR/CHE3]**

This study reports the enthalpies of formation and low-temperature heat capacities of synthetic samples of $Ni[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr), $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr), $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr), and $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr). The purity of phases was confirmed with X-ray diffractometry, the elemental composition was determined with an electron microscope equipped with an EDAX energy-dispersive analyser. However, the exact stoichiometry of studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($UO_3$(cr, γ), $KH_2PO_4$(cr), $KH_2AsO_4$(cr), $K_2SO_4$(cr), $H_2O$(l), $NiSO_4 \cdot 6H_2O$(cr), $CuSO_4 \cdot 5H_2O$(cr), $Ni[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr), $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(Cr), $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr), and $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr)) in an aqueous HCl solution (the molar ratio $HCl:H_2O$ 1:10, *i.e.* the HCl molality is 5.55). The thermochemical cycle employed resulted in the following values for the reactions:

$$2KH_2PO_4(cr) + 2UO_3(cr) + NiSO_4 \cdot 6H_2O(cr) + 2H_2O(l) \rightleftharpoons Ni[(UO_2)(PO_4)]_2 \cdot 10H_2O(cr) + K_2SO_4(cr) \quad (A.93)$$

$\Delta_r H_m = -(134.5 \pm 5.6)$ kJ·mol$^{-1}$;

$$2KH_2AsO_4(cr) + 2UO_3(cr) + NiSO_4 \cdot 6H_2O(cr) + 2H_2O(l) \rightleftharpoons Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O(cr) + K_2SO_4(cr) \quad (A.94)$$

$\Delta_r H_m = -(130.2 \pm 6.2)$ kJ·mol$^{-1}$;

$$2KH_2PO_4(cr) + 2UO_3(cr) + CuSO_4 \cdot 5H_2O(cr) + H_2O(l) \rightleftharpoons Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr) + K_2SO_4(cr) \quad (A.95)$$

$\Delta_r H_m = -(175.2 \pm 5.7)$ kJ·mol$^{-1}$;

$$2KH_2AsO_4(cr) + 2UO_3(cr) + CuSO_4 \cdot 5H_2O(cr) + H_2O(l) \rightleftharpoons Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr) + K_2SO_4(cr) \quad (A.96)$$

$\Delta_r H_m = -(168.8 \pm 5.5)$ kJ·mol$^{-1}$.

This review used the following auxiliary data (in kJ·mol$^{-1}$): $-(1223.8 \pm 1.2)$ kJ·mol$^{-1}$ for $UO_3$(cr) [2003GUI/FAN]; $-(2683.817 \pm 1.014)$ for α-$NiSO_4 \cdot 6H_2O$(cr) [2005GAM/BUG]; $-(1437.7 \pm 0.5)$ kJ·mol$^{-1}$ for $K_2SO_4$(cr) [1982GLU/GUR]; $-(2280.38 \pm 1.29)$ for $CuSO_4 \cdot 5H_2O$(cr)—see the comment at the end of this review; $-(1574.5 \pm 2.0)$ for $KH_2PO_4$(cr)—see the review for [1993KAR/CHE]; and for $KH_2AsO_4$(cr) $\Delta_f H_m^o = -(1181.3 \pm 4.2)$, obtained as discussed in Section 9.6.3.1. Calculations of $\Delta_f H_m^o$ for uranyl phosphates were done as described in review of [1994KAR/CHE], [1996KAR/CHE], with $\overline{L}_1 = -0.53$ kJ·mol$^{-1}$ in 5.55 m HCl solutions. Results are shown in Table A-60 (in kJ·mol$^{-1}$ for $\Delta_f H_m^o$, $\Delta_f G_m^o$, and in J·K$^{-1}$·mol$^{-1}$ for $C_{p,m}^o$, $S_m^o$, $\Delta_f S_m^o$).

Table A-60: Thermodynamic properties of uranyl phosphates and arsenates of Cu(II) and Ni(II) at 298.15 K, recalculated in this review. These thermodynamic quantities are not included among the selected values based on a comparison with the Gibbs energies of formation and the molar entropies, *cf.* the main text.

| Compound | $-\Delta_f H_m^o$ | $C_{p,m}^o$ | $S_m^o$ | $S_m^o$ (estim) [(a)] | $-\Delta_f S_m^o$ [(b)] | $-\Delta_f G_m^o$ [(b)] |
|---|---|---|---|---|---|---|
| $Ni[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr) | (7549.9 ± 7.4) | 799.9 | 774.9 | (806 ± 63) | (3001.0 ± 30) | (6655.2 ± 11.6) |
| $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | (6759.2 ± 10.8) | 773.8 | 782.9 | (839 ± 63) | (2981.0 ± 30) | (5870.4 ± 14.0) |
| $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr) | (6900.8 ± 7.4) | 627.3 | 644.3 | (718 ± 52) | (2668.4 ± 30) | (6105.2 ± 11.6) |
| $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | (6108.0 ± 10.4) | 629.6 | 660.7 | (751 ± 52) | (2640.0 ± 30) | (5320.9 ± 13.7) |

(a) Estimated by the Latimer method [1951LAT] as outlined in Appendix D
(b) Values are calculated in this review

The authors also determined the low-temperature heat capacity of phases at 80-300 K with an adiabatic vacuum calorimeter. Data are extrapolated to 0 K and numerically integrated to evaluate the entropy at 298.15 K (in $J \cdot K^{-1} \cdot mol^{-1}$)—see Table A-60. The uncertainties of $S_m^o$ are estimated ± 30 in $J \cdot K^{-1} \cdot mol^{-1}$ due to lack of exact compositions of samples. The following values of $S_m^o$ of elements from the NEA database were used by this review to calculate $\Delta_f S_m^o$ in the Table above (in $J \cdot K^{-1} \cdot mol^{-1}$): (205.152 ± 0.005) for $O_2$(g); (130.680 ± 0.003) for $H_2$(g); (50.20 ± 0.20) for U(cr); (41.09 ± 0.25) for P(cr); (35.10 ± 0.60) for As(cr); (29.87 ± 0.20) for Ni(cr); (33.15 ± 0.08) for Cu(cr)—this is the CODATA value [1989COX/WAG]. The values of $\Delta_f G_m^o$ are calculated using the Gibbs-Helmholtz relation. They can be used for scoping calculations only.

The value of the enthalpy of formation of $CuSO_4 \cdot 5H_2O$(cr) used in this review was evaluated as follows: the handbook [1971NAU/RYZ] based on available data recommends for reaction $CuSO_4(cr) + 5H_2O(l) \rightleftharpoons CuSO_4 \cdot 5H_2O(cr)$ the value $\Delta_r H_m^o$ (298.15 K) = – (79.83 ± 0.42) $kJ \cdot mol^{-1}$. Combining this value with the CODATA-based [1989COX/WAG] enthalpies of formation $CuSO_4$(cr) – (771.4 ± 1.2) and $H_2O$(l) – (285.83 ± 0.04), this review calculates for $CuSO_4 \cdot 5H_2O$(cr) $\Delta_f H_m^o$ (298.15 K) = – (2280.38 ± 1.29) $kJ \cdot mol^{-1}$.

**[2002KAR/CHE5]**

This study reports the enthalpies of formation and low-temperature heat capacities of synthetic samples of $La[(UO_2)(PO_4)]_3 \cdot 14H_2O$(cr) and $La[(UO_2)(AsO_4)]_3 \cdot 15H_2O$(cr). The purity of phases was confirmed with X-ray diffractometry and by an unspecified analysis for La and U. The water content was determined gravimetrically by calcination at 500 °C for ten hours. However, the exact stoichiometry of the studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($LaCl_3$(cr), $UO_3$(cr, γ),

$KH_2PO_4$(cr), $KH_2AsO_4$(cr), KCl(cr), $H_2O$(l), $La[(UO_2)(PO_4)]_3{\cdot}14H_2O$(cr) and $La[(UO_2)(AsO_4)]_3{\cdot}15H_2O$(cr)) in an aqueous HCl solution (the molar ratio HCl:$H_2O$ 1:20, *i.e.* the HCl molality is 2.78). The thermochemical cycle employed resulted in the following values for the reactions:

$$LaCl_3(cr) + 3UO_3(cr) + 3KH_2PO_4(cr) + 11H_2O(l) \rightleftharpoons 3KCl(cr) + La[(UO_2)(PO_4)]_3{\cdot}14H_2O(cr) \quad \text{(A.97)}$$

$\Delta_r H^o_m = -(303.6 \pm 4.6)$ kJ·mol$^{-1}$;

$$LaCl_3(cr) + 3UO_3(cr) + 3KH_2AsO_4(cr) + 12H_2O(l) \rightleftharpoons 3KCl(cr) + La[(UO_2)(AsO_4)]_3{\cdot}15H_2O(cr) \quad \text{(A.98)}$$

$\Delta_r H^o_m = -(296.9 \pm 3.7)$ kJ·mol$^{-1}$.

This review used the following auxiliary data (in kJ·mol$^{-1}$): $-(1223.8 \pm 1.2)$ for $UO_3$(cr), $-(436.461 \pm 0.129)$ for KCl(cr) [2003GUI/FAN]; $-(1071.1 \pm 0.7)$ for $LaCl_3$(cr) from Glushko *et al.* (1965-1981) [1978GLU/GUR]; $-(1574.5 \pm 2.0)$ for $KH_2PO_4$(cr)—see the review for [1993KAR/CHE]; and for $KH_2AsO_4$(cr) $\Delta_f H^o_m = -(1181.3 \pm 4.2)$, obtained as discussed in Section 9.6.3.2. Calculations of $\Delta_f H^o_m$ for uranyl phosphates was done as described in review of [1994KAR/CHE], [1996KAR/CHE], with $\overline{L}_1 = -0.13$ kJ·mol$^{-1}$ in 2.78 m HCl solutions. Results are shown in Table A-61(in kJ·mol$^{-1}$) for $\Delta_f H^o_m$, $\Delta_f G^o_m$, and in J·K$^{-1}$·mol$^{-1}$ for $C^o_{p,m}$, $S^o_m$, $\Delta_f S^o_m$):

Table A-61: Thermodynamic properties of uranyl phosphate and arsenate of La(III) at 298.15 K, recalculated in this review.

| Compound | $-\Delta_f H^o_m$ | $C^o_{p,m}$ | $S^o_m$ (exp) | $S^o_m$ (estim)[(a)] | $-\Delta_f S^o_m$ [(b)] | $-\Delta_f G^o_m$ |
|---|---|---|---|---|---|---|
| $La[(UO_2)(PO_4)]_3{\cdot}14H_2O$ | 11605.8 ± 8.4 | 1302 | 1209 ± 4 | 1156 ± 89 | 4234 ± 40 | 10343 ± 15 |
| $La[(UO_2)(AsO_4)]_3{\cdot}15H_2O$ | 10705.4 ± 13.7 | 1398 | 1273 ± 4 | 1251 ± 94 | 4385 ± 40 | 9398 ± 18 |

(a) Estimated by the Latimer (1951) method as outlined in Appendix D;
(b) Uncertainties are estimated in the current review;
(c) Values are calculated in this review, the authors' estimation of uncertainties.

The authors also determined the low-temperature heat capacity of phases at 80-300 K with an adiabatic vacuum calorimeter. Data are extrapolated to 0 K and numerically integrated to evaluate the entropy at 298.15 K (in J·K$^{-1}$·mol$^{-1}$)—see Table A-61. The authors' uncertainties of ± 4 J·K$^{-1}$·mol$^{-1}$ were increased in this review to ± 40 J·K$^{-1}$·mol$^{-1}$ mainly due to lack of exact stoichiometry of the studied samples.

The following values of $S^o_m$ of elements from the NEA database were used by this review to calculate $\Delta_f S^o_m$ in Table A-61 (in J·K$^{-1}$·mol$^{-1}$): (205.152 ± 0.005) for $O_2$(g); (130.680 ± 0.003) for $H_2$(g); (50.20 ± 0.20) for U(cr); (41.09 ± 0.25) for P(cr); (35.10 ± 0.60) for As(cr); (56.7 ± 0.60) for La(cr) as given in [1982GLU/GUR]. The values of $\Delta_f G^o_m$ are calculated using the Gibbs-Helmholtz relation.

These values are not selected; they are given for information only.

**[2002SUL/KAR]**

The vapor pressures over the solid phases of the systems $Na[(UO_2)(PO_4)]$-$H_2O$ and $K[(UO_2)(PO_4)]$-$H_2O$ were determined using isopiestic and tensimetric methods at 40-210 °C (the temperature range was estimated from plots in the paper, no primary vapor pressure data are reported). These data and the results of TGA showed the existence of the following crystalline phases: $Na[(UO_2)(PO_4)]\cdot(3.1 \pm 0.2)H_2O$(cr), $Na[(UO_2)(PO_4)]\cdot(1.30 \pm 0.05)H_2O$(cr), $Na[(UO_2)(PO_4)]\cdot(1.01 \pm 0.01)H_2O$(cr), $Na[(UO_2)(PO_4)]$(cr), $K[(UO_2)(PO_4)]\cdot(3.0 \pm 0.1)H_2O$(cr), $K[(UO_2)(PO_4)]\cdot(0.45 \pm 0.05)H_2O$(cr), and $K[(UO_2)(PO_4)]$(cr). Vapor pressure results over coexisting phases were fitted by the authors with the equation ($\ln P = A + B/T$), and using the tabulated coefficients of this equation the current review calculated for the reaction:

$$Na[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons Na[(UO_2)(PO_4)](cr) + 3H_2O(g) \quad (A.99)$$

at 298.15 K $\Delta_r G_m^o = (48.0 \pm 5.7)$ kJ·mol$^{-1}$;

and for the reaction:

$$K[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons K[(UO_2)(PO_4)](cr) + 3H_2O(g) \quad (A.100)$$

at 298.15 K $\Delta_r G_m^o = (43.1 \pm 5.7)$ kJ·mol$^{-1}$, uncertainties are estimated in this review. Details of calculations can be shown on an example of dehydration of $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr), which takes place through two reactions:

$$K[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons K[(UO_2)(PO_4)]\cdot 0.5H_2O(cr) + 2.5H_2O(g) \quad (A.101)$$

for which $\Delta_r G_m^o(A.101) = -RT\ln K^o = -2.5\,RT\ln P(A.102)/P^{\otimes}$, and

$$K[(UO_2)(PO_4)]\cdot 0.5H_2O(cr) \rightleftharpoons K[(UO_2)(PO_4)](cr) + 0.5H_2O(g) \quad (A.102)$$

for which $\Delta_r G_m^o(A.102) = -RT\ln K^o = -2.5\,RT\ln P(A.102)/P^{\otimes}$, where $P$(A.101) and $P$(A.102) are vapor pressure over corresponding monovariant phase associations, and $P^{\otimes}$ is the standard state pressure. The sum of Reactions (A.101) and (A.102) gives Reaction (A.100), for which $\Delta_r G_m^o(A.100) = \Delta_r G_m^o(A.101) + \Delta_r G_m^o(A.102)$. Analogous results can be calculated for dehydration reactions involving $Na[(UO_2)(PO_4)]\cdot 1.3H_2O$(cr), $Na[(UO_2)(PO_4)]\cdot H_2O$(cr), and $K[(UO_2)(PO_4)]\cdot 0.5H_2O$(cr). The uncertainties are estimated in this review, and they could be conservative, taking into account rather long extrapolations (up to 100 K) necessary to evaluate vapor pressures at 298.15 K.

In addition, the authors performed calorimetric experiments in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($UO_3$(cr), $KH_2PO_4$(cr), $H_2O$(l), NaCl(cr), KCl(cr), $Na[(UO_2)(PO_4)]\cdot 3H_2O$(cr) and $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr)) in concentrated HF solutions (molar ratio HF:$H_2O$ 166:569, *i.e.* ~16.2 m HF). The thermochemical cycle employed resulted in the following values of $\Delta_r H_m^o$ for the reactions

$$KH_2PO_4(cr) + UO_3(cr) + NaCl(cr) + 2H_2O(l) \rightleftharpoons Na[(UO_2)(PO_4)]\cdot 3H_2O(cr) + KCl(cr) \quad (A.103)$$

$\Delta_r H^o_m = -(77.6 \pm 4.6)$ kJ·mol$^{-1}$ (in the paper this value is misprinted as $-(171.4 \pm 4.6)$ kJ·mol$^{-1}$, the correct value is calculated from primary calorimetric data);

and

$$KH_2PO_4(cr) + UO_3(cr) + 2H_2O(l) \rightleftharpoons K[(UO_2)(PO_4)]\cdot 3H_2O(cr) \quad (A.104)$$

$\Delta_r H^o_m = -(84.0 \pm 4.1)$ kJ·mol$^{-1}$.

Using the following auxiliary data for $\Delta_f H^o_m$ (in kJ·mol$^{-1}$): $-(1574.5 \pm 2.0)$ for $KH_2PO_4$(cr), see the discussion in the review of [1993KAR/CHE]; $-(1223.8 \pm 1.2)$ for $UO_3$(cr), $-(285.83 \pm 0.04)$ for $H_2O$(l), $-(411.26 \pm 0.12)$ for NaCl(cr), $-(436.461 \pm 0.129)$ for KCl(cr), all from [2003GUI/FAN]; as well as the value of the relative partial molar enthalpy of water, $L_1$, equal to $-0.54$ kJ·mol$^{-1}$ in 16.2 m HF, evaluated from [1965PAR] data as explained in the review of [2002KAR/CHE]; this review calculated the values of $\Delta_f H^o_m$ summarised in Table A-62.

Table A-62: Enthalpies of formation of uranyl phosphates of Na and K, recalculated in this review from [2002SUL/KAR].

| Compound | $\Delta_f H^o_m$ /kJ·mol$^{-1}$ |
|---|---|
| $Na[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | $-(3423.4 \pm 5.2)$ |
| $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | $-(3455.0 \pm 4.7)$ |
| $Na[(UO_2)(PO_4)]$(cr) | $-(2518.2 \pm 5.5)$ |
| $K[(UO_2)(PO_4)]$(cr) | $-(2553.1 \pm 4.7)$ |

The authors also measured enthalpies of hydration of $Na[(UO_2)(PO_4)]\cdot 1.3H_2O$(cr), $Na[(UO_2)(PO_4)]\cdot H_2O$(cr), $Na[(UO_2)(PO_4)]$(cr), $K[(UO_2)(PO_4)]\cdot 0.5H_2O$(cr) and $K[(UO_2)(PO_4)]$(cr) (presumably in the pure water medium). From obtained results, the current review has accepted the enthalpy changes for the dehydration reactions:

$$Na[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons Na[(UO_2)(PO_4)](cr) + 3H_2O(l) \quad (A.105)$$

at 298.15 K $\Delta_r H^o_m$ (A.105) = $(47.7 \pm 1.9)$ kJ·mol$^{-1}$;

and for the reaction:

$$K[(UO_2)(PO_4)]\cdot 3H_2O(cr) \rightleftharpoons K[(UO_2)(PO_4)](cr) + 3H_2O(l) \quad (A.106)$$

at 298.15 K $\Delta_r H^o_m$ (A.106) = $(44.4 \pm 0.1)$ kJ·mol$^{-1}$. These values were employed to calculate the enthalpies of formation of anhydrous compounds—see Table A-62.

**[2003CHE/SUL]**

This study reports the enthalpies of formation of synthetic $M^{II}[(UO_2)(PO_4)]_2{\cdot}nH_2O$(cr) ($M^{II}$ = Mn, Fe, Co, Ni, Cu, Zn, Cd). The purity of the studied phases was confirmed with X-ray diffractometry, the elemental composition was determined with an electron microscope equipped with an EDAX energy-dispersive analyser. However, the exact stoichiometry of the investigated samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($UO_3$(cr), $KH_2PO_4$(cr), $K_2SO_4$(cr), $H_2O$(l), $M^{II}SO_4{\cdot}kH_2O$(cr), $M^{II}[(UO_2)(PO_4)]_2{\cdot}nH_2O$(cr)) in 4 M (~ 4.36 m) aqueous HCl solution. The thermochemical cycle employed resulted in the following $\Delta_r H_m^o$ values (in kJ·mol$^{-1}$) for the reaction:

$$2UO_3(cr) + 2KH_2PO_4(cr) + M^{II}SO_4{\cdot}kH_2O(cr) + (n-k-2)H_2O(l) \rightleftharpoons M^{II}[(UO_2)(PO_4)]_2{\cdot}nH_2O(cr) + K_2SO_4(cr) \quad \text{(A.107)}$$

(see Table A-63).

Table A-63: Values of $\Delta_r H_m$ for Reaction (A.107) for uranyl phosphates of some transition metals at 298.15 K measured in [2003CHE/SUL].

| Compound | $\Delta_r H_m$ /kJ·mol$^{-1}$ | Compound | $\Delta_r H_m$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mn[(UO_2)(PO_4)]_2{\cdot}7H_2O$(cr) | – (160.1 ± 5.8) | $Mn[(UO_2)(PO_4)]_2$(cr) | – (31.1 ± 5.9) |
| $Fe[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | – (138.1 ± 5.6) | $Fe[(UO_2)(PO_4)]_2$(cr) | (27.8 ± 5.6) |
| $Co[(UO_2)(PO_4)]_2{\cdot}7H_2O$(cr) | – (116.5 ± 5.6) | $Co[(UO_2)(PO_4)]_2$(cr) | (36.4 ± 5.7) |
| $Ni[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | – (134.5 ± 5.6) | $Ni[(UO_2)(PO_4)]_2$(cr) | (59.1 ± 5.6) |
| $Cu[(UO_2)(PO_4)]_2{\cdot}8H_2O$(cr) | – (175.2 ± 5.7) | $Cu[(UO_2)(PO_4)]_2$(cr) | (24.8 ± 7.2) |
| $Zn[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | – (152.4 ± 6.3) | $Zn[(UO_2)(PO_4)]_2$(cr) | (19.6 ± 6.5) |
| $Cd[(UO_2)(PO_4)]_2{\cdot}8H_2O$(cr) | – (146.1 ± 6.1) | $Cd[(UO_2)(PO_4)]_2$(cr) | – (66.0 ± 5.8) |

This review used the following auxiliary data (in kJ·mol$^{-1}$): – (1223.8 ± 1.2) for $UO_3$(cr) [2003GUI/FAN], – (2683.817 ± 1.014) for α-$NiSO_4{\cdot}6H_2O$(cr) [2005GAM/BUG]; – (3012.512 ± 0.602) for $FeSO_4{\cdot}7H_2O$(cr) [2013LEM/BER]; – (1729.30 ± 0.80) for $CdSO_4{\cdot}8/3H_2O$(cr), as accepted in NEA TDB; – (1437.7 ± 0.5) for $K_2SO_4$(cr) [1982GLU/GUR]; – (2685.2 ± 2.1) for $CoSO_4{\cdot}6H_2O$(cr) [1972GLU/MED], – (2280.38 ± 1.29) for $CuSO_4{\cdot}5H_2O$(cr)—see review of [2003KAR/CHE3]); – (3076.85 ± 0.67) for $ZnSO_4{\cdot}7H_2O$(cr)—see the comment at the end of this review; – (1574.5 ± 2.0) for $KH_2PO_4$(cr)—see the review of [1993KAR/CHE]. Calculations have not been performed for the Mn phases as no satisfactory value of $\Delta_f H_m^o$ have been found for for $MnSO_4{\cdot}H_2O$(cr). Calculation of $\Delta_f H_m^o$ for uranyl phosphates was done as described in review of [1994KAR/CHE], [1996KAR/CHE], with $\overline{L}_1$ = – 0.34 kJ·mol$^{-1}$ in 4.36 m HCl solutions. Results are shown in Table A-64.

Table A-64: Values of $\Delta_f H_m^o$ for various uranyl phosphates of some transition metals at 298.15 K, recalculated in this review.

| Compound | $-\Delta_f H_m^o$ /kJ·mol$^{-1}$ | Compound | $-\Delta_f H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Fe[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | (7595.7 ± 7.3) | $Fe[(UO_2)(PO_4)]_2$(cr) | (4568.1 ± 7.4) |
| $Co[(UO_2)(PO_4)]_2{\cdot}7H_2O$(cr) | (6674.4 ± 7.6) | $Co[(UO_2)(PO_4)]_2$(cr) | (4518.3 ± 7.6) |
| $Ni[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | (7549.6 ± 7.4) | $Ni[(UO_2)(PO_4)]_2$(cr) | (4494.3 ± 7.4) |
| $Cu[(UO_2)(PO_4)]_2{\cdot}8H_2O$(cr) | (6900.7 ± 7.5) | $Cu[(UO_2)(PO_4)]_2$(cr) | (4411.3 ± 8.7) |
| $Zn[(UO_2)(PO_4)]_2{\cdot}10H_2O$(cr) | (7674.3 ± 8.0) | $Zn[(UO_2)(PO_4)]_2$(cr) | (4640.6 ± 8.1) |
| $Cd[(UO_2)(PO_4)]_2{\cdot}8H_2O$(cr) | (6988.2 ± 7.7) | $Cd[(UO_2)(PO_4)]_2$(cr) | (4618.7 ± 7.5) |

The uncertainties are calculated using rules of propagation of errors, see Appendix C. Note that the authors reported larger uncertainties, from 11 to 14 kJ·mol$^{-1}$.

The value of the enthalpy of formation of $ZnSO_4{\cdot}7H_2O$(cr) used in recalculation was evaluated in this review as follows: the handbook [1971NAU/RYZ] based on available data recommends for reaction $ZnSO_4{\cdot}7H_2O(cr) \rightleftharpoons Zn^{2+} + SO_4^{2-} + 7H_2O(l)$ the value $\Delta_r H_m^o$ (298.15 K) = (13.31 ± 0.42) kJ·mol$^{-1}$. Combining this value with the CODATA-based [1989COX/WAG] enthalpies of formation of $Zn^{2+}$ – (153.39 ± 0.20), $SO_4^{2-}$ – (909.34 ± 0.40) and $H_2O$(l) – (285.83 ± 0.04), this review calculates for $ZnSO_4{\cdot}7H_2O$(cr) $\Delta_f H_m^o$ (298.15 K) = – (3076.85 ± 0.67) kJ·mol$^{-1}$.

Some auxiliary data used in calculations were not scrutinised by the NEA team, and the $\Delta_f H_m^o$ values for uranyl phosphates of Fe, Co, Ni, Cu, Zn, and Cd are given for information only.

**[2003CHE/SUL2]**

Chernorukov *et al.* have measured the solubility at (25 ± 2) °C of the compounds $M[(UO_2)(XO_4)]_2{\cdot}nH_2O$(cr); M = $Mn^{2+}$, $Fe^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and X = P, As. The solid phases were characterised by X-ray diffraction and elemental analyses by X-ray fluorescence; the analyses of the test solutions in equilibrium with the solid phases were made using standard methods. A crucial point in experiments of this type is to ascertain that the dissolution is congruent and this can be judged by the mole ratio M : U : P/As. These data are reported by Chernorukov *et al.* in their Tables 1 and 2, which clearly show that the dissolution is *not* congruent and that the dissolution reaction is not defined. For this reason the solubility products, Gibbs energies of reaction and the Gibbs energy of formation are not accepted by the present review.

**[2003CHE/SUL3]**

This is the study of solubility of synthetic compounds $A^I[(UO_2)(PO_4)]{\cdot}nH_2O$(cr), where $A^I$ = H, Li, Na, K, Rb, Cs, in water and dilute aqueous sulfuric acid (0.05-5 × 10$^{-5}$ M) in

polyethylene vessels at 25 °C with stirring for 7-10 days (a sufficient time to attain the steady-state). The concentrations of U and P were determined photometrically: for P(V) with molybdophosphoric heteropoly acid; for U(VI)-with arsenazo III. Concentrations of alkali metals were not measured. It was found that the concentrations of U and P coincide within experimental error, *i.e.* the solubility was congruent. The measured solubility was used to calculate the solubility products according to the Reaction (A.108):

$$A^{I}[(UO_2)(PO_4)]\cdot nH_2O(cr) \rightleftharpoons A^{+}(aq) + UO_2^{2+}(aq) + PO_4^{3-}(aq) + nH_2O(l) \qquad (A.108)$$

When calculating solubility products, the measured concentrations of U and P were corrected for the hydrolysis and formation of sulfate and phosphor-containing complexes of U(VI) using the corresponding stability constants from the Russian handbook Thermal Constants of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981. The activity coefficients of ions were calculated with the Debye-Hückel equations (in all cases $I < 0.10$ M). The activity of water was also calculated (it is very close to unity in the studied solutions). Results are presented in Table A-65.

Table A-65: Values of solubility products at $I = 0$ of uranyl phosphates of alkali metals and of chernikovite, calculated in [2003CHE/SUL3].

| Compound | $\log_{10} K^{o}$ | Compound | $\log_{10} K^{o}$ |
|---|---|---|---|
| $H[(UO_2)(PO_4)]\cdot 4H_2O$(cr) | (25.9 ± 1.0) | $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | (26.2 ± 0.5) |
| $Li[(UO_2)(PO_4)]\cdot 4H_2O$(cr) | (25.4 ± 0.1) | $Rb[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | (26.2 ± 0.5) |
| $Na[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | (25.8 ± 0.3) | $Cs[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | (26.4 ± 0.7) |

These results are in a reasonable agreement (within one $\log_{10}$ unit) with other published values ([1965VES/PEK], [1985MAG/JES], [1996HAV/VOC], [2005FEL/XIA], [2011CHE/NIP]) and were considered for the selection of thermodynamic data by the current review.

**[2003SUL/KAR]**

This study reports the low-temperature heat capacity of synthetic samples of $Sr[(UO_2)(PO_4)]_2\cdot 8H_2O$(cr) and $Sr[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr). The phase's compositions were confirmed with X-ray diffractometry. The elemental composition was determined with an EDAX 9900 energy dispersive analyser (the accuracy was 2-5 at %). However, the exact compositions of studied samples were not given.

The heat capacity is measured at 6-300 K for $Sr[(UO_2)(PO_4)]_2\cdot 8H_2O$(cr) and at 80-300 K for $Sr[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr) with an adiabatic vacuum calorimeter. Data are extrapolated to 0 K and numerically integrated to evaluate the entropy (in $J\cdot K^{-1}\cdot mol^{-1}$): at 298.15 K for $Sr[(UO_2)(PO_4)]_2\cdot 8H_2O$(cr) $S^{o}_{m} = (717.4 \pm 20)$ and $C^{o}_{p,m} = 707.8$; for $Sr[(UO_2)(AsO_4)]_2\cdot 8H_2O$(cr) $S^{o}_{m} = (758.4 \pm 20)$ and $C^{o}_{p,m} = 720.9$. The

uncertainties are estimated in this review considering the $S_m^o$ results of [2003SUL/KAR] semi-quantitative due to lack of data on the exact composition of phases and information on the water content. The estimates of $S_m^o$ by the Latimer method [1951LAT], as outlined in Appendix D, are equal to (723 ± 52) and (756 ± 52) $J \cdot K^{-1} \cdot mol^{-1}$, respectively.

Using the auxiliary $S_m^o$ data for elements from the NEA database (U(cr) (50.20 ± 0.20); $H_2$(g) (130.680 ± 0.003); $O_2$(g) (205.152 ± 0.005); P(white) (41.09 ± 0.25); As(cr) (35.10 ± 0.60); Sr(cr) (55.70 ± 0.21)), this review calculated: for $Sr[(UO_2)(PO_4)]_2 \cdot 8H_2O$(cr) $\Delta_f S_m^o = -(2617.8 \pm 20)$ in $J \cdot K^{-1} \cdot mol^{-1}$ and for $Sr[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) $\Delta_f S_m^o = -(2564.9 \pm 20)$ in $J \cdot K^{-1} \cdot mol^{-1}$.

**[2004MAJ/BAL]**

Majdumar and Balasubramanian have studied the structure and vibration spectra of $UO_2(H_2SiO_4) \cdot 3H_2O$(cr), $UO_2(HPO_4) \cdot 3H_2O$(cr) and $UO_2(HAsO_4) \cdot 3H_2O$(cr), by using quantum chemistry calculations at the DFT/B3LYP and MP2 levels. The structure models are based on those found in the solid state. The bond distances between the two quantum chemistry methods differ somewhat, but both are in good agreement with experimental information from EXAFS spectra. There are some differences in the vibration spectra related to modes in the different anions; the frequency shifts in the uranyl stretch vibrations are small and hardly useful for comparison with experimental data. The chemical bonding is discussed and the authors note that these effects are small. There are no thermodynamic data of use for the present review.

**[2005FEL/XIA]**

The solubility product of $Na[UO_2(PO_4)] \cdot nH_2O$(cr) was discussed in [1992GRE/FUG] but no value was selected. Felmy *et al.* have returned to this problem using solubility measurements over a wide pH range using three sets of test solutions, 0.50 M $NaNO_3$ + 0.010 M phosphate, 3.00 M $NaNO_3$ + 0.010 M phosphate and 0.50 M $NaNO_3$ + 0.010 M phosphate + 0.010 M carbonate. They have in all cases made a careful structure characterisation of the solid phase both before and after equilibrium. Time Resolved Laser Fluorescence Spectroscopy (TRLFS) analysis of non-carbonate solutions outside of the acidic region (at $p[H^+] < 4$) revealed the presence of uranium phosphate nanoparticles that apparently passed through the filters. The addition of carbonate ion removes some of the experimental problems. Felmy *et al.* have used the Pitzer ion-interaction approach to calculate the equilibrium constant at zero ionic strength. As most extrapolations of this type are made using the SIT in the present reviews, we have recalculated the experimental data as follows:

- All experimental $\log_{10} K_s$-values in 0.5 M $NaNO_3$ were recalculated to zero ionic strength using the SIT model.

- The mass balance equations for U and P were solved (for runs with the added $CO_2$(g), the $P_{CO2}$ was varied to achieve an agreement with the measured analytical total carbon concentrations).

The equilibrium concentration quotient for the Reaction (A.109) in 0.5 M $NaNO_3$ medium

$$Na[UO_2PO_4]\cdot 4H_2O(cr) + 2H^+ \rightleftharpoons Na^+ + UO_2^{2+} + H_2PO_4^- + 4H_2O(l) \qquad (A.109)$$

was extrapolated to $I = 0$ using $\Delta Z^2 = 4$ and $\Delta\varepsilon = -0.02$ (from the NEA selected SIT interaction coefficients), and the water activity in 0.5 M $NaNO_3$ equal to 0.984. Using the selected protonation constants of $PO_4^{3-}$ from the NEA database, $\log_{10}{}^*K^o$ values of the Reaction (A.109) were recalculated to $\log_{10} K^o$ for the Reaction (A.110)

$$Na[UO_2PO_4]\cdot 4H_2O(cr) \rightleftharpoons Na^+ + UO_2^{2+} + PO_4^{3-} + 4H_2O(l) \qquad (A.110)$$

see Table A-66.

Table A-66: Recalculated solubility product for $Na[UO_2PO_4]\cdot 4H_2O$(cr), $\log_{10}{}^*K^o$ (A.110).

| Table in [2005FEL/XIA] | $pC_{H+}$ | $-\log_{10}{}^*K^o$ (A.110) |
|---|---|---|
| A1 | 3.470 | 23.26 |
| A1 | 3.850 | 23.04 |
| A3 | 3.826 | 23.08 |
| A3 | 6.536 | 20.12 |
| A3 | 8.361 | 23.32 |
| A3 | 8.662 | 23.53 |
| A3 | 8.712 | 23.42 |
| A3 | 8.731 | 23.56 |
| A3 | 8.827 | 23.41 |

Excluding a strongly deviating point at $pC_{H+}$=6.536, the unweighted average results in $\log_{10}{}^*K_{so} = -(23.33 \pm 0.38)$, where the uncertainty is given as $1.96\sigma_X$, and $\sigma_X$ is the standard deviation associated with $\log_{10} K^o$ (see Appendix C). This value is in excellent agreement with the one obtained by Felmy *et al.*, $\log_{10}{}^*K_s^o = -23.6$, using the Pitzer ion-interaction approach, but this review prefers value obtained using the SIT because it also provides an estimate of the uncertainty.

Felmy *et al.* have also determined the equilibrium constant for the solubility reaction

$$Na_4[UO_2(CO_3)_3](cr) \rightleftharpoons 4Na^+ + UO_2(CO_3)_3^{4-} \qquad (A.111)$$

The analysis of these solubility data is based both on accurate information of the equilibrium constant for the uranyl(VI) carbonate complexes (the values selected in

previous reviews were used for this purpose) and on proper activity coefficient data. The latter were obtained by using the Pitzer approach, which required a determination of Pitzer parameters for $UO_2(CO_3)_3^{4-}$ and $(UO_2)_3(CO_3)_6^{6-}$ using the solubility data of Blake *et al.* [1956BLA/COL]. Using these data, Felmy *et al.* were able to describe the experimental solubility of $Na[UO_2(PO_4)]\cdot nH_2O$(cr) in five different media: $NaClO_4$; $Na_2CO_3$; NaCl; $Na_2SO_4$ and mixed $Na_2CO_3$ + NaCl solutions using the following equilibrium constant (no uncertainty estimate was made):

$\log_{10} K^o$(A.111) = – 4.08.

The value of $\log_{10}K^o$(A.111) differs significantly from the one selected in previous reviews, $\log_{10}K^o$(A.111) = – (5.34 ± 0.16) ([1992GRE/FUG], [2003GUI/FAN]).

**[2005RAI/XIA]**

Rai *et al.* studied the solubility of $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) in the $H^+$-$Na^+$-$OH^-$-phosphate system in test solutions where the phosphate concentration varied between 0.001 and 0.010 M over a wide range of pH (2.5-10.5) in long-running experiments (up to 870 days); the use of test solutions with different concentrations of phosphate is important in order to determine the speciation.

In a similar study by Sandino [1991SAN] only one phosphate concentration was used. The experimental methods and data analysis follow the same pattern as in [2005FEL/XIA]. The system has previously been discussed in [1992GRE/FUG] where some shortcomings in the published data were pointed out, in [1965VES/PEK] a solubility product of – (49.36 ± 0.30) was obtained—the present study makes it possible to obtain a better understanding of the chemistry and more accurate equilibrium data, in particular the identification of the stoichiometry of the complex responsible for the increase in solubility at higher total concentration of phosphate. Rai *et al.* use the Pitzer model for estimates of activity coefficients, and report the solubility product $\log_{10}K_s^o$(A.112) = – (49.08 ± 0.48), which is close to one selected in [1992GRE/FUG], $\log_{10}K_s^o$ = – (49.36 ± 0.30). The modelling of the solubility data was performed considering the equilibrium constants for U(VI) hydrolysis and phosphate complexation as selected in [2003GUI/FAN], except for the complex $UO_2PO_4^-$ predominating in alkaline conditions (see text below).

$$(UO_2)_3(PO_4)_2\cdot 4H_2O(cr) \rightleftharpoons 3UO_2^{2+} + 2PO_4^{3-} + 4H_2O(l) \qquad \text{(A.112)}$$

Rai *et al.* reported that only three phosphate complexes become relevant in the conditions of their experiments, namely $UO_2H_2PO_4^+$, $UO_2HPO_4$(aq) and $UO_2PO_4^-$, where the equilibrium constants for the first two complexes were those selected in [2003GUI/FAN], while the one for the formation of the third, according to the Reaction (A.113):

$$UO_2^{2+} + PO_4^{3-} \rightleftharpoons UO_2PO_4^- \quad \text{(A.113)}$$

was found to be $\log_{10}\beta^o = (11.01 \pm 0.48)$. This value is significantly different from the one in [1992GRE/FUG] and [2003GUI/FAN], $\log_{10}\beta^o = (13.23 \pm 0.15)$, but the present review considers it more reliable as the solubility curves in Figure 6 of [2005RAI/XIA] cannot be described using the selected value in [2003GUI/FAN]. The Gibbs energy of formation calculated from the solubility product in [2005RAI/XIA] is $\Delta_f G^o((UO_2)_3(PO_4)_2{\cdot}4H_2O, cr, 298.15\ K) = -(6137.40 \pm 2.73)\ kJ{\cdot}mol^{-1}$; this value is close to the one selected in [1992GRE/FUG] and [2003GUI/FAN], $\Delta_f G^o((UO_2)_3(PO_4)_2{\cdot}4H_2O, cr, 298.15\ K) = -(6138.97 \pm 6.35)\ kJ{\cdot}mol^{-1}$. The selected value for the Reaction (A.113) is $\log_{10}\beta^o = (11.01 \pm 0.48)$, and the corresponding Gibbs energy of reaction, $\Delta_r G^o(A.113) = -(62.845 \pm 2.740)\ kJ{\cdot}mol^{-1}$, and $\Delta_f G^o(UO_2PO_4^-, 298.15\ K) = -(2040.887 \pm 3.611)\ kJ{\cdot}mol^{-1}$.

**[2006CHE/NIP]**

In this study, Chernorukov and Nipruk have made a summary of three of their previous studies on the solubility of uranyl(VI) phases, with the general composition $M^{n+}[UO_2X]_n{\cdot}nH_2O(cr)$, where X = $VO_4^{3-}$, $PO_4^{3-}$, $AsO_4^{3-}$, $HSiO_3^{3-}$, $BO_3^{3-}$ and M is an alkali, alkaline-earth or 3*d* transition element. The phases were characterised by X-ray diffraction before and after equilibration with an aqueous phase within a pH range of 2-10 and containing different concentrations of complexing agents like sulfate and carbonate. There was evidence of phase decomposition when the pH increased. The following general observations were made: the solubility increased with increasing concentration of sulfate, with increasing ionic strength, but decreased somewhat with increasing temperature. Solubility products were obtained from the measured equilibrium concentration of the components and the pH, taking the speciation and activity factors into account, the former by using published equilibrium constants and the latter using the Debye-Hückel equation. The solubility products reported are given in Table A-67.

Table A-67: Solubility products of some uranyl borates, phosphates, arsenates and silicates of alkali metals given in the review paper [2006CHE/NIP]. Chemical formulae as reported in the original publication.

| Substance | $pSP = -\log_{10} SP$ | Substance | $pSP = -\log_{10} SP$ |
|---|---|---|---|
| $KBUO_5 \cdot H_2O$ (cr) | (28.7 ± 0.5) | $LiHSiUO_6 \cdot 1.5H_2O$ (cr) | (28.4 ± 0.6) |
| $KHSiUO_6 \cdot H_2O$ (cr) | (31.7 ± 0.5) | $NaHSiUO_6 \cdot H_2O$ (cr) | (29.5 ± 0.5) |
| $KAsUO_6 \cdot 3H_2O$ (cr) | (23.4 ± 0.2) | $RbHSiUO_6 \cdot H_2O$ (cr) | (30.6 ± 0.6) |
| $KPUO_6 \cdot 3H_2O$ (cr) | (26.2 ± 0.5) | $CsHSiUO_6 \cdot H_2O$ (cr) | (29.2 ± 0.5) |
| $KPUO_6$ (cr) | (31.8 ± 0.1) | $NH_4HSiUO_6 \cdot H_2O$ (cr) | (28.7 ± 0.7) |

There is no detailed information on the source of the equilibrium constants.

**[2006SAV]**

Savenko has determined the solubility of $UO_2HPO_4$(cr) (in a personal communication, Savenko reported this phase to be $UO_2HPO_4 \cdot 4H_2O$(cr)) in normal seawater with a salinity of 3.5 % as a function of pH and the added amount of phosphate. Two series of measurements were made, the first without the added phosphate and the second where phosphate was added. Analysis of uranium and phosphate in the equilibrium solutions indicated that the dissolution was congruent at pH > 7.2 and that a phase-transformation to $UO_2(H_2PO_4)_2$(cr) took place at lower pH. Savenko has calculated the product $[UO_{2,total}][PO_{4total}]$ that varies between $(0.12\text{-}54.6) \times 10^{-10}$ under the conditions used—she points out that this variation is a result of a neglect of soluble uranyl complexes; accordingly the reported product of the total concentrations of U(VI) and phosphate cannot be used to obtain the solubility product.

**[2006SUL/CHE]**

This study reports the low-temperature heat capacity of the synthetic samples of $A^{II}[(UO_2)(B^{V}O_4)]_2 \cdot nH_2O$(cr) ($A^{II}$ = Mg, Ca); $B^{V}$ – P, As) at 80-300 K measured with an adiabatic vacuum calorimeter. Phases were confirmed with X-ray diffractometry. The elemental composition was determined with an energy dispersive analyser (the accuracy was 2-5 at %). However, the exact compositions of studied samples were not given. Measured heat capacities data are extrapolated to 0 K and numerically integrated to evaluate the entropy at 298.15 K (in $J \cdot K^{-1} \cdot mol^{-1}$), see Table A-68.

Table A-68: Thermodynamic properties of uranyl phosphates and arsenates of Mg and Ca based on data of [2006SUL/CHE].

| Compound | $C^{o}_{p,m}$ (298.15 K)[(a)] /J·K$^{-1}$·mol$^{-1}$ | $S^{o}_{m}$ (298.15 K)[(a)] /J·K$^{-1}$·mol$^{-1}$ | $S^{o}_{m}$ (298.15 K)[(b)] /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|
| $Mg[(UO_2)(PO_4)]_2 \cdot 10H_2O$(cr) | 802.1 | (756 ± 30)[(c)] | (794 ± 63) |
| $Ca[(UO_2)(PO_4)]_2 \cdot 6H_2O$(cr) | 620.2 | (667 ± 30)[(c)] | (622 ± 41) |
| $Mg[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | 765.4 | (766 ± 40)[(c)] | (827 ± 63) |
| $Ca[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) | 939.7 | (874 ± 40)[(c)] | (834 ± 63) |

(a) Experimental value;
(b) Estimated with the Latimer method [1951LAT] as outlined in Appendix D;
(c) The uncertainties are estimated in this review, the authors' value of ± 5 J·K$^{-1}$·mol$^{-1}$ is considered unrealistic due to lack of exact stoichiometries of the studied samples.

The difference in entropies of $Mg[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) and $Ca[(UO_2)(AsO_4)]_2 \cdot 10H_2O$(cr) exceeds 100 in $J \cdot K^{-1} \cdot mol^{-1}$, which appears unrealistic: according to the Glushko's handbook [1981GLU/GUR], for most solid compounds of Mg and Ca this difference is about 15 $J \cdot K^{-1} \cdot mol^{-1}$. The fourth column of Table gives $S^{o}_{m}$ (298.15 K) estimated by the Latimer [1951LAT] method as outlined in Appendix D. Based on these observations and the fact that there is no exact information on the

stoichiometry of the samples, this review increases uncertainties of $S_m^o$ (298.15 K) values to ± 30-40 $J \cdot K^{-1} \cdot mol^{-1}$. These values are given for information only.

**[2006SUL/CHE2]**

This study reports the low-temperature heat capacity of synthetic samples of $Ba[(UO_2)(PO_4)]_2 \cdot 6H_2O$(cr) and $Ba[(UO_2)(AsO_4)]_2 \cdot 7H_2O$(cr) at 80-300 K measured with a TAU-1 adiabatic vacuum calorimeter. The purity of the solid phases was checked by X-ray diffraction, the composition was determined with an electron microscope equipped with an EDAX energy-dispersive analyser (accuracy 2-5 at %). No exact chemical compositions of the studied samples are presented. Measured heat capacities data are extrapolated to 0 K and numerically integrated to evaluate the entropy at 298.15 K (in $J \cdot K^{-1} \cdot mol^{-1}$), see Table A-69.

Table A-69: Thermodynamic properties of uranyl phosphate and arsenate of Ba based on data of [2006SUL/CHE2].

| Compound | $C_{p,m}^o$ (298.15 K)[(a)] /$J \cdot K^{-1} \cdot mol^{-1}$ | $S_m^o$ (298.15 K)[(a)] /$J \cdot K^{-1} \cdot mol^{-1}$ | $S_m^o$ (298.15 K)[(b)] /$J \cdot K^{-1} \cdot mol^{-1}$ |
|---|---|---|---|
| $Ba[(UO_2)(PO_4)]_2 \cdot 6H_2O$(cr) | 655.3 | (686.4 ± 30)[(c)] | (641 ± 41) |
| $Ba[(UO_2)(AsO_4)]_2 \cdot 7H_2O$(cr) | 700.8 | (738.3 ± 30)[(c)] | (718 ± 47) |

(a) Experimental value;
(b) Estimated with the Latimer method [1951LAT] as outlined in Appendix D;
(c) The uncertainties are estimated in this review, the authors' value of ± 9 $J \cdot K^{-1} \cdot mol^{-1}$ is considered unrealistic due to lack of exact stoichiometries of studied samples.

The fourth column of Table A-69 gives $S_m^o$ (298.15 K) estimated by the Latimer [1951LAT] method as outlined in Appendix D. Based on the fact that there is no exact information on the stoichiometry of the samples, this review increases uncertainties of $S_m^o$ (298.15 K) values to ± 30 $J \cdot K^{-1} \cdot mol^{-1}$. These values are given for information only.

**[2007DAC/CLA]**

Dacheux *et al.* report X-ray structures of $Th(OH)PO_4$(cr), $U(OH)PO_4$(cr) and $Th_2(O)(PO_4)_2$(cr) and suggest a mechanism for formation of the latter. The paper contains Raman data for the solids but no thermodynamic information.

**[2007DUF/CLA]**

Dufou de Kernel *et al.* have identified the solubility controlling phases during dissolution of phosphate ceramics; no thermodynamic information is reported.

**[2007VAZ/DOD]**

Vazquez *et al.* have investigated the interactions between $UO_2^{2+}$ and linear polyphosphate with a chain length of 10-13 phosphate units. They report potentiometric titrations and EXAFS analyses of precipitates formed. The solution chemical information is qualitative and difficult to analyse—one solid piece of information is that the equilibrium solubility in the pH range 3-8 is approximately constant at 0.3 mM. This review cannot extract more useful information.

**[2007WEL/GUN]**

Wellman *et al.* studied the dissolution kinetics of the mineral $Ca[(UO_2)(PO_4)]_2{\cdot}H_2O$(cr) and synthetic $Na_2[(UO_2)(PO_4)]_2{\cdot}H_2O$(cr) between pH 2 and 4 and analysed the steady-state concentrations of uranium and phosphorus. The dissolution is non-congruent and the authors suggest that this is due to the formation of $[(UO_2)_3(PO_4)_2]{\cdot}nH_2O$(cr) that was also identified by SEM-EDS. There is no thermodynamic information in this communication. There are graphs of the predicted solubility of $[(UO_2)_3(PO_4)_2]{\cdot}nH_2O$(cr) that could be tested using the equilibrium constants from the NEA reviews.

**[2008MAT/WEL]**

Mattigod *et al.* have identified secondary minerals, like meta-autunite that might be formed in Portland cement used to immobilise nuclear waste. They have measured the solubility of meta-autunite in the pH range 8-13 at concentrations of phosphate that vary from 0.001 to 0.1 M, but these data cannot be used to extract thermodynamic information.

**[2008REY/GIM]**

Rey *et al.* determined the rate of dissolution of $UO_2$(cr) and formation of secondary phases on its surface in phosphate media with concentrations ranging from $10^{-6}$ to $10^{-4}$ M and a pH between 7.3-7.5, under an atmosphere of "synthetic air". They observed the formation of chernikovite $[(UO_2)_2(HPO_4)_2]{\cdot}8H_2O$(cr) in a solution, containing $10^{-4}$ M of total phosphate at pH = 7.2 (but not at concentrations of $10^{-5}$, and $10^{-6}$ M of U). In solutions that contained 0.92 mM $HCO_3^-$ no secondary phase formation took place, which the authors suggest is due to the formation of the uranyl tris-carbonato complex. There is no thermodynamic information but the conclusions on phase stability should be checked using the selected thermodynamic data in this review.

**[2009ARM], [2010ARM/FEL]**

Armstrong's Ph. D. thesis comprises a discussion of synthesis, spectroscopic and thermodynamic studies of uranyl and neodymium phases, where only the former are of interest for this review. The following items have been discussed:

- Transformation of chernikovite $(H_3O)[UO_2(PO_4)]\cdot 3H_2O$(cr) to $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr).

- Solubility of $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) at 25 and 50 °C with determination of the solubility product of the phase.

- Studies of the state of hydration of the mineral meta-autunite $Ca[UO_2PO_4]_2\cdot 6.5H_2O$(cr) and synthetic $Na[UO_2PO_4]\cdot nH_2O$(cr) and meta-autunite $Ca[UO_2PO_4]_2\cdot nH_2O$(cr) have been made using DTA and DSC (digital scanning calorimetry).

The phase characterisation has been performed using powder X-ray data, IR spectroscopy and thermal analyses, important for the solubility studies which are of main interest for this review.

The solubility experiments were made at a hydrogen ion concentration of 10 mM in solutions of $HClO_4/NaClO_4$ with ionic strength 0.1, 1, 2 and 5 m, using equilibration time up to 82 days. The solubility was measured by using both the total concentration of uranium and phosphorous. The solid phase after equilibration was characterised by powder X-ray and IR spectra. The number of data points is too small to allow an independent analysis of the speciation and the composition of the solution phase has therefore been described using the equilibrium constants selected in [1992GRE/FUG] and [2003GUI/FAN]; extrapolation of the solubility data to zero ionic strength was made using the Pitzer model. Armstrong noted that $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) was transformed to $Na[UO_2PO_4]\cdot 3H_2O$(cr) at $Na^+$-concentrations larger than 0.1 M and that only data at $I = 0.10$ m could be used to estimate the solubility product for $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr). There is, however, only a single solubility measurement on which to base the solubility product. The measured concentrations of U and P are consistent with a congruent dissolution and the estimated solubility product $\log_{10} K_s^o$ (23 °C) = – 49.7 and at 50 °C – 51.3. The value at 23 °C is consistent with the one selected in [1992GRE/FUG], $\log_{10} K_s^o = -(49.4 \pm 0.3)$ and the one reported by Rai *et al.* [2005RAI/XIA], $\log_{10} K_s^o = -(49.08 \pm 0.48)$. The fact that the solubility product increases with increasing temperature suggests that the dissolution is endothermic, but as the uncertainty in the solubility products is unknown it is not meaningful to estimate an enthalpy of reaction.

This review considers that the uncertainty in the measured solubility in the test solutions at $I$ = 1, 2 and 5 m is too large to make it meaningful to estimate a solubility product for $Na[UO_2PO_4]\cdot 3H_2O$(cr). Armstrong reports $\log_{10} K_s^o$ (23 °C) = – 24.4, for

Reaction (A.114) which is in good agreement with the value reported in [2005FEL/XIA], but this review considers the latter better supported.

$$Na[(UO_2)(PO_4)]\cdot nH_2O(cr) \rightleftharpoons Na^+ + UO_2^{2+} + PO_4^{3-} + nH_2O(l) \quad (A.114)$$

**[2009GOR/SHV]**

Gorman-Lewis *et al.* have made an extensive study of the thermodynamics of synthetic samples of $UO_2HPO_4\cdot 3H_2O$(cr), $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) and of a natural sample of $Ca[UO_2(PO_4)]_2\cdot 3H_2O$(cr) using the oxide-melt solution calorimetry to determine the enthalpies of formation of the different phases and solubility measurements to determine the Gibbs energies of dissolution; a combination of these data allows calculation of the Gibbs energy of formation and the entropies of the phases. Note that the XRD data of $UO_2HPO_4\cdot 3H_2O$(cr) is identical to mineral chernikovite $UO_2HPO_4\cdot 4H_2O$(cr), according to the reference file card 75-1106 from the Joint committee on Powder Diffraction Standards-International Centre for Diffraction Data (provided in Supporting materials to the paper).

Calorimetric measurements of enthalpies of addition of $UO_2HPO_4\cdot 3H_2O$(cr) and $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) to a sodium molybdate melt at 702 °C gave the enthalpy changes for the following reactions:

$$UO_2HPO_4\cdot 3H_2O(cr) \rightleftharpoons UO_3(cr) + 1/2P_2O_5(cr) + 3.5H_2O(l) \quad (A.115)$$

$\Delta_r H_m^o$ (298.15 K) = (240.95 ± 3.89) kJ·mol$^{-1}$;

$$(UO_2)_3(PO_4)_2\cdot 4H_2O(cr) \rightleftharpoons 3UO_3(cr) + P_2O_5(cr) + 4H_2O(l) \quad (A.116)$$

$\Delta_r H_m^o$ (298.15 K) = (681.51 ± 13.82) kJ·mol$^{-1}$. The authors calculated from these results the following values of $\Delta_f H_m^o$, in kJ·mol$^{-1}$: – (3223.22 ± 3.99) for $UO_2HPO_4\cdot 3H_2O$(cr), and – (7001.01 ± 13.90) for $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr), using the handbook [1995ROB/HEM] as source of the auxiliary data (however, this handbook does not report thermodynamic values of $UO_3$(cr)). This review recalculated enthalpies of formation of uranyl phosphates using the following auxiliary $\Delta_f H_m^o$ data, in kJ·mol$^{-1}$: – (1223.8 ± 1.2) for $UO_3$(cr), – (285.83 ± 0.04) for $H_2O$(l), from the NEA database; – (3010.1 ± 3.2) for $P_4O_{10}$(cr) from the handbook [1978GLU/GUR] and obtained $\Delta_f H_m^o$ ($UO_2HPO_4\cdot 3H_2O$, cr, 298.15 K) = – (3217.68 ± 4.15) kJ·mol$^{-1}$ and $\Delta_f H_m^o$ ($(UO_2)_3(PO_4)_2\cdot 4H_2O$, cr, 298.15 K) = – (7001.28 ± 14.37) kJ·mol$^{-1}$, see Table A-70.

The solubility experiments have been made in the pH range 3-3.8 for $Ca[UO_2(PO_4)]_2\cdot 3H_2O$(cr) and at 4.2-4.5 for the other two phases, all at 25 °C and without ionic medium (the ionic strength is very low, less than 0.01 M) for both under- and oversaturation. The concentrations at steady-state were measured for U, P and Ca and this showed clearly that the dissolution was incongruent, except for

$Ca[UO_2(PO_4)]_2{\cdot}3H_2O(cr)$ and $(UO_2)_3(PO_4)_2{\cdot}4H_2O(cr)$ in the undersaturation experiments. Experimental data were used to evaluate solubility products at infinite dilution, $\log_{10}K_s^o \pm 2\sigma$, for the following reactions (the concentrations of $UO_2^{2+}$ and $PO_4^{3-}$ have been calculated from the measured total concentrations using the known speciation based on equilibrium constants in [2003GUI/FAN]):

$$Ca[UO_2(PO_4)]_2{\cdot}3H_2O(cr) \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 2PO_4^{3-} + 3H_2O(l) \quad \text{(A.117)}$$
$$\log_{10}K_s^o\,(A.117) = -\,(48.36 \pm 0.03)$$

$$UO_2HPO_4{\cdot}3H_2O(cr) \rightleftharpoons UO_2^{2+} + HPO_4^{2-} + 3H_2O(l) \quad \text{(A.118)}$$
$$\log_{10}K_s^o\,(A.118) = -\,13.17(-\,0.11/+0.07)$$

$$(UO_2)_3(PO_4)_2{\cdot}4H_2O(cr) \rightleftharpoons 3UO_2^{2+} + 2PO_4^{3-} + 4H_2O(l) \quad \text{(A.119)}$$
$$\log_{10}K_s^o\,(A.119) = -\,49.36(-\,0.04/+0.02).$$

The authors emphasised that in all cases the $\log_{10}K_s^o$ values determined from either under- or oversaturated experiments, or conducted at different pH were within experimental uncertainty of each other for every mineral phase investigated. As an explanation, the authors suggested the steady state condition between an aqueous solution and an outer leached layer of a mineral and between the outer leached layer and the inner bulk material. Such a suggestion may explain the constancy of $\log_{10}K_s^o$ even at incongruent dissolution of a mineral. The reported solubility products were used to calculate the Gibbs energy of formation of these phases using the auxiliary values for ions and $H_2O(l)$ from the NEA sources, see Table A-70 below, which lists thermodynamic properties of compounds based on data of this work.

Table A-70: Thermodynamic data for solid phases studied in [2009GOR/SHV]. For reasons given in comments a and b these values have not been selected and are included for information only.

| Compound | $-\Delta_f G_m^o \pm 2\sigma$ /kJ·mol$^{-1}$ | $-\Delta_f H_m^o \pm 2\sigma$ /kJ·mol$^{-1}$ | $-\Delta_f S_m^o \pm 2\sigma$ /J·mol$^{-1}$·K$^{-1}$ | $S_m^o \pm 2\sigma$ /J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|
| $Ca[UO_2(PO_4)]_2{\cdot}3H_2O(cr)$ | (5496.35 ± 9.67)[(a)] | | | |
| $UO_2HPO_4{\cdot}3H_2O(cr)$ | (2835.14 ± 4.89)[(b)] | (3217.68 ± 4.15) | (1283.1 ± 21.2) | (188.8 ± 21.5) |
| $(UO_2)_3(PO_4)_2{\cdot}4H_2O(cr)$ | **(6138.968 ± 6.355)**[(c)] | (7001.28 ± 14.37) | (2892.3 ± 63.0) | – (290.4 ± 63.0) |
| | | **(6739.105 ± 9.136** )[(c)] | | |

(a) First, for the calcium uranyl phosphate hydrate the finally selected value of $\log_{10}K_s^o = -\,(50.000 \pm 1.000)$ (based on 5 studies), while the value of $\log_{10}K_s^o$ from this study is – 48.36;
(b) For $UO_2HPO_4{\cdot}3H_2O(cr)$ no $\Delta_f G$ value is selected in the current review. For the solubility constant of $UO_2HPO_4{\cdot}4H_2O(cr)$, the selected value (from [2003GUI/FAN] differs by more than 1 log unit from the value in this work;
(c) From [2003GUI/FAN].

Using the auxiliary $S_m^o$ data for elements from the NEA database (U(cr) (50.20 ± 0.20); $H_2$(g) (130.680 ± 0.003); $O_2$(g) (205.152 ± 0.005); P(cr, white) (41.09 ± 0.25), this review calculated $S_m^o$ values, given in the last column of Table. The negative value of $S_m^o$ for $(UO_2)_3(PO_4)_2{\cdot}4H_2O$(cr) is clearly unphysical, and it differs by more than 800 $J{\cdot}mol^{-1}{\cdot}K^{-1}$ from the value $S_m^o$ = (589 ± 22) $J{\cdot}mol^{-1}{\cdot}K^{-1}$ estimated in [1992GRE/FUG] using the Latimer [1951LAT] method. An estimate of $S_m^o$ for $UO_2HPO_4{\cdot}3H_2O$(cr) with the same method, see Appendix D, gives $S_m^o$ = (301 ± 25) $J{\cdot}mol^{-1}{\cdot}K^{-1}$, which is significantly larger than the value in Table. The values of $\Delta_f G_m^o$ (or $\log_{10} K_s^o$ for Reactions (A.117)-(A.119)) are close to results of other studies and they are considered in the thermodynamic evaluation by this review. However, this review considers $\Delta_f H_m^o$ results in error and does not select them.

**[2010ILT/ZAC]**

Ilton *et al.* have determined the solubility of natural meta-torbernite, $Cu[(UO_2)(PO_4)]_2{\cdot}8H_2O$(cr) under a $N_2$ atmosphere as a function of pH (pH 2.5 and 3) and the phosphate concentration; this was done by measuring the solubility by addition of $HNO_3$ or phosphoric acid. These data were used to determine the solubility product. Ilton *et al.* have ascertained that the dissolution is stoichiometric and approached equilibrium from both over- and under-saturation and in this way established that equilibrium has been attained. The experimental temperature was (22 ± 1) °C. Activity coefficients correction was made with the Pitzer model. This is a careful experimental study that results in the following solubility product based on equilibration times longer than seven days; the values are averages of data from over- and under-saturation. Values of $\log_{10}{}^{*}K_s^o$ refer to Reaction (A.120):

$$Cu[(UO_2)(PO_4)_2]{\cdot}8H_2O(cr) + 2H^+ \rightleftharpoons Cu^{2+} + 2UO_2^{2+} + 2HPO_4^{2-} + 8H_2O(l) \qquad (A.120)$$

Table A-71: Solubility constants for the dissolution of $Cu[(UO_2)(PO_4)_2]{\cdot}8H_2O$(cr) in $HNO_3$ and phosphoric acid.

| Sample | $\log_{10}{}^{*}K_s^o$ | |
|---|---|---|
| | pH = 2.5 | pH = 3.0 |
| Sample 1 /$HNO_3$ diss. | – (28.6 ± 0.4) | – (27.8 ± 0.3) |
| Sample 2 /$HNO_3$ diss. | – (28.4 ± 0.3) | – (27.6 ± 0.2) |
| Sample 1 /$H_3PO_4$ diss. | – (28.0 ± 0.2) | – (27.7 ± 0.4) |
| Sample 2 /$H_3PO_4$ diss. | – (28.0 ± 0.3) | – (27.8 ± 0.4) |

The solubility products seem to be slightly larger at higher pH; based on these data the present review calculates the solubility product $\log_{10} K_s^o$ = – (28.0 ± 0.3) where the estimated uncertainty is significantly larger than the one reported by Ilton *et al.* For the reaction $M[(UO_2)(PO_4)]_2{\cdot}xH_2O(cr) \rightleftharpoons 2UO_2^{2+} + M^{2+} + 2PO_4^{3-} + xH_2O(l)$, the value

of $\log_{10} K_s^o = -(52.7 \pm 0.3)$ is calculated by using $\log_{10}{}^* K_s^o = -12.35$ for the reaction $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ [2003GUI/FAN].

**[2010LEH/GEI]**

Lehman *et al.* used time-resolved laser fluorescent spectroscopy (TRLFS) to study the complex formation between U(IV) and phosphate. The study was made at different pH where those at the highest acidity are the most reliable as they minimise the effect of hydrolysis. The fluorescence decay was in all cases mono-exponential indicating a single emitting species. The ratio U(IV)/phosphate was equal to 1 within the experimental uncertainty; in a separate experiment the number of protons released in the Reaction (A.121)

$$U^{4+} + H_3PO_4(aq) \rightleftharpoons UH_nPO_4^{1+n} + (3-n)H^+ \qquad \text{(A.121)}$$

was used to establish a value of $n = 2$ (only the data at pH > 0 should be used). To conclude, Lehman *et al.* provide convincing evidence for the formation of a single complex $UH_2PO_4^{3+}$ with an equilibrium constant $\log_{10}K^o(\text{A.121}) = (4.7 \pm 0.7)$. By combining this value with the first dissociation constant of $H_3PO_4$, $\log_{10}K^o = -2.14$ this review obtains for Reaction (A.122), $\log_{10} K^o\,(\text{A.122}) = (6.8 \pm 0.7)$.

$$U^{4+} + H_2PO_4^- \rightleftharpoons UH_2PO_4^{3+} \qquad \text{(A.122)}$$

Lehman *et al.* have reported a value of $\log_{10}K^o(\text{A.122}) = 26.36$, because they have used the equilibrium constant for the reaction $H_3PO_4 \rightleftharpoons PO_4^{3-} + 3H^+$, with $\log_{10}K^o = 21.70$ instead of the correct value.

There are no previous determinations of the equilibrium constants in the U(IV)-phosphate system. The present review notes that $\log_{10}K^o(\text{A.122}) = (6.8 \pm 0.7)$ is close to the equilibrium constant for formation of $USO_4^{2+}$ with $\log_{10}K^o = 6.58$ at $I = 0$ [2003GUI/FAN], consistent with the fact that both ligands are coordinated in a bidentate fashion through oxygen donors.

**[2011CHE/NIP]**

Chernorukov *et al.* have studied phase transformations in $(H_3O)[(UO_2)(PO_4)]\cdot 3H_2O(cr)$ and $M[UO_2PO_4]\cdot 3H_2O(cr)$, M = Li, Na, K, Rb, Cs, $NH_4$ as a function of pH. They have used powder X-ray, IR and elemental composition of the solid phases to characterise them. The speciation in solution was obtained by using selected equilibrium constants for the hydroxide complexes from [1992GRE/FUG] and [2003GUI/FAN], for the protonation of phosphate from [1996BRE/GEI] and for the binary M(II)-hydroxide and phosphate systems from the "old" Glushko handbook (Thermal constants, 1965-1981, issues I-X). Using these data the speciation in solution was established, which together with the measured solubility allowed calculation of the solubility products.

Chernorukov *et al.* noted the following sequence of phases: at pH < 3 the stable phase is $(H_3O)[(UO_2)(PO_4)]\cdot 3H_2O$(cr) and all $M[UO_2PO_4]\cdot 3H_2O$(cr) phases are transformed to this. At pH > 3, $(H_3O)[(UO_2)(PO_4)]\cdot 3H_2O$(cr) is transformed to $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr). The results are similar for the $M[UO_2PO_4]\cdot 3H_2O$(cr) phases with the difference that uranate phases, $M_2U_2O_7$(cr) are formed at pH > 8. These findings are consistent with the known chemistry in these systems. Chernorukov *et al.* also report solubility products of these phases, these are based on few experimental solubility measurements and are listed in the table below together with solubility products for $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr), $UO_3\cdot 2H_2O$(cr) and $Na_2U_2O_7$(cr).

Table A-72: Values of solubility products at $I = 0$ of some uranyl phases calculated in [2011CHE/NIP].

| Solid phase | $\log_{10} K_s^o$ | Solid phase | $\log_{10} K_s^o$ |
|---|---|---|---|
| $H_3O[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | – (25.15 ± 0.50) | $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) | – 50.6 |
| $Li[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | – (25.70 ± 0.40) | $UO_3\cdot 2H_2O$(cr) | – 21.32 |
| $Na[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | – (26.19 ± 0.40) | $Na_2U_2O_7$(cr) | – 55.1 |
| $K[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | – (26.47 ± 0.40) | | |
| $Rb[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | – (26.53 ± 0.40) | | |
| $Cs[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | – (26.73 ± 0.40) | | |
| $NH_4[(UO_2)(PO_4)]\cdot 3H_2O$(cr) | – (25.69 ± 0.40) | | |

The solubility product of $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) is consistent with the value in [2005RAI/XIA] and [2003GUI/FAN].

**[2011NIP/CHE]**

Nipruk *et al.* have used the same methodology as in the previous communication by Chernorukov *et al.* [2011CHE/NIP] and they have compared phase transformations and structures in the uranyl(VI)-phosphate and uranyl(VI)-arsenate systems resulting from changes in pH. The two systems are very similar, but $(UO_2)_3(AsO_4)_2\cdot 4H_2O$(cr) has a very narrow range of existence between pH 1.8-2.0 and at pH higher than 2 it transforms to $(UO_2)_3(AsO_4)_2\cdot 12H_2O$(cr), a phase that has not been identified in the phosphate system. At pH > 1.8 both the phosphate and arsenate phases transform to $H_3O[(UO_2)(PO_4)]\cdot 3H_2O$(cr) and $H_3O[(UO_2)(AsO_4)]\cdot 3H_2O$(cr). $UO_3\cdot 2H_2O$(cr) is the stable phase in the range 8 < pH < 11.8 and above pH 11.8 the stable phase is an uranate like $Na_2U_2O_7$(cr). Nipruk *et al.* have also measured the solubility of $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) and $(UO_2)_3(AsO_4)_2\cdot 12H_2O$(cr) in the pH range where these phases are stable and they report the following solubility products: $\log_{10} K_s^o$ ($(UO_2)_3(PO_4)_2\cdot 4H_2O$, cr) = – (50.39 ± 0.47) and $\log_{10} K_s^o$ ($(UO_2)_3(AsO_4)_2\cdot 12H_2O$, cr) = – (45.33 ± 0.3). The solubility product for $(UO_2)_3(PO_4)_2\cdot 4H_2O$(cr) is in good agreement with the value reported in [2011CHE/NIP] and it is consistent with the values reported in [2005RAI/XIA] and [2003GUI/FAN].

**[2011NIP/PYK]**

Nipruk *et al.* have studied the stability of $M[(UO_2)(PO_4)]_2{\cdot}nH_2O$(cr), M = Mg, Ca, Sr, and Ba phases and determined their solubility products, the methodology is the same as in previous studies by these authors. The phases are stable over the range 1 < pH < 11, where they dissolve congruently. At pH < 1 they transform to $H_3O[(UO_2)(PO_4)]{\cdot}3H_2O$(cr), and at pH > 11 to uranates. The speciation in solution was obtained by using selected equilibrium constants for the hydroxide complexes from [1992GRE/FUG] and [2003GUI/FAN], for protonation of phosphate from [1996BRE/GEI] and for the binary M(II)-hydroxide and phosphate systems from Glushko *et al.* (Thermal constants, 1965-1981, issues I-X). The following solubility products at zero ionic strength, were reported:

$\log_{10} K_s^o$ ($Mg[(UO_2)(PO_4)]_2{\cdot}8H_2O$, cr) = – (50.3 ± 0.4);

$\log_{10} K_s^o$ ($Ca[(UO_2)(PO_4)]_2{\cdot}8H_2O$, cr) = – (50.4 ± 0.4);

$\log_{10} K_s^o$ ($Sr[(UO_2)(PO_4)]_2{\cdot}8H_2O$, cr) = – (50.7 ± 0.4);

$\log_{10} K_s^o$ ($Ba[(UO_2)(PO_4)]_2{\cdot}7H_2O$, cr) = – (51.3 ± 0.4).

The corresponding Gibbs energies of formation are given by the authors as:

$\Delta_f G_m^o$ ($Mg[(UO_2)(PO_4)]_2{\cdot}8H_2O$, cr, 298.15 K) = – (6136 ± 30) kJ·mol$^{-1}$;

$\Delta_f G_m^o$ ($Ca[(UO_2)(PO_4)]_2{\cdot}8H_2O$, cr, 298.15 K) = – (6139 ± 30) kJ·mol$^{-1}$;

$\Delta_f G_m^o$ ($Sr[(UO_2)(PO_4)]_2{\cdot}8H_2O$, cr, 298.15 K) = – (6145 ± 30) kJ·mol$^{-1}$;

$\Delta_f G_m^o$ ($Ba[(UO_2)(PO_4)]_2{\cdot}7H_2O$, cr, 298.15 K) = – (5909 ± 30) kJ·mol$^{-1}$.

There is no explanation in the paper why the authors selected such large uncertainties in the Gibbs energy of formation.

Nipruk *et al.* also report equilibrium constants for the following reactions:

$H_3O[(UO_2)(PO_4)]{\cdot}3H_2O(cr) \rightleftharpoons UO_2^{2+} + PO_4^{3-} + 4H_2O + H^+$; $\log_{10} K_s^o = -25.15$;

$Na_2U_2O_7(cr) + 3H_2O \rightleftharpoons 2Na^+ + 2UO_2^{2+} + 6OH^-$; $\log_{10} K_s^o = -55.03$;

$SrU_2O_7(cr) + 3H_2O \rightleftharpoons Sr^{2+} + 2UO_2^{2+} + 6OH^-$; $\log_{10} K_s^o = -57.57$;

$BaU_2O_7(cr) + 3H_2O \rightleftharpoons Ba^{2+} + 2UO_2^{2+} + 6OH^-$; $\log_{10} K_s^o = -56.96$.

The corresponding Gibbs energies of formation are given by the authors as:

$\Delta_f G_m^o$ ($(H_3O)[(UO_2)(PO_4)]{\cdot}3H_2O$, cr, 298.15 K) = – (2783 ± 2.4) kJ·mol$^{-1}$;

$\Delta_f G_m^o$ ($Na_2U_2O_7$, cr, 298.15 K) = – (3070 ± 2.5) kJ·mol$^{-1}$;

$\Delta_f G_m^o$ ($SrU_2O_7$, cr, 298.15 K) = – (3084 ± 2.8) kJ·mol$^{-1}$;

$\Delta_f G_m^o$ ($BaU_2O_7$, cr, 298.15 K) = – (3081 ± 3.6) kJ·mol$^{-1}$.

The values for these four phases cannot be verified. The text of the paper says: "Calculated from data on solubility of individual compounds". However, the solubility of these phases was not reported in this paper.

**[2012NIP/CHE]**

Nipruk *et al.* have studied the solubility, solubility products and phase transformations of the compounds $M[(UO_2)(PO_4)]_2 \cdot nH_2O(cr)$; M = Mn, Co, Ni, Cu, Zn, Cd, Pb, at 25 °C. The solubility measurements were made in test solutions with the concentrations of $HClO_4$ equal to 100, 10, 1 and 0.1 mM, pure water and 1000, 100, 10, 1 and 0.1 mM NaOH and measuring the pH after equilibration. The phase composition before and after equilibration was determined using X-ray diffraction; the solubility was measured using the total concentrations of M(II), U and P; the M(II) analyses were only made in the solutions with the concentration of $HClO_4$ equal to 100, 10 and 1 mM. Only in the 1 mM $HClO_4$ test solution was there clear evidence of congruent dissolution and only these were used to determine solubility products reported in Table A-73 for the Reactions (A.123)

$$M[(UO_2)(PO_4)]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2PO_4^{3-} + nH_2O(l) \qquad (A.123)$$

Only the data from the Cu, Co, Zn, and Ni phases (for which there are data from independent labs) were considered and we note that the difference between the reported $\log_{10}{}^{*}K_s$-values and the finally selected ones is about 0.6 for the Co, Zn, Ni phases and more than 4 orders for the Cu phase. This review considers the reliability of the latter value to be questionable.

Table A-73: Solubility products and Gibbs energy of formation for $M[(UO_2)(PO_4)]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2PO_4^{3-} + nH_2O(l)$; the uncertainties are those reported by the authors. The values of $\Delta_f G_m^o$ are given for information only.

| Solid phase | $-\log_{10} K_s^o$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| $Mn[(UO_2)(PO_4)]_2 \cdot 10H_2O(cr)$ | (50.22 ± 0.40) | – (6614 ± 20) |
| $Co[(UO_2)(PO_4)]_2 \cdot 12H_2O(cr)$ | (49.08 ± 0.40) | – (7082 ± 20) |
| $Ni[(UO_2)(PO_4)]_2 \cdot 12H_2O(cr)$ | (49.34 ± 0.40) | – (7083 ± 20) |
| $Cu[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$ | (48.85 ± 0.40) | – (6132 ± 20) |
| $Zn[(UO_2)(PO_4)]_2 \cdot 12H_2O(cr)$ | (49.28 ± 0.40) | – (7083 ± 20) |
| $Cd[(UO_2)(PO_4)]_2 \cdot 10H_2O(cr)$ | (49.85 ± 0.50) | – (6612 ± 20) |
| $Pb[(UO_2)(PO_4)]_2 \cdot 8H_2O(cr)$ | (50.34 ± 0.30) | – (6141 ± 20) |

When analysing the solubility data by determination of the speciation in the test solutions in equilibrium with the solid phase(s) the authors used the same data as in [2012CHE/NIP], except for the protonation constants of phosphate for which the values selected in the NEA reviews were used; activity coefficients were estimated using the SIT method where the main contribution is given by the Debye-Hückel term.

The phase analysis suggested the following phase transformations:

In the range 8 < pH < 11

$$\mathrm{M[(UO_2)(PO_4)]_2 \cdot \mathit{n}H_2O(cr) + 6NaOH(sln) \rightleftharpoons 2UO_3 \cdot 2H_2O(cr) + M(OH)_2(cr) + 2Na_3PO_4(cr) + (\mathit{n}-2)H_2O(l)} \quad \text{(A.124)}$$

At pH > 11

$$\mathrm{M[(UO_2)(PO_4)]_2 \cdot \mathit{n}H_2O(cr) + 6NaOH(sln) \rightleftharpoons Na_2U_2O_7(cr) + M(OH)_2(cr) + 2Na_2HPO_4(cr) + (\mathit{n}+1)H_2O(l)} \quad \text{(A.125)}$$

The authors present in their Figure 3 plots of the measured solubility over the pH range 1-14 together with full-drawn curves that are obtained by using the known equilibrium constants, but it is not clear to this review how such a calculation is possible when several solid phases are present. Of interest is that the minimum solubility in all systems is close to $10^{-7}$ M around pH = 6-8.

The authors provide detailed information on experimental methods and data analysis. The use of hydrolysis data from the Glushko tables presents no problem for the current review, even if these data have not been critically reviewed by NEA, because the correction is very small as discussed in [2012NIP/CHE]. The constants proposed by Nipruk *et al.* have been considered for the selection of thermodynamic data for $M[(UO_2)(PO_4)]_2 \cdot nH_2O$(cr), with M = Co, Ni and Zn.

**[2012SHV/FEI]**

Shvareva *et al.* make a review of the previously published thermodynamic data for hydrous oxides, phosphates, silicates and carbonates that provide important information. Shvareva *et al.* report data based on oxide-melt solution calorimetry that are summarised in Table A-74. These values are given per uranium atom and should be multiplied by the corresponding stoichiometric coefficient to be comparable with the values per formula unit given in [1992GRE/FUG] and [2003GUI/FAN]. Some of the reported values are significantly different from those reported in [2009GOR/SHV]; some of the Russian studies have not been reviewed, *e.g.* [2011CHE/NIP] and [2011NIP/PYK].

Table A-74: Thermodynamic properties of uranyl-bearing phases given in the review [2012SHV/FEI]. These data are given for information only.

| Phase | $-\Delta_f H_m^\circ$ /kJ·mol$^{-1}$ | $-\Delta_f G_m^\circ$ /kJ·mol$^{-1}$ | $-\Delta_f S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^\circ$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| Metaschoepite $UO_3 \cdot 2H_2O$(cr) | (1791.0 ± 3.2) | (1632.4 ± 7.4) | (532.5 ± 8.1) | (1356.6 ± 8.1) |
| β-$UO_2(OH)_2$ | (1536.2 ± 2.8) | – | – | – |
| Becquerelite | (1898.2 ± 2.3) | (1717.6 ± 4.4) | (605.8 ± 5.0) | (1407.8 ± 5.0) |

(Continued on next page)

Table A-74 (continued)

| Phase | $-\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $-\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $-\Delta_f S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | $S_m^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| Clarkeite | (1724.7 ± 5.1) | (1635.1 ± 23.4) | (300.5 ± 23.9) | (891.0 ± 23.9) |
| Na-compreignite | (1822.7 ± 2.4) | (1674.3 ± 4.1) | (497.9 ± 5.0) | (1286.9 ± 5.0) |
| Curite | (1645.4 ± 4.3) | – | – | – |
| Studtite | (2344.7 ± 4.3) | – | – | – |
| Rutherfordine | (1716.4 ± 4.2) | – | – | – |
| Andersonite | (5593.6 ± 9.1) | – | – | – |
| Grimselite | (4431.6 ± 15.3) | – | – | – |
| $UO_2HPO_4·3H_2O$(cr) | (3223.2 ± 4.0) | (3072.3 ± 4.8) | (1302.3 ± 21.2) | (2774.1 ± 21.2) |
| $(UO_2)_3(PO_4)_2·4H_2O$(cr) | (2337.7 ± 4.6) | (2046.3 ± 12.02) | (974.3 ± 6.2) | (1831.6 ± 20.6) |
| Soddyite | (2022.7 ± 2.5) | (1826.1 ± 2.1) | (635.4 ± 10.9) | (1338.4 ± 10.9) |
| K-boltwoodite | (2768.1 ± 6.5) | (2758.6 ± 3.8) | (27.5 ± 7.3) | (1075.0 ± 7.3) |
| Na-boltwoodite | (2947.2 ± 4.0) | (2725.2 ± 2.6) | (352.5 ± 7.2) | (1386.6 ± 7.2) |
| Uranophane | (3399.7 ± 4.0) | (3099.3 ± 5.6) | (1007.6 ± 12.0) | (2321.0 ± 12.2) |

**[2013CRE/SZE]**

Cretaz *et al.* studied the solubility of synthetic and natural samples of meta-torbernite (the idealised formula $Cu[(UO_2)(PO_4)]_2·8H_2O$(cr)) in solutions of $HNO_3$, HCl and $H_2SO_4$. The real chemical formula of both samples was $(H_3O)_{0.4}Cu_{0.8}[(UO_2)(PO_4)]_2·7.6H_2O$(cr) (samples differed by the specific surface area, which was by six times less for the synthetic sample compared to the natural sample, as measured by BET method). Phases were characterised by X-ray diffraction, scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (EDS), Raman spectroscopy, thermogravimetric analyses (TGA) and differential thermal analyses (DTA). Elemental composition was determined by ICP-AES. Equilibrium solubility was approached from both supersaturation (in 1 M of $HNO_3$, HCl and $H_2SO_4$ solutions) and undersaturation (from $HNO_3$, HCl and $H_2SO_4$-containing solutions having the ionic strength set to 1 M and the equilibrium pH around 0.7), both methods lead to the same saturation index. Chemical analyses were made by ICP-AEA, pH values (the concentrations of hydrogen ions) have also been measured. Experiments were performed at seven temperatures between 277 and 333 K. Experimental data were treated to calculate the equilibrium constant for the reaction

$$(H_3O)_{0.4}Cu_{0.8}[(UO_2)(PO_4)]_2·7.6H_2O(cr) \rightleftharpoons 0.4H_3O^+ + 0.8Cu^{2+} + 2UO_2^{2+} + 2PO_4^{3-} + 7.6\ H_2O(l) \quad \text{(A.126)},$$

taking into account the hydrolysis and complexation and using the SIT model to evaluate the activity coefficients. At 298.15 K, the value of $\log_{10}{}^*K^o = -(52.9 \pm 0.1)$ was calculated for the Reaction (A.126), whereas $\Delta_r H_m^o = (40 \pm 3)$ kJ·mol$^{-1}$ and $\Delta_r S_m^o = -(879 \pm 7)$ J·mol$^{-1}$·K$^{-1}$ were determined assuming that $\Delta_r H_m^o$ and $\Delta_r S_m^o$ are temperature independent.

The current review increases the uncertainties of derived thermodynamic properties for the Reaction (A.126) (for example, the authors made no corrections for

deviations of water activity from unity, while it is ~ 0.96-0.97 in 1 m solutions of $HNO_3$, HCl and $H_2SO_4$, *i.e.* contributing ~ 0.10-0.15 $\log_{10}$ units into $\log_{10}{}^{*}K^{o}$ value):

$\log_{10}{}^{*}K^{o} = -(52.9 \pm 0.3)$;

$\Delta_r G^{o}_{m} = (302.0 \pm 1.7)$ kJ·mol$^{-1}$;

$\Delta_r H^{o}_{m} = (40 \pm 8)$ kJ·mol$^{-1}$;

$\Delta_r S^{o}_{m} = -(879 \pm 27)$ J·mol$^{-1}$·K$^{-1}$.

The thermodynamic data from this study was considered in the main text as one of the most reliable.

**[2013FAN/YOO]**

Fanizza *et al.* have made a modeling study where they evaluate the rate of precipitation of uranyl(VI) phosphate minerals in micro-fluidic pore networks and the effect on the mobility of uranium in such systems by blocking flow-pathways. The model uses thermodynamic data on relevant uranyl(VI) phosphate minerals. There is an extensive review of relevant literature that includes thermodynamic data from [1992GRE/FUG] and [2003GUI/FAN]. The focus is on modeling and there are no new thermodynamic data presented. Transport modelling is important but the model uncertainties are so large that it is rarely possible to use them for validation of the thermodynamic input parameters and this is the case in [2013FAN/YOO].

**[2013JAC/GUT]**

Jackson *et al.* have made a detailed quantum chemistry study of reactions in the uranyl(VI)-phosphate system using DFT and different models to describe the water solvent. They report geometries of a large number of possible structures where the mode of coordination of $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$ varies with the number of coordinated water ligands in such a way that five-coordination is retained in the equatorial plane of the uranyl ion. The results indicate that the bidentate coordination of the ligands results in the most stable structures. The reaction energies are strongly dependent on the model used and cannot be used as proxies for experimental data. One also notes that the calculated vibration spectra deviate somewhat from experimental observations, care is needed when using them for structural assignments.

**[2013WAN/NI]**

The paper contains a large number of predominance area diagrams relating to the U- $PO_4^{3-}$ -NaCl-$H_2O$ system at 25 °C based on equilibrium constants of unknown origin. This study does not contain new information useful for the present review.

**[2014MEH/MAI]**

Mehta *et al.* discuss the possibility of remediation of uranium contaminated subsurface systems by precipitation of phosphate solids. This is done by using batch experiments where the total concentrations of U(VI), phosphate and carbonate were 0.1, 1 and 1 mM, respectively in the pH range 4 to 8. The concentrations of $Na^+$ and $Ca^{2+}$ varied from 0 to 5 mM. The total concentrations in the aqueous phases after equilibration have been reported as well as the solid phases. Based on these data and published equilibrium constants for the dissolved species and solubility products for the solid phases in the model, they could check the consistency of the experimental data and the equilibrium constants used. This information is important for the present review. Many of the equilibrium constants used are taken from previous NEA reviews, but there are some important differences.

The selected solubility product for metaschoepite, $UO_3{\cdot}2H_2O$(cr) was $\log_{10}K_s^o = 5.60$, taken from [2008GOR/FEI], which is significantly different from the value 4.81 from [1992GRE/FUG]. The latter resulted in a calculated uranium concentration that was ten times larger than the experimental value, while the one from [2008GOR/FEI] was in good agreement. The solubility product for chernikovite, $\log_{10}K_s^o = -25.50$ and for Ca-autunite, $Ca[UO_2PO_4]$(cr), $\log_{10}K_s^o = -48.36$, both are from [2009GOR/SHV]. The solubility product for Na-autunite, $\log_{10}K_s^o = -47.41$ is from [1978LAN] and finally the solubility product for $UO_2CO_3$(cr) is from [2003GUI/FAN]. Mehta *et al.* have also included the following two aqueous complexes $Ca[UO_2(CO_3)_3]^{2-}$, $\log_{10}K^o = 27.18$ and $Ca_2[UO_2(CO_3)_3]$(aq), $\log_{10}K^o = 30.70$ from [2006DON/BRO].

## A-1.5.3 Uranium arsenates

**[1956CHU/SHA]**

Chukhlantsev and Sharova have synthesised $M[(UO_2)(AsO_4)]{\cdot}xH_2O$(cr) (M = Li, Na, K, $NH_4$) and $UO_2HAsO_4{\cdot}xH_2O$(cr) by precipitation from aqueous solutions. The samples were characterised by chemical analyses, and the deviations from the ideal M:U:As stoichiometries were always within 2 %, however, the water content of the studied samples was not determined. The solubility was studied at (20 ± 0.1) °C by the "shake-flask" method in dilute $H_2SO_4$ or $HNO_3$ solutions over the pH range (2.0-5.3). For each phase six data points at various pH values were obtained. The authors measured pH and the concentration of U, the concentrations of M and As were calculated assuming the congruent dissolution of the solid phases. For the interpretation of data the authors used the following values of the stepwise dissociation of the arsenic acid (in the parentheses the corresponding values from Grenthe *et al.* [1992GRE/FUG] are given) : $\log_{10}K_1^o$ = 2.25 (2.24); $\log_{10}K_2^o$ = 6.77 (6.76); $\log_{10}K_3^o$ = 11.53 (11.60). The hydrolysis of uranyl ion was not taken into account and this approximation is correct only at the lowest pH in the test solutions.

The authors calculated the equilibrium concentration quotients from their solubility data. These were extrapolated by this review to infinite dilution using the SIT model with only the Debye-Hückel term.

For the Reaction (A.127)

$$M[(UO_2)(AsO_4)]\cdot xH_2O(cr) \rightleftharpoons M^+ + UO_2^{2+} + AsO_4^{3-} + xH_2O \qquad (A.127)$$

the obtained results are given in Table A-75, these values were considered in the main text together with other literature data. However, the finally selected values differ from the ones in this work, in some case by more than 1 log unit.

Table A-75: Values of $\log_{10} K_s^o$ of Reaction (A.127) extrapolated to $I = 0$ in this review based on data reported in [1956CHU/SHA].

| Compound | Ionic strength | Number of points | $\log_{10}{}^*K^o$(A.127) |
|---|---|---|---|
| $Li[(UO_2)(AsO_4)]\cdot xH_2O(cr)$ | $I < 0.01$ M | 6 | $-(19.30 \pm 0.64)$[(a)] |
| $Na[(UO_2)(AsO_4)]\cdot xH_2O(cr)$ | $I < 0.01$ M | 6 | $-(22.28 \pm 0.65)$[(a)] |
| $K[(UO_2)(AsO_4)]\cdot xH_2O(cr)$ | $I < 0.01$ M | 6 | $-(22.99 \pm 0.51)$[(a)] |
| $(NH_4)[(UO_2)(AsO_4)]\cdot xH_2O(cr)$ | $I < 0.01$ M | 6 | $-(24.22 \pm 0.46)$[(a)] |

(a) Uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10}{}^*K^o$, see Appendix C.

For the reaction:

$$UO_2HAsO_4\cdot xH_2O(cr) \rightleftharpoons UO_2^{2+} + HAsO_4^{2-} + xH_2O(l) \qquad (A.128)$$

$\log_{10}K^o(A.128) = -(10.73 \pm 0.56)$, as determined in this review by extrapolating six equilibrium concentration quotients, tabulated by the authors, to infinite dilution using the SIT model with only the Debye-Hückel term, the uncertainty is $1.96\ \sigma_X$. For the reaction:

$$UO_2HAsO_4\cdot xH_2O(cr) \rightleftharpoons UO_2^{2+} + H^+ + AsO_4^{3-} + xH_2O(l) \qquad (A.129)$$

the value of $\log_{10}{}^*K^o(A.129) = -(22.3 \pm 0.6)$ was obtained by combining $\log_{10}K^o(A.128)$ with the value of $\log_{10}K_3^o = 11.60$ for the third step of the dissociation of arsenic acid from [1992GRE/FUG]. These values were discussed in the main text together with other literature data.

**[1984VOC/GOE]**

Vochten *et al.* have synthesised minerals of the meta-zeunerite and meta-kirchenerite type ($Cu[(UO_2)(AsO_4)]_2\cdot 8H_2O(cr)$; $Co[(UO_2)(AsO_4)]_2\cdot 7H_2O(cr)$; $Ni[(UO_2)(AsO_4)]_2\cdot 7H_2O(cr)$) and characterised them using X-ray powder diffraction and chemical analyses. They have also studied their solubility at 25 °C in the $p[H^+]$ range 1-4 and calculated the solubility product for Reaction (A.130):

$$M[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2AsO_4^{3-} + nH_2O(l) \qquad (A.130)$$

In the p[$H^+$] range 1-3 one expects $H_3AsO_4$ and $H_2AsO_4^-$ to be the predominant arsenate ion while the predominant uranyl species is $UO_2^{2+}$. The experimental data have been used by Vochten *et al.* to determine the solubility product for Reaction (A.130). They note that a plot of $-\log_{10}s$ *vs.* p[$H^+$] ($s$ is the measured solubility, based on the total concentration of M, which in the p[$H^+$] range used is equal to $M^{2+}$) is linear with a slope of about 1.1, but it is obvious from Eqn. (A.131) that this is a coincidence as arsenate is present both as $H_3AsO_4$ and $H_2AsO_4^-$ in this p[$H^+$] range. From the total concentration of arsenate, As = 2$s$, and the protonation constants for $AsO_4^{3-}$ they then calculate the solubility product as:

$$K_s = \{s\}\{2s\}^2\{2s(\,1 + K_1^H[H^+] + K_1^H K_2^H[H^+]^2 + K_1^H K_2^H K_3^H[H^+]^3); \qquad (A.131)$$

The protonation constants ($\log_{10}K_1^H = 11.50$; $\log_{10}K_2^H = 6.94$, $\log_{10}K_3^H = 2.19$) used by Vochten *et al.* are taken from Flies *et al.* 1959FLI/MIS are in good agreement with those tabulated by Perrin (D. D. Perrin, *Ionization constants of inorganic acids and bases in aqueous solution*, IUPAC, Chemical Data Series, No 29), but slightly different from the values selected in [1992GRE/FUG] (11.60, 6.76 and 2.24). Vochten *et al.* report p$K_s$($Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$, cr) = 49.20, p$K_s$($Co[(UO_2)(AsO_4)]_2 \cdot 7H_2O$, cr) = 45.34, and p$K_s$($Ni[(UO_2)(AsO_4)]_2 \cdot 7H_2O$, cr) = 45.10; these are conditional equilibrium constants valid in test solutions where the ionic strength varies between $10^{-1}$ and $10^{-3.5}$ M. By using the NEA selected values, this review obtains the same solubility products as Vochten *et al.*, well within an estimated uncertainty of about 0.2 log for each studied compound. The extrapolation to $I = 0$ was performed in this review using SIT (with only the Debye-Hückel term) for Reaction (A.130) (see Table A-76). These values were discussed in the main text together with other literature data. However, the finally selected values differ from the ones in this work, in some case by more than 2 log units.

Table A-76: Values of $\log_{10}K_s^o$ (A.130) extrapolated to $I = 0$ in this review based on data reported in [1984VOC/GOE].

| Compound | Ionic strength | Number of points | $\log_{10}K^o$(A.130) |
|---|---|---|---|
| $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr) | $I < 0.10$ M | 5 | $-(50.9 \pm 1.6)$[(a)] |
| $Co[(UO_2)(AsO_4)]_2 \cdot 7H_2O$(cr) | $I < 0.10$ M | 6 | $-(47.5 \pm 1.8)$[(a)] |
| $Ni[(UO_2)(AsO_4)]_2 \cdot 7H_2O$(cr) | $I < 0.06$ M | 6 | $-(46.33 \pm 0.75)$[(a)] |

(a) Recalculated in this review, uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10}{}^*K^o$, see Appendix C.

**[1986VOC/GRA]**

This study includes synthesis, crystallographic and spectroscopic data, solubility and electrokinetic properties of metakhalerite, $Fe[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr), and manganese uranylarsenate, $Mn[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr). For metakhalerite,

$Fe[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr), the solubility was studied in a $N_2$ atmosphere and for manganese uranylarsenate under ambient atmospheric conditions. The analytical procedures and evaluation methods are the same as in previous studies by these authors. Data were corrected for hydrolysis of arsenate ion, but not for hydrolysis or complex formation with arsenate for metal ions. The concentration solubility products were recalculated to $I = 0$ in this review (the SIT model with the electrostatic term only) and averaged (see Table A-77); these values were taken into account in the main text.

Table A-77: Values of $\log_{10} K_s^o$ extrapolated to $I = 0$ in this review based on data reported in [1986VOC/GRA].

| Compound | Medium | Number of data points | $\log_{10} K^o$ |
|---|---|---|---|
| $Fe[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) | $I < 0.10$ M | 9 | $-(46.1 \pm 2.2)^{(a)}$ |
| $Mn[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) | $I < 0.10$ M | 6 | $-(43.6 \pm 2.2)^{(a)}$ |

(a) Recalculated in this review, , uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10} {}^*K^o$, see Appendix C.

The values of $\log_{10} {}^*K^o$ depend strongly on pH and change for about 3 $\log_{10}$ units when pH increases from ~ 1 to ~ 4, resulting in large uncertainties of averaged $\log_{10} {}^*K^o$.

**[1987ZHI/POL]**

Zhiltsova *et al.* studied the solubility of synthetic samples of uranyl arsenates: hydrogen uranospinite, of the stoichiometry $(H_3O)_2[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr); uranospinite, $Ca[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr); nováčekite, $Mg[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr), and zeunerite, $Cu[(UO_2)(AsO_4)]_2{\cdot}10H_2O$(cr). The phases were characterised by X-ray diffraction. Solubility studies were conducted at 25 °C in HCl solutions of pH 1.3-3.0 (2-3 solutions for each phase) in polyethylene flasks with periodic manual shaking. Concentrations of U, As, Mg, Ca, and Cu were measured: U—by vanadatometric titration; Ca, Mg, As, U and Cu—by Plasmatron torch; in addition, Mg and Ca—by Atomic absorption spectroscopy (AAS), and Cu—by the polarographic method. pH values (the activity scale) were also reported. The steady-state concentrations were reached in 12-20 days; the solubility of all phases was congruent.

Data were used used to evaluate solubility products of uranoarsenates. Activity coefficients were calculated using the extended Debye-Hückel equation. Hydrolysis and formation of the chloride complex of uranyl ion (but not of arsenate complexes) were taken into account. Results are presented in Table A-78:

Table A-78: Values of solubility products of uranyl arsenates at $I = 0$ reported in [1987ZHI/POL] and averaged in this review.

| Compound | Ionic strength | Number of points | $\log_{10}{}^{*}K^{o}$ |
|---|---|---|---|
| $(H_3O)_2[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) | $I < 0.01$ M | 2 | – (45.58 ± 0.17)[(a)] |
| $Ca[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) | $I < 0.01$ M | 2 | – (45.76 ± 0.14)[(a)] |
| $Mg[(UO_2)(AsO_4)]_2{\cdot}8H_2O$(cr) | $I < 0.01$ M | 2 | – (44.44 ± 0.29)[(a)] |
| $Cu[(UO_2)(AsO_4)]_2{\cdot}10H_2O$(cr) | $I < 0.05$ M | 3 | – (46.33 ± 0.37)[(a)] |

(a) Recalculated in this review—uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10}{}^{*}K^{o}$, see Appendix C. These values were discussed in the main text together with other literature data. However, the finally selected values differ from the ones in this work and most likely represent the upper boundary of $\log_{10}K^{o}$, because the complexation of metals with arsenate was neglected.

**[1994KAR/CHE2]**

This study determined the enthalpies of formation of synthetic samples of $M^{I}[(UO_2)(AsO_4)]{\cdot}nH_2O$(cr) ($M^{I}$ = Li, Na, K, Rb, Cs, $n = 4$ for Li and $n = 3$ for Na-Cs). The compounds were analysed by X-ray diffraction, IR spectroscopy and thermogravimetry, however, the exact stoichiometry of the studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions involving $UO_3$(cr), $KH_2AsO_4$(cr), $M^{I}NO_3$(cr) where $M^{I}$ = Na, K, Rb, Cs, $M^{I}[(UO_2)(AsO_4)]{\cdot}nH_2O$(cr) in concentrated HF solutions, ~18 m HF. The thermochemical cycle employed resulted in the following values of $\Delta_r H_m$ for the reaction:

$$KH_2AsO_4(cr) + UO_3(cr) + M^{I}NO_3(cr) + (n-1)H_2O(l) \rightleftharpoons M^{I}[(UO_2)(AsO_4)]{\cdot}nH_2O(cr) + KNO_3(cr) \quad \text{(A.132)}$$

(see values in kJ·mol$^{-1}$ in Table A-79).

Table A-79: Values of the enthalpy change for Reaction (A.132) and the enthalpy of formation $\Delta_f H_m^{o}$ of uranyl arsenates of alkali metals recalculated in this review based on data [1994KAR/CHE2]. These values are given for information only.

| Compound | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_f H_m^{o}$ /kJ·mol$^{-1}$ |
|---|---|---|
| $Li[(UO_2)(AsO_4)]{\cdot}4H_2O$(cr) | – (74.87 ± 2.66) | – (3328.1 ± 5.2) |
| $Na[(UO_2)(AsO_4)]{\cdot}3H_2O$(cr) | – (39.88 ± 2.61) | – (2991.5 ± 5.1) |
| $K[(UO_2)(AsO_4)]{\cdot}3H_2O$(cr) | – (37.02 ± 2.89) | – (3015.0 ± 5.3) |
| $Rb[(UO_2)(AsO_4)]{\cdot}3H_2O$(cr) | – (37.73 ± 1.95) | – (3016.5 ± 4.9) |
| $Cs[(UO_2)(AsO_4)]{\cdot}3H_2O$(cr) | – (34.21 ± 1.52) | – (3023.2 ± 4.7)[(a)] |

(a) – (2880.0 ± 4.7) in the case of a solid with the composition $Cs[(UO_2)(AsO_4)]{\cdot}2.5H_2O$(cr).

These $\Delta_r H_m$ values in 18 m HF medium were used to calculate $\Delta_f H_m^{o}$ for uranyl arsenates as described for [1994KAR/CHE], [1996KAR/CHE], *i.e.* with the relation

$$\Delta_f H_m^o = \Delta_r H_m^o - \Delta_f H_m^o(KNO_3, cr) + \Delta_f H_m^o(KH_2AsO_4, cr) + \Delta_f H_m^o(UO_3, cr) + \Delta_f H_m^o(M^INO_3, cr) + (n-1)(\Delta_f H_m^o(H_2O(l) + \overline{L}_1))$$

where the relative partial molar enthalpy of water, $\overline{L}_1$, is equal to – 0.63 kJ·mol$^{-1}$ in 18 m HF, see the review of [2002KAR/CHE2] for explanations. The current review used the following $\Delta_f H_m^o$ auxiliary data (in kJ·mol$^{-1}$): – (1223.8 ± 1.2) for $UO_3$(cr), – (467.58 ± 0.41) for $NaNO_3$(cr) and – (285.83 ± 0.04) for $H_2O$(l) from [2003GUI/FAN]; – (482.7 ± 0.5) for $LiNO_3$(cr); – (494.0 ± 0.5) for $KNO_3$(cr); – (494.7 ± 0.5) for $RbNO_3$(cr); – (505.0 ± 0.5) for $CsNO_3$(cr), all from [1982GLU/GUR]; and for $KH_2AsO_4$(cr) $\Delta_f H_m^o$ = – (1181.3 ± 4.2), obtained as discussed in Section 9.6.3.2. The resulting values of $\Delta_f H_m^o$ (in kJ·mol$^{-1}$) are given in the last column of Table A-79. The uncertainties are calculated using rules of propagation of errors, see Appendix C. Note that the authors gave larger uncertainties to their $\Delta_f H_m^o$ results, 8-9 kJ·mol$^{-1}$.

**[1994KAR/CHE3]**

This study determined the enthalpies of formation of synthetic samples of $M^I[(UO_2)(AsO_4)]$(cr) ($M^I$ = Li, Na, K, Rb, Cs). The anhydrous compounds were obtained by calcination of corresponding hydrates at 400 °C for five hours. Compounds were analysed by chemical analysis and by X-ray diffraction. However, the exact stoichiometry of the studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions involving $UO_3$(cr), $KH_2AsO_4$(cr), $M^INO_3$(cr) where $M^I$ = Na, K, Rb, Cs, $M^I[(UO_2)(AsO_4)]\cdot nH_2O$(cr) in concentrated HF solutions, ~18 m HF. The thermochemical cycle employed resulted in the following values of $\Delta_r H_m$ for the reactions:

$$KH_2AsO_4(cr) + UO_3(cr) + M^INO_3(cr) \rightleftharpoons M^I[(UO_2)(AsO_4)](cr) + KNO_3(cr) + H_2O(l) \quad \text{(A.133)}$$

(see values in kJ·mol$^{-1}$ in Table A-80).

Table A-80: Values of the enthalpy change for Reaction (A.133) and the enthalpy of formation $\Delta_f H_m^o$ of uranyl arsenates of alkali metals recalculated in this review based on data reported in [1994KAR/CHE3]. These values are given for information.

| Compound | $\Delta_f H_m$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| $Li[(UO_2)(AsO_4)]$(cr) | – (8.99 ± 2.28) | – (2116.3 ± 5.0) |
| $Na[(UO_2)(AsO_4)]$(cr) | – (8.88 ± 2.49) | – (2101.1 ± 5.1) |
| $K[(UO_2)(AsO_4)]$(cr) | – (12.90 ± 2.29) | – (2131.5 ± 4.9) |
| $Rb[(UO_2)(AsO_4)]$(cr) | – (17.09 ± 2.21) | – (2136.4 ± 4.9) |
| $Cs[(UO_2)(AsO_4)]$(cr) | – (17.49 ± 2.42) | – (2147.1 ± 5.0) |

These $\Delta_r H_m$ values in 18 m HF medium were used to calculate $\Delta_f H_m^o$ for uranyl arsenates as described for [1994KAR/CHE2], see the last column of Table A-80. The uncertainties are calculated using rules of propagation of errors, see Appendix C. Note that the authors gave larger uncertainties to their $\Delta_f H_m^o$ results, 8-9 kJ·mol$^{-1}$.

**[1996KAR/CHE4]**

This study reports the enthalpies of formation of synthetic samples of $M^{II}[(UO_2)(AsO_4)]_2$(cr) (M = Ca, Sr, Ba). The phases were obtained by calcination of the corresponding synthetic crystallohydrates at 500 °C. As the compounds were highly hygroscopic, samples were prepared in a dry Ar atmosphere. The exact composition of the studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($UO_3$(cr, γ), $KH_2AsO_4$(cr, tetr), $CaCO_3$(cr, hex), $K_2CO_3$(cr, monocl), $SrCO_3$(cr, rhomb), $BaCO_3$(cr, rhomb), $Ca[(UO_2)(AsO_4)]_2$(cr), $Sr[(UO_2)(AsO_4)]_2$(cr), $Ba[(UO_2)(AsO_4)]_2$(cr)) in an aqueous HCl solution (the exact HCl concentration was not reported in the paper, however, this is an analogous study to [1996KAR/CHE], so, this review assumes the medium to be 4 M (~ 4.36 m) HCl).

The values of $\Delta_f H_m^o$ of $M^{II}[(UO_2)(AsO_4)]_2$(cr) were evaluated from the reaction:

$$2KH_2AsO_4(cr, tetr) + 2UO_3(cr, \gamma) + MCO_3(cr) \rightleftharpoons M[(UO_2)(AsO_4)]_2(cr) + K_2CO_3(cr) + 2H_2O(l) \quad (A.134)$$

(see Table A-81) where the values are given for information only.

Table A-81: Values of the enthalpy change for Reaction (A.134) and $\Delta_f H_m^o$ of uranyl arsenates of Ca, Sr, and Ba recalculated in this review based on data reported in [1996KAR/CHE4].

| Compound | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| $Ca[(UO_2)(AsO_4)]_2$(cr) | (50.69 ± 1.35) | – (4243.2 ± 9.0) |
| $Sr[(UO_2)(AsO_4)]_2$(cr) | (27.66 ± 1.87) | – (4284.7 ± 9.4) |
| $Ba[(UO_2)(AsO_4)]_2$(cr) | (7.14 ± 1.38) | – (4292.3 ± 9.3) |

The auxiliary $\Delta_f H_m^o$ data used in this review are same as in the review for [1996KAR/CHE], and for $KH_2AsO_4$(cr) $\Delta_f H_m^o = -(1181.3 \pm 4.2)$, obtained as discussed in Section 9.6.3.2. The calculations were done as discussed in [1996KAR/CHE]. Results are given in the last column of Table A-81. The uncertainties are calculated using rules of propagation of errors, see Appendix C.

**[1998KAR/CHE3]**

This study determined the low-temperature heat capacities of synthetic samples of anhydrous uranoarsenates $A^I[(UO_2)(AsO_4)](cr)$ ($A^I$ = Li, Na, K, Rb, and Cs), obtained by calcination of their crystallohydrates. However, the exact compositions of the studied samples were not reported.

The heat capacities were measured at 80-320 K, data were extrapolated to 0 K and numerically integrated to evaluate at 298.15 K the following values of the thermodynamic functions in $J \cdot K^{-1} \cdot mol^{-1}$ (see Table A-82).

Table A-82: Thermodynamic properties of uranyl arsenates of alkali metals reported in [1998KAR/CHE3]. These data are provided for information only.

| Compound | $C^o_{p,m}$ (298.15 K)[(a)] /J·K$^{-1}$·mol$^{-1}$ | $S^o_m$ (298.15 K)[(a)] /J·K$^{-1}$·mol$^{-1}$ | $S^o_m$ (298.15 K)[(b)] /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|
| $Li[(UO_2)(AsO_4)](cr)$ | 182.2 | 228.8 | (189 ± 12) |
| $Na[(UO_2)(AsO_4)]$ (cr) | 172.8 | 230.0 | (206 ± 12) |
| $K[(UO_2)(AsO_4)]$ (cr) | 178.7 | 233.9 | (213 ± 12) |
| $Rb[(UO_2)(AsO_4)]$ (cr) | 177.3 | 236.2 | (224 ± 12) |
| $Cs[(UO_2)(AsO_4)]$ (cr) | 190.3 | 249.2 | (231 ± 12) |

(a) Experimental value;
(b) Estimated with the Latimer (1951) method, as outlined in Appendix D.

Values of $S^o_m(298.15\ K)$ for these compounds are also reported in [2000KAR/CHE]. Data of the two studies from the same laboratory are only in a moderate agreement: for Li, Na and K uranoarsenates the difference in the entropy values is within 3-5 %, increasing to ~ 8 % for $Rb[(UO_2)(AsO_4)](cr)$ and ~ 15 % for $Cs[(UO_2)(AsO_4)](cr)$. Results of [1998KAR/CHE3] are considered by this review semi-quantitative due to lack of data on the exact composition of phases; their estimated uncertainty is about ± 20 $J \cdot K^{-1} \cdot mol^{-1}$.

**[2002CHE/SUL]**

This study determined the enthalpies of formation of synthetic samples of $M^{II}[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr)$ ($M^{II}$ = Mn, Fe, Co, Ni, Cu, Zn, Cd). The purity of phases was confirmed with X-ray diffractometry, the elemental composition was determined with an electron microscope equipped with an EDAX energy-dispersive analyser. However, the exact stoichiometry of studied samples was not reported.

Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($UO_3(cr)$, $KH_2AsO_4(cr)$, $K_2SO_4(cr)$, $H_2O(l)$, $M^{II}SO_4 \cdot kH_2O(cr)$, $M^{II}[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr)$) in 4 M (~ 4.36 m) aqueous HCl solution. The thermochemical cycle employed resulted in the following $\Delta_r H_m$ values (in $kJ \cdot mol^{-1}$) for the Reaction:

$$2UO_3(cr) + 2KH_2AsO_4(cr) + M^{II}SO_4 \cdot kH_2O(cr) + (n-k-2)H_2O(l) \rightleftharpoons M^{II}[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr) + K_2SO_4(cr) \quad \text{(A.135)}$$

(see Table A-83). These results are discussed in the section of the main text dedicated to transition metal uranyl arsenates.

Table A-83: Values of the enthalpy change for Reaction (A.135) and $\Delta_f H_m^o$ of uranyl arsenates of some transition metals recalculated in this review based on data reported in [2002CHE/SUL]. The data are provided for information only.

| Compound | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| $Mn[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr)$ | – (178.0 ± 5.7) | |
| $Fe[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr)$ | – (135.2 ± 5.5) | – (6234.0 ± 10.4) |
| $Co[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr)$ | – (118.1 ± 5.5) | – (6175.8 ± 10.5) |
| $Ni[(UO_2)(AsO_4)]_2 \cdot 10H_2O(cr)$ | – (130.2 ± 5.6) | – (6757.9 ± 10.5) |
| $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr)$ | – (181.5 ± 5.6) | – (6120.5 ± 10.5) |
| $Zn[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr)$ | – (126.3 ± 6.5) | – (6289.5 ± 10.9) |
| $Cd[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr)$ | – (150.4 ± 5.5) | – (6206.1 ± 10.4) |

The auxiliary $\Delta_f H_m^o$ data used in this review to calculate enthalpies of formation of uranyl arsenates are same as in the review for [2003CHE/SUL], and for $KH_2AsO_4(cr)$ $\Delta_f H_m^o = -(1181.3 \pm 4.2)$, obtained as discussed in Section 9.6.3.2. The calculations were done as described in the review for [2003CHE/SUL]. Results are given in the last column of Table A-83. Calculations have not been performed for the Mn phase as no satisfactory value of $\Delta_f H_m^o$ was found for $MnSO_4 \cdot H_2O(cr)$. The uncertainties are calculated using rules of propagation of errors, see Appendix C. Some auxiliary data used in calculations were not scrutinised by the NEA team, and these $\Delta_f H_m^o$ cannot be selected, however, they can be used for scoping calculations.

**[2003SUL/CHE]**

The vapor pressures over the solid phases of the systems $M[(UO_2)(AsO_4)]$-$H_2O$ (M = Li, Na, K, Rb, Cs) were determined using isopiestic and tensimetric methods at 60-270 °C (the temperature range was estimated from plots in the paper, no primary vapor pressure data are reported). These data showed the existence of the following crystalline phases: $Li[(UO_2)(AsO_4)] \cdot 4H_2O(cr)$, $Li[(UO_2)(AsO_4)] \cdot 3H_2O(cr)$, $Li[(UO_2)(AsO_4)] \cdot H_2O(cr)$, $Li[(UO_2)(AsO_4)](cr)$, $Na[(UO_2)(AsO_4)] \cdot 3H_2O(cr)$, $Na[(UO_2)(AsO_4)] \cdot 1.5H_2O(cr)$, $Na[(UO_2)(AsO_4)] \cdot H_2O(cr)$, $Na[(UO_2)(AsO_4)](cr)$, $K[(UO_2)(AsO_4)] \cdot 3H_2O(cr)$, $K[(UO_2)(AsO_4)] \cdot 0.5H_2O(cr)$, $K[(UO_2)(AsO_4)](cr)$, $Rb[(UO_2)(AsO_4)] \cdot 3H_2O(cr)$, $Rb[(UO_2)(AsO_4)] \cdot H_2O(cr)$, $Rb[(UO_2)(AsO_4)] \cdot 0.5H_2O(cr)$, $Rb[(UO_2)(AsO_4)](cr)$, $Cs[(UO_2)(AsO_4)] \cdot 2.5H_2O(cr)$, $Cs[(UO_2)(AsO_4)] \cdot H_2O(cr)$, $Cs[(UO_2)(AsO_4)] \cdot 0.5H_2O(cr)$, and $Cs[(UO_2)(AsO_4)](cr)$. Vapor pressures over coexisting phases are shown only on plots in the paper.

In addition, the authors performed calorimetric experiments in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds ($UO_3$(cr), $KH_2AsO_4$(cr), $H_2O$(l), MCl(cr) (M = Li, Na, K, Rb, Cs), $M[(UO_2)(AsO_4)]\cdot xH_2O$(cr), $Li_2CO_3$(cr), and $K_2CO_3$(cr)) in concentrated HF solutions (molar ratio HF:$H_2O$ 289:1230, *i.e.* ~13.0 m HF). The thermochemical cycle employed resulted in the following values of $\Delta_r H_m$ for the reactions:

$$KH_2AsO_4(cr) + UO_3(cr) + 0.5Li_2CO_3(cr) + 3H_2O(l) \rightleftharpoons Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr) + 0.5K_2CO_3(cr) \quad \text{(A.136)}$$

$\Delta_r H_m = -(53.2 \pm 2.1)$ kJ·mol$^{-1}$;

$$KH_2AsO_4(cr) + UO_3(cr) + MCl(cr) + 2H_2O(l) \rightleftharpoons M[(UO_2)(AsO_4)]\cdot 3H_2O(cr) + KCl(cr) \quad \text{(A.137)}$$

$\Delta_r H_m = -(69.4 \pm 2.3)$ kJ·mol$^{-1}$ for M = Na;

$\Delta_r H_m = -(68.5 \pm 2.9)$ kJ·mol$^{-1}$ for M = K;

$\Delta_r H_m = -(76.1 \pm 2.5)$ kJ·mol$^{-1}$ for M = Rb,

$$KH_2AsO_4(cr) + UO_3(cr) + CsCl(cr) + 1.5H_2O(l) \rightleftharpoons Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr) + KCl(cr) \quad \text{(A.138)}$$

$\Delta_r H_m = -(67.1 \pm 2.5)$ kJ·mol$^{-1}$.

These results were used in this review to calculate $\Delta_f H_m^o$ of uranyl arsenates as it was done in reviews for [1994KAR/CHE], [1996KAR/CHE]. The following auxiliary data were used (in kJ·mol$^{-1}$): $-(1223.8 \pm 1.2)$ for $UO_3$(cr), $-(285.83 \pm 0.04)$ for $H_2O$(l), $-(411.26 \pm 0.12)$ for NaCl(cr), all from NEA database [2003GUI/FAN]; $-(1214.1 \pm 1.0)$ for $Li_2CO_3$(cr), $-(1151.5 \pm 2.0)$ for $K_2CO_3$(cr), $-(436.49 \pm 0.13)$ for KCl(cr), $-(435.22 \pm 0.16)$ for RbCl(cr), $-(442.31 \pm 0.16)$ for CsCl(cr), all from [1982GLU/GUR]; and for $KH_2AsO_4$(cr) $\Delta_f H_m^o = -(1181.3 \pm 4.2)$, obtained as discussed in Section 9.6.3.2. The used value of the relative partial molar enthalpy of water, $\overline{L}_1$, is equal to – 0.31 kJ·mol$^{-1}$ in 13.0 m HF, evaluated as explained in the review of [2002KAR/CHE2]. Results are shown in Table A-84. These results are discussed in the section for alkali metal uranyl arsenates of the main text.

Table A-84: Values of $\Delta_f H_m^o$ of uranyl arsenates of alkali metals recalculated in this review based on data reported in [2003SUL/CHE]. Data are provided for information only.

| Compound | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | Compound | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O$(cr) | $-(3348.0 \pm 5.0)$ | $K[(UO_2)(AsO_4)]$(cr) | $-(2137.4 \pm 5.4)$ |
| $Li[(UO_2)(AsO_4)]$(cr) | $-(2123.3 \pm 5.5)$ | $Rb[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | $-(3052.2 \pm 5.1)$ |
| $Na[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | $-(3021.6 \pm 4.9)$ | $Rb[(UO_2)(AsO_4)]$(cr) | $-(2152.2 \pm 5.1)$ |
| $Na[(UO_2)(AsO_4)]$(cr) | $-(2095.1 \pm 5.3)$ | $Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O$(cr) | $-(2907.2 \pm 5.0)$ |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | $-(3045.9 \pm 5.2)$ | $Cs[(UO_2)(AsO_4)]$(cr) | $-(2153.0 \pm 5.2)$ |

The authors also measured heat effects of reactions of water with lower hydrates and unhydrated compounds. This review accepted the enthalpy changes, $\Delta_r H_m^o$, in kJ·mol$^{-1}$, for the following dehydration reactions at 25 °C:

$$Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr) \rightleftharpoons Li[(UO_2)(AsO_4)](cr) + 4H_2O(l) \quad (A.139)$$

$$\Delta_r H_m^o \text{ (A.139)} = (80.1 \pm 2.2);$$

$$Na[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons Na[(UO_2)(AsO_4)](cr) + 3H_2O(l) \quad (A.140)$$

$$\Delta_r H_m^o \text{ (A.140)} = (68.1 \pm 2.0);$$

$$K[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons K[(UO_2)(AsO_4)](cr) + 3H_2O(l) \quad (A.141)$$

$$\Delta_r H_m^o \text{ (A.141)} = (50.1 \pm 1.5);$$

$$Rb[(UO_2)(AsO_4)]\cdot 3H_2O(cr) \rightleftharpoons Rb[(UO_2)(AsO_4)](cr) + 3H_2O(l) \quad (A.142)$$

$$\Delta_r H_m^o \text{ (A.142)} = (41.6 \pm 1.0);$$

$$Cs[(UO_2)(AsO_4)]\cdot 2.5H_2O(cr) \rightleftharpoons Cs[(UO_2)(AsO_4)](cr) + 2.5H_2O(l) \quad (A.143)$$

$$\Delta_r H_m^o \text{ (A.143)} = (38.9 \pm 1.5).$$

Note that there are also data for intermediate hydrates. Combining these $\Delta_r H_m^o$ with values of $\Delta_r H_m^o$ of hydrates of uranyl arsenates and liquid water, this review calculated the enthalpies of formation of unhydrated phases—see Table A-84. The uncertainties are calculated using rules of propagation of errors, see Appendix C.

**[2006CHE/SUL]**

This paper reports solubility data for uranyl arsenates $M[(UO_2)(AsO_4)]\cdot nH_2O(cr)$ in water and dilute (0.1-0.0001 M) $HClO_4$ solutions at 25 °C (M = $H^+$, $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $NH_4^+$); the test solutions were equilibrated during several weeks with intermittent stirring (the equilibrium was reached in 10-14 days). The phase purity of the synthesised uranyl arsenates was checked by X-ray diffraction, the elemental composition was determined with an electron microscope equipped with an EDAX energy-dispersive analyser. The solubilities are congruent in $HClO_4$ solutions, except for $Li[(UO_2)(AsO_4)]\cdot 4H_2O(cr)$ systems with $HClO_4$ concentrations below 0.01 M. In water the solubilities are incongruent.

Experimental data were used to calculate the solubility products according to the reaction $M[(UO_2)(AsO_4)]\cdot nH_2O(cr) \rightleftharpoons M^+ + UO_2^{2+} + AsO_4^{3-} + nH_2O(l)$. The formation of monomeric and polymeric hydroxocomplexes of the uranyl ion (the corresponding stability constants were taken from the Russian handbook Thermal Constants of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981), the dissociation of arsenic acid (Chemist's Handbook, Moscow, Khimiya, 1964, Vol.3, in Russian), and the formation of arsenate complexes of the uranyl ion (based on data of

[1999RUT/GEI]) were accounted for. No details of the calculation of activity coefficients are given, however, in other papers of this group the activity coefficients were calculated with the Debye-Hückel or the SIT equations. The calculated solubility products are presented in Table A-85, These values were discussed in the main text together with other literature data. However, the finally selected values usually differ from the ones in this work.

Table A-85: Solubility products of uranyl arsenates reported in [2006CHE/SUL].

| Compound | $\log_{10} K_s^o$ | Compound | $\log_{10} K_s^o$ |
|---|---|---|---|
| $H[(UO_2)(AsO_4)]\cdot 4H_2O$(cr) | – (23.1 ± 0.4) | $Rb[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | – (24.6 ± 0.2) |
| $Li[(UO_2)(AsO_4)]\cdot 4H_2O$(cr) | – (21.0 ± 0.2) | $Cs[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | – (25.2 ± 0.8) |
| $Na[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | – (23.0 ± 0.2) | $NH_4[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | – (24.9 ± 0.3) |
| $K[(UO_2)(AsO_4)]\cdot 3H_2O$(cr) | – (23.4 ± 0.2) | | |

**[2009CHE/NIP]**

Chernorukov *et al.* have studied the stability and solubility products of $M[UO_2AsO_4]_2\cdot nH_2O$(cr), M = Mg, Ca, Sr, Ba, phases. The composition is similar to those of the minerals novacekite, $Mg[UO_2AsO_4]_2\cdot 12H_2O$(cr), uranospinite, $Ca[UO_2AsO_4]_2\cdot 10H_2O$(cr) and heinrichite, $Ba[UO_2AsO_4]_2\cdot(10\text{-}12H_2O)$(cr). The solid phases were characterised by X-ray diffraction and the elemental composition was determined by energy dispersive X-ray fluorescence both before and after equilibrium with aqueous phases at different pH. The phases are claimed to be stable over a broad pH range $3 < pH < 11$ but are transformed to $H_3O[UO_2AsO_4]\cdot 3H_2O$(cr) at lower pH. The experimental methods are discussed in the Appendix A entry to [2011NIP/PYK]. Solubility was approached from both over- and under-saturation, but the $\log_{10}S$ data differ systematically by about 0.5 units, where those from under-saturation are systematically higher. The shape of the curves is approximately the same, but the discrepancy in the solubility data results in a significant uncertainty in the calculated value of the solubility products $pK_s^o$ for the Reaction (A.144), reported in Table A-86.

The authors have assumed congruent dissolution of the solid phases, but this is not evident from the elemental analyses of the aqueous phase. The X-ray diffraction data on the solid phase after equilibrium cannot be used as evidence for phase-transformation if only a small amount of a new phase is formed. The calculation of the solubility products requires corrections for the speciation of the components in the aqueous phase and an estimate of the activity factors. Chernorukov *et al.* describe the details, but this review notes that not all auxiliary data have been critically reviewed by NEA. The values of $pK_s^o$ reported in Table A-86 are discussed in the main text together with other literature data.

$$M[UO_2AsO_4]_2\cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + AsO_4^{3-} + nH_2O(l) \qquad (A.144)$$

Table A-86: Solubility products for the $M[UO_2AsO_4]_2{\cdot}nH_2O$(cr) as reported in [2009CHE/NIP].

| Solid phase | $pK_s^o$ |
|---|---|
| $Mg[UO_2AsO_4]_2{\cdot}10H_2O$(cr) | (44.7 ± 0.3) |
| $Ca[UO_2AsO_4]_2{\cdot}10H_2O$(cr) | (44.4 ± 0.3) |
| $Sr[UO_2AsO_4]_2{\cdot}8H_2O$(cr) | (45.1 ± 0.3) |
| $Ba[UO_2AsO_4]_2{\cdot}7H_2O$(cr) | (44.7 ± 0.3) |

Chernorukov *et al.* have also calculated the equilibrium constants for a number of phase transitions that are given in Table A-87.

Table A-87: Equilibrium constants for phase transformations in the $M[UO_2AsO_4]_2{\cdot}nH_2O$(cr) systems determined in [2009CHE/NIP]. Chemical formulae as reported in the original publication.

| Reaction | $K^o$ |
|---|---|
| $Mg(AsUO_6)_2{\cdot}10H_2O(solid) + 2H^+(sln) \rightleftharpoons 2HAsUO_6{\cdot}4H_2O(solid) + Mg^{+2}(sln) + 2H_2O(l)$ | $8.39 \times 10^1$ |
| $Ca(AsUO_6)_2{\cdot}10H_2O(solid) + 2H^+(sln) \rightleftharpoons 2HAsUO_6{\cdot}4H_2O(solid) + Ca^{+2}(sln) + 2H_2O(l)$ | $1.63 \times 10^2$ |
| $Sr(AsUO_6)_2{\cdot}8H_2O(solid) + 2H^+(sln) \rightleftharpoons 2HAsUO_6{\cdot}4H_2O(solid) + Sr^{+2}(sln)$ | $3.40 \times 10^1$ |
| $Ba(AsUO_6)_2{\cdot}8H_2O(solid) + 2H^+(sln) + H_2O(l) \rightleftharpoons 2HAsUO_6{\cdot}4H_2O(solid) + Ba^{+2}(sln)$ | $8.79 \times 10^1$ |
| $3Mg(AsUO_6)_2{\cdot}10H_2O(solid) + 18NaOH(sln) \rightleftharpoons 3Na_2U_2O_7{\cdot}6H_2O(solid) + Mg_3(AsO_4)_2(sln) + 4Na_3AsO_4(sln) + 21H_2O(l)$ | $2.78 \times 10^{15}$ |
| $3Ca(AsUO_6)_2{\cdot}10H_2O(solid) + 18NaOH(sln) \rightleftharpoons 3Na_2U_2O_7{\cdot}6H_2O(solid) + Ca_3(AsO_4)_2(sln) + 4Na_3AsO_4(sln) + 21H_2O(l)$ | $5.37 \times 10^{15}$ |
| $Sr(AsUO_6)_2{\cdot}8H_2O(solid) + 6NaOH(sln) \rightleftharpoons SrU_2O_7{\cdot}4H_2O(solid) + 2Na_3AsO_4(sln) + 7H_2O(l)$ | $1.44 \times 10^{15}$ |
| $Ba(AsUO_6)_2{\cdot}7H_2O(solid) + 6NaOH(sln) \rightleftharpoons BaU_2O_7{\cdot}4H_2O(solid) + 2Na_3AsO_4(sln) + 6H_2O(l)$ | $1.34 \times 10^{15}$ |

The solubility of the uranyl(VI) arsenate phases are significantly larger than those of the corresponding phosphate phases.

We note that the Gibbs energies of formation are in good agreement with previous studies, [2006SUL/CHE] and [1996KAR/CHE].

$\Delta_f G_m^o$ ($Mg[UO_2AsO_4]_2{\cdot}10H_2O$, cr, 298.15 K) = – (6292 ± 30) kJ mol$^{-1}$

$\Delta_f G_m^o$ ($Ca[UO_2AsO_4]_2{\cdot}10H_2O$, cr, 298.15 K) = – (6386 ± 30) kJ mol$^{-1}$

$\Delta_f G_m^o$ ($Sr[UO_2AsO_4]_2{\cdot}8H_2O$, cr, 298.15 K) = – (5927 ± 30) kJ mol$^{-1}$

$\Delta_f G_m^o$ ($Ba[UO_2AsO_4]_2{\cdot}7H_2O$, cr, 298.15 K) = – (5670 ± 30) kJ mol$^{-1}$.

**[2012CHE/NIP]**

Chernorukov *et al.* have studied the solubility, solubility products and phase transformations of the compounds $M[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr)$; M = Mn, Co, Ni, Cu, Zn, Cd, Pb, at 25 °C. The solubility determinations were made in test solutions with the concentrations of $HClO_4$ equal to 100, 10, 1 and 0.1 mM, pure water and 1000, 100, 10, 1 and 0.1 mM NaOH, and measuring the pH after equilibration. The phase composition before and after equilibration was determined using X-ray diffraction; the solubility was measured using the total concentrations of U and As. The equilibrium concentrations of U and As were approximately equal in the test solutions with 100, 10 and 1 mM $HClO_4$ and only these data could be used to determine solubility products for Reaction (A.145):

$$M[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2AsO_4^{3-} + nH_2O(l) \qquad (A.145)$$

The phase-analyses demonstrated that the following reactions took place:

At pH < 1.5 for Pb and 2.2 for Mn and the other compounds:

$$M[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr) + 2H^+ \rightleftharpoons (H_3O)_2[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr) + M^{2+} + (n-2)H_2O(l) \qquad (A.146)$$

This is an ion exchange reaction as shown by the identification of $H_3O^+$ using IR.

The data in the intermediate pH range ≈ 1.5 – 2.2 < pH < 7 are the ones where the dissolution Reaction (A.145) is congruent. At higher pH the phase analysis identified the formation of $UO_3 \cdot 2H_2O(cr)$, $Na_2U_2O_7(cr)$ and $Ni(OH)_2(cr)$ corresponding to the reactions below. In the range 8 < pH < 11

$$M[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr) + 6NaOH \rightleftharpoons UO_3 \cdot 2H_2O(cr) + M(OH)_2(cr) + 2Na_3AsO_4(cr) + (n-2)H_2O(l) \qquad (A.147)$$

At pH > 11

$$M[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr) + 6NaOH \rightleftharpoons NaU_2O_7(cr) + M(OH)_2(cr) + 2Na_2HAsO_4(cr) + (n+1)H_2O(l) \qquad (A.148)$$

There are only six to eight experimental solubility values where the dissolution of the solid phase is congruent as shown by the total concentration of U and As and these were corrected for the actual speciation in the test solutions using the protonation constants of $AsO_4^{3-}$ from [1999RUT/GEI] that are in fair agreement with the ones selected in [1992GRE/FUG], for the speciation of U(VI) the hydroxide and phosphate equilibrium constants from [1992GRE/FUG] and [2003GUI/FAN], the solubility products and hydrolysis constants for the M(II) ions were taken from Glushko *et al.* (Thermal Constants of Substances, Akad. Nauk SSSR, 1965-1981). The only constants that can be compared with the hydrolysis constants from Baes and Mesmer [1976BAE/MES], and the NEA selected values in [2005GAM/BUG] were the first

hydrolysis constant for $NiOH^+$ – (9.86 ± 0.03) and – (9.54 ± 0.14), respectively; and the corresponding values for the solubility product of $Ni(OH)_2$(cr) are, $\log_{10} K_s^o$ = – (17.2 ± 0.1) and – (17.0 ± 0.3), respectively. The corresponding quantities in the Glushko tables are – 10.75 and – 17.23, respectively, the difference in the first hydrolysis constant is significant. The hydrolysis of Pb(II) is the strongest one among the M(II) ions and will affect the speciation (including the U(VI) arsenate complex) at pH > 6, according to Figure 5 in [2012CHE/NIP], however the hydrolysis constant for $PbOH^+$ used, – 6.15 is much larger than the one suggested by Baes and Mesmer, – (7.71 ± 0.1), resulting in a correction for hydrolysis that is too large. The hydrolysis of the other M(II) ions are much smaller than those of Pb(II) suggesting that the corrections of the solubility data for hydrolysis of M(II) ions, made in [2012NIP/CHE] has no significant effect on the magnitude of the U(VI) arsenate equilibrium constants. Chernorukov *et al.* have calculated the activity coefficients of the dissolved species using SIT and the NEA selected values and report the solubility products and Gibbs energies of reaction in Table A-88. These values were discussed in the main text together with other literature data. However, the finally selected values differ from the ones in this work, up to 1 log unit.

Table A-88: Solubility products and Gibbs energy of formation for $M[(UO_2)(AsO_4)]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2AsO_4^{3-} + nH_2O(l)$.

| Solid phase | $-\log_{10} K_s^o$ | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| $Mn[(UO_2)(AsO_4)]_2 \cdot 12H_2O(cr)$ | (45.14 ± 0.40) | – (6305 ± 20) |
| $Co[(UO_2)(AsO_4)]_2 \cdot 12H_2O(cr)$ | (45.52 ± 0.40) | – (6307 ± 20) |
| $Ni[(UO_2)(AsO_4)]_2 \cdot 12H_2O(cr)$ | (45.56 ± 0.40) | – (6308 ± 20) |
| $Cu[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr)$ | (44.97 ± 0.40) | – (5356 ± 20) |
| $Zn[(UO_2)(AsO_4)]_2 \cdot 12H_2O(cr)$ | (45.05 ± 0.40) | – (6305 ± 20) |
| $Cd[(UO_2)(AsO_4)]_2 \cdot 10H_2O(cr)$ | (45.42 ± 0.40) | – (5893 ± 20) |
| $Pb[(UO_2)(AsO_4)]_2 \cdot 8H_2O(cr)$ | (46.25 ± 0.40) | – (5363 ± 20) |

The authors provide detailed information on experimental methods and data analysis. The present review has not scrutinised the auxiliary data on the M(II) hydroxides. For this reason, we have not made any calculation of the solubility data using the selected protonation constants of arsenate and Ni hydroxides. A recalculation using another set of auxiliary data would not change the relative values of $-\log_{10} K_s^o$ and for this reason the data reported by Chernorukov *et al.* are considered for the thermodynamic selection of the transition metal uranyl(VI) arsenate compounds .

**[2012GEZ/HEN]**

Gezahegne *et al.* studied the structure of uranyl(VI) arsenate complexes in solid state and solution using EXAFS, and employing quantum chemistry calculations at the DFT level for additional information. Uranyl arsenate phases are sparingly soluble under the

conditions used, despite the fact that available thermodynamic data from [2003GUI/FAN] indicate a significant solubility; Gezahegne *et al.* suggest that this is due to the lack of data on trögerite $H_3O[UO_2AsO_4]\cdot 3H_2O$(cr). In this case the modeling should be made by using an estimate of the solubility product based on the chemical analogue $H_3O[UO_2PO_4]\cdot 3H_2O$(cr). In order to obtain structure information on the mode of coordination of the arsenate, Gezahegne *et al.* mixed uranyl and arsenate solutions rapidly at pH with a "flash" cooling of the resulting solution. The rate of nucleation was sufficiently slow to allow the soluble species that are formed very rapidly, to be "frozen"; the resulting glass was then used in the EXAFS experiment. The important finding was that arsenate is coordinated in bidentate fashion as shown by the U-As distance 3.39 Å, distinctly different from the value 3.69 Å, found in solids with monodentate coordination. The conclusions from the quantum chemistry modeling of structures are essentially the same as in [2013JAC/GUT] on the corresponding phosphate systems. No thermodynamic data are reported in this study, except for energy differences between isomers with different location of protons in the coordinated arsenate.

**[2012GEZ/HEN2]**

This is a review of experimental methods, mainly based on fluorescence spectroscopy, used to study uranyl(VI)-arsenate complex formation. The experimental results have been discussed in previous publications by the authors.

## A-1.6 Uranium compounds and complexes with group 14 elements

### A-1.6.1 Carbonate compounds and complexes

**[1956BLA/COL]**

The experiments were made by dissolving $UO_2CO_3$(s) in sodium carbonate solutions. The solubility was measured by the total concentration of U(VI) using standard spectrophotometry. From the evaluation of the data, it is obvious that the predominant complex must have the ratio 1:2 between U(VI) and carbonate and the only possible complex is then $[(UO_2)_3(CO_3)_6]^{6-}$. This is demonstrated in Figure A.1 on p. 570 of [1992GRE/FUG]. However, the experimental data are not sufficiently accurate to allow a determination of the equilibrium constant for Reaction (A.149)

$$3UO_2CO_3(s) + 3CO_3^{2-} \rightleftharpoons (UO_2)_3(CO_3)_6^{6-} \qquad \text{(A.149)}$$

The experimental data of the solubility of $UO_2CO_3(s)$ in sodium carbonate solutions at 26 °C from Table 1 in [1956BLA/COL] are plotted in Figure A1, p. 570 in [1992GRE/FUG].

Blake *et al.* have also measured the solubility of $Na_4[UO_2(CO_3)_3](s)$, Reaction (A.150) and their data are shown in Table A-89.

$$Na_4[UO_2(CO_3)_3](s) \rightleftharpoons 4Na^+ + UO_2(CO_3)_3^{4-} \qquad (A.150)$$

Table A-89: Solubility of $Na_4[UO_2(CO_3)_3](s)$ in water and $NaClO_4$ solutions.

| Solution | Solubility /M |
|---|---|
| Water | 0.286 |
| 0.50 M $NaClO_4$ | 0.134 |
| 1.5 M $NaClO_4$ | 0.056 |
| 2.0 M $NaClO_4$ | 0.028 |
| 2.5 M $NaClO_4$ | 0.015 |
| 3.0 M $NaClO_4$ | 0.008 |
| 3.5 M $NaClO_4$ | 0.005 |
| 4.0 M $NaClO_4$ | 0.002 |

The solubility is high in pure water, which is consistent with the observations of Karyakin *et al.* [2004KAR/CHE], but decreases strongly at increased concentrations of $Na^+$. As shown in [1992GRE/FUG], Figure V.21, p. 328, the SIT extrapolation depends strongly on the activity factors, $\log_{10} K_{s,3}(A.150) - 20D = \log_{10} K^o_{s,3} - \Delta\varepsilon \cdot m_{Na+}$ ($D$ is the Debye-Hückel factor). The resulting value of $\log_{10} K^o_{s,3}(A.150) = -(5.34 \pm 0.16)$ is very different from the value determined by calorimetry in [2004KAR/CHE], $\log_{10} K^o_{s,3}(A.150) = -(1.968 \pm 0.588)$. This review has checked the analysis in [1992GRE/FUG] and agrees with the conclusions there. Karyakin *et al.* [2004KAR/CHE] has used an anhydrous phase that is properly characterised in their study, but this is not the case in [1956BLA/COL] and the different results for the solubility product might be due to the use of a hydrated phase in the Blake study. This review has not found information on such a phase in the literature, but notes that $NaK_3[UO_2(CO_3)_3](s)$ exists in both a hydrated and anhydrous phase, the same is true for the $M_2[UO_2(CO_3)_3](s)$ phases and $CaNa_2[UO_2(CO_3)_3](s)$, *cf.* [2005KAR/CHE], [2005KAR/CHE2], [2009CHE/KNY]. The present review has not included $\log_{10} K^o_{s,3}(A.149) = -(5.34 \pm 0.16)$ among the selected values.

Felmy *et al.* [2005FEL/XIA] have also determined the equilibrium constant for the solubility reaction:

$$Na_4[UO_2(CO_3)_3](cr) \rightleftharpoons 4Na^+ + UO_2(CO_3)_3^{4-} \qquad (A.151)$$

The analysis of these solubility data is based both on accurate information of the equilibrium constant for the uranyl(VI) carbonate complexes (the values selected in previous reviews were used for this purpose) and on proper activity coefficient data.

The latter were obtained by using the Pitzer approach, which required a determination of Pitzer parameters for $UO_2(CO_3)_3^{4-}$ and $(UO_2)_3(CO_3)_6^{6-}$ using the solubility data of Blake *et al.* [1956BLA/COL]. Felmy *et al.* found $\log_{10} K^{\circ}$ (A.151) = – 4.08, which differs significantly from $\log_{10} K^{\circ}_{s,3}$ (A.149) = – (5.34 ± 0.16).

As discussed in the section on Group 14 compounds and complexes in the main text, these values have not been accepted by the present review.

**[1980ALW/WIL]**

The authors point out the importance of carbonate for the formation of a large number of minerals and give a brief literature survey of their occurrence and formation in nature. They point out that their thermodynamic stability is not understood. The experimental part of this study consists of synthesis of the different minerals according to published methods followed by equilibration with an aqueous phase. Equilibrium was attained within 48 hours, but no information on the phase composition after equilibrium is provided. Analyses of the total concentration of the solutes were made and these data together with measured pH were used to calculate the speciation in solution using known equilibrium constants. The authors report Gibbs energies of formation from the measured solubilities but no details are given. They report the following values:

Table A-90: Thermodynamic quantities at 298.2 K for the minerals of the liebigite group

| Mineral | Formula | $\Delta_f G^{\circ}$ /kJ·mol$^{-1}$ | $\Delta_f H^{\circ}$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| liebigite | $Ca_2UO_2(CO_3)_3 \cdot 10H_2O$(cr) | – (6226 ± 12) | – (7037 ± 24) |
| swartzite | $CaMgUO_2(CO_3)_3 \cdot 12H_2O$(cr) | – (6607 ± 8) | – (7535 ± 20) |
| bayleyite | $Mg_2UO_2(CO_3)_3 \cdot 18H_2O$(cr) | – (7924 ± 8) | – (9192 ± 20) |
| andersonite | $Na_2CaUO_2(CO_3)_3 \cdot 6H_2O$(cr) | – (5651 ± 24) | – (5916 ± 36) |

Insufficient details are provided in the description this study. This review notes that the formation of ternary complexes $M_n[UO_2(CO_3)_3]^{2n-4}$ was not considered in [1980ALW/WIL] for the interpretation of the solubility data. The reported $\Delta_f G^{\circ}_m$ and $\Delta_f H^{\circ}_m$ are not accepted by this review. The data from this study have been re-evaluated in [2016END/LEG].

**[1983DEV/YEF]**

This is an important experimental study that was referred to in [1992GRE/FUG] both as [1982DEV/YEF] and [1983DEV/YEF], but no Appendix A review was given. In this study Devina *et al.* reports experimental solution calorimetric data obtained with the high-precision LKB-7000 instrument. The following reaction is studied and discussed:

$$UO_2(NO_3)_2\cdot 6H_2O(cr) + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} + 2NO_3^- + 6H_2O(l) \quad \text{(A.152)}$$

The calorimetric experiments were made at four different temperatures, 15, 25, 35 and 45 °C and different ionic strengths, up to 5 M at 25 °C and between 0.2 and 1.50 M, at the other temperatures. This allowed a determination of the enthalpy of reaction at zero ionic strength by using a SIT-type model, resulting in $\Delta_r H^o$ (A.152) values reported in Table A-91.

Table A-91: Reaction enthalpies, $\Delta_r H^o$ (A.152) and $\Delta_r H^o$ (A.154) at different temperatures.

| $T$ /K | $-\Delta_r H^o$ (A.152) /kJ·mol$^{-1}$ | $-\Delta_r H^o$ (A.154) /kJ·mol$^{-1}$ |
|---|---|---|
| 288.34 | (22.295 ± 0.380) | (42.280 ± 0.460) |
| 298.15 | (21.440 ± 0.125) | (40.620 ± 0.130) |
| 308.08 | (18.060 ± 0.220) | (36.175 ± 0.250) |
| 317.80 | (15.810 ± 0.190) | (32.630 ± 0.250) |

Devina *et al.* [1983DEV/YEF] also measured the enthalpy of reaction for:

$$UO_2(NO_3)_2\cdot 6H_2O(cr) \rightleftharpoons UO_2^{2+} + 2NO_3^- + 6H_2O(l) \quad \text{(A.153)}$$

This reaction was used to select the enthalpy of formation, $\Delta_f H^o(UO_2(NO_3)_2\cdot 6H_2O, cr) = -(3167.5 \pm 1.5)$ kJ·mol$^{-1}$.

Combination of Reactions (A.152) and (A.153) allows the determination of the enthalpy of reaction, $\Delta_r H^o$ (A.154) = – (40.620 ± 0.130) kJ·mol$^{-1}$ for Reaction (A.154), which is in excellent agreement with the value obtained by direct reaction calorimetry, $\Delta_r H^o$ (A.154) = – (39.20 ± 4.10) kJ·mol$^{-1}$ selected in [2003GUI/FAN].

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \quad \text{(A.154)}$$

Based on the entropy of reaction obtained from the enthalpy of Reaction (A.154), Devina *et al.* [1983DEV/YEF] also discuss the standard molar entropy of $UO_2(CO_3)_3^{4-}(aq)$. Based on the value, $\log_{10}\beta_3 = 21.2$, they report $\Delta_r G^o$ (A.154) = – (121.03 ± 0.14) kJ·mol$^{-1}$, which together with $\Delta_r H^o$ (A.154) = – (40.62 ± 0.13) kJ·mol$^{-1}$ gives $\Delta_r S^o$((A.154), 298.15 K) = – (269.70 ± 0.64) J·K$^{-1}$·mol$^{-1}$ as compared to – (286.6 ± 13.8) J·K$^{-1}$·mol$^{-1}$ selected in [2003GUI/FAN]. A value of $S_m^o(UO_2(CO_3)_3^{4-}, aq)$ = (24.5 ± 6.8) J·K$^{-1}$·mol$^{-1}$ was obtained from the data in [1983DEV/YEF] as compared to $S_m^o(UO_2(CO_3)_3^{4-}, aq)$ = (38.4 ± 14.4) J·K$^{-1}$·mol$^{-1}$ in [2003GUI/FAN]. The two sets of data agree within the estimated uncertainties, but the present review prefers the selected data in [2003GUI/FAN].

Devina *et al.* report $\Delta_r C_{p,m}^o$ ((A.154), 298.15 K) = (380 ± 58) J·K$^{-1}$·mol$^{-1}$, a value that is reported for information only. Using literature data they find the partial molal specific heat capacity $C_{p,m}^o(UO_2(CO_3)_3^{4-}, aq)$ = – (298 ± 77) J·K$^{-1}$·mol$^{-1}$, this value is reported for information only.

Based on a report by Rafal'skiy [1973RAF] (this report in Russian was not available to the present review), Devina *et al.* discuss the equilibrium constant for Reaction (A.155) at temperatures 100, 120, 140, 170 and 200 °C. Equilibrium constants were extrapolated to zero ionic strength using Vasil'yev equation, which has the same structure as the corresponding SIT expression.

$$0.5Na_2U_2O_7(cr) + 3HCO_3^- \rightleftharpoons UO_2(CO_3)_3^{4-} + Na^+ + 1.5H_2O(l) \quad \text{(A.155)}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad \text{(A.156)}$$

Combining Reactions (A.154), (A.155) and (A.156) gives Reaction (A.157):

$$0.5Na_2U_2O_7(cr) + 3H^+ \rightleftharpoons UO_2^{2+} + Na^+ + 1.5H_2O(l) \quad \text{(A.157)}$$

The temperature dependence of Reactions (A.154), (A.155) and (A.156) is known, and from these the temperature dependent equilibrium constant for Reaction (A.157) was calculated.

The temperature dependence of Reactions (A.154), (A.155) and (A.157) reported by Devina *et al.* is summarised in Table A-92.

Table A-92: Temperature dependence of equilibrium constants for Reactions (A.152), (A.154) and from [1983DEV/YEF].

| $t$ /°C | $\log_{10}K_s^o$ (A.155) | $\log_{10}\beta_3^o$ (A.154) | $\log_{10}K_s^o$ (A.157) |
|---|---|---|---|
| 100 | – 3.0 | 18.2 | 9.2 |
| 120 | – 3.4 | 18.8 | 8.5 |
| 140 | – 2.9 | 20.1 | 7.9 |
| 170 | – 3.8 | 20.6 | 7.0 |
| 200 | – 4.6 | 21.2 | 6.4 |

The solubility constants for Reaction (A.157) can be used to obtain the solubility constant at 298.15 K, but the long temperature extrapolation means that the constant, $\log_{10}K_s^o$ ((A.157), 298.15 K) = (13 ± 2), is not very accurate. We note however that it is of the same order of magnitude as the the more accurate value reported in [2017ALT/YAL].

The most important information for this review is that the data from Devina *et al.* provides a check of the consistency of data for the carbonate, nitrate and hydroxide systems.

**[2002AMA]**

The doctoral dissertation of Amayri provides a detailed and very useful description of preparation, structures and spectroscopic properties (IR, Raman and fluorescence spectra) of solid $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr), M = Mg, Ca, Sr, Ba, compounds. The thesis

also includes a detailed literature review. Amayri has also studied the complexation in aqueous $M^{2+}$- $UO_2^{2+}$ -carbonate systems and used time resolved laser fluorescence spectroscopy to determine the stoichiometry and equilibrium constants of the complexes formed. The structures have been deduced from a combination of EXAFS spectra from solutions and information on the solid state structures obtained by X-ray diffraction and EXAFS. There is also useful comparisons of the synthetic $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr) phases with corresponding minerals. In the present review we have focused on the solution chemical data.

The solubility of the various phases decrease in the order ≈ 200, 150, 7 to 0.1 mM from Mg to Ba as exemplified by the data at a pH of 8 (note that the solubility varies with pH); Amayari's analyses demonstrate clearly that the dissolution is congruent, but that the dissolution is slow, requiring about 20-40 days to ensure equilibrium.

Amayari has studied the following equilibrium in a 0.10 M $NaClO_4$ ionic medium:

$$pM^{2+} + UO_2(CO_3)_3^{4-} \rightleftharpoons M_p[UO_2(CO_3)_3]^{2p-4} \quad \text{(A.158)}$$

The analysis of the experimental data has been made using the two mass-balance conditions:

$$U_{tot} = [UO_2(CO_3)_3^{4-}] + [M_pUO_2(CO_3)_3^{2p-4}] \quad \text{(A.159)}$$

$$M_{tot} = [M^{2+}] + p[M_pUO_2(CO_3)_3^{2p-4}] \quad \text{(A.160)}$$

Using the equilibrium condition for Equation (A.158), one obtains:

$$\log_{10}\frac{[M_pUO_2(CO_3)_3^{2p-4}]}{[M^{2+}][UO_2(CO_3)_3]} = \log_{10}\frac{[M_pUO_2(CO_3)_3^{2p-4}]}{[M^{2+}]^p\{U_{tot} - [M_pUO_2(CO_3)_3^{2p-4}]\}} =$$

$$\log_{10}R = p\log_{10}[M^{2+}] + \log_{10}\beta \text{ (A.158)} \quad \text{(A.161)}$$

$$pM^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons M_p[UO_2(CO_3)_3]^{2p-4} \quad \text{(A.162)}$$

The concentration of $M_pUO_2(CO_3)_3^{2p-4}$ is measured by fluorescence spectroscopy, where it is important to note that the fluorescence intensity is not significantly affected by other U(VI) species. Amayri has used Equation (A.161) to obtain a value of the stoichiometric coefficient *p*, as exemplified in Figure A-9. A slope close to one suggests that the predominant complex is $MUO_2(CO_3)_3^{2-}$. The equilibrium constants reported by Amayri are listed in Table A-93.

Figure A-9: Slope analysis in [2002AMA] for the determination of the *p* stoichiometric coefficient in $Sr_pUO_2(CO_3)_3^{2p-4}$. (Reprinted with permission from the author. Copyright (2002)).

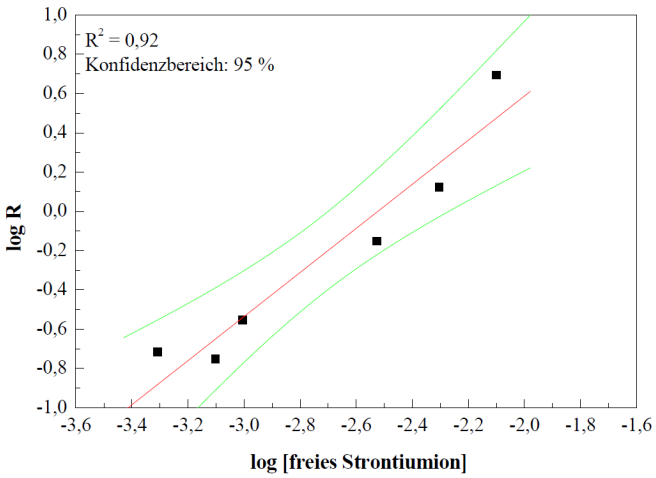



Table A-93: Equilibrium constants for Reaction (A.158) at $I$ = 0.1 and 0 M and the equilibrium constant for Reaction (A.162) at zero ionic strength using the NEA selected value for formation of $UO_2(CO_3)_3^{4-}$. The extrapolation to $I$ = 0 has been made by this review using SIT. The equilibrium constant for the formation of $CaUO_2(CO_3)_3^{2-}$ is from [2001BER/GEI].

| Complex | $\log_{10} \beta$ (A.158) /$I$ = 0.1 M | $\log_{10} \beta$ (A.158) /$I$ = 0 | $\log_{10} \beta$ (A.162) /$I$ = 0 |
|---|---|---|---|
| $MgUO_2(CO_3)_3^{2-}$ | (0.09 ± 0.05) | (1.27 ± 0.07) | (23.11 ± 0.07) |
| $CaUO_2(CO_3)_3^{2-}$ | | | 25.4 [2001BER/GEI] |
| $SrUO_2(CO_3)_3^{2-}$ | (2.50 ± 0.22) | (3.68 ± 0.22) | (25.52 ± 0.22) |
| $BaUO_2(CO_3)_3^{2-}$ | (2.61 ± 0.26) | (3.79 ± 0.26) | (25.63 ± 0.26) |

Amayari has used the equilibrium constants in Table A-93 and the equilibrium constants for U(VI) hydroxide and carbonate complexes to calculated the species distribution, an example is Figure 6.18 in his thesis, which demonstrates that the predominant U(VI) complex in the absence of M(II) is the tris-carbonato complex.

The Ca(II)-U(VI)-carbonate system has been extensively studied by Bernhard, Geipel *et al.* [1996BER/GEI], [1997BER/GEI], [1997AMA/GEI], [2001BER/GEI] and these studies were discussed in [2003GUI/FAN], but as the results were not consistent no equilibrium constants were selected.

**[2003CHE/KNY5]**

Chernorukov *et al.* have synthesised the compounds $Li_4[UO_2(CO_3)_3]\cdot 1.5H_2O$(cr), $Na_4[UO_2(CO_3)_3]$(cr), $K_4[UO_2(CO_3)_3]$, $NaK_3[UO_2(CO_3)_3]$(cr) by the reaction of $UO_2CO_3$(cr) with the aqueous solutions of the corresponding alkali metal carbonates. The compound $(NH_4)_4[UO_2(CO_3)_3]$(cr) was prepared by reaction of a solution of uranyl nitrate with a solution of ammonium carbonate. The phase purity was checked by X-ray diffraction. The chemical composition was studied by chemical (unspecified), gravimetric, thermal, and IR-spectra analyses. The lithium, potassium and ammonium derivatives crystallise in the monoclinic system, and grimselite ($NaK_3[UO_2(CO_3)_3]$) and tetrasodium tricarbonatouranylate—in the hexagonal system.

The thermochemical properties have been studied in "an upgraded calorimeter of S.M. Skuratov's design" by measuring enthalpies of solution of several compounds in 13.5 M HF at 298.15 K, see Table A-94.

Table A-94: Enthalpies of solution, $\Delta_s H^o$, of compounds in 13.5 M HF at 298.15 K.

| Compound | $\Delta_s H^o$ /kJ·mol$^{-1}$ | Compound | $\Delta_s H^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $UO_2CO_3$(cr) | – (54.0 ± 1.4) | $Li_4[UO_2(CO_3)_3]\cdot 1.5H_2O$(cr) | – (141.0 ± 1.2) |
| $Li_2CO_3$(cr) | – (44.5 ± 0.2) | $Na_4[UO_2(CO_3)_3]$ (cr) | – (99.9 ± 0.4) |
| $Na_2CO_3$(cr) | – (49.6 ± 0.1) | $NaK_3[UO_2(CO_3)_3]$(cr) | – (133.8 ± 0.4) |
| $K_2CO_3$(cr) | – (43.1 ± 0.1) | $K_4[UO_2(CO_3)_3]$(cr) | – (113.4 ± 1.3) |
| $H_2O$ | 0 | $(NH_4)_4[UO_2(CO_3)_3]$(cr) | – (64.0 ± 0.3) |
| $NH_4Cl$(cr) | (10.9 ± 0.3) | KCl(cr) | (3.4 ± 0.2) |

Obtained results have been combined to determine the enthalpies of formation of tricarbonatouranylates, see Table A-95. As auxiliary data the enthalpies of formation, in kJ·mol$^{-1}$, of several compounds from the old Glushko handbook ([1968GLU/MED], [1978GLU/GUR], [1981GLU/MED]) were employed: $UO_2CO_3$(cr) – (1698.0 ± 8.0), $Na_2CO_3$(cr) – (1129.43 ± 0.25), $Li_2CO_3$(cr) – (1215.5 ± 1.2), $K_2CO_3$(cr) – (1153.0 ± 2.0), KCl(cr) – (436.6 ± 0.3), $NH_4Cl$(cr) – (314.22 ± 0.33). The NEA database has different values for auxiliary compounds: $UO_2CO_3$(cr) – (1691.3 ± 1.8) [2003GUI/FAN], $Na_2CO_3$(cr) – (1129.25 ± 0.30) (see Chapter 14), $Li_2CO_3$(cr) – (1214.1 ± 1.0) [1982GLU/GUR], $K_2CO_3$(cr) – (1151.5 ± 2.0) [1982GLU/GUR], KCl(cr) – (436.461 ± 0.129) [2005GAM/BUG], $NH_4Cl$(cr) – (315.12 ± 0.50) (see Chapter 14), and the current review recalculated $\Delta_f H^o$ of tricarbonatouranylates to provide consistency with the NEA database, see the last column of Table A-95. For the case of the lithium phase the value of the relative partial molar enthalpy of water in the HF medium, $L_1$ = – 0.34 kJ mol$^{-1}$, was accounted for.

Table A-95: Enthalpies of formation, $\Delta_f H^o$, (kJ·mol$^{-1}$) of compounds at 298.15 K. Original results of the authors of [2003CHE/KNY5] are given in parentheses; the recalculated in this review values are selected and given in bold.

| Compound | Original values of [2003CHE/KNY5] | Values recalculated in this review |
|---|---|---|
| $Li_4[UO_2(CO_3)_3]\cdot 1.5H_2O$(cr) | – (4558.5 ± 8.5) | **– (4550.8 ± 3.3)** |
| $Na_4[UO_2(CO_3)_3]$(cr) | – (4009.5 ± 8.0) | **– (4003.1 ± 2.4)** |
| $NaK_3[UO_2(CO_3)_3]$(cr) | – (4001.0 ± 8.5) | **– (3992.8 ± 3.8)** |
| $K_4[UO_2(CO_3)_3]$(cr) | – (4030.0 ± 8.5) | **– (4021.1 ± 4.8)** |
| $(NH_4)_4[UO_2(CO_3)_3]$(cr) | – (3560.5 ± 8.5) | **– (3555.1 ± 4.6)** |

Analogous data have been reported in later works of this research group: [2004KAR/CHE] for $Na_4[UO_2(CO_3)_3]$(cr), [2005KAR/CHE] for $K_4[UO_2(CO_3)_3]$(cr), [2005KAR/CHE2] for $NaK_3[UO_2(CO_3)_3]$(cr).

**[2003DEV/SER]**

This is a careful experimental study of rutherfordine, $UO_2CO_3$(cr) and schoepite, $UO_2(OH)_2$(cr, α) phases using calorimetric and solubility data; the authors have also made a detailed review of the previous literature that includes several of their own studies. Based on their survey of the literature they also question the CODATA value of the Gibbs energy and molar entropy of $UO_2^{2+}(aq)$. The study is based on [1983DEV/YEF] that was referred to, but not reviewed in [1992GRE/FUG].

Reaction calorimetry was used to study Reaction (A.163) at different $Na_2CO_3$ concentrations from 0.40, 0.80 and 1.9 M (corresponding to ionic strength from 1.2 to 5.7 M), with the experimental enthalpies of reaction are shown in Table A-96.

$$UO_2CO_3(cr) + 2CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \qquad (A.163)$$

Table A-96: Experimental dissolution enthalpy of $UO_2CO_3$(cr, rutherfordine) in $Na_2CO_3$ solutions at 298.15 K: $UO_2CO_3(cr, rutherfordine) + 2CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-}$.

| $UO_2CO_3$(cr) sample weight | | $I$ | $\varepsilon \times 10^{-3}$ | $Q$ | $Q - Q_{amp}$ | $\Delta_r H$(l) |
|---|---|---|---|---|---|---|
| g | mol × 10$^4$ | | J·Ω$^{-1}$ | J | | kJ·mol$^{-1}$ |
| 0.10881 | 3.2968 | 1.253 | 10762.50 | 11.139 | 11.181 | – 33.912 |
| 0.13326 | 4.0377 | 1.256 | 10765.49 | 12.771 | 12.812 | – 31.731 |
| 0.10246 | 3.1044 | 2.508 | 10764.44 | 10.310 | 10.352 | – 33.345 |
| 0.17836 | 5.4043 | 2.508 | 11125.15 | 16.440 | 16.480 | – 30.495 |
| 0.13281 | 4.0240 | 2.511 | 10850.14 | 14.090 | 14.131 | – 35.118 |
| 0.10801 | 3.2726 | 5.750 | 11030.01 | 9.387 | 9.428 | – 28.810 |
| 0.11946 | 3.6196 | 5.750 | 11047.73 | 12.358 | 12.399 | – 34.256 |

Note: $I$ is ionic strength of the solution. $\varepsilon$ is heat capacity of the calorimeter. $Q$ is the heat effect of the reaction. $Q - Q_{amp}$ is heat effect of the reaction with a correction for the heat effect of the broken empty ampoule, and $\Delta_r H$(l) is the enthalpy of the reaction.

The samples of $UO_2CO_3$(cr) used by the authors were carefully analysed and had a phase purity around 99.9 %, hence the scatter of the experimental heats of reaction are most likely due to systematic errors; *e.g.*, in the slow rate of dissolution in the calorimeter that could take more than one hour, which will make corrections for heat exchange with the surrounding difficult (it is not clear from the paper if the calibration to determine the heat equivalent of the calorimeter was made over such long periods of time). From the data in their Table A-96 it is clear that the systematic error in the experiments can amount to between 3 and 5.5 kJ·mol$^{-1}$. Slow dissolution will result in a less negative heat of reaction and one should therefore not use an average of the experimental values, but the most negative one; Devina *et al.* have instead used the average of all experiments and extrapolated the experimental heats of reaction, $\Delta_r H$ at 298.15 to zero ionic strength using an equation based on the Debye-Hückel theory from the doctoral thesis of Igor Khodakovskii and report $\Delta_r H$ ((A.163), $I = 0$) = – (37.66 ± 2.8) kJ·mol$^{-1}$. As details of the latter were not available to the reviewers, we have used Equation IX.72 from *Modelling in Aquatic Chemistry* [1997GRE/PLY2] to extrapolate the data at $I$ = 1.25 and 2.50 M to zero ionic strength. The present review has not included the experimental enthalpy of reaction at the highest ionic strength, 5.75 M and obtains the following enthalpies of reaction at zero ionic strength were, $\Delta_r H^o_m$ ((A.163), 1.25 M) = – (38.0 ± 3.0) kJ·mol$^{-1}$ and $\Delta_r H^o_m$ ((A.163), 2.50 M) = – (40.7 ± 3.0) kJ·mol$^{-1}$. Based on these, we find the average value – (39.4 ± 3.0) kJ·mol$^{-1}$, which within the estimated uncertainty is identical with the value reported by Devina *et al.*

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \qquad \text{(A.164)}$$

$$UO_2CO_3(\text{cr, rutherfordine}) \rightleftharpoons UO_2^{2+} + CO_3^{2-} \qquad \text{(A.165)}$$

The enthalpy of reaction, $\Delta_r H^o_m$ ((A.164), 298.15 K) = – (40.6 ± 0.5) kJ·mol$^{-1}$ used in [2003DEV/SER] is taken from the study by Devina *et al.* [1983DEV/YEF] that report – (40.63 ± 0.13) kJ·mol$^{-1}$; this value is slightly different from that selected in [2003GUI/FAN], $\Delta_r H^o_m$ ((A.164), 298.15 K) = – (39.2 ± 4.1) kJ·mol$^{-1}$ that was based on a larger number calorimetric studies and the present review has for this reason preferred this value and corrected the data in [2003DEV/SER] accordingly.

The enthalpy of dissolution of rutherfordine in Reaction (A.165), reported by Devina *et al.* is $\Delta_r H^o_m$ ((A.165), 298.15 K) = (2.9 ± 2.8) kJ·mol$^{-1}$. Based on our enthalpies of reaction, we prefer a slightly different value, $\Delta_r H^o_m$ ((A.165), 298.15 K) = – (0.2 ± 5.1) kJ·mol$^{-1}$. Using this value and the selected enthalpies of formation of $UO_2^{2+}$(aq) and $CO_3^{2-}$(aq), this review calculates the standard enthalpy of formation of $UO_2CO_3$(s), $\Delta_f H^o_m$($UO_2CO_3$, cr, 298.15 K) = – (1694.0 ± 5.3) kJ·mol$^{-1}$. This value is consistent, within the estimated uncertainty, with the selected value in [1992GRE/FUG] and [2003GUI/FAN], $\Delta_f H^o_m$($UO_2CO_3$, cr, 298.15 K) = – (1691.3 ± 1.8) kJ·mol$^{-1}$, which is retained by the present review. However, the difference is significant from the value

reported by Kubatko *et al.* [2005KUB/HEL], $\Delta_f H_m^o(UO_2CO_3, cr, 298.15\ K) = -(1716.4 \pm 4.2)\ kJ{\cdot}mol^{-1}$.

Equilibria in the $UO_3$-$CO_2(g)$-$H_2O(l)$ system has been investigated by Sergeyeva *et al.* [1972SER/NIK] that studied Reaction (A.166) over the temperature range 25-200 °C.

$$UO_2CO_3(cr, rutherfordine) + H_2O(l) \rightleftharpoons UO_2(OH)_2(cr, \alpha) + CO_2(g) \qquad (A.166)$$

From the temperature dependence of the equilibrium constant they report, $\Delta_r H$ (A.166) = $(55.65 \pm 7.5)\ kJ{\cdot}mol^{-1}$. Using this value and the selected enthalpies of formation of $UO_2CO_3$(cr), $H_2O$(l) and $CO_2$(g) this review finds, $\Delta_f H_m^o(UO_2(OH)_2, cr, 298.15\ K) = -(1528.0 \pm 7.7)\ kJ{\cdot}mol^{-1}$. The thermodynamics of hydrated $UO_3$ phases was discussed in [2003GUI/FAN] that suggest an enthalpy of formation for $UO_3{\cdot}H_2O \equiv UO_2(OH)_2$, $\Delta_f H_m^o(UO_2(OH)_2, cr, \alpha, 298.15\ K) = -(1536.4 \pm 1.9)\ kJ{\cdot}mol^{-1}$, $\Delta_f H_m^o(UO_2(OH)_2, cr, \beta, 298.15\ K) = -(1533.8 \pm 1.3)\ kJ{\cdot}mol^{-1}$ and $\Delta_f H_m^o(UO_2(OH)_2, cr, \gamma, 298.15\ K) = -(1531.4 \pm 1.3)\ kJ{\cdot}mol^{-1}$; all these values agree within the estimated uncertainty, confirming the reliability of the studies and also that the enthalpies of formation of $UO_2CO_3$(cr) and $UO_2(OH)_2$(cr) are consistent.

The solubility product of rutherfordine has been determined in several investigations that are reviewed by Devina *et al.* in their Table 6; from these data they have selected the solubility product, $\log_{10} K_s^o = -(14.37 \pm 0.10)$ for Reaction (A.165) using a different extrapolation method than SIT. This value is in good agreement with that selected in [1992GRE/FUG], $\log_{10} K_s^o = -(14.49 \pm 0.04)$, but not with the value selected in [2003GUI/FAN], $\log_{10} K_s^o = -(14.76 \pm 0.02)$. The difference between the selected values in the two NEA reviews may be a result of a higher solubility for a less crystalline solid as argued by Guillaumont *et al.*, the present review agrees and therefore accepts their selection in [2003GUI/FAN] and the corresponding Gibbs energy of reaction, $\Delta_r G_m^o$ (A.165) = $(84.25 \pm 0.11)\ kJ{\cdot}mol^{-1}$.

Devina *et al.* note that there is a discrepancy between the enthalpy of formation of $UO_2CO_3$(cr) obtained from their solubility data and the entropy $S_m^o(UO_2CO_3, cr, 298.15\ K)$ and the value obtained by calorimetry and they speculate that one reason for the discrepancy might be related to the CODATA value for $UO_2^{2+}$. To explore this idea they have a detailed discussion of the thermodynamics of Reaction (A.166) for which the thermodynamics does not depend on the enthalpy of formation and the entropy of $UO_2^{2+}$; their arguments were discussed in detail in [2003GUI/FAN].

The comparison uses solubility data for the two phases, the enthalpy of formation of $UO_2(OH)_2$(cr, α) and the third law method, to calculate enthalpy of formation of $UO_2CO_3$(cr, rutherfordine); the enthalpy of formation of $UO_2(OH)_2$(cr, α) is based on the data from Gurevich *et al.* [1997GUR/SER]. The resulting enthalpy of reaction, $\Delta_f H_m^o(UO_2CO_3, cr, 298.15\ K) = -(1690.8 \pm 1.7)\ kJ{\cdot}mol^{-1}$ is marginally different from the one obtained by calorimetry. This review has made the same

calculation but instead using the selected Gibbs energy of Reaction (A.165) from [2003GUI/FAN] and then finds $\Delta_f H_m^o(UO_2CO_3, cr, 298.15\ K) = -(1693.0 \pm 3.2)$ kJ·mol$^{-1}$. It is not obvious to this review that there is an error in the CODATA values of the Gibbs energy of formation and entropy of $UO_2^{2+}$.

The enthalpy of formation of $UO_2(OH)_2$(cr, α) is discussed in some detail in [2003GUI/FAN] and also in the present review. The value of the solubility constant, $\log_{10}{}^*K_s^o = (5.96 \pm 0.1)$ used in [2003DEV/SER] is based on the data from Sandino and Bruno [1992SAN/BRU], that report $\log_{10}{}^*K_s^o = (6.23 \pm 0.14)$.

$$UO_2(OH)_2 \cdot H_2O(cr, \text{schoepite}) + 2H^+ \rightleftharpoons UO_2^{2+} + 3H_2O \qquad (A.167)$$

$$UO_2(OH)_2(cr, \alpha) + 2H^+ \rightleftharpoons UO_2^{2+} + H_2O \qquad (A.168)$$

Devina *et al.* used their data to calculate the phase stability at different temperatures. At partial pressures of $CO_2$(g) $\log P_{co2} \geq -1.3$ and temperatures below 333 K rutherfordine is the stable phase and at higher temperature and $P_{co2} < -1.3$, the stable phase is $UO_2(OH)_2$(cr, α).

**[2003VAZ/BO]**

Vázquez *et al.* have used quantum chemistry at the DFT level to study the structures of uranyl(VI) carbonate, acetate and malonate complexes, where only the carbonate complexes are relevant for the present review. The bond distances in $UO_2(CO_3)_3^{4-}$ agree both with experimental EXAFS data and other quantum chemistry calculations. The most interesting information concerns the geometry of $Ca_2[UO_2(CO_3)_3]$ where the quantum chemistry value of the U-Ca distances is consistent with the one in an EXAFS study, 3.94 Å; in the structure $Ca^{2+}$ acts as a bridge between adjacent carbonate ligands.

**[2004KAR/CHE]**

Karyakin *et al.* have determined the enthalpy of formation of $Na_4[UO_2(CO_3)_3]$(cr) using reaction calorimetry. The thermodynamic cycle used involves determination of the heats of solution of the following reactions:

$$UO_2CO_3(cr) + HF(13.5\ M) \rightleftharpoons sln1 \qquad (A.169)$$

the enthalpy of reaction is denoted $\Delta_r H$(A.169).

$$Na_2CO_3(cr) + sln1 \rightleftharpoons sln2 \qquad (A.170)$$

the reaction products are $UO_2(CO_3)_3^{4-}$, fluoride and $CO_2$(g)/$HCO_3^-$ with the enthalpy of reaction $\Delta_r H$(A.170).

$$Na_4[UO_2(CO_3)_3](cr) + HF(13.5\ M) \rightleftharpoons sln\ 3 \qquad (A.171)$$

with the enthalpy of reaction $\Delta_r H$(A.171).

Conditions are arranged in such a way that the compositions of solutions 1 and 3 are very near the same. Using Hess law the enthalpy of reaction $\Delta_r H$(A.172) is calculated with experimental uncertainties within parenthesis.

$$UO_2CO_3(cr) + 2Na_2CO_3(cr) \rightleftharpoons Na_4[UO_2(CO_3)_3](cr) \qquad (A.172)$$

$\Delta_r H$(A.172) = $\Delta_r H$(A.171) – $\Delta_r H$(A.169) – 2 × $\Delta_r H$(A.170) = (99.9 ± 0.4) – (49.6 ± 0.1) – 2 × (54.0 ± 1.4) = – (53.3 ± 2.8) kJ·mol$^{-1}$.

Using the known enthalpies of formation of $UO_2CO_3$(cr) and $Na_2CO_3$(cr) one obtains:

$\Delta_r H$(A.172) = $\Delta_f H^o$($Na_4[UO_2(CO_3)_3]$, cr) – $\Delta_f H^o$($UO_2CO_3$, cr) – 2 × $\Delta_f H^o$($Na_2CO_3$, cr).

The following enthalpies of formation were used by Karyakin *et al.*: $\Delta_f H^o$($UO_2CO_3$, cr) = – (1698.0 ± 8.0) kJ·mol$^{-1}$ and $\Delta_f H^o$($Na_2CO_3$, cr) = – (1129.43 ± 0.25) kJ·mol$^{-1}$, the latter from Robie and Hemingway [1995ROB/HEM], to give $\Delta_f H$($Na_4[UO_2(CO_3)_3]$, cr) = – (53.3 – 1698.0 – 2 × 1129.43) = – (4010.2 ± 8.0) kJ·mol$^{-1}$. This review has used the NEA selected values, $\Delta_f H^o$($UO_2CO_3$, cr) = – (1691.30 ± 1.80) kJ·mol$^{-1}$ and $\Delta_f H^o$($Na_2CO_3$, cr) = – (1129.3 ± 0.30) kJ·mol$^{-1}$, to recalculate the value from Karyakin *et al.* and the present review obtains $\Delta_f H$($Na_4[UO_2(CO_3)_3]$, cr) = – (4003.0 ± 2.4) kJ·mol$^{-1}$. Note that these results are very similar but not identical to ones reported earlier in [2003CHE/KNY5].

Karyakin *et al.* have also determined the heat capacity, molar entropy and thermodynamic functions for $Na_4[UO_2(CO_3)_3]$(cr). They report the heat capacity at 298.15 K, $C_p$ = (420.1 ± 2.1) J·K$^{-1}$·mol$^{-1}$, $S^o$($Na_4[UO_2(CO_3)_3]$, cr, 298.15 K) = (451.3 ± 3) J·K$^{-1}$·mol$^{-1}$ and $\Delta_f S$($Na_4[UO_2(CO_3)_3]$, cr) = – (949.0 ± 3.1) J·K$^{-1}$·mol$^{-1}$, this review obtains a value of – (949.656 ± 3.126) J·K$^{-1}$·mol$^{-1}$, using the same data and the NEA selected values. There are two phase transitions amorphous → crystal I → crystal II at (60.5 ± 0.5) K and (386 ± 5), respectively with $\Delta_{tr} H$(60.5 K) = 1.5 kJ·mol$^{-1}$ and $\Delta_{tr} S$(60.5 K) = 33 J·K$^{-1}$·mol$^{-1}$; at 386.5 K, $\Delta_{tr} H$(386.5 K) = (50.2 ± 0.1) kJ·mol$^{-1}$ and $\Delta_{tr} S$(386.5 K) = (18.0 ± 0.2).

Karyakin *et al.* have calculated the Gibbs energy of formation $\Delta_f G^o$($Na_4[UO_2(CO_3)_3]$, cr) = – (3727.0 ± 8.5) kJ·mol$^{-1}$, which was recalculated by this review to – (3719.960 ± 2.575) kJ·mol$^{-1}$; the latter value is not consistent with the selected value in [2003GUI/FAN], $\Delta_f G^o$($Na_4[UO_2(CO_3)_3]$, cr) = – (3737.7 ± 2.3) kJ·mol$^{-1}$, which was based on the solubility product from [1956BLA/COL]. Because of lack of information on the solid phase used by Blake *et al.*, the present review prefers the Gibbs energy of formation based on the recalculated calorimetric data from Karyakin *et al.* $\Delta_f G^o$($Na_4[UO_2(CO_3)_3]$, cr) = **– (3719.960 ± 2.575)** kJ·mol$^{-1}$ that is more accurate and this is therefore the new selected value.

$$Na_4[UO_2(CO_3)_3](cr) \rightleftharpoons 4Na^+(aq) + UO_2^{2+}(aq) + 3CO_3^{2-}(aq) \qquad (A.173)$$

$$4Na^+(aq) + UO_2(CO_3)_3^{4-}(aq) \rightleftharpoons Na_4[UO_2(CO_3)_3](cr) \qquad (A.174)$$

The solubility product $\log_{10}K_s$(A.173) = – (23.79 ± 0.59), calculated from the calorimetric data differs significantly from the corresponding value from [1956BLA/COL], $\log_{10}K_s$(A.173) = – (26.18 ± 0.20). The present review has for this reason selected $\log_{10}K_s$(A.173) = **– (23.790 ± 0.590)**, for the solubility product of $Na_4[UO_2(CO_3)_3]$(cr) according to Reaction (A.173).

Karyakin *et al.* have also calculated the enthalpy of reaction $\Delta_rH$(A.174) = (41.0 ± 9.0) kJ·mol$^{-1}$, using auxiliary data, $\Delta_fH^o(Na^+)$ = – (240.41 ± 0.13) and $\Delta_fH^o(UO_2(CO_3)_3^{4-})$ = – (3089.5 ± 3.8) kJ·mol$^{-1}$ from the Glushko tables; the present review has used the selected value $\Delta_fH^o(Na_4[UO_2(CO_3)_3]$, cr) = – (4003.1 ± 2.4) kJ·mol$^{-1}$, $\Delta_fH^o(Na^+)$ = – (240.34 ± 0.06) and $\Delta_fH^o(UO_2(CO_3)_3^{4-})$= – (3083.890 ± 4.430) kJ·mol$^{-1}$ to obtain the selected value, $\Delta_rH$(A.174) = **(42.150 ± 5.040)** kJ·mol$^{-1}$.

**[2005KAR/CHE]**

Karyakin *et al.* have used the same experimental technique as in [2004KAR/CHE] and report $\Delta_fH^o(K_4[UO_2(CO_3)_3]$, cr) = – (4030.0 ± 8.5) kJ·mol$^{-1}$, using their enthalpy of Reaction (A.175), $\Delta_rH^o$(A.175) = – (26.9 ± 2.0) kJ·mol$^{-1}$ and auxiliary data taken from the Glushko tables.

$$UO_2CO_3(cr) + 2K_2CO_3(cr) \rightleftharpoons K_4[UO_2(CO_3)_3](cr) \qquad (A.175)$$

The auxiliary data used by the authors are: $\Delta_fH^o(UO_2CO_3$, cr) = – (1698.0 ± 8.0) kJ·mol$^{-1}$ and $\Delta_fH^o(K_2CO_3$, cr) = – (1153.1 ± 2.1) kJ·mol$^{-1}$. Recalculation using the NEA selected values, $\Delta_fH^o(UO_2(CO_3)$, cr) = – (1691.30 ± 1.80) kJ·mol$^{-1}$ and $\Delta_fH^o(K_2CO_3$, cr) = – (1151.5 ± 2.0) kJ·mol$^{-1}$, this review finds $\Delta_fH^o(K_4[UO_2(CO_3)_3]$, cr) = **– (4021.100 ± 4.800)** kJ·mol$^{-1}$, which is our selected value. Note that these results are identical to ones reported earlier in [2003CHE/KNY5].

Karyakin *et al.* report the molar heat capacity and entropy for $K_4[UO_2(CO_3)_3]$(cr), $C_p$(298.15 K) = (362.6 ± 1.8) J·K$^{-1}$·mol$^{-1}$ and $S^o$(298.15 K) = (447.8 ± 3.0) J·K$^{-1}$·mol$^{-1}$. From the experimental entropy and the entropies of the elements (identical with the NEA selected values), Karyakin *et al.* obtain $\Delta_fS^o(K_4[UO_2(CO_3)_3]$, cr) = – (1006.1 ± 3.0) J·K$^{-1}$·mol$^{-1}$. The corresponding Gibbs energy of formation calculated using the standard enthalpy of formation is $\Delta_fG^o(K_4[UO_2(CO_3)_3]$, cr) = – (3730.0 ± 9.0) kJ·mol$^{-1}$. This value was recalculated by this review using the selected enthalpy of formation, to give $\Delta_fG^o(K_4[UO_2(CO_3)_3]$, cr) = **– (3720.960 ± 4.890)** kJ·mol$^{-1}$, which is the selected value. There is a phase transition at (403.5 ± 0.5) K, with $\Delta H_{tr}^o$ = (6.9 ± 0.1) kJ·mol$^{-1}$ and $\Delta S_{tr}^o$ = 17.1 J·K$^{-1}$·mol$^{-1}$.

Based on the thermodynamic data for $Na_4[UO_2(CO_3)_3]$(cr), $K_4[UO_2(CO_3)_3]$(cr) and $NaK_3[UO_2(CO_3)_3]$(cr), Karyakin *et al.* have calculated the enthalpy and entropy of reaction for the formation of grimselite $NaK_3[UO_2(CO_3)_3]$(cr):

$$1/4Na_4[UO_2(CO_3)_3](cr) + 3/4K_4[UO_2(CO_3)_3](cr) \rightleftharpoons K_3Na[UO_2(CO_3)_3](cr) \qquad (A.176)$$

$\Delta H^{o}_{tr}$(A.176) = (24 ± 11) kJ·mol$^{-1}$; $\Delta G^{o}_{tr}$(A.176) = (13.0 ± 11.5) kJ·mol$^{-1}$; $\Delta S^{o}_{tr}$(A.176) = (37.0 ± 3.0) J·K$^{-1}$·mol$^{-1}$, which recalculated by this review results in $\Delta H^{o}_{tr}$(A.176) = **(23.800 ± 5.300)** kJ·mol$^{-1}$, $\Delta G^{o}_{tr}$(A.176) = **(12.900 ± 5.400)** kJ·mol$^{-1}$; $\Delta S^{o}_{tr}$(A.176) = **(37.200 ± 13.100)** J·K$^{-1}$·mol$^{-1}$.

**[2005KAR/CHE2]**

Karyakin *et al.* have used the same experimental technique as in [2004KAR/CHE] and [2005KAR/CHE] and report $\Delta_f H^{o}$($NaK_3[UO_2(CO_3)_3]$, cr) = – (4001.0 ± 8.5) kJ·mol$^{-1}$. This value is based on the enthalpy of reaction, $\Delta_r H^{o}$(A.177) = – (9.7 ± 1.5) kJ·mol$^{-1}$ and the auxiliary values, $\Delta_f H^{o}$($[UO_2CO_3]$, cr) = – (1698.0 ± 8.0) kJ·mol$^{-1}$, $\Delta_f H^{o}$($K_2CO_3$, cr) = – (1153.1 ± 2.1) kJ·mol$^{-1}$ and $\Delta_f H^{o}$($Na_2CO_3$, cr) = – (1129.43 ± 0.25) kJ·mol$^{-1}$. This enthalpy of formation was recalculated using the NEA selected values, except for $Na_2CO_3$(cr) and $K_2CO_3$(cr), which are accepted even if no NEA review has been made; the recalculated value is $\Delta_f H^{o}$($NaK_3[UO_2(CO_3)_3]$, cr) **= – (3992.800 ± 3.800)** kJ·mol$^{-1}$ and this has been selected by the present review. Note that these results are identical to the ones reported earlier in [2003CHE/KNY5].

$$UO_2CO_3(cr) + 1.5K_2CO_3(cr) + 0.5Na_2CO_3(cr) \rightleftharpoons NaK_3[UO_2(CO_3)_3](cr) \qquad (A.177)$$

Karyakin *et al.* have determined the molar heat capacity and entropy of $NaK_3[UO_2(CO_3)_3]$(cr) using calorimetry and report $C^{o}_{p}$($NaK_3[UO_2(CO_3)_3]$, cr, 298.15 K) = (389 ± 2.0) J·K$^{-1}$·mol$^{-1}$ and $S^{o}$($NaK_3[UO_2(CO_3)_3]$, cr, 298.15 K) = (485.0 ± 2.1) J·K$^{-1}$·mol$^{-1}$. From this entropy value and those of the elements they obtain $\Delta_f S^{o}$($NaK_3[UO_2(CO_3)_3]$, cr) = – (955.5 ± 2.1) J·K$^{-1}$·mol$^{-1}$, a value accepted by the present review. Using their values of $\Delta_f H^{o}$($NaK_3[UO_2(CO_3)_3]$, cr) and $\Delta_f S^{o}$($NaK_3[UO_2(CO_3)_3]$, cr), Karyakin *et al.* find $\Delta_f G^{o}$($NaK_3[UO_2(CO_3)_3]$, cr) = – (3716.0 ± 9.0) kJ·mol$^{-1}$. The latter has been recalculated by the present review that finds $\Delta_f G^{o}$($NaK_3[UO_2(CO_3)_3]$, cr) = **– (3707.740 ± 3.857)** kJ·mol$^{-1}$, which is our selected value.

There is one phase transition at (395 ± 1) K with $\Delta_{tr} S$ = 2.0 JK$^{-1}$mol$^{-1}$ and $\Delta_{tr} H$ = (0.8 ± 0.1) kJ·mol$^{-1}$.

**[2005KUB/HEL]**

The enthalpy of formation of rutherfordine, $UO_2CO_3$(cr), andersonite, $CaNa_2[UO_2(CO_3)_3]·5H_2O$(cr) and grimselite, $NaK_3[UO_2(CO_3)_3]·H_2O$(cr) have been determined using drop-solution calorimetry in a high temperature oxide melt in combination with auxiliary data for the enthalpy of formation of $UO_3$(cr, γ), $Na_2O$(cr), CaO(cr), $K_2O$(cr), $CO_2$(g), $H_2O$(l) $Na_2CO_3$(cr), and $K_2CO_3$(cr) that are described in detail in Table 3 of the publication. These data are taken from Glushko and Robie and

Hemingway and have not been evaluated by the present review. The following reactions are of interest for this review:

$$UO_3(cr, 298.15\ K) + CO_2(g, 298.15\ K) \rightleftharpoons UO_2CO_3(cr, 298.15\ K)$$

$$\Delta_r H = -(99.1 \pm 4.2)\ kJ \cdot mol^{-1}.$$

$$UO_2CO_3(cr, 298.15\ K) + CaCO_3(cr, 298.15\ K) + Na_2CO_3(cr, 298.15\ K) + 5H_2O(l, 298.15\ K) \rightleftharpoons CaNa_2[UO_2(CO_3)_3] \cdot 5H_2O(cr)$$

$$\Delta_r H = -(111.7 \pm 0.2)\ kJ \cdot mol^{-1}.$$

$$UO_2CO_3(cr, 298.15\ K) + 3/2K_2CO_3(cr, 298.15\ K) + 1/2Na_2CO_3(cr, 298.15\ K) + H_2O(l, 298.15\ K) \rightleftharpoons NaK_3[UO_2(CO_3)_3] \cdot H_2O(cr)$$

$$\Delta_r H = -(139.6 \pm 16.1)\ kJ \cdot mol^{-1}.$$

Using the corresponding auxiliary data, Kubatko *et al.* obtain the following enthalpies of formation:

$\Delta_f H^o(UO_2CO_3, cr, 298.15\ K) = -(1716.4 \pm 4.2)\ kJ \cdot mol^{-1}$;

$\Delta_f H^o(CaNa_2[UO_2(CO_3)_3 \cdot 5H_2O, cr, 298.15\ K) = -(5593.6 \pm 9.1)\ kJ \cdot mol^{-1}$;

$\Delta_f H^o(NaK_3[UO_2(CO_3)_3] \cdot H_2O, cr, 298.15\ K) = -(4431.6 \pm 15.3)\ kJ \cdot mol^{-1}$.

The enthalpy of formation of rutherfordine differs significantly from the value selected in [2003GUI/FAN], and from the one in this review based on the analysis of [2003DEV/SER]. Kubatko *et al.* have not paid sufficient attention to the large number of accurate determinations of the solubility of rutherfordine and the enthalpy of formation reported in previous studies as discussed in the review of [2003DEV/SER]. The enthalpy of formation from [2005KUB/HEL] combined with the accurate data for the entropy, $S^o(UO_2CO_3, cr, 298.15\ K) = (120.10 \pm 0.1)\ J \cdot K^{-1} \cdot mol^{-1}$ from [1987GUR/SER], will result in a solubility that is orders of magnitude larger than observed experimentally. A possible explanation for the large discrepancy in the enthalpy of formation of $UO_2CO_3$(cr) might be related to uncertainties in the auxiliary data. As there are a large number of independent studies that result in a significantly different enthalpy of formation of $UO_2CO_3$(cr), the present review has not included the data from [2005KUB/HEL] in our selection, but notes that it is highly desirable to evaluate the enthalpies of formation for $Na_2O$(cr), $K_2O$(cr) and the carbonates of the alkali and alkaline earths.

The enthalpy of formation of grimselite refers to a mono-hydrate, and is thus not the same phase as the one studied by Karyakin *et al.* that report $\Delta_f H^o(NaK_3[UO_2(CO_3)_3], cr, 298.15\ K) = -(4001.0 \pm 8.5)\ kJ \cdot mol^{-1}$. Thermodynamic data for $Na_4[UO_2(CO_3)_3] \cdot H_2O$(cr) and andersonite, $CaNa_2[UO_2(CO_3)_3 \cdot 5H_2O$(cr) were not selected in previous reviews, and the new data have therefore been included in the discussion in the main text.

**[2005MIZ/GRE]**

The mechanism for carbonate exchange in the reaction:

$$UO_2(CO_3)_3^{5-} + {}^*CO_3^{2-} \rightleftharpoons UO_2({}^*CO_3)_3^{5-} + CO_3^{2-} \qquad \text{(A.178)}$$

was studied using NMR spectroscopy; the asterisk denotes C-13 enriched carbonate. These data indicate a dissociative exchange mechanism, but there are no new thermodynamic data reported that relates to the complex formation.

**[2006DON/BRO], [2008DON/BRO]**

In both studies, Dong and Brooks measured the distribution of uranyl(VI) between an anion exchanger (R) and an aqueous solution of $UO_2^{2+}$, $CO_3^{2-}$ and $M^{2+}$, where M = Mg, Ca, Sr and Ba, to study the formation of ternary complexes, $M[UO_2(CO_3)_3]^{2-}$ and $M_2UO_2(CO_3)_3(aq)$. In the first study, the experiments were made at 25 °C and pH = 8.1, in a 0.1 M $NaNO_3$ ionic medium and in the second at different ionic strength from 0.1 to 0.5 M, in this case only the Mg(II) system was studied. The experimental method is straightforward, but rests on the assumption that the activities in the resin phase are constant and that only the complex $UO_2(CO_3)_3^{4-}$ is sorbed; the constant activity condition is essential in the analysis of the ionic strength dependence of the equilibria in the Mg(II) system ([2008DON/BRO]). In the absence of $Mg^{2+}$, the equilibrium distribution of $UO_2(CO_3)_3^{4-}$ varies strongly with the ionic strength, from $2 \times 10^4$ L·kg$^{-1}$ in 0.101 M $NaNO_3$ to 40 L·kg$^{-1}$ in 0.509 M $NaNO_3$ ([2008DON/BRO]). This review has compared this experimental variation with the one expected by applying SIT on the distribution equilibrium ($\log_{10}D_o$), taking only the changes in activity in the aqueous phase into account.

$$4R\text{-}NO_3 + UO_2(CO_3)_3^{4-}(aq) \rightleftharpoons R_4\text{-}(UO_2(CO_3)_3) + 4NO_3^- \qquad \text{(A.179)}$$

We find an expected variation in $\log_{10}D_o = 0.78$, which is much smaller than the experimental value and conclude that the activities in the ion exchange phase are not constant when the concentration of $NaNO_3$ varies. Accordingly, the only conditional equilibrium constants at a constant ionic medium, in this case $I = 0.102$ M, can be used to obtain equilibrium constants at zero ionic strength.

There is a lack of experimental details in the communication and it had been helpful to have information on the total concentration of carbonate in the test solutions used; the carbonate concentration seems to have been defined by bubbling air through the test solutions and under these conditions one might have some $UO_2(CO_3)_2^{2-}$ formed in the absence of $M^{2+}$. The equilibrium data reported by Dong and Brooks, $\log_{10}\beta^o$(A.180) and $\log_{10}K^o$(A.181), have been obtained using Davies equation and these constants (see Table A-97) are in good agreement with previous observations and in excellent agreement with a later publication by Lee *et al.* [2013LEE/YUN]. The

difference between the extrapolated values using Davies equation and SIT is small in 0.102 M $NaNO_3$.

$$UO_2^{2+} + nM^{2+} + 3CO_3^{2-} \rightleftharpoons M_n[UO_2(CO_3)_3]^{2n-4} \; ; n = 1, 2 \qquad \text{(A.180)}$$

$$nM^{2+} + UO_2(CO_3)_3^{4-} \rightleftharpoons M_n[UO_2(CO_3)_3]^{2n-4}; n = 1, 2 \qquad \text{(A.181)}$$

Table A-97: Equilibrium constants at zero ionic strength obtained for Reactions (A.180) ($\log_{10}\beta_n^o$) and (A.181) ($\log_{10}K_n^o$), using the Davies equation from data in [2006DON/BRO], [2008DON/BRO].

| [2006DON/BRO] | $Mg^{2+}$ | | $Ca^{2+}$ | | $Sr^{2+}$ | | $Ba^{2+}$ | |
|---|---|---|---|---|---|---|---|---|
| *N* | $\log_{10}\beta_n^o$ | $\log_{10}K_n^o$ | $\log_{10}\beta_n^o$ | $\log_{10}K_n^o$ | $\log_{10}\beta_n^o$ | $\log_{10}K_n^o$ | $\log_{10}\beta_n^o$ | $\log_{10}K_n^o$ |
| 1 | 26.11 ± 0.04 | 4.27 ± 0.01 | 27.18 ± 0.06 | 5.34 ± 0.04 | 26.86 ± 0.04 | 5.02 ± 0.01 | 26.68 ± 0.04 | 4.84 ± 0.04 |
| 2 | – | – | 30.70 ± 0.05 | 8.86 ± 0.04 | – | – | 29.75 ± 0.07 | 7.91 ± 0.06 |
| [2008DON/BRO] $n = 1$ | 25.8 ± 0.5 | | | | | | | |

Only the experimental data in the Ca-system provide clear evidence for the formation of $M_2[UO_2(CO_3)_3](aq)$, because the equilibrium constant in the Ba-system is based on only one experimental point.

The ionic strength dependence of $\log_{10}\beta_1$ for the formation of $Mg[UO_2(CO_3)_3]^{2-}$ reported in [2008DON/BRO] provides clear indication that the variation of the conditional equilibrium constants in different ionic media, cannot be described by using SIT (or Davies equation). Application of SIT results in an interaction coefficient for Reaction (A.180), $\Delta\varepsilon = -3.4$ kg·mol$^{-1}$, which in turn would result in an interaction coefficient between $Mg[UO_2(CO_3)_3]^{2-}$ and $Na^+$ equal to $-3.0$ kg·mol$^{-1}$, which is unreasonably large (one can also note that the experimental value of $\log_{10}\beta_1$ is nearly independent of the ionic strength). This review notes that this equilibrium constant differs significantly between the two studies of Dong and Brooks, which might indicate an unknown systematic error in their studies. This review notes that $\log_{10}\beta_n^o$ has a maximum for $Ca^{2+}$, which might be related to the structure of the complex; the $M^{2+}$-ions act as bridges between adjacent carbonate ligands and this may provide a geometric constraint that in turn facilitates coordination of the ion with a proper ionic radius to provide the "best" fit. Because of the shortcomings above, the present review has not accepted the equilibrium constants in [2006DON/BRO] and [2008DON/BRO].

**[2007MEL/CHE]**

Mellah *et al.* have calculated the Gibbs energy change for the formation of $(NH_4)_4[UO_2(CO_3)_3](cr)$ using published enthalpies of reaction; these data provide information on the thermodynamic driving force for the precipitation that is of some interest for its kinetics, but not for the present review.

**[2008GEI/AMA]**

Geipel *et al.* have used TRLFS spectroscopy to study the Reactions (A.182) and (A.183)

$$n\mathrm{M}^{2+} + \mathrm{UO_2(CO_3)_3^{4-}} \rightleftharpoons \mathrm{M}_n[\mathrm{UO_2(CO_3)_3}]^{2n-4}; \quad \text{(A.182)}$$

$\mathrm{M}^{2+}$ = Mg, Sr and Ba, $n$ = 1, 2.

$$n\mathrm{M}^{2+} + \mathrm{UO_2^{2+}} + 3\mathrm{CO_3^{2-}} \rightleftharpoons \mathrm{M}_n[\mathrm{UO_2(CO_3)_3}]^{2n-4}; \quad \text{(A.183)}$$

$\mathrm{M}^{2+}$ = Mg, Sr and Ba, $n$ = 1, 2.

Their test solutions are better defined than in [2006DON/BRO] and [2008DON/BRO]. The experiment started with a test solution of 8 mM $\mathrm{HCO_3^-/CO_3^{2-}}$ that was adjusted to pH 8.0, after which U(VI) was added to a total concentration of $5 \times 10^{-5}$ M. The fluorescence intensity was measured as a function of added $\mathrm{M}^{2+}$ to obtain concentrations ranging from 0 to 10 mM. From the change in fluorescence intensity, the equilibrium constants in Table A-98 were obtained, where the equilibrium constant for formation of $\mathrm{UO_2(CO_3)_3^{4-}}$ is from [2003GUI/FAN].

Table A-98: Equilibrium constants from [2008GEI/AMA], [2006DON/BRO] and [2001BER/GEI].

| Complex formed | $\log_{10}K_{exp}$ [2008GEI/AMA] | $\log_{10}\beta_n^o$ [2008GEI/AMA] | $\log_{10}K_{exp}$ [2006DON/BRO] | $\log_{10}K_{exp}$ [2001BER/GEI] |
|---|---|---|---|---|
| $Mg[UO_2(CO_3)_3]^{2-}$ | (2.61 ± 0.09) | (26.24 ± 0.13) | (2.56 ± 0.01) | – |
| $Ca[UO_2(CO_3)_3]^{2-}$ | – | – | (3.63 ± 0.04) | (3.30 ± 0.21) |
| $Ca_2UO_2(CO_3)_3$ | – | – | (6.29 ± 0.04) | (6.26 ± 0.24) |
| $Sr[UO_2(CO_3)_3]^{2-}$ | (2.44 ± 0.09) | (26.07 ± 0.13) | (3.30 ± 0.01) | – |
| $Sr_2UO_2(CO_3)_3$ | (5.20 ± 0.43) | (29.73 ± 0.47) | – | – |
| $Ba[UO_2(CO_3)_3]^{2-}$ | (2.52 ± 0.27) | (26.16 ± 0.32) | (3.13 ± 0.02) | – |
| $Ba_2UO_2(CO_3)_3$ | (5.23 ± 0.70) | (29.76 ± 0.75) | (5.34 ± 0.06) | – |

The uncertainty in the equilibrium constants vary greatly and seems, at least for the Mg and Sr complexes, to be underestimated (the constant is obtained from the graph in their Figure 2, that is expected to be linear with unity slope, but the experimental values are scattered, they give a slope of (0.99 ± 0.20) but with a large uncertainty. The values of $\log_{10}K_{exp}$ for the formation of $M_2[UO_2(CO_3)_3](aq)$ suggest that the equilibrium constant for Reaction (A.184) is larger than for the formation of $M[UO_2(CO_3)_3]^{2-}$, which seems very unlikely.

$$\mathrm{M[UO_2(CO_3)_3]^{2-}} + \mathrm{M^{2+}} \rightleftharpoons \mathrm{M_2[UO_2(CO_3)_3](aq)} \quad \text{(A.184)}$$

**[2009CHE/KNY]**

Chernorukov *et al.* have described the synthesis of crystalline $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr), M = Mg, Ca, Sr and Ba and $n$ = 0-18, they have made chemical, gravimetric and X-ray analysis of the compounds and made a proper structure characterisation of the different phases. The dissociation temperatures have been determined using DTA analysis, and the heats of dissolution are quantified for both the hydrated and anhydrous compounds. The most important result is the enthalpy of formation determined by the reaction calorimetry cycle leading to Reaction (A.185). The thermodynamic cycle is based on heats of dissolution of $MCO_3$(cr), $UO_2CO_3$(cr) and $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr) in 13.5 M $HNO_3$, see Table A-99.

$$UO_2CO_3(cr) + 2MCO_3(cr) + nH_2O(aq, HNO_3, 13.5\ M) \rightleftharpoons M_2[UO_2(CO_3)_3]\cdot nH_2O(cr) \quad (A.185)$$

Chernorukov *et al.* report the following enthalpies of dissolution:

Table A-99: The enthalpy of dissolution, $\Delta_r H^o$, of $MCO_3$(cr), $UO_2CO_3$(cr) and $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr) (M = Mg, Ca, Sr and Ba) in 13.5 M $HNO_3$ as reported in [2009CHE/KNY].

| Compound | $\Delta_r H^o$ /kJ·mol$^{-1}$ | Compound | $\Delta_r H^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $MgCO_3$(cr) | – (49.2 ± 1.4) | $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr) | – (92.6 ± 0.2) |
| $CaCO_3$(cr) | – (51.5 ± 0.4) | $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) | – (113.3 ± 1.5) |
| $SrCO_3$(cr) | – (56.9 ± 1.4) | $Sr_2[UO_2(CO_3)_3]\cdot 8H_2O$(cr) | – (121.8 ± 1.1) |
| $BaCO_3$(cr) | – (90.7 ± 1.5) | $Ba_2[UO_2(CO_3)_3]\cdot 6H_2O$(cr) | – (213.4 ± 0.9) |
| $UO_2CO_3$(cr) | – (70.5 ± 1.4) | | |

These data were used by Chernorukov *et al.* to calculate the enthalpies of formation of tricarbonatouranylate hydrates by combining $\Delta_r H^o$ with the enthalpies of formation of $UO_2CO_3$(cr), $MCO_3$(cr) and $H_2O$ (see Table A-100). The authors gave no numerical values of $\Delta_f H^o$ for auxiliary compounds, just references to the old Glushko handbook (1968-1981).

The present review has recalculated data by using the following enthalpies of formation of auxiliary compounds (all in kJ·mol$^{-1}$): $UO_2CO_3$(cr) – (1691.3 ± 1.8) [2003GUI/FAN], $MgCO_3$(cr) – (1112.4 ± 1.0) ([NEA TDB review on Ancillary Data – to be published]), $CaCO_3$(cr, calcite) – (1207.5 ± 1.5) (see Chapter 14), $SrCO_3$(cr) – (1226.0 ± 2.0) (see Chapter 14), $BaCO_3$(cr) – (1213.0 ± 2.0) (see Chapter 14). In addition, the relative partial molar enthalpy of water in 13.5 M $HNO_3$ $\bar{L}_1$ = – 1.99 kJ·mol$^{-1}$ obtained from the heats of dilution in [1965PAR], was accounted for. The correction for the relative partial enthalpy of water is important as it results in an

enthalpy of formation of water in 13.5 M $HNO_3$ equal to – (285.83 ± 0.04) – 1.99 = – 287.82 kJ·mol$^{-1}$. The values recalculated in this review are also given in Table A-100.

Table A-100: Enthalpies of formation for the $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr) compounds as reported in [2009CHE/KNY] and recalculated by this review.

| Compound | $\Delta_f H^o$ /kJ·mol$^{-1}$ [2009CHE/KNY] | $\Delta_f H^o$ /kJ·mol$^{-1}$ Recalculated by this review |
|---|---|---|
| $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr) | – (9110 ± 9) | **– (9173.2 ± 4.2)** |
| $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) | – (7029 ± 8) | **– (7044.7 ± 3.7)** |
| $Sr_2[UO_2(CO_3)_3]\cdot 8H_2O$(cr) | – (6497 ± 10) | **– (6508.4 ± 5.5)** |
| $Ba_2[UO_2(CO_3)_3]\cdot 6H_2O$(cr) | – (5873 ± 10) | **– (5882.8 ± 5.6)** |

Chernorukov *et al.* have used differential thermal analysis to study the decomposition of the $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr) compounds and in this way determined the enthalpy of formation for the anhydrous $M_2[UO_2(CO_3)_3]$(cr) phases using the enthalpies of dehydration for Reaction (A.186) reported in Table A-101.

$$M_2[UO_2(CO_3)_3]\cdot nH_2O(cr) \rightleftharpoons M_2[UO_2(CO_3)_3](cr) + nH_2O(g) \quad \text{(A.186)}$$

Table A-101: Standard enthalpies of dehydration of $M_2[UO_2(CO_3)_3]\cdot nH_2O$(cr) compounds, M = Mg, Ca, Sr, Ba in kJ·mol$^{-1}$.

| Compound | $\Delta_{dehydr}H^o$ /kJ·mol$^{-1}$ |
|---|---|
| $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr) | (631 ± 4) |
| $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) | (391 ± 4) |
| $Sr_2[UO_2(CO_3)_3]\cdot 8H_2O$(cr) | (342 ± 4) |
| $Ba_2[UO_2(CO_3)_3]\cdot 6H_2O$(cr) | (214 ± 4) |

From the data in Table A-100 and Table A-101, the enthalpies of formation of the anhydrous $M_2[UO_2(CO_3)_3]$(cr) have been obtained; these are reported in Table A-102, where the second column are the values from Chernorukov *et al.* and the third the values corrected by this review.

Table A-102: Standard enthalpies of formation, $\Delta_f H^o(M_2[UO_2(CO_3)_3], cr)$, as reported in [2009CHE/KNY] and recalculated by this review.

| Compound | $\Delta_f H^o$ /kJ·mol$^{-1}$ [2009CHE/KNY] | $\Delta_f H^o$ /kJ·mol$^{-1}$ Recalculated by this review |
|---|---|---|
| $Mg_2[UO_2(CO_3)_3]$(cr) | – (5388 ± 10) | **– (5451.3 ± 5.8)** |
| $Ca_2[UO_2(CO_3)_3]$(cr) | – (4220 ± 9) | **– (5017.4 ± 5.5)** |
| $Sr_2[UO_2(CO_3)_3]$(cr) | – (4904 ± 11) | **– (4915.8 ± 6.8)** |
| $Ba_2[UO_2(CO_3)_3]$(cr) | – (4636 ± 11) | **– (4645.8 ± 6.9)** |

**[2009KUB/HAL]**

Kubicki *et al.* [2009KUB/HAL] have made an extensive quantum chemistry study of structures of aqua-ions, hydroxide, phosphate and carbonate complexes of U(VI), U(V) and U(IV), that include coordination number and mode of coordination of $PO_4^{3-}$, $HPO_4^{2-}$ and $H_2PO_4^-$, redox reactions between uranium carbonato complexes, and calculations of IR, Raman and NMR chemical shifts; a detailed discussion of these data is outside the scope of the present review. However, the following points are of interest:

- The constitution of the aqua-ions are $UO_2(OH_2)_6^{2+}$ and $UO_2(OH_2)_6^{+}$ (their Table 1 claims a coordination number of 7, but the reported structure has a coordination number of six), whereas other quantum chemistry studies claim $UO_2(OH_2)_5^{2+}$ or $UO_2(OH_2)_4^{2+}$; $UO_2(OH_2)_5^{+}$ and $U(OH_2)_9^{4+}$, *cf.* discussion in Section 9.2 on simple aqua-ions.
- The most stable phosphate structures have bidentate coordination of $PO_4^{3-}$, $HPO_4^{2-}$ (in $UO_2(HPO_4)_2$ one ligand is bidentate and the second monodentate coordinated); $H_2PO_4^-$ is monodentate coordinated: these results indicate that the phosphate ligand is coordinated in a similar way as in sulfate complexes. The quantum chemistry results are supported by EXAFS data in [2005HEN/TUT].
- The structure of $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_3^{5-}$ are consistent with EXAFS information.
- The structure of $Ca_2[UO_2(CO_3)_3]$ is in good agreement with the X-ray structure of the mineral liebigite [2002LOC/BUR]. Kubicki *et al.* have also calculated reaction energies but in general, these deviate very much from experimental data; this is also often the case between experimental and calculated IR/Raman frequencies and NMR data on $^{13}C$ and $^{17}O$ chemical shifts.

**[2010HEN/IKE]**

Hennig *et al.* have studied the structure of the complex $[U(CO_3)_5]^{6-}$ in solution using EXAFS and in the solid state using an X-ray structure determination of $K_6[U(CO_3)_5]\cdot 12H_2O$(cr); the agreement between bond distances in solution and solid phase is excellent as one often finds when the complex is present as a discreet unit in the solid state. The structure and composition of the complexes $[An(CO_3)_5]^{6-}$ are now well established for the An(IV) actinides. There are no thermodynamic data in this study.

**[2008GOT/GEI], [2011GOT/GEI]**

In the first study by Götz *et al.* [2008GOT/GEI], the authors use the temperature variation of the UV/VIS spectra of $UO_2(CO_3)_4^{4-}$ to calculate the enthalpy of reaction $\Delta_r H^o$(A.187) by measuring the variation of the spectra with the temperature in the range 5-70 °C. Götz *et al.* report $\Delta_r H^o$(A.187) = – (36.25 ± 4.31)

kJ·mol$^{-1}$, which is identical with the value selected in [1992GRE/FUG] and [2003GUI/FAN], $\Delta_r H^o(\text{A.187}) = -(35.9 \pm 0.8)$ kJ·mol$^{-1}$. This agreement is not surprising because Götz *et al.* have used this value when they have calculated the equilibrium constant $K$(A.187).

$$UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \qquad \text{(A.187)}$$

The study by Götz *et al.* does not provide any new thermodynamic information, but, at best, a confirmation of the selected values of $\Delta_r H^o$(A.187) and $\log_{10} K^o$(A.187) from previous reviews. In their second study [2011GOT/GEI], Götz *et al.* have focused on a comparison of UV/VIS and fluorescence spectra/lifetimes of U(VI) hydroxide and carbonate complexes over the pH range 2-11. The lifetimes have been investigated in frozen solutions, solid compounds and aqueous solution. The lifetimes in solution are very short, 6 to 12 ns for $UO_2(CO_3)_4^{4-}$, 4.2 ns for $Ca_2[UO_2(CO_3)_3](aq)$ and 18 ns for $Mg_2[UO_2(CO_3)_3](aq)$, the latter lifetime provides strong support for the formation of $M^{2+}$ complexes in solution, but not about their stoichiometry. From the experimental molar absorptivities it seems clear that the possibility to use direct spectrophotometry to identify U(VI) carbonate complexes in solution is limited, which is due to their small molar absorptivity compared to those of the hydroxide complexes. There are no new thermodynamic data in these two studies.

**[2011NAI/MER]**

Nair and Merkel have studied the sorption of U(VI) on quartz in carbonate solutions and how this is affected by the presence of $Mg^{2+}$, $Ca^{2+}$ and $Sr^{2+}$. The sorption decreases significantly in the presence of $M^{2+}$ which is ascribed to the formation of $M_x[UO_2(CO_3)_3]^{4-2x}$ complexes. There are no new thermodynamic data relating to the sorption process.

**[2013LEE/YUN]**

The equilibria in the Ca-U(VI)-carbonate system was investigated by using time resolved laser fluorescence spectroscopy in test solutions where initially all U(VI) is present as $Ca_x[UO_2(CO_3)_3]^{4-2x}$ complexes. By adding a solution of $EDTA^{4-}$ the following reaction takes place:

$$Ca_x[UO_2(CO_3)_3]^{4-2x} + EDTA^{4-} \rightleftharpoons CaEDTA^{2-} + UO_2(CO_3)_3^{4-} + (x-1)Ca^{2+} \qquad \text{(A.188)}$$

The resulting large change in fluorescence intensity, together with the known equilibrium constants for formation of binary U(VI) carbonato and EDTA complexes provides information on the equilibrium constants for Reactions (A.189) and (A.190) using an iteration method that seems satisfactory by this review.

$$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Ca[UO_2(CO_3)_3]^{2-} \qquad \text{(A.189)}$$

$$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Ca_2[UO_2(CO_3)_3](aq) \qquad (A.190)$$

This study avoids the complications encountered in experiments based on distribution equilibria between an aqueous solution and an anion-exchanger and is therefore not affected by the uncertainties discussed in the studies by Dong and Brooks, [2006DON/BRO], [2008DON/BRO]. The present review has therefore considered the equilibrium constants by Lee and Yun extrapolated to zero ionic strength, $\log_{10}\beta^o$(A.189) = (27.27 ± 0.14) and $\log_{10}\beta^o$(A.190) = (29.81 ± 0.19), as more accurate; the first constant is in good agreement with the one reported by Dong and Brooks [2006DON/BRO], but the second differs significantly.

**[2014END/RAO]**

Endrizzi and Rao have studied the interactions between $Ca^{2+}$ and $Mg^{2+}$ with the tris-carbonato complex $UO_2(CO_3)_3^{4-}$ in 0.10 and 0.50 M NaCl ionic media and determined equilibrium constants for the formation of $Mg[UO_2(CO_3)_3]^{2-}$, $Ca[UO_2(CO_3)_3]^{2-}$ and $Ca_2[UO_2(CO_3)_3](aq)$; for the Ca-complexes the enthalpies of reaction were also determined.

The Mg(II)-U(VI)-carbonate system was studied using UV/VIS spectrophotometry and a single complex, $Mg[UO_2(CO_3)_3]^{2-}$ was identified with an equilibrium constant $\log_{10}\beta_{113}$ = (24.53 ± 0.04), in 0.10 M NaCl, and $\log_{10}\beta_{113}$ = (23.62 ± 0.07) in 0.50 M NaCl, for Reaction (A.191)

$$Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Mg[UO_2(CO_3)_3]^{2-} \qquad (A.191)$$

The Ca(II)-U(VI)-carbonate system was studied using potentiometry with a Ca-selective electrode, resulting in the following equilibrium constants for Reaction (A.192) $\log_{10}\beta_{113}$ = (25.26 ± 0.04), in 0.10 M NaCl, and $\log_{10}\beta_{213}$ = (28.26 ± 0.04), for Reaction (A.192) in 0.10 M NaCl and $\log_{10}\beta_{113}$ = (24.28 ± 0.07), and $\log_{10}\beta_{213}$ = (26.81 ± 0.07), in 0.50 M NaCl.

$$nCa^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Ca_n[UO_2(CO_3)_3]^{2n-4}\ ;\ n = 1, 2 \qquad (A.192)$$

Based on the data Endrizzi and Rao, calculated the equilibrium constants at zero ionic strength using the ion-interaction coefficients, listed in their Table 2, mainly from NEA, and report:

$\log_{10}\beta^o_{113}$(Ca) = (27.00 ± 0.04), $\log_{10}\beta^o_{213}$(Ca) = (30.84 ± 0.04), $\log_{10}\beta^o_{113}$(Mg) = (26.25 ± 0.04).

Endrizzi and Rao provide detailed information on experimental procedures and data analysis and the reported equilibrium constants are, in the opinion of the present review, the most precise ones published to-date.

The enthalpy of Reaction (A.192) was measured using micro calorimetry and the authors report the following values in 0.10 M NaCl:

$\Delta_r H^o(Ca[UO_2(CO_3)_3]^{2-}) = -(47 \pm 6)$ kJ·mol$^{-1}$;

$\Delta_r H^o(Ca_2[UO_2(CO_3)_3]) = -(47 \pm 7)$ kJ·mol$^{-1}$.

Because of the low ionic strength, the present review accepts the claim of the authors that these values are also applicable at zero ionic strength.

**[2016END/LEG]**

The authors have made a careful literature review of thermodynamic data for the mineral phases liebigite ($Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr)), swartzite ($MgCa[UO_2(CO_3)_3]\cdot 12H_2O$(cr)) and bayleyite ($Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr)). The selection by the authors is mostly based on the recalculation of the values reported by [1980ALW/WIL], see Table A-103.

Table A-103: Solubility products and the corresponding Gibbs energies of formation selected in the literature review by [2016END/LEG]. These values are reported for information only.

| Mineral | $\log_{10} K_s^o \pm 3\sigma$ | $-\Delta_f G^o \pm 3\sigma$ /kJ·mol$^{-1}$ |
|---|---|---|
| Liebigite $Ca_2[UO_2(CO_3)_3]\cdot 10H_2O$(cr) | – (33.9 ± 3.0) | (5820 ± 9) |
| Swartzite $CaMg[UO_2(CO_3)_3]\cdot 12H_2O$(cr) | – (33.4 ± 6.0) | (6199 ± 9) |
| Bayleyite $Mg_2[UO_2(CO_3)_3]\cdot 18H_2O$(cr) | – (31.7 ± 4.5) | (6682 ± 4) |

**[2017LEE/VES]**

The complex formation in the ternary Mg-$UO_2$-$CO_3^{2-}$ system in weakly alkaline solutions has been studied by time-resolved laser-fluorescence spectroscopy, and EXAFS. Two different complexes were identified, $Mg[UO_2(CO_3)_3]^{2-}$ and $Mg_2[UO_2(CO_3)_3]$(aq) with equilibrium constants at zero ionic strength equal to $\log_{10}\beta_{113}$(A.193) = (25.8 ± 0.3) and $\log_{10}\beta_{213}$(A.194) = (27.1 ± 0.6), respectively; both constants are accepted by this review but we note that the Mg-complexes are significantly weaker than those for the other alkali-earth metal ions.

$$Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Mg[UO_2(CO_3)_3]^{2-} \quad \text{(A.193)}$$

$$2Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} \rightleftharpoons Mg_2[UO_2(CO_3)_3](aq) \quad \text{(A.194)}$$

The predominant reactions in the test solutions used are:

$$Mg^{2+} + UO_2(CO_3)_3^{4-} \rightleftharpoons Mg[UO_2(CO_3)_3]^{2-} \quad \text{(A.195)}$$

$$2Mg^{2+} + UO_2(CO_3)_3^{4-} \rightleftharpoons Mg_2[UO_2(CO_3)_3](aq) \quad \text{(A.196)}$$

The corresponding equilibrium constants used is the selected equilibrium constant for formation of $UO_2(CO_3)_3^{4-}$, $\log_{10}\beta_3$ = (21.84 ± 0.04) is $\log_{10}K^{o}_{113}$ (A.195) = (4.0 ± 0.3) and $\log_{10}K^{o}_{213}$ (A.196) = (5.3 ± 0.6), respectively. The authors have made an extensive discussion of fluorescence lifetimes that have been used to determine the equilibrium constants. The EXAFS data are consistent with the known structures, such as the mineral liebigite. This is a carefully made study that confirms previous studies with more details.

## A-1.6.2 Silicate compounds and complexes

**[2002GIA/HER]**

The stirred test solutions containing 0.01 M $NaNO_3$ at pH 6, initially equilibrated with atmospheric $CO_2$, were used to investigate the dissolution and transformation of soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O$(cr). At longer times, above 365 hours, the initially congruent dissolution was changed, suggesting the precipitation of a new solubility-controlling phase, the mineral clarkeite, $Na(UO_2)O(OH){\cdot}(H_2O)_{0\text{-}1}$(cr) in the form of 1-2 μm long needle-like crystals. For the clarkeite the authors evaluated the solubility product according to the reaction (omitting for convenience water of hydration):

$$Na(UO_2)O(OH)(cr) + 3H^+ \rightleftharpoons Na^+ + UO_2^{2+} + 2H_2O(l) \quad \text{(A.197)}$$

The measured average equilibrium concentration of dissolved U corresponds to a solubility product $\log_{10}{}^{*}K^{o}_{s}$ = 9.02, for the Reaction (A.197).

The authors also calculated the solubility product $\log_{10}{}^{*}K^{o}_{s}$ of soddyite according to the following reaction:

$$(UO_2)_2SiO_4{\cdot}2H_2O(cr) + 4H^+ \rightleftharpoons 2UO_2^{2+} + SiO_2(aq) + 4H_2O(l) \quad \text{(A.198)}$$

using the experimental data from [1992NGU/SIL], [1996MOL/GEI] and [1997PER/CAS], see Table A-104. When calculating the concentrations of $UO_2^{2+}$, they took into account the formation of ten hydroxy and four carbonate complexes of U(VI) using stability constants from [1992GRE/FUG] and the equilibrium constant for one silicate complex from [1992SAT/CHO]. The activity coefficients were calculated using the Davies equation. The results of their reinterpretation are given in Table A-104 (note the large difference between the recalculated values and those from original studies, demonstrating the large difference in $\log_{10}{}^{*}K^{o}_{s}$ depending on the data treatment).

Table A-104: Values of $\log_{10}{}^{*}K_{s}^{o}$ for the Reaction (A.198) reported in [1992NGU/SIL], [1996MOL/GEI] and [1997PER/CAS], and recalculated in [2002GIA/HER].

| Reference | pH | Atmosphere | $I$ /M | [U] /μm | [Si] /μm | $\log_{10}{}^{*}K_{s}^{o}$ | |
|---|---|---|---|---|---|---|---|
| | | | | | | Published | Recalculated |
| [1992NGU/SIL] | 3.0 | Ar | 0.08 | 19.3 | 5.12 | (5.74 ± 0.21) | 5.35 |
| [1996MOL/GEI] | 3.0 | $N_2$ | 0.14 | 18.0 | 9.00 | (6.03 ± 0.45) | 5.39 |
| | 3.0 | Air | 0.14 | 19.5 | 10.0 | (6.15 ± 0.53) | 5.50 |
| [1997PER/CAS] | 8.54-9.11 | Air | 0.009-0.033 | 0.29-2.24 | Calculated | (2.58 -6.36) | 2.76-6.99 |

**[2002KAR/CHE2]**

This study presents results of determination of the enthalpy of formation and the entropy of sodium uranosilicate hydrate, Na-boltwoodite, which formula is given by the authors as $Na(UO_2)(SiO_3OH)\cdot H_2O(cr)$. However, as shown below, the numerical value of the entropy of the investigated sample suggests that it contains more than 1 mole of water. Indeed, many researchers, for example, [2006ILT/LIU], [2010WAL/CLA], found the formula of the synthesised sodium boltwoodite to be $Na(UO_2)(SiO_3OH)\cdot 1.5H_2O(cr)$, while in [1992NGU/SIL] the composition of the studied phase was determined as $Na(UO_2)(SiO_3OH)\cdot 2H_2O(cr)$. The sample, investigated in [2002KAR/CHE2], contained more than 98.8 wt % of the main component. This review notes that the uncertainty in the stoichiometry of the investigated sample represents a large and difficult-to-account-for contribution to the measured thermodynamic properties.

The enthalpies of reactions were measured in a custom-made adiabatic calorimeter, with a random error below 1.5 %, as estimated by determining the standard heat of solution of KCl. Two thermochemical schemes were used to calculate the standard enthalpy of formation of sodium boltwoodite. The thermochemical cycle #1 included the measurements of heats of the following reactions at 298.15 K:

1) The enthalpy of solution of sodium uranosilicate monohydrate in a concentrated (approximately 18 m) HF solution:

$$Na(UO_2)(SiO_3OH)\cdot H_2O(cr) + 7HF(sln) \rightleftharpoons NaF(sln) + SiF_4(sln) + UO_2F_2(sln) + 5H_2O(l) \quad \text{(A.199)}$$

$\Delta_r H_m$ (A.199) = – (400.34 ± 2.03) kJ·mol$^{-1}$. The enthalpy of reaction is much more negative than the ones for similar reactions with K-, Rb-, and Cs uranosilicate monohydrates (– 249.95, – 241.23 and – 234.47 kJ·mol$^{-1}$—see [2002KAR/CHE], [2003KAR/CHE2], [2003KAR/CHE3], respectively). This review considers this as strong evidence that the investigated sample contains more than 1 mole of water.

2) The enthalpy of solution of a stoichiometric mixture of crystalline sodium nitrate, uranium (VI) oxide, and finely dispersed powder of amorphous silica in the same HF solution according to Reaction (A.200):

$$NaNO_3(cr) + UO_3(cr) + SiO_2(am, fine) + 7HF(sln) \rightleftharpoons NaF(sln) + SiF_4(sln) + UO_2F_2(sln) + 3\ H_2O(l) + HNO_3(sln) \quad \text{(A.200)}$$

$\Delta_r H_m$ (A.200) = – (237.55 ± 1.99) kJ·mol$^{-1}$.

Subtracting $\Delta_r H_m$ (A.200) from $\Delta_r H_m$ (A.199) yields $\Delta_r H_m$ (A.201) = – (162.79 ± 2.84) kJ·mol$^{-1}$ for the following reaction:

$$Na(UO_2)(SiO_3OH)\cdot H_2O(cr) + HNO_3(sln) \rightleftharpoons UO_3(cr) + SiO_2(am, fine) + NaNO_3(cr) + 2H_2O(l) \quad \text{(A.201)}$$

Using the following literature values of the standard enthalpies of formation (in kJ·mol$^{-1}$): – (1228.3 ± 3.0) for $UO_3$(cr), – (468.2 ± 0.5) for $NaNO_3$(cr), – (896.8 ± 1.5) for finely dispersed amorphous silica, – (285.84 ± 0.04) for liquid water, – (207.4 ± 0.5) for an infinitely diluted solution of $HNO_3$, the authors calculated for the standard enthalpies of formation of crystalline sodium uranosilicate monohydrate, $\Delta_f H_m^o$ (298.15 K) = – (2795.0 ± 4.5) kJ·mol$^{-1}$.

However, as the reaction medium was not pure water but a ~ 18 m HF solution, two additional corrections are needed. First, the relative partial molar enthalpy of water in 18 m HF solution, $\overline{L_1}$, which can be calculated as

$$\overline{L_1} = -\frac{m^2}{n_w}\left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_m} \approx -0.63 \text{ kJ·mol}^{-1},$$

where $\phi_L$ is the apparent relative enthalpy of HF solutions, tabulated in [1965PAR]. This correction has to be added to the enthalpy of formation of pure water and multiplied by the number of moles of water in the Reaction (A.201). The second correction concerns the change of the enthalpy of dilute solutions of $HNO_3$ in 18 m HF given by $\overline{L_2}$. However, there are no relevant calorimetric data available and it is therefore not possible to calculate $\overline{L_2}$. However, this quantity is expected to be large: for example, values of

$$\overline{L_2} = \phi_L + m\left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_w},$$

evaluated for HF and $HNO_3$ in their binary mixtures with water at 18 m [1965PAR], are equal to 16.6 and 17.6 kJ·mol$^{-1}$, respectively. In addition, there should be a contribution to the uncertainty in the $\Delta_f H_m^o$ value due to a non-stoichiometric composition of the synthesised sample of $Na(UO_2)(SiO_3OH)\cdot H_2O$(cr) (the exact chemical composition of the investigated sample was not given in the publication). For these reasons, this review expects that the uncertainty of the enthalpy of formation of sodium boltwoodite should be increased to at least ± 20 kJ·mol$^{-1}$.

The thermochemical cycle #2 involved the measurements of the enthalpy of the reaction of a stoichiometric mixture of crystalline sodium metasilicate, uranium (VI)

oxide, and finely dispersed powder of amorphous silica in the same HF solution at 298.15 K (Reaction (A.202)):

$$0.5Na_2SiO_3(cr) + UO_3(cr) + 0.5SiO_2(am, fine) + 7HF(sln) \rightleftharpoons NaF(sln) + SiF_4(sln) + UO_2F_2(sln) + 3.5\ H_2O(l) \quad \text{(A.202)}$$

$\Delta_r H_m$ (A.202) = – (310.14 ± 1.25) kJ·mol$^{-1}$.

Subtracting $\Delta_r H_m$ (A.202) from $\Delta_r H_m$ (A.199) yields $\Delta_r H_m$ (A.203) = – (90.2 ± 2.4) kJ·mol$^{-1}$ for the following reaction:

$$Na(UO_2)(SiO_3OH)\cdot H_2O(cr) \rightleftharpoons 0.5Na_2SiO_3(cr) + UO_3(cr) + 0.5SiO_2(am,fine) + 1.5H_2O(l) \quad \text{(A.203)}$$

Using the enthalpy of formation of $Na_2SiO_3$(cr) equal to – (1563.6 ± 5.0) kJ·mol$^{-1}$ from [1981GLU/MED], the authors calculated the enthalpy of formation for sodium uranyl silicate monohydrate, $\Delta_f H_m^o$ (298.15 K) = – (2797.0 ± 4.5) kJ·mol$^{-1}$, in a good agreement with the value from the thermochemical cycle #1.

Finally, the authors selected the mean value of $\Delta_f H_m^o$ (298.15 K) = – (2796.0 ± 6.0) kJ·mol$^{-1}$.

This review recalculated the authors's result as described below:

First, we note that the value of $\Delta_f H_m^o$ (298.15 K) calculated with the thermochemical cycle #2, requires a correction for 1.5 $\overline{L_l}$, which in 18 m HF solution is about – 0.9 kJ·mol$^{-1}$, see above. In addition, the NEA value of $\Delta_f H_m^o$ = – (1223.8 ± 1.2) kJ·mol$^{-1}$ should be used for $UO_3$(cr). We also employed $\Delta_f H_m^o$ – (896.6 ± 1.5) for finely dispersed amorphous silica (based on $\Delta_f H_m^o$ of α-quartz in [2003GUI/FAN] and the difference in the enthalpies of formation of α-quartz and finely dispersed amorphous silica given as (14.1 ± 1.5) kJ·mol$^{-1}$ from heats of solution in HF solutions in the handbook [1970GLU/MED]). The value of the enthalpy of formation of $Na_2SiO_3$(cr) was evaluated as follows: the handbook [1971NAU/RYZ] recommends for reaction $Na_2CO_3(cr) + SiO_2(quartz) \rightleftharpoons Na_2SiO_3(cr) + CO_2(g)$ the value $\Delta_r H_m^o$ (298.15 K) = (90.58 ± 0.96) kJ·mol$^{-1}$. Combining this value with the CODATA-based [1989COX/WAG] enthalpies of formation of quartz – (910.7 ± 1.0) and $CO_2$(g) – (393.51 ± 0.13), and the enthalpy of formation of $Na_2CO_3$(cr) from [NEA TDB review on Ancillary Data – to be published] – (1129.25 ± 0.30), one calculates for $Na_2SiO_3$(cr) $\Delta_f H_m^o$ (298.15 K) = – (1555.86 ± 2.1) kJ·mol$^{-1}$.

The recalculated value of $\Delta_f H_m^o$ ($Na(UO_2)(SiO_3OH)\cdot H_2O$, cr, 298.15 K) = – (2789.52 ± 3.74) kJ·mol$^{-1}$. However, as discussed above, this review is not confident that the composition of the studied sample corresponds to a monohydrate, but to a phase with a higher water content.

The heat capacity of the studied phase was measured in the adiabatic vacuum calorimeter BKT-3 in the temperature range 7-300 K (in all there are 97 measurements).

The error in $C_p$ measurements was 2 % below 15 K, 0.5 % at 15-40 K, and 0.2 % at $T$ = 40-300 K. These values were extrapolated to $T < 7$ K using the $T^3$ function. The numerical integration of the $C_p$ values gave $S^o_m(298.15\ K) = 291.7\ J{\cdot}mol^{-1}{\cdot}K^{-1}$. This value is incompatible with entropies of uranosilicate monohydrates of K, Rb, and Cs, which are equal to 258.7, 259.7, and 265.3 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, respectively, see [2002KAR/CHE], [2003KAR/CHE2], [2003KAR/CHE3]. In many alkali metal containing phases the increase in entropy, $S^o_m(298.15\ K)$, between the various compounds is about 10 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ between each alkali-ion phase [1982GLU/GUR]; therefore, the fact that the entropy of the Na phase is higher than those of the K, Rb, and Cs monohydrate phases is a strong indication that the Na phase is not a monohydrate.

Summing up, this review concludes that the uncertainty in composition of the studied sample, in particular the content of water, results in such large uncertainty in the enthalpy of formation, $\Delta_f H^o_m(298.15\ K)$, and the corresponding entropy, $S^o_m(298.15\ K)$, that they have not be selected in the present review.

**[2002KAR/CHE], [2003KAR/CHE2], [2003KAR/CHE3]**

These three studies from the same laboratory present results of a determination of the enthalpy of formation and the entropy of potassium [2002KAR/CHE], rubidium [2003KAR/CHE2], and caesium [2003KAR/CHE3] uranosilicate monohydrate of a common idealised formula $M(UO_2)(SiO_3OH){\cdot}H_2O(cr)$, where M = (K, Rb, or Cs). The K phase is known as a mineral boltwoodite.

The thermochemical cycles used included the measurements of heats of the following reactions at 298.15 K:

1) The enthalpy of solution of uranosilicate monohydrate in a concentrated (approximately 18 m) HF solution:

$$M(UO_2)(SiO_3OH){\cdot}H_2O(cr) + 7HF(sln) \rightleftharpoons MF(sln) + SiF_4(sln) + UO_2F_2(sln) + 5H_2O(l) \quad \text{(A.204)}$$

$\Delta_r H_m$ (A.204) = – (249.95±1.94) $kJ{\cdot}mol^{-1}$, where M = K;

$\Delta_r H_m$ (A.204) = – (241.23±2.65) $kJ{\cdot}mol^{-1}$; where M = Rb;

$\Delta_r H_m$ (A.204) = – (234.47±1.89) $kJ{\cdot}mol^{-1}$; where M = Cs.

2) The enthalpy of solution of stoichiometric mixture of crystalline potassium nitrate, or rubidium nitrate, or cesium nitrate, uranium (VI) oxide, and fine disperse powder of amorphous silica in the same HF solution:

$$MNO_3(cr) + UO_3(cr) + SiO_2(am, fine) + 7HF(sln) \rightleftharpoons MF(sln) + SiF_4(sln) + UO_2F_2(sln) + 3H_2O(l) + HNO_3(sln) \quad \text{(A.205)}$$

$\Delta_r H_m$ (A.205) = – (223.90 ± 1.96) kJ·mol$^{-1}$, where M = K;

$\Delta_r H_m$ (A.205) = – (223.89 ± 1.56) kJ·mol$^{-1}$, where M = Rb;

$\Delta_r H_m$ (A.205) = – (220.13 ± 1.75) kJ·mol$^{-1}$, where M = Cs.

Subtracting $\Delta_r H_m$ (A.205) from $\Delta_r H_m$ (A.204) yields $\Delta_r H_m$ (A.206) kJ mol$^{-1}$ for the final reaction:

$$M(UO_2)(SiO_3OH)\cdot H_2O(cr) + HNO_3(sln) \rightleftharpoons UO_3(cr) + SiO_2(am, fine) + MNO_3(cr) + 2H_2O(l) \quad \text{(A.206)}$$

$\Delta_r H_m$ (A.206) = – (26.05 ± 2.76) kJ·mol$^{-1}$, where M = K;

$\Delta_r H_m$ (A.206) = – (17.34 ± 3.08) kJ·mol$^{-1}$, where M = Rb;

$\Delta_r H_m$ (A.206) = – (15.34 ± 2.58) kJ mol$^{-1}$, where M = Cs.

Using the following literature values of the standard enthalpies of formation (in kJ·mol$^{-1}$): – (1228.3 ± 3.0) or $UO_3$(cr), – (494.6 ± 0.5) for $KNO_3$(cr), – (495.1 ± 0.5) for $RbNO_3$(cr), – (505.7 ± 0.6) for $CsNO_3$(cr), – (896.8 ± 1.5) for finely dispersed amorphous silica, – (285.84 ± 0.04) for liquid water, – (207.40 ± 0.5) for an infinitely diluted solution of $HNO_3$, the authors calculated the following standard enthalpies of formation:

$\Delta_f H_m^o$ (298.15 K) = – (2958.0 ± 4.5) kJ·mol$^{-1}$ for potassium uranosilicate monohydrate;

$\Delta_f H_m^o$ (298.15 K) = – (2967.0 ± 5.0) kJ·mol$^{-1}$ for rubidium uranosilicate monohydrate;

$\Delta_f H_m^o$ (298.15 K) = – (2980.0 ± 4.5) kJ·mol$^{-1}$ for cesium uranosilicate monohydrate.

The auxiliary data used are revised in this review as follows (in kJ·mol$^{-1}$): – (1223.8 ± 1.2) for $UO_3$(cr); – (206.85 ± 0.40) for an infinitely diluted solution of $HNO_3$ (or $NO_3^-$); – (285.83 ± 0.04) for $H_2O$(l) (all from [2003GUI/FAN]); – (494.0 ± 0.5) for $KNO_3$(cr), – (494.7 ± 0.5) for $RbNO_3$(cr), – (505.0 ± 0.5) for $CsNO_3$(cr) as recommended in [1982GLU/GUR], – (896.6 ± 1.5) for finely dispersed amorphous silica (based on $\Delta_f H_m^o$ of α-quartz in [2003GUI/FAN] and the difference in the enthalpies of formation of α-quartz and finely dispersed amorphous silica given as (14.1 ± 1.5) kJ·mol$^{-1}$ in the handbook [1970GLU/MED]). For Reaction (A.206) the recalculated values are:

$\Delta_f H_m^o$ (298.15 K) = – (2953.2 ± 3.4) kJ·mol$^{-1}$ for potassium uranosilicate monohydrate;

$\Delta_f H_m^o$ (298.15 K) = – (2962.6 ± 3.7) kJ·mol$^{-1}$ for rubidium uranosilicate monohydrate;

$\Delta_f H_m^o$ (298.15 K) = – (2974.9 ± 3.3) kJ·mol$^{-1}$ for cesium uranosilicate monohydrate.

However, as discussed in the review of [2002KAR/CHE2], these results have to be corrected for $2\overline{L_1}$ (the relative partial molar enthalpy of water) in ~18 m HF aqueous solution, this correction will make the calculated $\Delta_f H_m^o$ values by 1.2-1.3

kJ·mol$^{-1}$ more negative. The second correction is for $\overline{L_2}$, the relative partial molar enthalpy of the dilute solutions of $HNO_3$ in ~ 18 m HF. The value of $\overline{L_2}$ is not known, however, it may be large, up to 20 kJ·mol$^{-1}$, thus making accurate calculations of enthalpies of formation of alkali metal uranyl silicates impossible. For these reasons, this review expects that the uncertainties should be increased up to 20 kJ·mol$^{-1}$:

$\Delta_f H_m^o$ (298.15 K) = – (2953.2 ± 20.0) kJ·mol$^{-1}$ for potassium uranosilicate monohydrate;

$\Delta_f H_m^o$ (298.15 K) = – (2962.6 ± 20.0) kJ·mol$^{-1}$ for rubidium uranosilicate monohydrate;

$\Delta_f H_m^o$ (298.15 K) = – ( 2974.9 ± 20.0) kJ·mol$^{-1}$ for cesium uranosilicate monohydrate.

The heat capacity of crystalline potassium, rubidium and casium uranosilicate monohydrates were measured in the adiabatic vacuum calorimeter BKT-3 in the temperature range ~ 6-300 K (in all there are about 100 measurements for each phase). The error in $C_p$ measurements was 2 % below 15 K, 0.5 % at 15-40 K, and 0.2 % at $T$ = 40-300 K. The heat capacity values were extrapolated to $T < 7$ K using the $T^3$ function. The numerical integration of $C_p$ values gave the following values of $S_m^o$ (298.15 K):

$S_m^o$ (298.15 K) = (258.7 ± 12.0) J·mol$^{-1}$·K$^{-1}$ for potassium uranosilicate monohydrate;

$S_m^o$ (298.15 K) = (259.7 ± 12.0) J·mol$^{-1}$·K$^{-1}$ for rubidium uranosilicate monohydrate;

$S_m^o$ (298.15 K) = (265.3 ± 12.0) J·mol$^{-1}$·K$^{-1}$ for cesium uranosilicate monohydrate.

As no compositions of the investigated samples were reported, this review uses conservative estimates of the uncertainty of $S_m^o$ equal to ± 12 J·mol$^{-1}$·K$^{-1}$.

Using the values of the entropies of elements in their standard states accepted in NEA TDB (in J·mol$^{-1}$·K$^{-1}$): (64.68 ± 0.20) for K(cr), (76.78 ± 0.30) for Rb(cr), (85.23 ± 0.40) for Cs(cr), (130.680 ± 0.003) for $H_2$(g), (18.81 ± 0.08) for Si(cr), (50.20 ± 0.20) for U(cr), and (205.152 ± 0.005) for $O_2$(g), this review calculates:

$\Delta_f S_m^o$ (298.15 K) = – (789.0 ± 12.0) J·mol$^{-1}$·K$^{-1}$ for potassium uranosilicate monohydrate;

$\Delta_f S_m^o$ (298.15 K) = – (800.1 ± 12.0) J·mol$^{-1}$·K$^{-1}$ for rubidium uranosilicate monohydrate;

$\Delta_f S_m^o$ (298.15 K) = – (803.0 ± 12.0) J·mol$^{-1}$·K$^{-1}$ for cesium uranosilicate monohydrate;

and for the Gibbs energy of formation:

$\Delta_f G_m^o$ (298.15 K) = – (2718 ± 20) kJ·mol$^{-1}$ for potassium uranosilicate monohydrate;

$\Delta_f G_m^o$ (298.15 K) = – (2724 ± 20) kJ·mol$^{-1}$ for rubidium uranosilicate monohydrate;

$\Delta_f G_m^o$ (298.15 K) = – (2735 ± 20) kJ·mol$^{-1}$ for cesium uranosilicate monohydrate.

This review has accepted the experimentally determined values of the entropies of these alkali metal uranyl silicates, but not their enthalpies and Gibbs energies of formation.

**[2003WHE/MAJ]**

Wheaton *et al.* [2003WHE/MAJ] have used quantum chemical ab initio methods to study the structure, vibration frequencies and bonding characteristics in $UO_2H_2SiO_4$ and $UO_2(H_4Si_2O_7)$ complexes in gas-phase where the silicate is bidentate coordinated in the first complex as compared to monodentate in the second—this is claimed to be consistent with experimental EXAFS information. As there are only two oxygens from coordinated silicate in these structures, the present review finds this agreement entirely coincidental. The same is true for the proposed agreement between quantum chemical and experimental vibration frequencies. The two uncharged complexes have not been identified in solution and no thermodynamic data are reported.

**[2004CHE/KNY]**

Chernorukov *et al.* have determined the enthalpy of formation of U(VI) silicate, germanate and borate phases using dissolution calorimetry. First, we discuss the enthalpy of formation of $UO_2(BO_2)_2$(cr). The authors report the synthesis and the analysis of the solid where the latter is in excellent agreement with the stoichiometric formula. Based on calorimetric heats of solution of $UO_3$(γ, cr), $B(OH)_3$(cr) and $UO_2(BO_2)_2$(cr) they have calculated the enthalpy of reaction $\Delta_r H^\circ$ (A.207) and from the enthalpies of formation of $UO_3$(γ, cr), $B(OH)_3$(cr) and $H_2O$(l) the enthalpy of formation $\Delta_f H^\circ(UO_2(BO_2)_2, cr)$.

$$UO_3(\gamma, cr) + 2B(OH)_3(cr) \rightleftharpoons UO_2(BO_2)_2(cr) + 3H_2O(l) \qquad (A.207)$$

Chernorukov *et al.* report $\Delta_r H^\circ$ (A.207) = (12.8 ± 1.1) kJ·mol$^{-1}$, based on the measured heats of dissolution. The same experimental data have been used in a later study [2006CHE/SMI4], with the same heats of dissolution and uncertainties, except for the dissolution of $UO_2(BO_2)_2$(cr) for which the uncertainty has been increased from 0.5 to 2.5 kJ·mol$^{-1}$. This review assumes that the lower value is a misprint, and has accepted the higher value. Chernorukov *et al.* reported the value $\Delta_f H^\circ(UO_2(BO_2)_2, cr)$ = – (2542.5 ± 3.5) kJ·mol$^{-1}$. From $\Delta_f H^\circ$ (A.207) = (12.8 ± 2.7) kJ·mol$^{-1}$ and the NEA accepted enthalpies of formation $\Delta_f H^\circ(UO_3, \gamma, cr)$ = – (1223.8 ± 1.2) kJ·mol$^{-1}$; $\Delta_f H^\circ(B(OH)_3, cr)$ = – (1094.8 ± 0.8) kJ·mol$^{-1}$ (a slightly different value – (1094.2 ± 0.8) kJ·mol$^{-1}$, was used in [2004CHE/KNY]); $\Delta_f H^\circ(H_2O, l)$ = – (285.83 ± 0.04) kJ·mol$^{-1}$ and a correction $\overline{L_1}$ in 16.5 m HF ($\overline{L_1}$ = – 0.56 kJ·mol$^{-1}$), this review obtains $\Delta_f H^\circ(UO_2(BO_2)_2, cr)$ = – (2541.4 ± 3.4) kJ·mol$^{-1}$. This review has included our recalculated value among the selected data.

Chernorukov *et al.* have also prepared and characterised a synthetic analog of soddyite, $(UO_2)_2SiO_4$(cr) and the corresponding germanium phase, $(UO_2)_2GeO_4$(cr). They report elemental analyses, X-ray diffraction data, IR spectra, thermogravimetric data. The synthetic soddyite and its germanium analog had the compositions of $(UO_2)_{1.986}SiO_4 \cdot 1.971H_2O$(cr) and $(UO_2)_{1.986}GeO_4 \cdot 1.976H_2O$(cr), respective, as calculated from this review from results of chemical analyses of the phases. The authors determined calorimetrically enthalpies of solution of solid phases in 13.5 M HF (~ 16.5 m HF) medium. From these data (see Table 5 in the paper) the current review calculated the enthalpy changes of Reactions (A.208) and (A.209):

$$2UO_3(cr,\gamma) + SiO_2(cr,\text{cristobalite}) + 2H_2O(l) \rightleftharpoons (UO_2)_2SiO_4 \cdot 2H_2O(cr) \qquad \text{(A.208)}$$

$\Delta_r H_m$ (A.208) = (68.3 ± 2.6) kJ·mol$^{-1}$;

$$2UO_3(cr,\gamma) + GeO_2(cr,hex) + 2H_2O(l) \rightleftharpoons (UO_2)_2GeO_4 \cdot 2H_2O(cr) \qquad \text{(A.209)}$$

$\Delta_r H_m$ (A.209) = – (8.6 ± 2.5) kJ·mol$^{-1}$.

The authors calculated from their data the enthalpies of formation of $(UO_2)_2GeO_4 \cdot 2H_2O$(cr), $\Delta_f H^o_m$ = – (3936.0 ± 4.0) kJ·mol$^{-1}$ using auxiliary data mainly from the Glushko (1965-1981) tables. For soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O$(cr), the authors obtained $\Delta_f H^o_m$ = – (3859.0 ± 4.0) kJ·mol$^{-1}$, and, combining this value with $\Delta_f G°_m$ = – (3658 ± 4.8) kJ·mol$^{-1}$ from [1992NGU/SIL], calculated for soddyite the entropy value of $S^o_m$ = (758.4 ± 2.2) J·mol$^{-1}$·K$^{-1}$. The current review considers this value unrealistic for this phase: as discussed in the review of [2007GOR/MAZ], the expected value of $S^o_m$ for $(UO_2)_2SiO_4 \cdot 2H_2O$(cr) is around 320 J·mol$^{-1}$·K$^{-1}$. This suggests that the enthalpy value for the Reaction (A.208) is about 130 kJ·mol$^{-1}$ too large.

The recalculation using a slightly different value of the enthalpy of formation of $SiO_2$(cr, cristobalite), accepted in NEA, – (907.7 ± 1.1) kJ·mol$^{-1}$, and a correction for $\overline{L_1}$ in 16.5 m HF ($\overline{L_1}$ = – 0.56 kJ·mol$^{-1}$), resulted in a similar value of $\Delta_f H^o_m$ ($(UO_2)_2SiO_4 \cdot 2H_2O$, cr, 298.15 K) = – (3859.70 ± 3.7) kJ·mol$^{-1}$, not affecting the conclusions presented above. Indeed, we note that the large positive value of $\Delta_r H_m$ of Reaction (A.208) suggests that soddyite is metastable relative to the oxides, which obviously contradicts both mineralogical and laboratory observations.

There are also data for amorphous $(UO_2)_2SiO_4$(am) and $(UO_2)_2GeO_4$(am), which are not of interest for the current review.

**[2004CHE/NIP], [2004CHE/NIP2]**

The study [2004CHE/NIP2] presents only part of the experimental data published in [2004CHE/NIP], and therefore both studies are reviewed together. Both studies report the solubility of synthetic uranosilicates of the general formula $M^I(UO_2)(SiO_3OH) \cdot nH_2O$(cr) (boltwoodites) in water and dilute $HClO_4$ ($10^{-2}$, $10^{-3}$, and

$10^{-4}$ M) solutions at 25 °C (M = $Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$, $NH_4^+$). The test solutions were prepared by adding 300 mg of a solid phase to water or $HClO_4$ solutions. The mixture was allowed to stand for several weeks with intermittent stirring (the equilibrium was reached in ten days). The concentrations of elements were determined spectrophotometrically: for Si(IV) using the molybdate method; for U(VI)–using arsenazo III. The experimental results are presented as values of pH, and concentrations of U and Si. The experimental data show congruent dissolution, with solubilities that decrease with increasing pH in the examined range of pH 3.2-7.4.

The experimental data were used to calculate the solubility constants of uranosilicates according to the reaction:

$$M^{I}(UO_2)(SiO_3OH)\cdot nH_2O(cr) + 3H^+ \rightleftharpoons M^+ + UO_2^{2+} + Si(OH)_4(aq) + nH_2O(l) \quad (A.210)$$

When calculating the activities of the ions, the authors took into account the formation of monomeric and polymeric hydroxo complexes of the uranyl ion (the corresponding stability constants were taken from the Russian handbook Thermal Constants of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981), the dissociation and polymerisation constants of silicic acid (up to $SiO_4^{4-}$ and the formation of tetramers), in addition to the equilibrium constant for the formation of the complex $UO_2OSi(OH)_3^+$ from [1998MOL/GEI]. The activity coefficients were calculated with the Debye-Hückel equations, and the values of the water activity were assumed equal to one. The calculated data are presented in Table A-105 (apparently, values of the Gibbs energy of formation of ions are taken from the Glushko handbook, Thermal Constants of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981).

This review recalculated the values of $\log_{10}{}^*K_s^o$ for Reaction (A.210) using equilibrium constants for all hydroxo-, carbonate, mixed hydroxo-carbonate complexes of uranyl, and $UO_2SiO(OH)_3^+$, selected or retained in this review. Note that the concentrations of alkali metal ion, $M^+$, was not measured, and this review assumed that the molality of $M^+$ was equal to the half the sum of total concentrations of silica and U(VI). The SIT model was used to evaluate activity coefficients (note that the ionic strength was always less than 0.01 m), and the water activity was therefore taken equal to 1. The average values of $\log_{10}{}^*K_s^o$ for Reaction (A.210) and $\Delta_f G_m^o$ of uranosilicates calculated with the use of $\Delta_f G_m^o$ for the reaction products taken from [2003GUI/FAN] (except for $Si(OH)_4$, which was taken from [NEA TDB review on Ancillary Data – to be published] are given in Table A-105. Values of $\log_{10}{}^*K_s^o$, given in the paper and recalculated in this review, are in satisfactory agreement, however, the Gibbs energies of formation of the solid phases differ considerably. The reason for the discrepancy may be the fact that $\Delta_f G_m^o$ for uranosilicates in [2004CHE/NIP] were calculated using a thermochemical cycle involving the $SiO_4^{4-}$ ion as a reactant (its thermodynamic properties are expected to be very uncertain).

Calculations, performed in this review, showed that in practically all cases (except for K-boltwoodite) the solutions were oversaturated with respect to soddyite,

$(UO_2)_2SiO_4{\cdot}2H_2O$(cr), and for this reason the data have not been selected. It should also be noted that the values of ${}^{*}K_s^o$ for K-boltwoodite, based on data of [2004CHE/NIP], are several orders of magnitude lower than the value reported in [2011SHV/MAZ].

Table A-105: Values of $\log_{10}{}^{*}K_s^o$ for Reaction (A.210) and $\Delta_f G_m^o$ of uranosilicates based on data [2004CHE/NIP].

| Compound | $\log_{10}{}^{*}K_s^{o\,(a)}$ | $-\Delta_f G_m^{o\,(b)}$ /kJ·mol$^{-1}$ | $\log_{10}{}^{*}K_s^{o\,(c)}$ | $-\Delta_f G_m^{o\,(c)}$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $Li(UO_2)(SiO_3OH){\cdot}1.5H_2O$(cr) | (4.5 ± 0.6) | (2833 ± 20) | (4.03 ± 1.43) | (2887.4 ± 8.4) |
| $Na(UO_2)(SiO_3OH){\cdot}H_2O$(cr) | (3.5 ± 0.5) | (2691 ± 20) | (3.58 ± 0.40) | (2740.4 ± 3.1) |
| $K(UO_2)(SiO_3OH){\cdot}H_2O$(cr) | (1.5 ± 0.5) | (2723 ± 20) | (1.61 ± 0.75) | (2772.2 ± 4.7) |
| $Rb(UO_2)(SiO_3OH){\cdot}H_2O$(cr) | (2.2 ± 0.6) | (2718 ± 20) | (2.37 ± 0.53) | (2769.4 ± 3.6) |
| $Cs(UO_2)(SiO_3OH){\cdot}H_2O$(cr) | (3.6 ± 0.5) | (2719 ± 20) | (3.70 ± 0.81) | (2769.2 ± 5.1) |
| $NH_4(UO_2)(SiO_3OH){\cdot}H_2O$(cr) | (4.1 ± 0.7) | (2384 ± 20) | (4.66 ± 1.24) | (2551.7 ± 7.4) |

(a) Values calculated in [2004CHE/NIP];
(b) Calculations of $\Delta_f G_m^o$ in [2004CHE/NIP] are based on the values of the solubility products involving the $SiO_4^{4-}$ ion as the reaction participant (its thermodynamic is expected to be very uncertain);
(c) Values evaluated in this review, uncertainties are given $1.96\sigma_X$.

The current review does not credit data from this study, and no value was selected.

**[2005CHE/NIP2]**

This study presents data on solubility of uranosilicates of the uranophane-kasolite structural group ($Mg[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O$(cr), $Ca[(UO_2)(SiO_3OH)]_2{\cdot}5H_2O$(cr) (the mineral uranophane), $Sr[(UO_2)SiO_4]{\cdot}H_2O$(cr), $Ba[(UO_2)SiO_4]{\cdot}H_2O$(cr), and $Pb[(UO_2)SiO_4]{\cdot}H_2O$(cr) (the mineral kasolite) in water and dilute $HClO_4$ ($10^{-2}$, $10^{-3}$, and $10^{-4}$ M) solutions at 25 °C.

Synthesis of calcium and magnesium uranosilicates was described elsewhere; kasolite $Pb[(UO_2)SiO_4]{\cdot}H_2O$(cr) and its structural Sr and Ba analogs were precipitated from high-temperature solutions at pH 6-8. The phase purity before and after the solubility runs was checked by X-ray diffraction, and there was no indication of phase transformations during the experiment. The exact compositions of the investigated phases were not reported.

The test solutions were prepared by adding 300 mg of solid phase to water or $HClO_4$ solutions and using an equilibration time of 25-30 days with intermittent stirring. The concentrations of elements were determined spectrophotometrically: for Si(IV) with the molybdate method; for U(VI) – with arsenazo III. Experimental results are presented in Tables (pH, concentrations of U and Si). The dissolution is congruent and the solubility decreases with increasing pH in the examined range of pH 4-7.

Experimental data were used to calculate the solubility constants ( $\log_{10}{}^{*}K_{s}^{o}$ ) of uranosilicates according to the reactions:

$$M^{II}[(UO_2)(SiO_3OH)]_2 \cdot nH_2O(cr) + 6H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2Si(OH)_4(aq) + nH_2O(l) \quad (A.211)$$

where $M^{II}$ = Ca, Mg, and

$$M^{II}[(UO_2)SiO_4] \cdot nH_2O(cr) + 4H^+ \rightleftharpoons M^{2+} + UO_2^{2+} + Si(OH)_4(aq) + nH_2O(l) \quad (A.212)$$

where $M^{II}$ = Sr, Ba, Pb.

Calculations of equilibrium constants by the authors were done as described in the Appendix A entry of [2004CHE/NIP].

This review recalculated $\log_{10}{}^{*}K_{s}^{o}$ values for Reactions (A.211) and (A.212) from data [2005CHE/NIP2] using a chemical model that included all hydroxo-, carbonate, mixed hydroxo-carbonate complexes of uranyl, $UO_2SiO(OH)_3^+$, selected in this review, products of dissociation of $CO_2$ (from [2003GUI/FAN]) and $Si(OH)_4$ from [NEA TDB review on Ancillary Data – to be published], and the following values of the logarithms of stability constants of hydroxide, carbonate and hydrogencarbonate complexes of Mg, Ca, Sr, Ba, and Pb: $MgHCO_3^+$ – 1.07 [1977SIE/HOS], $MgCO_3(aq)$ – 2.92, $MgOH^+$ – 2.58 (both from [1976SMI/MAR]); $CaHCO_3^+$ – 1.11, $CaCO_3(aq)$ – 3.22 (both from [1982PLU/BUS]), $CaOH^+$ – 1.30 [1976SMI/MAR]; $SrHCO_3^+$ – 1.18, $SrCO_3(aq)$ – 2.81 (both from [1984BUS/PLU]), $SrOH^+$ – 0.82 [1976SMI/MAR]; $BaHCO_3^+$ – 0.98, $BaCO_3(aq)$ – 2.71 (both from [1986BUS/PLU]), $BaOH^+$ – 0.64 [1976SMI/MAR]; $PbCO_3(aq)$ – 6.87 [2013WOO/MIL], $PbOH^+$ – 6.4 [1976SMI/MAR]. The activity coefficients were calculated with the SIT model, however the ionic strength is very low $I < 0.02$ M, and therefore the results are determined mainly by the electrostatic term and are not very sensitive to the numerical values of the SIT interaction coefficients. The system was open to $CO_2$, and $P(CO_2) = 10^{-3.50}$ atm. Results are given in Table A-106.

Values of $\log_{10}{}^{*}K_{s}^{o}$ from both evaluations are close to each other. However, the calculated values of $\Delta_f G_m^o$ of uranosilicates differ significantly, the reason is that calculations in [2005CHE/NIP2] are based on the thermochemical cycle involving the $SiO_4^{4-}$ ion as the reaction participant (the existence of such an ion is in doubt and its thermodynamic properties are expected to be very uncertain). This review also notes that in practically all cases the solutions were oversaturated with respect to soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O(cr)$. These data are not selected as our recalculations showed that these experiments were performed outside of fields of stability of these phases.

Table A-106: Values of $\log_{10}{}^{*}K_s^o$ for Reaction (A.212) and $\Delta_f G_m^o$ of uranosilicates as reported in [2005CHE/NIP2] and recalculated in this review.

| Compound | $\log_{10}{}^{*}K_s^{o\ (a)}$ | $-\Delta_f G_m^{o\ (a)}$ /kJ·mol$^{-1}$ | $\log_{10}{}^{*}K_s^{o\ (b)}$ | Oversaturated in soddyite | $-\Delta_f G_m^{o\ (b,d)}$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Mg[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O$(cr) | (11.3 ± 0.9) | (6239 ± 30) | (11.53 ± 1.11) | Yes | (6335.9 ± 7.1) |
| $Ca[(UO_2)(SiO_3OH)]_2{\cdot}5H_2O$(cr) | (8.0 ± 2.0) | (6118 ± 40) | (8.71 ± 2.44) | Yes | (6212 ± 14) |
| $Sr[(UO_2)SiO_4]{\cdot}H_2O$(cr) | (9.6 ± 0.4) | (2958 ± 20) | (9.59 ± 0.50) | Yes/No[(c)] | (3008.0 ± 3.6) |
| $Ba[(UO_2)SiO_4]{\cdot}H_2O$(cr) | (8.0 ± 0.2) | (2950 ± 20) | (8.04 ± 0.39) | Yes | (3010.7 ± 4.0) |
| $Pb[(UO_2)SiO_4]{\cdot}H_2O$(cr) | (6.4 ± 0.2) | (2437 ± 20) | (6.48 ± 0.40) | Yes | (2486.1 ± 3.1) |

(a) Calculations of $\Delta_f G_m^o$ are based on the values of the solubility products involving the $SiO_4^{4-}$ ion as the reaction participant (its thermodynamic data are expected to be very uncertain);

(b) Values evaluated in this review, uncertainties are given $1.96\sigma_X$;

(c) The solution in pure water is undersaturated with respect to soddyite;

(d) Auxiliary $\Delta_f G_m^o$ data (in kJ·mol$^{-1}$): $UO_2^{2+}$ – (952.55 ± 1.75), $Mg^{2+}$ – (455.38 ± 1.34), $Ca^{2+}$ – (552.81 ± 1.05), $Sr^{2+}$ – (563.86 ± 0.78), $Ba^{2+}$ – (557.66 ± 2.58), all from [2003GUI/FAN]; $Si(OH)_4$(aq) – (1309.20 ± 1.02) [NEA TDB review on Ancillary Data – to be published]; $Pb^{2+}$ – (24.20 ± 0.30) [1989COX/WAG].

**[2005YUS/FED]**

This study is a spectrophotometric investigation of the uranyl ions hydrolysis and the interaction of the uranyl ion with the orthosilicic acid and polymeric silicic acids (PSA) at (23 ± 1) °C in 0.1-0.3 M $NaClO_4$ medium. The spectra were recorded in the wavelength range 270-600 nm, pH (the activity scale) was measured in equilibrated solutions.

First, the authors studied the hydrolysis reaction $2UO_2^{2+} + 2H_2O \rightleftharpoons (UO_2)_2(OH)_2^{2+} + 2H^+$ in 0.1 M $NaClO_4$ medium at conditions (uranyl concentrations, pH range) where the formation of other hydrolytic uranyl species ($UO_2OH^+$, $(UO_2)_3(OH)_5^+$, *etc.*) can be neglected. The best fit gave $\log_{10}{}^{*}K_{2,2}$ = – (5.95 ± 0.10) (note that the review [2003GUI/FAN] recommends in this medium a value of $\log_{10}{}^{*}K_{2,2}$ = – (5.83 ± 0.04)). The obtained value, which slightly differs from the [2003GUI/FAN] value was used in interpretation of experiments with orthosilicic acid.

Solutions of orthosilicic acid were prepared by quick acidification of the stock solution (1.0 M $Na_2SiO_3$ + 0.25 M NaOH) with $HClO_4$ to pH 1.7-2.0 immediately before use. Such a procedure allows preparing oversaturated $Si(OH)_4$ solutions, in which the polymers are not formed in appreciable amounts during a certain period. The total Si concentration and the degree of silica polymerisation were determined by the molybdate method. The reaction of the complex formation is as follows: $UO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons UO_2SiO(OH)_3^+ + H^+$. The appreciable formation of the silica-uranyl complex occurs at the $Si(OH)_4$ concentrations in excess of 0.01 M and in the pH range 3-4 (at higher pH values the rate of polymerisation of silica drastically increased). Measurements were made at wavelengths of 422.5, 322,290 and 270 nm. The initial $UO_2^{2+}$ concentration varied in a range of (0.32-7.25) × 10$^{-3}$ M, the pH range was 1.75-4.25, the total silica concentration in the accepted runs varied within a range of

(0.0115-0.088) M. At the lowest silica concentrations it existed as a monomer, then as a monomer plus a dimer, and at highest concentrations a tetramer (and oligomers) also formed. It appears that the authors used the total silica concentration when calculating the equilibrium constant of the reaction above, not the concentration of the monomeric species. Nevertheless, the $\log_{10}{}^{*}K$ values of the reaction above remained practically constant over the whole range of the silica concentrations, and the average value of $\log_{10}{}^{*}K = -(2.56 \pm 0.09)$ (3σ) is valid for 0.1 M $NaClO_4$ (nine data points) and 0.2 M $NaClO_4$ (one point) media.

A separate series was performed to study the interaction of the uranyl ion with polymeric silicic acids (PSA), $[Si_x(OH)_{4-2x}]_n$, with $n$ = 100-300 and more than 1000 in some samples, which means a concentration 1000 times larger than in the monomer solutions. In this series the initial uranyl concentration amounted to $7.2 \times 10^{-3}$ M, the pH range was 1.50-3.97, and the total silica concentration – 0.083 M. The ionic medium was 0.3 M $NaClO_4$. The apparent constant of the reaction decreases with an increase in the degree of polymerisation. The authors also noticed the changes in the spectra at higher pH (7-7.5), which were interpreted as the formation of a complex $UO_2(\equiv SiO)_2(\equiv SiOH)_{m-2}$ with the equilibrium constant $\log_{10} K \geq -8$.

This review accepts $\log_{10}{}^{*}K$ values (– 2.35, – 2.59, – 2.52) for the three lowest silica concentrations (0.0057-0.014 M), where the silica monomer prevailed in the course of the measurements as confirmed by the "molybdate" method. The average value is $\log_{10}{}^{*}K = -(2.49 \pm 0.24)$ (1.96σ). This is the "mixed" equilibrium constant where pH refers to the activity scale. The value of the equilibrium constant in terms of concentrations was calculated by evaluating the activity coefficient of the hydrogen ion with the SIT using $\varepsilon(H^+, ClO_4^-) = 0.14$ kg·mol$^{-1}$, and obtaining $\log_{10}\gamma_{H^+} = -0.095$ in the 0.1 M $NaClO_4$ ionic medium. Therefore, the recalculated data were discussed together with other literature data, but the finally selected value differs from this one by more than 0.5 log unit from the value of the molar equilibrium constant, $\log_{10}{}^{*}K = -(2.39 \pm 0.40)$, the uncertainty is increased to account for possible systematic errors. The extrapolation to $I = 0$ using the SIT model $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$, $\varepsilon(Si(OH)_4, Na^+, ClO_4^-) = (0.13 \pm 0.04)$, $\varepsilon(UO_2SiO(OH)_3^+, ClO_4^-) = 0.3$, $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$, all in kg·mol$^{-1}$, results in $\log_{10}{}^{*}K^{o} = -(2.18 \pm 0.40)$.

**[2006CHE/KNY]**

This paper presents results of thermodynamic measurements to determine the enthalpy of formation and the entropy of calcium uranosilicate pentahydrate, α-$Ca[(UO_2)(SiO_3OH)]_2 \cdot 5H_2O$(cr), the mineral uranophane. The synthesis of the sample used was prepared by hydrothermal (200 °C) ion exchange between the crystalline phase $K(UO_2)(SiO_3OH) \cdot H_2O$(cr) and a calcium nitrate solution. The formation of uranophane was confirmed by XRD. The exact stoichiometry of the studied phase was

not given. The synthesis of the unhydrated $Ca[(UO_2)(SiO_3OH)]_2$(cr) phase was not discussed in the paper.

The enthalpies of reactions and processes were measured in a custom-made adiabatic calorimeter. The thermochemical cycle to determine $\Delta_f H_m^o$ (298.15 K) of uranophane included the measurements at 298.15 K of heat effects of the dissolution of $K(UO_2)(SiO_3OH)\cdot H_2O$(cr), $Ca(NO_3)_2\cdot 4H_2O$(cr), $Ca[(UO_2)(SiO_3OH)]_2\cdot nH_2O$(cr) ($n = 0$ and 5), $KNO_3$(cr), and $H_2O$(l) in a mixture of concentrated $HNO_3$, HF (13.5 M), and $H_2O$ taken in a volume ratio of 2.5:1:9, to give for the reaction:

$$2K(UO_2)(SiO_3OH)\cdot H_2O(cr) + Ca(NO_3)_2\cdot 4H_2O(cr) \rightleftharpoons Ca[(UO_2)(SiO_3OH)]_2\cdot nH_2O(cr) + 2KNO_3(cr) + (6-n)H_2O(l) \quad \text{(A.213)}$$

$\Delta_r H_m^o = (130.1 \pm 3.3)$ kJ·mol$^{-1}$ and $\Delta_r H_m^o = -(6.3 \pm 3.0)$ kJ·mol$^{-1}$ for $n = 0$ and 5, respectively.

The authors calculated for $Ca[(UO_2)(SiO_3OH)]_2\cdot 5H_2O$(cr) $\Delta_f H_m^o = -(6781.0 \pm 9.5)$ kJ·mol$^{-1}$, using auxiliary values from [1979GLU/MED], Vol. IX, [1981GLU/MED], Vol. X, and for $K(UO_2)(SiO_3OH)\cdot H_2O$(cr) from [2002KAR/CHE].

We note that the value of $\Delta_f H_m^o$ for $K(UO_2)(SiO_3OH)\cdot H_2O$(cr), selected in the current review, differs from the value given in [2002KAR/CHE] by more than 190 kJ·mol$^{-1}$. In addition, the correction for the relative partial molar enthalpy of water, $\overline{L_1}$, in the concentrated aqueous $HNO_3$ and HF mixture should be made when calculating $\Delta_f H_m^o$ of $Ca[(UO_2)(SiO_3OH)]_2\cdot 5H_2O$(cr), however, an exact evaluation of $\overline{L_1}$ is not possible, but the expected contribution is only about 1 kJ·mol$^{-1}$ and can be neglected, at least for the hydrated uranophane phase. No selection of $\Delta_f H_m^o$ of $Ca[(UO_2)(SiO_3OH)]_2\cdot 5H_2O$(cr) based on data of [2006CHE/KNY] is made in the current review, due to concerns about the composition of the studied phase, see below.

The low-temperature heat capacity was measured in the adiabatic vacuum calorimeter at 80-260 K. At higher temperatures the onset of dehydration distorted the measurement results, and the authors used a linear in $T$ function to extrapolate data, obtained at 200-250 K, to 300 K. The extrapolation $C_p$ values from 80 to 0 K was done with the Kelley-Parks procedure (a linear relation between $C_p$ of a given solid and reference phases) using $K(UO_2)(SiO_3OH)\cdot H_2O$(cr) as a reference phase. At 298.15 K the evaluated $C_{p,m}^o$ and $S_m^o$ are equal to 628.8 and 727.3 J·K$^{-1}$·mol$^{-1}$, respectively. The latter value appears suspect. First, the authors observed the onset of dehydration at $T > 260$ K, while the thermal instability of uranophane at such low temperatures was not observed in other experimental studies. Second, the obtained $S_m^o$ is significantly higher than several estimates: the Latimer [1951LAT] method (as outlined in Appendix D) gives ~ 584 J·K$^{-1}$·mol$^{-1}$; while the approximation of $S_m^o$ of uranophane equals the sum of entropies of 2 K-boltwoodite ($S_m^o = 259$), three moles of hydrated water ($S_m^o \approx$ 40-45 each, see [1951LAT]), one mole of $CaCl_2$(cr) ($S_m^o = 108.4$ [1981GLU/GUR]), minus 2 moles of KCl(cr) ($S_m^o = 82.57$ each

[1982GLU/GUR]), gives ~ 587, all values in $J \cdot K^{-1} \cdot mol^{-1}$. It could be that the investigated sample contained additional water. Regrettably, the exact composition of studied samples was not reported.

For reasons discussed above the values of $S_m^o$ and $\Delta_f H_m^o$ from this study were not selected in the current review.

**[2006ILT/LIU]**

The solubility of a synthetic Na-boltwoodite, $Na(UO_2)(SiO_3OH) \cdot 1.5H_2O(cr)$, was studied at 23(± 2) °C in the 0.05 M $NaNO_3/NaHCO_3$ medium. Na-boltwoodite was precipitated from uranyl acetate and sodium metasilicate solutions, and the resulting solid was vacuum-dried and then heated with water at 150 °C for seven days. BET analysis of the solid yielded a surface area of 30.78 $m^2 \cdot g^{-1}$. Solution compositions were determined with an inductively coupled plasma-atomic emission spectrometer, ICP-AES. Dissolution of the synthetic materials in nitric acid yielded U/Si = (1.011 ± 0.014) (1σ), U/Na = (1.039 ± 0.020) (1σ), and only traces of K and Ca.

Dissolution experiments were conducted for seven days at 23(± 2) °C from undersaturation in continually stirred batch reactors. Samples (0.25 g) of Na-boltwoodite reacted with 100 ml of solution (a 0.05 M $NaNO_3/NaHCO_3$ medium) containing different concentrations of $NaHCO_3$ (0-50 mM) at pH from 6.76 to 9.63, experiments were open to the atmosphere. Three series of experiments were performed: 1) kinetic runs; 2) seven-day experiments; 3) experiments with a solid pretreated for 24 hours with a 0.05 M $NaHCO_3$ solution. Experimental results (pH, concentrations of Si and U) are presented in Tables. Generally, the solubility data do not indicate congruent dissolution, especially at $NaHCO_3$ concentrations below 10 mM, which suggests a precipitation of a U-rich, Si-poor phase. Due to the minuscule amounts of the new phase it could not be identified with methods used to characterise solids: XRD, laser induced fluorescence spectroscopy (LIFS), high resolution transmission electron microscopy (HRTEM), and X-Ray photoelectron spectroscopy (XPS). However, a pretreatment of the starting materials with 50 mM bicarbonate solutions yielded near congruent dissolution behaviour in 6 and 50 mM of $NaHCO_3$. The authors suggest that this pretreatment removes a U-rich, Si-deficient contaminant, and provides evidence that Na-boltwoodite dissolves congruently, in accordance with the XPS analysis.

The authors calculated the solubility constant of Na-boltwoodite for the reaction

$$Na(UO_2)(SiO_3OH) \cdot 1.5H_2O(cr) + 3H^+ \rightleftharpoons UO_2^{2+} + Na^+ + Si(OH)_4(aq) + 1.5H_2O(l) \quad \text{(A.214)}$$

When calculating the concentrations of reaction participants, the authors took into account the formation of hydroxo, carbonate, mixed hydroxo-carbonate, the silicate

and the nitrate complexes of uranyl ion [2003GUI/FAN], the dissociation of carbonic and silicic acid [2003GUI/FAN], and the formation of the carbonate and bicarbonate complexes of $Na^+$ (the NIST database). Two models were used to calculate activity coefficients: the Davies equation and the Pitzer model with necessary parameters from [2005FEL/XIA]. Ten experimental data points were selected for the calculation of the equilibrium constants, $\log_{10}{}^{*}K_s^o$, for Reaction (A.214), although in three of them the concentrations of U and Si differed by more than one order of magnitude, demonstrating a strongly incongruent dissolution. The average $\log_{10}{}^{*}K_s^o = (5.86 \pm 0.24)$ (1σ) or $(5.85 \pm 0.26)$ (1σ) were obtained using the Pitzer model or the Davies equation, respectively.

The current review used the same 10 data points to calculate $\log_{10}{}^{*}K_s^o$, employing the SIT model with all equilibrium constants selected or retained in the present review, and obtained values were in a very good agreement with authors' evaluations and selected, $\log_{10}{}^{*}K_s^o = (5.87 \pm 0.50)$, where the uncertainty is given as $1.96\sigma_X$. It was verified that all test solutions were undersaturated with respect to soddyite $(UO_2)_2SiO_4{\cdot}2H_2O$(cr).

**[2006PAT/CHO]**

This paper is also discussed in the Am section and a separate review is given there; it is a study of the complexation between $UO_2^{2+}$, $Cm^{3+}$, $Eu^{3+}$ and orthosilicic acid (*o*-SA) by the extraction method at 5-45(± 1) °C in the 0.20 M $NaClO_4$ medium. Extractant solutions were prepared by dissolving bis(2-ethylhexyl) phosphoric acid (HDEHP) in *n*-heptane and were pre-equilibrated with an aqueous phase without *o*-SA. Fresh SA solutions were prepared by dissolving sodium metasilicate in water. The concentrations of *o*-SA, as measured by the molybdate method, varied between $(0\text{-}10) \times 10^{-3}$ M, where no polymeric species were detected. $^{233}U$ and $^{244}Cm$ were purified from decay products by ion exchange. The concentrations of metals in equilibrated aqueous and organic phases were determined by liquid scintillation counting, and the material balance of metals was preserved within ± 5 %. The initial concentrations of U(VI), Cm(III) and Eu(III) were $5 \times 10^{-5}$, $3 \times 10^{-4}$ and $3 \times 10^{-4}$ M, respectively. Their aqueous solutions had pcH (the negative logarithm of the molar concentrations of $H^+$ calculated from pH-meter readings) values of (3.60 ± 0.05), (3.40 ± 0.05), and (3.15 ± 0.05), respectively at $I = 0.20$ M $NaClO_4$. The water-organic mixtures were shaken for an hour, which was sufficient to achieve equilibrium. The analysis of the dependence of the metal distribution coefficients on the *o*-SA concentrations showed the formation of only monosilicate (M/L=1) $M(OSi(OH)_3)$ complexes with the following values of the equilibrium constants $\beta_1$ (see Table A-107).

Table A-107: Values of stability constants of monosilicate complexes of $UO_2^{2+}$, $Cm^{3+}$, $Eu^{3+}$ and the enthalpy changes for reaction $M^{n+} + Si(OH)_4(aq) \rightleftharpoons MSiO(OH)_3^{(n-1)} + H^+$ reported in [2006PAT/CHO] and enthalpies of reaction calculated from the temperature dependence of the equilibrium constants.

| Metal | $\log_{10}\beta_1$ | | | | | $\Delta_r H$ [(a)] |
|---|---|---|---|---|---|---|
| ion / t (°C) | 5 | 15 | 25 | 35 | 45 | /kJ·mol$^{-1}$ |
| $UO_2^{2+}$ | (6.78 ± 0.01) | (6.82 ± 0.01) | (6.87 ± 0.02) | (6.92 ± 0.02) | (6.99 ± 0.02) | (8.3 ± 0.7) |
| $Cm^{3+}$ | (7.67 ± 0.01) | (7.77 ± 0.01) | (7.83 ± 0.02) | (7.91 ± 0.03) | (8.07 ± 0.02) | (15.8 ± 2.0) |
| $Eu^{3+}$ | (7.61 ± 0.02) | (7.67 ± 0.01) | (7.79 ± 0.01) | (7.86 ± 0.03) | (7.93 ± 0.01) | (14.5 ± 1.0) |

(a) The error limits correspond to one standard deviation.

For recalculating $\log_{10}\beta_1$ to the value of the equilibrium constant of the reaction $M^{n+} + Si(OH)_4(aq) \rightleftharpoons MSiO(OH)_3^{(n-1)} + H^+$ one needs to know the value of the equilibrium constant, $\log_{10}{}^*K$, of the reaction $Si(OH)_4(aq) \rightleftharpoons SiO(OH)_3^- + H^+$ in 0.2 M $NaClO_4$ ionic medium. This value was evaluated using $\log_{10}{}^*K^\circ_m = -(9.824 \pm 0.11)$; the molality/molarity ratio, *m*/c, for 0.2 M $NaClO_4$ is equal to 1.012; $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol$^{-1}$; $\varepsilon(Na^+, SiO(OH)_3^-) = (0.00 \pm 0.05)$ kg·mol$^{-1}$; $\varepsilon(Si(OH)_4, Na^+, ClO_4^-) = (0.13 \pm 0.04)$ kg·mol$^{-1}$: first, in 0.202 m $NaClO_4$ $\log_{10}{}^*K_m = -9.55$; and then in 0.2 M $NaClO_4$ $\log_{10}{}^*K_c = \log_{10}K_m - \Sigma\nu_B \log_{10}\varrho = -9.56$. Therefore, for the reaction $UO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons UO_2SiO(OH)_3^+ + H^+$ $\log_{10}{}^*K_c = -(2.69 \pm 0.11)$; for the reaction $Cm^{3+} + Si(OH)_4(aq) \rightleftharpoons CmSiO(OH)_3^{2+} + H^+$ $\log_{10}{}^*K_c = -(1.73 \pm 0.11)$; for the reaction $Eu^{3+} + Si(OH)_4(aq) \rightleftharpoons EuSiO(OH)_3^{2+} + H^+$ $\log_{10}{}^*K_c = -(1.77 \pm 0.11)$. The values of equilibrium constant were extrapolated to $I = 0$ using the SIT with $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol$^{-1}$, $\varepsilon(Si(OH)_4, Na^+, ClO_4^-) = (0.13 \pm 0.04)$ kg·mol$^{-1}$, $\varepsilon(UO_2SiO(OH)_3^+, ClO_4^-) = 0.3$ kg·mol$^{-1}$, $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol$^{-1}$, $\varepsilon(Am^{3+}, ClO_4^-) = (0.49 \pm 0.03)$ kg·mol$^{-1}$, $\varepsilon(AmSiO(OH)_3^{2+}, ClO_4^-) = (0.39 \pm 0.04)$ kg·mol$^{-1}$ (from [2003GUI/FAN] and [NEA TDB review on Ancillary Data – to be published]). It was assumed that $\varepsilon$ values for interactions involving $Cm^{3+}$, $Eu^{3+}$ and their complexes are identical to corresponding $\varepsilon$ values for $Am^{3+}$ and its complexes): for the reaction $UO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons UO_2SiO(OH)_3^+ + H^+$ $\log_{10}{}^*K^\circ = -(2.43 \pm 0.5)$; for the reaction $Cm^{3+} + Si(OH)_4(aq) \rightleftharpoons CmSiO(OH)_3^{2+} + H^+$ $\log_{10}{}^*K^\circ = -(1.20 \pm 0.5)$; and for the reaction $Eu^{3+} + Si(OH)_4(aq) \rightleftharpoons EuSiO(OH)_3^{2+} + H^+$ $\log_{10}{}^*K^\circ = -(1.24 \pm 0.5)$. The uncertainties were increased to reflect a large scatter of $\log_{10}{}^*K$ from extraction experiments and a fact that the value for $Cm^{3+}$ is about 0.4 $\log_{10}$ larger than the selected value in [2003GUI/FAN].

The values of the enthalpy change for the formation of complexes (see the last column of the Table above) were evaluated by the authors from the temperature dependence of the stability constants. These values of $\Delta_r H$, which refer to 0.2 M $NaClO_4$, were extrapolated in this review to $I = 0$ using the SIT-model as outlined in [1996PLY/GRE], [1997GRE/PLY2] according to the relation:

$$\Delta_r H^o = \Delta_r H - \frac{3}{4}\frac{A_L \Delta Z^2 I^{0.5}}{1+1.5I^{0.5}} - RT^2 m\Delta\varepsilon_L ,$$

where $A_L = 1.986$ kJ·kg$^{1/2}$·mol$^{-3/2}$ is the Debye-Hückel limiting slope for the relative partial molar enthalpies, and $\varepsilon_L$ refers to the temperature derivative of the SIT parameter as

$$\varepsilon_L = \ln(10)\left(\frac{\partial \varepsilon}{\partial T}\right)_T .$$

The contribution of the last term was neglected (its expected contribution is less than 1 kJ·mol$^{-1}$). The obtained values of $\Delta_r H^o_m$ for the reaction $M^{n+} + SiO(OH)_3^- \rightleftharpoons MSiO(OH)_3^{n-1} + H^+$ are equal to (9.9 ± 3), (18.2 ± 4), (16.9 ± 3) kJ·mol$^{-1}$ for $M^{n+} = UO_2^{2+}$, $Cm^{3+}$, and $Eu^{3+}$, respectively (uncertainties are estimated). Combining these values with $\Delta_r H^o_m = (29.73 \pm 0.50)$ kJ·mol$^{-1}$ for the reaction $Si(OH)_4(aq) \rightleftharpoons SiO(OH)_3^- + H^+$ ([NEA TDB review on Ancillary Data – to be published]), this review evaluates for the reaction $UO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons UO_2SiO(OH)_3^+ + H^+$ the value of $\Delta_r H^o_m = (39.6 \pm 3.0)$ kJ·mol$^{-1}$; for the reaction $Cm^{3+} + Si(OH)_4(aq) \rightleftharpoons CmSiO(OH)_3^{2+} + H^+$ the value of $\Delta_r H^o_m = (47.9 \pm 4.0)$ kJ·mol$^{-1}$; and for the reaction $Eu^{3+} + Si(OH)_4(aq) \rightleftharpoons EuSiO(OH)_3^{2+} + H^+$ the value of $\Delta_r H^o_m = (46.6 \pm 3.0)$ kJ·mol$^{-1}$.

**[2007GOR/MAZ]**

This paper presents results of a study of the enthalpy of formation (through drop solution calorimetry measurements) and the Gibbs energy of formation (through solubility measurements) of synthetic soddyite, $(UO_2)_2SiO_4 \cdot 2H_2O$(cr). Soddyite was synthesised under mild hydrothermal condition ($T$ = 389 K) from aqueous solutions of uranyl acetate and sodium metasilicate and was investigated by XRD, Fourier transform infrared (FT-IR) spectroscopy, thermogravimetry, and chemical analysis.

The enthalpy of formation was measured by drop solution calorimetry in a melt of composition $3Na_2O \cdot 4MoO_3$ (saturated with $SiO_2$ prior to the experiment, also oxygen was bubbled through the melt to maintain an oxidising atmosphere) at 976 K using a custom-built Tian-Calvet high-temperature microcalorimeter. In total, 11 data points were obtained for soddyite and 6 for cristobalite (cristobalite, a polymorph of $SiO_2$, was found in the sodium molybdate solvent after soddyite dissolution). In order to close the thermochemical cycle, the authors used auxiliary $\Delta_f H^o_m$ data, in kJ·mol$^{-1}$, for $UO_3$(cr) – 1223.8 and $H_2O$(l) – 285.8, identical to ones accepted in NEA TDB, and for cristobalite(cr) the value of – (908.4 ± 2.1) from [1995ROB/HEM]. For soddyite the resulting $\Delta_f H^o_m$ = – (117.8 ± 4.3) kJ·mol$^{-1}$ (from oxides) and $\Delta_f H^o_m$ = – (4045.4 ± 5.4) kJ·mol$^{-1}$ (from elements), the uncertainty is calculated using the using rules for propagation of uncertainty, the authors value is ± 4.9 kJ·mol$^{-1}$. This review

recalculated the enthalpy of formation from elements using for cristobalite(cr) the value of – (907.7 ± 1.1) from [NEA TDB review on Ancillary Data – to be published]: $\Delta_f H^o_m$ = – (4044.8 ± 5.0) kJ·mol$^{-1}$ (from elements).

The solubility measurements were conducted as batch experiments in Teflon reaction vessels, which were slowly agitated at room temperature. Experimental runs were carried out both from undersaturation and supersaturation, between pH 3.0 and 3.6, in test solutions open to the atmosphere; pH was regulated by adding nitric acid. Equilibrium was attained within 20 days. Aliquots of solutions were filtered through 0.1 μm nylon filters, diluted and acidified for ICP-OES analysis for U and Si. Soddyite was stable under the experimental conditions, but amorphous silica was also formed and in many runs amorphous silica gel was added to enhance the kinetics of dissolution of soddyite. In all experiments the log of concentration of silica is rather constant, and varied within – 2.48 to – 2.68. The value of the solubility recommended by Palmer [NEA TDB review on Ancillary Data – to be published], is – 2.69. So, their results are just slightly oversaturated with respect to solubility of amorphous silica. XRD analysis of the mineral residue indicated that soddyite was the only crystalline phase present. In all there are 65 data points that were used to determine the solubility constant, $\log_{10}{}^{*}K^{o}_{s}$ for Reaction (A.215)

$$(UO_2)_2SiO_4 \cdot 2H_2O(cr) + 4H^+ \rightleftharpoons 2UO_2^{2+} + Si(OH)_4(aq) + 2H_2O(l) \qquad (A.215)$$

to give $\log_{10}{}^{*}K^{o}_{s}$ = (6.43 + 0.20/– 0.37) at the 1σ error level. The chemical model employed the equilibrium constants from [2003GUI/FAN] and included hydroxo-, carbonate and mixed hydroxo-carbonate complexes of U(VI) (the partial pressure of $CO_2$ was taken equal to $10^{-3.5}$ atm, *i.e.* the solutions were in an equilibrium with atmosphere), and the silicate complex $UO_2SiO(OH)_3^+$ (most, but not all values of stability constants were taken from [1992GRE/FUG]). The Debye-Hückel equation in the form of the third approximation for $RbNO_3$ solutions according to [1981HEL/KIR] was employed to evaluate activity coefficients.

The current review reinterpreted the original solubility data using the same model as in [2007GOR/MAZ] with all equilibrium constants selected or retained in the present review), and products of dissociation of $CO_2$ ([2003GUI/FAN]), and $Si(OH)_4$(aq) (from [NEA TDB review on Ancillary Data – to be published]). The activity coefficients, γ, were calculated with the SIT model, however, in most cases $I < 0.03$ M, and the main contribution to γ was therefore due to the electrostatic term. The input information consisted of pH values (in the activity scale), and total concentrations of U and Si. The concentrations of $NO_3^-$, the major anion in solutions, containing mostly U-containing cations at equilibrium pH 2.9-3.8, were calculated from the condition of electro neutrality of solutions. The average value of equilibrium constant of Reaction (A.215) from 65 data points is equal to $\log_{10}{}^{*}K^{o}_{s}$ = (6.14 ± 0.42), where the error is given as $1.96\sigma_X$.

For Reaction (A.215) $\Delta_r G_m^o = -RT \ln {}^*K_s^o = -(35.0 \pm 2.4)$ kJ·mol$^{-1}$, and using $\Delta_f G_m^o$, in kJ·mol$^{-1}$, for $UO_2^{2+}$ $-(952.55 \pm 1.75)$, for $H_2O(l)$ $-(237.14 \pm 0.04)$, all from [2003GUI/FAN], and for $Si(OH)_4(aq)$ $-(1309.20 \pm 1.02)$ from [NEA TDB review on Ancillary Data – to be published], this review evaluated for soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O(cr)$, $\Delta_f G_m^o = -(3653.5 \pm 4.4)$ kJ·mol$^{-1}$. Combining this value with $\Delta_f H_m^o = -(4044.8 \pm 5.0)$ kJ·mol$^{-1}$, one obtains $\Delta_f S_m^o = -(1312 \pm 22)$ J·mol$^{-1}$·K$^{-1}$ which is equal to the entropy change for the reaction of formation from the elements in their standard states, see below:

$$2U(cr) + Si(cr) + 2H_2(g) + 5O_2(g) \rightleftharpoons (UO_2)_2SiO_4 \cdot 2H_2O(cr) \qquad (A.216)$$

Using for elements at 298.15 K the following $S_m^o$ values (in J·mol$^{-1}$·K$^{-1}$, all from [2003GUI/FAN]): $(50.20 \pm 0.20)$ for U(cr), $(18.81 \pm 0.08)$ for Si(cr), $(130.680 \pm 0.003)$ for $H_2(g)$, $(205.152 \pm 0.005)$ for $O_2(g)$, this review obtains for soddyite $S_m^o = (94 \pm 22)$ J·mol$^{-1}$·K$^{-1}$, significantly different from the rough estimate of the entropy of soddyite by the Latimer [1951LAT] method, as outlined in Appendix D, 332 J·mol$^{-1}$·K$^{-1}$. An approximation of the entropy of soddyite as a sum of the entropy of forsterite, $M_2SiO_4$ ($S_m^o = 94.1$ J·mol$^{-1}$·K$^{-1}$ [1995ROB/HEM]), two entropies of $UO_3(cr)$, two contributions of the entropy of water in solid hydrates, about 40-45 J·mol$^{-1}$·K$^{-1}$ each [1951LAT], minus two entropies of MgO(cr), ($S_m^o = 26.95$ J·mol$^{-1}$·K$^{-1}$, [2003GUI/FAN]), gives a value of ~ 322 J·mol$^{-1}$·K$^{-1}$. The estimated $S_m^o$ values exceed the value calculated from $\Delta_f G_m^o$ and $\Delta_f H_m^o$ results by more than 200 J·mol$^{-1}$·K$^{-1}$. Therefore, it appears that values of $\Delta_r G_m^o$ and $\Delta_r H_m^o$ for Reaction (A.215) are mutually inconsistent by up to 60 kJ·mol$^{-1}$.

This review gives credit to $\log_{10} {}^*K_s^o$ (A.215) = $(6.14 \pm 0.42)$, $\Delta_r G_m^o$ (A.215) = $-(35.0 \pm 2.4)$ kJ·mol$^{-1}$, and the corresponding Gibbs energy of formation of soddyite, $(UO_2)_2SiO_4{\cdot}2H_2O(cr)$, $\Delta_f G_m^o = -(3653.5 \pm 4.4)$ kJ·mol$^{-1}$ as recalculated from [2007GOR/MAZ].

**[2007RED/WOO]**

This paper reports a solubility constant $\log_{10}{}^*K_s = 12.23$ for the reaction:

$$CaH_2(UO_2)_2(SiO_4)_2 \cdot 5H_2O(s) + 6H^+ \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 2SiO_2(aq) + 9H_2O(l)$$

As discussed in the Appendix A review in the hydroxide section, no equilibrium constant from this study is accepted by the present review.

**[2008PRI]**

This is a study of dissolution and growth of uranophane, $Ca(UO_2)_2(SiO_3OH)_2{\cdot}5H_2O(cr)$, in aqueous solutions at 20.5(± 2) °C and near-neutral pH (~ 6.0) in the ~ 0.01 M $CaCl_2$ and ~$10^{-3}$ M $SiO_2$ medium.

Uranophane was synthesised by conversion of boltwoodite $K(UO_2)(SiO_3OH)\cdot 1.5H_2O(cr)$ to uranophane by exchange of Ca for K. First, pale yellow acicular boltwoodite crystals were synthesised at pH 11.5 from solutions of uranyl nitrate and potassium chloride, containing natural rock crystal quartz fragments, by heating the mixture in the Teflon-lined reactor at 185 °C for four days. The synthesised boltwoodite was placed in the Teflon reactor with 2 M $CaCl_2$ solution, and heated to 125 °C for 15 days. The resulting solid consisted of fine (< 50 μm in length) yellow acicular crystals of uranophane, as confirmed by XRD. Bulk dissolution of the synthetic materials in 0.1 M HCl followed by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) for major cations (Ca, K, Si) and ICP mass spectrometry (ICP-MS) for uranium resulted in the Ca:Si:U ratio in the synthesised uranophane equal to 0.95(± 0.01):1.99(± 0.01):1.99(± 0.07) as compared with 1:2:2 for ideal uranophane.

Solubility experiments were conducted at near-neutral pH (~ 6.0) in the ~ 0.01 M $CaCl_2$ and ~ $10^{-3}$ M $SiO_2$ medium at various initial concentrations of uranium (from 0 to ~ $2\cdot 10^{-6}$ M) in solutions to approach uranophane equilibrium in aqueous solutions from both under- and supersaturation. Experiments were open to the atmosphere, pH was adjusted to ~ 6.0 by addition of $CaCO_3$. Experiments were conducted at 20.5(± 2) ºC, and the solutions were continuously agitated using a gyratory shaker. The duration of experiments was 10 weeks, where steady-state concentrations were reached after 4-5 weeks. Before sampling, test solutions were centrifuged and used to measure pH, and after acidifying with $HNO_3$ – to measure U by ICP-MS (an uncertainty ± 10 %) and cations by ICP-AES (an uncertainty of ± 2 %). Data are presented only graphically, however, plots are detailed enough to read values with a precision of a few per cent, except for U, which concentrations could be read with a precision of ~ 20 %.

Two series of experiments were performed: 1) Dissolution experiments, with the initial concentrations of U of (0 ~ $10^{-7}$ M), *i.e.* below the equilibrium concentration, which is equal to (1.84-3.06) × $10^{-7}$ M in this series. The equilibrium pH ranged from 5.86 to 5.92 (± 0.03); and 2) Precipitation experiments, with initial concentrations of U of ~ (1-2) × $10^{-6}$ M, *i.e.* above the equilibrium concentration, which is equal to (2.25-5.00) × $10^{-7}$ M in this series. The equilibrium pH ranged from 5.78 to 5.84 (± 0.03). The kinetic data in both sets of experiments suggest that in the early stages of the dissolution (up to week 3) the Si concentration decreased, suggesting precipitation of a Si-bearing phase. However, scanning electron microscopy did not reveal textures characteristic of leaching of uranophane, or growth of a new phase. The authors checked carefully for signs of formation of soddiyte, $(UO_2)_2SiO_4\cdot 2H_2O(cr)$, but found no evidence; this was confirmed by thermodynamic calculations that showed that the test solutions were undersaturated with respect to soddiyte.

The calculated equilibrium constant refers to the following dissolution Reaction (A.217):

$$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O(cr) + 6H^+ \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 2Si(OH)_4(aq) + 5H_2O(l) \quad \text{(A.217)}$$

The speciation was calculated using a variant of the EQ3 program with the database based on equilibrium constants from [1992GRE/FUG]. The values $\log_{10}{}^{*}K_s^o$ were in a range 10.79-11.06 for the dissolution experiments and 10.96-11.01 for precipitation ones. The author used an average midpoint value of (11.01 ± 0.09) (one standard deviation) to calculate the Gibbs energy of dissolution $\Delta_r G_m^o = -(62.8 \pm 0.5)$ kJ·mol$^{-1}$, and the Gibbs energy of formation $\Delta_f G_m^o = -(6196.1 \pm 0.5)$ kJ·mol$^{-1}$.

This review recalculated $\log_{10}{}^{*}K_s^o$ for Reaction (A.217) using the equilibrium constants selected or retained in this review for formation of all hydroxo-, carbonate, mixed hydroxo-carbonate complexes of uranyl, $UO_2SiO(OH)_3^+$, $UO_2Cl^+$, products of dissociation of $CO_2$ (from [2003GUI/FAN]) and $Si(OH)_4$ ([NEA TDB review on Ancillary Data – to be published]). The system was open to atmosphere with $P(CO_2) = 10^{-3.50}$ atm. The activity coefficients were calculated with the SIT model, ignoring the non-electrostatic contribution to activity factors at low ionic strength (~ 0.03 M). Equilibrium concentrations of Ca, Si (with the precision of 2-3 %), of U (with the precision of ~ 20 %), pH values (± 0.03 units, on the activity scale) were read from Figures 2-4 of the article for six experiments of a longest duration, four of them are from dissolution and two from the precipitation experiments (as a rule, values were taken from curves drawn by Prikryl through measured values). The average $\log_{10}{}^{*}K_s^o$ from all six points is equal to (11.52 ± 0.16), the uncertainties is given as $1.96\sigma_X$. The difference of about 0.5 $\log_{10}$ units in values $\log_{10}{}^{*}K_s^o$ calculated in [2008PRI] and in this review appears to be due to difference in the hydrolysis constants of uranyl in [1992GRE/FUG], used by Prikryl, and selected in the current review: the calculated concentrations of $UO_2^{2+}$ in [2008PRI] are about 1.4-1.5 times lower than in this review. The corresponding value of the Gibbs energy of dissolution Reaction (A.217) $\Delta_r G_m^o = -(65.757 \pm 0.913)$ kJ·mol$^{-1}$. This value was selected in the current review.

**[2011SHV/MAZ]**

This is a study of the enthalpy of formation through drop solution measurements, and the Gibbs energy of formation through solubility measurements, of synthetic boltwoodite, Na-boltwoodite and uranophane.

Na-boltwoodite was synthesised by combining solid uranyl acetate, water and a solution of sodium metasilicate at pH 11 and heating the mixture in a reaction vessel at 150 °C for seven days. Boltwoodite was prepared by combining solid uranyl acetate with the $SiO_2$ powder, water and a KOH solution and heating the mixture at 180 °C for seven days. Both final phases were light yellow powders. Uranophane was synthesised by combining a solid uranyl acetate, sodium metasilicate nonahydrate, and calcium acetate monohydrate with water and heating at 100 °C for three days, the resulting

product was also a yellow powder. Solid phases were characterised by X-ray powder diffraction (XRD), FT-IR analyses, and chemical analyses using inductively coupled plasma optical emission spectrometry (ICP-OES); the water content was determined from the weight loss using thermogravimetry/differential scanning calorimetry (TG/DSC). It was confirmed that each synthetic material consisted of only one crystalline phase of the following composition:

boltwoodite—$K_{0.75}(UO_2)(H_{0.80}SiO_4)_{0.86}{\cdot}0.97H_2O$(cr),

Na-boltwoodite—$Na_{0.93}(UO_2)(H_{0.85}SiO_4)_{0.93}{\cdot}1.25H_2O$(cr) and

uranophane—$Ca_{1.09}(UO_2)_2(H_{0.51}SiO_4)_{1.77}{\cdot}5.55H_2O$(cr).

Solubility measurements were conducted as batch experiments in Teflon vessels, which were slowly agitated at 22 °C. The experiments were performed from both undersaturation and oversaturation; pH was adjusted using minute quantities of $HNO_3$ and/or NaOH or KOH. The ionic medium was 0.05 M $KNO_3$ or 0.05 M $NaNO_3$ in the case of boltwoodite and Na-boltwoodite, respectively; the experiments with uranophane were made at varying ionic strengths. The experimental systems were open to atmospheric $CO_2$. Aliquots of solutions were filtered through 0.1 μm Millipore Millex filters, diluted and acidified for ICP-OES analysis for U, Si, Na, and K.

For boltwoodite, the undersaturated system reached steady-state conditions within 62 days and the supersaturated one within 23 days. The pH of the test solutions varied between 7.23 and 8.94. The concentration of Si in solution was always in excess of that of U by less than an order of magnitude, suggesting a non-congruent dissolution. By using XRD and FT-IR the boltwoodite was found to be the only crystalline phase. In all, there were 24 data points. For Na-boltwoodite the steady-state conditions were reached within five days from both the undersaturation and oversaturation; however, the extent of non-stoichiometric dissolution was much greater than in the boltwoodite system, the Si/U ratio exceeded 100, and the U concentration was similar for both systems. pH varied within 7.32-8.58; in all, there were 25 data points. Again, XRD and FT-IR methods found Na-boltwoodite to be the only crystalline phase. These findings do not exclude the formation of an amorphous phase, if its FT-IR spectra are very similar to that of the crystalline phase, as found in other studies (for example, [2008SOD/SKA]).

For uranophane, aqueous solutions reached a steady-state within ten days. The Si concentrations in all runs, with or without excess $SiO_2$ gel, were within the ranges reported for solubility of amorphous silica. The equilibrium pH values varied within 2.99-4.06; in all there were 68 data points. XRD after experiments indicated that uranophane was the only crystalline phase present and FT-IR data of the final mineral residues were similar to that of the starting materials.

Solubility constants, $\log_{10}{}^{*}K_s^o$, were calculated from each data point at steady-state conditions and averaged. The dissolution reaction for $M^+ = Na^+$, $K^+$ was as follows:

$$M(UO_2)(SiO_3OH)\cdot H_2O(cr) + 3H^+ \rightleftharpoons M^+ + UO_2^{2+} + Si(OH)_4(aq) + H_2O(l) \quad (A.218)$$

and that for uranophane:

$$Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O(cr) + 6H^+ \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 2Si(OH)_4 + 5H_2O(l) \quad (A.219)$$

The authors have assumed phases of idealised composition when calculating $\log_{10}{}^{*}K_s^o$. The chemical model used for speciation calculations included complexes from [2003GUI/FAN], the calculations were made at the partial pressure of $CO_2$ of $10^{-3.5}$ atm. The Debye-Hückel equation in the form of the third approximation for $RbNO_3$ solutions according to [1981HEL/KIR] was employed to evaluate activity coefficients.

This review recalculated the solubility products of K- and Na-boltwoodite uranosilicates employing a chemical model, which included hydroxo-, carbonate, mixed hydroxo-carbonate complexes of uranyl, $UO_2NO_3^+$ and $UO_2SiO(OH)_3^+$, with all equilibrium constants selected or retained in the present review, and products of dissociation of $CO_2$ ([2003GUI/FAN]), and $Si(OH)_4(aq)$ (from [NEA TDB review on Ancillary Data – to be published]). The system was open to atmospheric $CO_2$.

The SIT model was used for evaluating activity coefficients. The average $\log_{10}{}^{*}K_s^o$ values, see Table A-108, are somewhat different from ones recommended in [2011SHV/MAZ]. To check the calculations we compared our custom *Mathematica* program and the commercially available HCH package [2008SHV] (for one control point). The concentrations of dissolved species agree within 3 % between the different calculation methods used. It was verified that all test solutions for both K- and Na-boltwoodite were unsaturated with respect to soddyite, $(UO_2)_2SiO_4\cdot 2H_2O(cr)$.

Similar calculations were performed for uranophane. In addition to above given complex species, the chemical model also included $CaCO_3(aq)$, $CaHCO_3^+$, and $CaOH^+$ complexes, but their contribution always turned out to be negligible at the low experimental pH values (< 4). However, in many solutions the ionic strengths were rather high (up to 1.5 m), which made the evaluation of the equilibrium constant for Reaction (A.219) at infinite dilution uncertain. As a compromise, the present review decided to accept only $\log_{10}{}^{*}K_s^o$ values obtained from data in solutions with ionic strengths less than 0.4 m (38 data points from a total of 68). The average $\log_{10}{}^{*}K_s^o$ value is given in Table A-108; it is about one log unit lower than the value reported in [2011SHV/MAZ] that has been obtained using all 68 data points. However, no $\log_{10}{}^{*}K_s^o$ values were accepted in the current review as thermodynamic calculations showed that the test solutions were oversaturated with respect to soddyite.

Table A-108: Values of $\log_{10}{}^{*}K_s^o$ for Reactions (A.218) and (A.219) as reported in [2011SHV/MAZ] and recalculated in this review.

| Phase | Formula | Number of data points used | $\log_{10}{}^{*}K_s^o$ (a) | $\log_{10}{}^{*}K_s^o$ (b) |
|---|---|---|---|---|
| Boltwoodite | $K(UO_2)(SiO_3OH)\cdot H_2O$(cr) | 24 | 4.12(– 0.48/+ 0.30)(c) | (4.48 ± 1.17)(c) |
| Na-boltwoodite | $Na(UO_2)(SiO_3OH)\cdot H_2O$(cr) | 25 | 6.07(– 0.16/+ 0.26)(c) | (5.59 ± 0.95)(c) |
| Uranophane | $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$(cr) | 38 | 10.82(–0.62/+ 0.29)(d) | (9.8 ± 0.9)(d) |

(a) Authors' value, uncertainties are given for 2σ;
(b) Recalculated in this review, uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10}{}^{*}K_s^o$, see Appendix C, Section C.3;
(c) For Reaction (A.218);
(d) For Reaction (A.219).

Enthalpies of formation were measured by drop solution calorimetry in the sodium molybdate solvent (50 mg of $SiO_2$ as cristobalite was added to the solvent) at 702 °C using a custom-built Tian-Calvet high-temperature microcalorimeter. In total, ten data points were obtained for each solid phase. These results were used to calculate the enthalpy of formation from oxides and from elements of phases of the above indicated composition, see Table A-109.

Table A-109: $\Delta_f H_m^o$ of uranosilicates based on data [2011SHV/MAZ].

| Phase | Formula | $\Delta_{f,oxide} H_m^o$ (a) /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ (b) /kJ·mol$^{-1}$ |
|---|---|---|---|
| Boltwoodite | $K_{0.75}(UO_2)(H_{0.80}SiO_4)_{0.86}\cdot 0.97H_2O$(cr) | – (251.2 ± 5.9) | – (2766.8 ± 6.5) |
| Na-boltwoodite | $Na_{0.93}(UO_2)(H_{0.85}SiO_4)_{0.93}\cdot 1.25H_2O$(cr) | – (215.8 ± 6.0) | – (2948.8 ± 6.6) |
| Uranophane | $Ca_{1.09}(UO_2)_2(H_{0.51}SiO_4)_{1.77}\cdot 5.55H_2O$(cr) | – (322.2 ± 10.7) | – (6799.0 ± 11.5)(c) |

(a) Authors' value of the enthalpy of formation from oxides, uncertainties are given for 2σ;
(b) Authors' value of the enthalpy of formation from elements, uncertainties are given for 2σ.

These values were taken by the authors (see Table 3 in [2011SHV/MAZ]) as the enthalpies of formation of boltwoodite, Na-boltwoodite and uranophane of the idealised stoichiometric compositions. The assumption of an idealised composition is likely to introduce a large error in $\Delta_f H_m^o$ values. Indeed, for example, the value of $\Delta_r S_m^o = (\Delta_r H_m^o - \Delta_r G_m^o)/T$ for boltwoodite, given in [2011SHV/MAZ], is equal to – (27.5 ± 7.3) J·K$^{-1}$·mol$^{-1}$, which results in $S_m^o \approx 1020$ J·K$^{-1}$·mol$^{-1}$ for boltwoodite. This value is about 760 J·K$^{-1}$·mol$^{-1}$ larger than $S_m^o = 258.7$ J·K$^{-1}$·mol$^{-1}$, obtained by calorimetry in [2002KAR/CHE] (the Latimer method [1951LAT], as outlined in Appendix D, predicts a close value of $S_m^o = 244$ J·K$^{-1}$·mol$^{-1}$). In other words, there appears to be an error of about 220 kJ·mol$^{-1}$ in the value of $\Delta_f H_m^o$ reported in [2011SHV/MAZ] for boltwoodite.

The authors of [2011SHV/MAZ] indicated that there is a possibility to evaluate $\Delta_f H_m^o$ of phases of the idealised stoichiometric compositions "assuming that the enthalpy of formation from oxides is the same as that measured for the slightly non-

stoichiometric materials". This review calculated $\Delta_f H_m^o$ of uranyl silicates using this assumption and obtained the values, given in the last column of Table A-110. The following values of the enthalpies of formation (in kJ·mol$^{-1}$) have been employed for oxides: – (361.7 ± 4.0) for $K_2O$(cr) and – (414.57 ± 0.30) for $Na_2O$(cr) from [1982GLU/GUR], – (634.92 ± 0.9) for CaO(cr), – (1223.8 ± 1.2) for $UO_3$(cr) (from [2003GUI/FAN]) and – (907.7 ± 1.0) for $SiO_2$(cr, crystobalite) (based on data from the NEA TDB review on Ancillary Data – to be published). As can be seen from Table A-110, the difference between two sets of $\Delta_f H_m^o$ values is very large, emphasising the effect of deviations from the idealised composition on the value of the enthalpy of formation evaluted from experimental results.

Table A-110: $\Delta_f H_m^o$ of uranosilicates of idealised stoichiometric composition based on data [2011SHV/MAZ].

| Phase | Formula | $\Delta_f H_m^o$ (a) /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ (b) /kJ·mol$^{-1}$ |
|---|---|---|---|
| Boltwoodite | $K(UO_2)(SiO_3OH)\cdot H_2O$(cr) | – (2766.8 ± 6.5) | – (2992.3 ± 6.4) |
| Na-boltwoodite | $Na(UO_2)(SiO_3OH)\cdot H_2O$(cr) | – (2948.8 ± 6.6) | – (2983.3 ± 6.2) |
| Uranophane | $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$(cr) | – (6799.0 ± 11.5) | – (6935.1 ± 11.2) |

(a) Authors' values accepted to be equal to those measured for phases of non-stoichiometric compositions;
(b) Calculated assuming that the enthalpies of formation from oxides are equal for phases of the exact and of a slightly non-stoichiometric compositions.

The current review accepts from [2011SHV/MAZ] only equilibrium constants for the Reaction (A.218) for the dissolution of K- and Na-boltwoodite, recalculated in this review:

$$\log_{10}{}^*K^o = (4.480 \pm 1.170) \text{ for K-boltwoodite;}$$

$$\log_{10}{}^*K^o = (5.590 \pm 0.950) \text{ for Na-boltwoodite.}$$

**[2013ALE/SZY]**

Soddyite, $(UO_2)_2SiO_4\cdot 2H_2O$(cr), and boltwoodite, $(K,Na)(UO_2)(SiO_3OH)\cdot 1.5H_2O$(cr), were synthesised under mild hydrothermal conditions in the presence of aqueous Np(V) solutions. Electron microscopy and electron diffraction analyses show that the Np(V) is incorporated in the structure of soddyite, up to a mol fraction of 0.0091 in the $UO_2^{2+}$ vacancies, while in the case of boltwoodite, the Np(V) forms a second phase, nanoparticles of $Np_2O_5$(s).

The authors also studied solubility of soddyite or boltwoodite (with the addition of amorphous silica) in aqueous solutions, containing uranyl nitrate and sodium metasilicate in amounts below the equilibrium concentrations of U and Si. The solubility was measured at pH (3.30 ± 0.09) for soddyite and at (8.54 ± 0.04) for boltwoodite (both in the $NaNO_3$ medium, $I$ < 0.02 M). Solubility measurements were

conducted as batch experiments in slowly agitated Teflon reaction vessels open to the atmosphere, at room (?) temperature over 24 days (the steady-state was reached within ten days). The ICP-OES analysis was used for U and Si, and ICP-MS for Np. In experiments with boltwoodite the concentrations of U and Np are comparable, and $Np_2O_5$(s) most likely controls the aqueous concentrations of Np. In the experiments with soddyite, the equilibrium concentrations of Np are about three orders of magnitude smaller than the concentrations of U, hence, there are no reasons to expect that small impurities of Np will affect the distribution of aqueous U species. Therefore, it is not clear why the concentrations of U in this study are about 0.5-0.7 $\log_{10}$ units lower than those measured at similar pH values in [2007GOR/MAZ], performed in the same laboratory. This review calculated the solubility constants for the reaction:

$$(UO_2)_2SiO_4 \cdot 2H_2O(cr) + 4H^+ \rightleftharpoons 2UO_2^{2+} + Si(OH)_4(aq) + 2H_2O(l) \qquad \text{(A.220)}$$

from two solubility data points [2013ALE/SZY] in a nitrate medium at pH = 3.27 ($[U_{tot}] = 10^{-2.65}$ M, $[Si_{tot}] = 10^{-2.65}$ M) and pH = 3.32 ($[U_{tot}] = 10^{-2.61}$ M, $[Si_{tot}] = 10^{-2.48}$ M) and obtained $\log_{10}{}^{*}K_s^o = 4.63$ and 5.20, which are lower than values calculated from solubility data in other studies ([1992NGU/SIL], [1996MOL/GEI], and [2007GOR/MAZ]). The incorporation of small (less than 0.01 in the mole fraction) amounts of Np(V) into the structure of soddyite is unlikely to be the reason for a large discrepancy of calculated $\log_{10}{}^{*}K_s^o$ values.

**[2013NIP/CHE2]**

This is a study of the solubility and phase composition of uranosilicates $M(III)[(UO_2)(SiO_3OH)]_3 \cdot 10H_2O(cr)$ (M(III) = La-Lu, Y) in aqueous solutions (water, $HClO_4$, or NaOH) at 25 °C. The rare earth uranosilicates were synthesised by mixing solutions containing a REE nitrate, sodium metasilicate, and uranyl acetate in the molar ratio 1:3:3. The phase purity was checked by X-ray diffraction and the elemental composition by X-ray fluorescence energy-dispersive spectrometry.

In the solubility experiments approximately 100 mg of the solid phases were added to 5-100 ml of water, $HClO_4$ ($1 \times 10^{-3}$ -1 M) or NaOH ($1 \times 10^{-3}$ -1 M) solutions in sealed plastic vessels. The mixture was allowed to equilibrate at 25 °C for 5-6 months with intermittent stirring and pH monitoring. After a constant pH value was attained (about 200 days), the precipitate was separated by centrifugation, washed with water, dried at room temperature and examined by X-ray diffraction and X-ray fluorescence analysis. The saturated solutions were checked by nephelometry and turbidimetry to reveal the presence of suspended and colloidal particles: all solutions were clear with no appreciable concentrations of colloidal particles. The concentrations of elements were determined spectrophotometrically: Si(IV) with the molybdate method; U(VI)—with arsenazo III, and REE—by titration with a $10^{-3}$ M $Na_2EDTA$ solution using Xylenol

Orange as indicator. Experimental data (composition and volume of the initial solution, equilibrium pH, concentrations of Si, REE and U) are tabulated.

The analysis showed that uranosilicates are stable over a rather wide pH range: lanthanum uranosilicates in the range pH 4-12 and uranosilicates of Gd and heavier elements are stable at pH 4-13; at lower pH these compounds decompose with the formation of amorphous $SiO_2$. At pH 10-12, REE hydroxides start precipitating, and in strongly alkaline media, at pH > 12 the uranosilicates decompose and the solid phase consists of REE hydroxides and $Na_2U_2O_7$.

Data on the solubility of uranosilicates in water were used to calculate the solubility constants of Reaction (A.221):

$$\mathrm{M(III)[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr) + 3H^+ \rightleftharpoons M^{3+} + 3UO_2^{2+} + 3H_2SiO_4^{2-} + 10H_2O(l)} \quad \text{(A.221)}$$

When calculating the activities of the ions, the authors took into account the hydrolysis of uranyl using the equilibrium constants from [2003GUI/FAN], the various monomeric and polymeric (up to tetrameric) ionic species of silica also from [2003GUI/FAN], the equilibrium constant for formation of $UO_2SiO(OH)_3^+$ from [1998MOL/GEI], the equilibrium constants for hydrolysis of REE and solubility products of REE hydroxides at infinite dilution were taken from the Russian handbook Thermal Constants of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981. The SIT model was employed to calculate the activity coefficients of ions with the values of the SIT interaction coefficients taken from [1992GRE/FUG]. The results are presented in Table A-111.

Table A-111: Values of solubility products and the Gibbs energy of formation of uranyl silicates of REE reported in [2013NIP/CHE2].

| Compound | $\log_{10}{}^{*}K_s^o$ | $-\Delta_f G_m^o$ /kJ·mol$^{-1}$ |
|---|---|---|
| $La[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (53.8 ± 0.5) | (9746 ± 20) |
| $Ce[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (53.7 ± 0.6) | (9738 ± 20) |
| $Pr[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (53.1 ± 0.6) | (9737 ± 20) |
| $Nd[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (53.5 ± 0.5) | (9732 ± 20) |
| $Sm[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (54.2 ± 0.5) | (9727 ± 20) |
| $Eu[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (53.7 ± 0.6) | (9640 ± 20) |
| $Gd[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (55.9 ± 0.7) | (9734 ± 20) |
| $Tb[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (54.6 ± 0.6) | (9732 ± 20) |
| $Dy[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (54.4 ± 0.6) | (9727 ± 20) |
| $Ho[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (54.1 ± 0.6) | (9750 ± 20) |
| $Er[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (54.0 ± 0.6) | (9735 ± 20) |
| $Tm[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (54.4 ± 0.6) | (9737 ± 20) |
| $Yb[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (53.8 ± 0.6) | (9707 ± 20) |
| $Lu[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (54.0 ± 0.6) | (9695 ± 20) |
| $Y[(UO_2)(SiO_3OH)]_3\cdot 10H_2O(cr)$ | (54.1 ± 0.6) | (9753 ± 20) |

(a) Values of the Gibbs energy of formation of ions and water are taken from [2003GUI/FAN], and the Russian handbook Thermal Constants of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981.

The obtained $\log_{10}{}^{*}K_{s}^{o}$ for Reaction (A.221) were not selected in the current review due to absence of independent $\log_{10}{}^{*}K_{s}^{o}$ values to compare (and where such a comparision is possible—soddyite, boltwoodite, uranophane—results of this laboratory could not be selected).

**[2013NIP/CHE3]**

This is a study of the solubility and phase composition of uranosilicates $M(II)[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O(cr)$ (M(II) = Mn, Co, Ni, Cu, Zn) in aqueous solutions at 25 °C. Note that $Cu[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O(cr)$ is known as the mineral cuprosklodowskite. Uranosilicates were synthesised by mixing solutions containing $K(UO_2)(SiO_3OH){\cdot}H_2O(cr)$ and $M(II)(NO_3)_2(cr)$ in the molar ratio 1:15 and heating to 100 ºC for 15 hours. For the synthesis of $Mn[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O(cr)$, solutions of $Na_2SiO_3{\cdot}9H_2O$, $UO_2(CH_3COO)_2$ and $MnSO_4$ in the molar ratio Mn:Si:U 0.6:1:1 were heated to 130 ºC for seven hours. The phase purity was checked by X-ray diffraction.

The solubility experiments were conducted by adding 100 to 300 mg of solid phase to 5-100 ml of water, $HClO_4$ ($1 \times 10^{-3}$ -1 M) or NaOH ($1 \times 10^{-3}$ -1 M) solutions in sealed plastic vessels. The mixture was allowed to equilibrate at 25 °C for a few months with intermittent stirring and pH monitoring. After a constant pH was attained (about 75 days), the precipitate was separated by centrifugation, washed with water, dried at room temperature and examined by X-ray diffraction and X-ray fluorescence analysis. The concentrations of elements were determined spectrophotometrically: Si(IV) with the molybdate method; U(VI) – with arsenazo III, and for Mn, Co, Ni, Cu, and Zn by reactions with 4-(2-pyridylazo)-resorcinol, nitrox-R-salt, dimethylglyoxime, diethyldithiocarbamate, and sulfarzacene, respectively. Experimental data (an initial solution's composition, equilibrium pH, concentrations of Si, $M^{II}$ and U) are tabulated.

It was found that the uranosilicates are stable only in a limited pH range of ~ 4.0-11, depending on M(II). In more acidic media uranosilicates are converted into amorphous silica, at pH > 7.0-10.5 M(II) hydroxides start precipitating, and in strongly alkaline media, at pH > 12 the uranosilicates decompose and the solid phase consists of M(II) hydroxides and $Na_2U_2O_7$ (in the case of $Zn[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O(cr)$ at M(NaOH) ≥ 0.1 M the precipitated amphoteric $Zn(OH)_2$ dissolves completely).

The solubility data were used to calculate the solubility constants of the following reactions:

$$M^{II}[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O(cr) + 2H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2H_2SiO_4^{2-} + 6H_2O(l) \quad \text{(A.222)}$$

The calculations of equilibrium constants were performed by the authors as described in [2013NIP/CHE2], the equilibrium constants for the hydrolysis of M(II) and solubility products of M(II) were taken from the Russian handbook Thermal Constants

of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981. Results are presented in Table A-112.

Table A-112: Values of solubility products and the Gibbs energy of formation of uranyl silicates of Mn, Co, Ni, Cu, Zn reported in [2013NIP/CHE3].

| Compound | $\log_{10}{}^{*}K_s^o$ | $-\Delta_f G_m^o$ (a) /kJ·mol$^{-1}$ |
|---|---|---|
| $Mn[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O$(cr) | (36.08 ± 0.38) | (6116 ± 20) |
| $Co[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O$(cr) | (36.83 ± 0.30) | (5943 ± 20) |
| $Ni[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O$(cr) | (38.02 ± 0.55) | (5942 ± 20) |
| $Cu[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O$(cr) | (38.80 ± 0.59) | (5835 ± 20) |
| $Zn[(UO_2)(SiO_3OH)]_2{\cdot}6H_2O$(cr) | (36.91 ± 0.35) | (6037 ± 20) |

(a) Values of the Gibbs energy of formation of ions and water are taken from [2003GUI/FAN], and the Russian handbook Thermal Constants of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981.

The obtained $\log_{10}{}^{*}K_s^o$ for the Reaction (A.222) were not selected in the current review due to absence of independent $\log_{10}{}^{*}K_s^o$ values to compare (and where such a comparision is possible—soddyite, boltwoodite, uranophane—results of this laboratory could not be selected).

**[2013NIP/CHE4]**

This is a study of solubility and phase composition of synthetic uranosilicates and uranogermanates $A^IHB^{IV}UO_6{\cdot}nH_2O$(cr) ($A^I$ = Li, Na, K, Rb, Cs, $NH_4$), $B^{IV}$ = Si, Ge in aqueous solutions at 25 °C. Alkali metal uranosilicates were synthesised by mixing solutions containing $A^INO_3$ and $UO_2(NO_3)_2$, then adding $SiO_2$ dissolved in $A^IOH$ at the molar ratio $A^I$:U:Si of 10:1:2 and heating to 200 °C for 15 hours. For alkali metal uranogermanates, $GeO_2$ dissolved in water was used, and the heating was conducted at 130 °C for 12 hours. The phase identification was done by X-ray diffraction.

The solubility experiments were performed by adding 100 to 300 mg of solid phase to 5-100 ml of water, $HClO_4$ ($1 \times 10^{-3}$ -1 M) or NaOH ($1 \times 10^{-3}$ -1 M) solutions in sealed plastic vessels. The mixture was allowed to equilibrate at 25 °C for a few months with intermittent stirring and pH monitoring. After a constant pH was attained (about ~ 50 days), the precipitate was separated by centrifugation, washed with water, dried at room temperature and examined by X-ray diffraction. The concentrations of elements were determined spectrophotometrically: Si(IV) and Ge(IV) with the molybdate method; U(VI) – with arsenazo III. Experimental data (an initial solution, equilibrium pH, concentrations of U and $B^{IV}$) are tabulated.

It is worth comparing presented solubility results to older data from the same laboratory ([2004CHE/NIP]) obtained in solubility runs of shorter duration (ten days). The equilibrium pH may differ up to 0.8 $\log_{10}$ units both in water and $10^{-3}$ M $HClO_4$ solutions, although usually the difference is much lower. However, the solubility

data for various phases are rather close to older results, except for $NH_4(UO_2)(SiO_3OH)\cdot H_2O$(cr) in pure water, where solubility data of [2013NIP/CHE4] are approximately by two orders of magnitude lower compared with similar data of [2004CHE/NIP].

It was found that uranosilicates and uranogermanates are stable only in a limited pH range. In acidic media with pH < 3-6 the compounds decompose with the formation of crystalline germanium oxide or amorphous silica. In alkaline solutions at pH ≥ 11 uranogermanates start decomposing with the formation of diuranates $A^I_2U_2O_7$. The conversion of uranosilicates takes place only at hydroxide concentrations larger than 1 M.

The solubility data were used to calculate the equilibrium constants of the following reaction:

$$A^IHSi/GeUO_6\cdot nH_2O(cr) + H^+ \rightleftharpoons A^+ + UO_2^{2+} + H_2Si/GeO_4^{2-} + nH_2O(l) \qquad (A.223)$$

When calculating the activities of the ions, the authors took into account the hydrolysis of uranyl and silica with the formation of monomeric and polymeric forms (the infinite dilution constants are from [2003GUI/FAN]), the formation of silicate complex of the uranyl ion ([1998MOL/GEI]), the solubility product and hydrolysis constants of Ge(IV) from [1998POK/SCH], and the hydrolysis constants of alkali metal ions and $NH_4^+$ (the corresponding stability constants at infinite dilution were taken from the Russian handbook Thermal Constants of Substances, Ed. Glushko V.P., Moscow, Nauka, 1965-1981). The SIT model was employed to calculate the activity coefficients of ions with the values of the SIT interaction coefficients taken from [2003GUI/FAN]. The obtained $\log_{10}{}^*K_s^o$ for Reaction (A.223) and $\Delta_f G_m^o$ for uranosilicates are given in Table A-113.

This review independently treated the solubility data for alkali metal uranosilicates in water and $10^{-2}$ and $10^{-3}$ M of $HClO_4$. Results in 0.1 and 1 M solution of perchloric acid were not used because the solid phases decompose in such acid solutions. Equilibrium with atmosphere was assumed and the partial pressure of $CO_2$ was taken equal to $10^{-3.5}$ atm. Note that results of calculations in $10^{-2}$ and $10^{-3}$ M $HClO_4$ solutions, whether open or closed to atmospheric $CO_2$, are very similar due to negligibly low concentrations of carbonate ions. However, an assumption that the alkali solutions are open to atmospheric $CO_2$ results in unrealistically high concentrations of carbonate ions (for example, at pH=11 the calculated activity of $CO_3^{2-}$ in solution exceeds 2 m). As it is impossible to estimate the extent of equilibrium with atmospheric $CO_2$ in alkali solutions that will be determined by the rate of transfer of $CO_2$(g) to the solution, solubility data in alkali solutions were not used by this review. The chemical model used included all hydroxo-, carbonate, mixed hydroxo-carbonate complexes of the uranyl ion and $UO_2SiO(OH)_3^+$, all selected or retained in this review. Data were used to calculate values of $\log_{10}{}^*K_s^o$ for Reaction (A.224).

$$M^{I}(UO_2)(SiO_3OH)\cdot nH_2O(cr) + 3H^+ \rightleftharpoons M^+ + UO_2^{2+} + Si(OH)_4(aq) + nH_2O(l) \quad (A.224)$$

Note that the concentration of alkali metal ion, $M^+$, was not measured, and this review has assumed that its molality was equal to the half the sum of total concentrations of silica and U(VI). The SIT model was used to evaluate activity coefficients (note that the ionic strength was always less than 0.01 m), and the water activity was taken equal to 1. As explained above, only $\log_{10}{}^{*}K_s^o$ values calculated from solubility data in $HClO_4$ solutions and $H_2O$ were accepted in this review. The average values of $\log_{10}{}^{*}K_s^o$ for Reaction (A.224) and $\Delta_f G_m^o$ of uranosilicates calculated with the use of $\Delta_f G_m^o$ of the reaction participants from [2003GUI/FAN] (except for $Si(OH)_4$, which was taken from [NEA TDB review on Ancillary Data – to be published]) are given in Table A-113. Values of the Gibbs energies of formation of solid phases given in the paper and recalculated in this review are in a close agreement.

Table A-113: Values of $\log_{10}{}^{*}K_s^o$ for Reactions (A.223) and (A.224) and $\Delta_f G_m^o$ of uranosilicates and uranogermanates based on data [2013NIP/CHE4].

| Compound | $\log_{10}{}^{*}K_s^{o\ (a)}$ | $-\Delta_f G_m^{o\ (a)}$/kJ·mol$^{-1}$ | $\log_{10}{}^{*}K_s^{o\ (b)}$ | $-\Delta_f G_m^{o\ (b)}$/kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $Li(UO_2)(SiO_3OH)\cdot 1.5H_2O(cr)$ | 18.85 | (2884 ± 20) | (4.23 ± 1.02) | (2886.2 ± 6.3) |
| $Na(UO_2)(SiO_3OH)\cdot H_2O(cr)$ | 19.39 | (2738 ± 20) | (3.82 ± 1.34) | (2739.0 ± 7.9) |
| $K(UO_2)(SiO_3OH)\cdot H_2O(cr)$ | 22.40 | (2776 ± 20) | (1.28 ± 0.94) | (2774.1 ± 5.7) |
| $Rb(UO_2)(SiO_3OH)\cdot H_2O(cr)$ | 20.70 | (2768 ± 20) | (2.14 ± 0.50)[c] | (2770.7 ± 3.5) |
| $Cs(UO_2)(SiO_3OH)\cdot H_2O(cr)$ | 18.65 | (2763 ± 20) | (3.63 ± 0.51) | (2769.6 ± 3.5) |
| $NH_4(UO_2)(SiO_3OH)\cdot H_2O(cr)$ | 20.88 | (2564 ± 20) | (1.98 ± 1.44) | (2567.0 ± 8.5) |
| $Li[(UO_2)(GeO_3OH)]\cdot 3.5H_2O(cr)$ | 12.61 | (2989 ± 20) | | |
| $Na[(UO_2)(GeO_3OH)]\cdot 2.5H_2O(cr)$ | 14.53 | (2732 ± 20) | | |
| $K[(UO_2)(GeO_3OH)]\cdot 2H_2O(cr)$ | 17.40 | (2650 ± 20) | | |
| $Rb[(UO_2)(GeO_3OH)]\cdot 2H_2O(cr)$ | 16.20 | (2645 ± 20) | | |
| $Cs[(UO_2)(GeO_3OH)]\cdot 2H_2O(cr)$ | 14.55 | (2643 ± 20) | | |
| $NH_4[(UO_2)(GeO_3OH)]\cdot 2H_2O(cr)$ | 16.52 | (2442 ± 20) | | |

(a) Values calculated in [2013NIP/CHE4] for Reaction (A.223);
(b) Values evaluated in this review for Reaction (A.224), uncertainties are given as $1.96\sigma_X$, where $\sigma_X$ is the standard deviation associated with $\log_{10}{}^{*}K_s^o$, see Appendix C, Section C.3;
(c) The uncertainty is estimated in this review, it is increased compared with the statistical value of 0.10.

Calculations, performed in this review, showed that solutions in equilibrium with Li-, Na-, and Cs-boltwoodite, in practically all cases, were oversaturated with respect to soddyite, $(UO_2)_2SiO_4\cdot 2H_2O(cr)$. Solutions for Rb- and $NH_4$-boltwoodite appear to be close to equilibrium with soddyite, within a wide (± 0.7 $\log_{10}$ units) range of scattering of calculated values of the saturation index. Solutions in equilibrium with K-boltwoodite appear to be undersaturated with respect to soddyite, however, ${}^{*}K_s^o$ values for K-boltwoodite, calculated from data of [2013NIP/CHE4], are several orders of magnitude lower than the value reported in [2011SHV/MAZ]. Therefore, no results were selected by the current review.

**[2013SZE/COS]**

This is a study of the solubility of intermediate members of the $Th_{1-x}U_xSiO_4$ solid solutions in the 0.1 M HCl aqueous solution at temperatures from 298 to 346 K. The synthesis was performed in an inert glovebox flushed with Ar, by mixing solutions of Th(IV) and U(IV) chlorides with a $Na_2SiO_3$ solution and heating the resulting gel in an autoclave at 250 °C for 24 hours or longer. Solids were characterised by scanning electron microscopy (SEM), X-ray energy-dispersive spectroscopy (EDS) and powder X-ray diffraction (PXRD). In all, seven compositions ($x$ = 0, 0.09, 0.20, 0.26, 0.35, 0.45, 0.51) were used in solubility runs at (298 ± 2) K, and 3 ($x$ = 0, 0.2, 0.45) at temperatures 313, 332, and 346 K. For all compositions, the dissolution was congruent (stoichiometric), and a constant composition of the aqueous solution was reached after 50-200 days. The speciation in the equilibrated aqueous solution was calculated using a chemical model based mostly on values selected in NEA-TDB [2003GUI/FAN], and employing the Davies equation to estimate activity coefficients. Experimental data were used to calculate solubility products for intermediate compositions and for thorite, $ThSiO_4$(cr). For the reaction:

$$ThSiO_4(cr) + 4H^+ \rightleftharpoons Th^{4+} + Si(OH)_4(aq) \qquad \text{(A.225)}$$

the value of $\log_{10}{}^*K_s^o = -(5.62 \pm 0.08)$ was obtained. An analysis of results shows that the uranothorite solid solution is very close to ideal, so, each of intermediate compositions was used to calculate the solubility product of coffinite, $USiO_4$(cr), according to the reaction:

$$USiO_4(cr) + 4H^+ \rightleftharpoons U^{4+} + Si(OH)_4(aq) \qquad \text{(A.226)}$$

and $\log_{10}{}^*K_s^o = -(6.1 \pm 0.2)$ was obtained. The temperature dependence of equilibrium constants allowed to determine for Reaction (A.225) $\Delta_r H_m^o = (56 \pm 16)$ kJ·mol$^{-1}$, and for Reaction (A.226) $\Delta_r H_m^o = (53 \pm 12)$ kJ·mol$^{-1}$.

This route to determine the thermodynamic properties of coffinite was selected due to difficulties in synthesising large amounts of the single-phase $USiO_4$(cr) for solubility studies. Indeed, obtained data show that uranothorite solid solutions with $x$ > 0.26 are less stable than the corresponding mixture of binary oxides.

The values of $\Delta_f G_m^o$, $\Delta_f H_m^o$, $\Delta_f S_m^o$, and $S_m^o$ calculated in this review from reaction data in [2013SZE/COS] are given in Table A-114. The additional data are taken from [2003GUI/FAN]: for $U^{4+}$ $\Delta_f G_m^o = -(529.86 \pm 1.77)$ kJ·mol$^{-1}$, $\Delta_f H_m^o = -(591.2 \pm 3.3)$ kJ·mol$^{-1}$; from [2008RAN/FUG] for $Th^{4+}$ $\Delta_f G_m^o = -(704.78 \pm 5.30)$ kJ·mol$^{-1}$, $\Delta_f H_m^o = -(768.70 \pm 2.30)$ kJ·mol$^{-1}$; and from [NEA TDB review on Ancillary Data – to be published]: for $Si(OH)_4$(aq) $\Delta_f G_m^o = -(1309.20 \pm 1.02)$ kJ·mol$^{-1}$, $\Delta_f H_m^o = -(1461.07 \pm 1.24)$ kJ·mol$^{-1}$.

Table A-114: Values of $\Delta_f G_m^o$, $\Delta_f H_m^o$, $\Delta_f S_m^o$, and $S_m^o$ of thorite and coffinite calculated in this review from reaction data in [2013SZE/COS].

| Phase, formula | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $\Delta_f S_m^o$ /J·mol$^{-1}$·K$^{-1}$ | $S_m^o$ (a) /J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|
| Coffinite, $USiO_4$(cr) | – (1873.9 ± 2.3) | – (2105.3 ± 12.5) | – (776 ± 43) | – (297 ± 43) |
| Thorite, $ThSiO_4$(cr) | – (2046.1 ± 5.4) | – (2285.8 ± 16.2) | – (804 ± 57) | – (322 ± 57) |

(a) Auxiliary data used: $S_m^o$ (U, cr) = (50.20 ± 0.20) J·mol$^{-1}$·K$^{-1}$, $S_m^o$ (Si, cr) = (18.81 ± 0.08) J·mol$^{-1}$·K$^{-1}$, $S_m^o$ ($O_2$, g) = (205.152 ± 0.005) J·mol$^{-1}$·K$^{-1}$ (all from [2003GUI/FAN]), $S_m^o$ (Th, cr, α) = (52.64 ± 0.50) J·mol$^{-1}$·K$^{-1}$ [2008RAN/FUG].

The negative values of the entropies of coffinite and thorite have no physical meaning. This suggests that the enthalpies of the dissolution reactions are grossly in error (at least by 100 kJ·mol$^{-1}$), as it was confirmed by a later calorimetric study [2015GUO/SZE] of coffinite. As a matter of fact, to provide the positive values of $S_m^o$ for solid phases, the enthalpy change for Reactions (A.225) and (A.226) must be negative, or, in other words, the solubility should decrease with temperature. As it is not clear, which data are in error (those at low temperatures or at high temperatures), the current review does not select any thermodynamic data from this study. In addition, as was pointed out in a later study [2016SZE/MES], the $\log_{10}{}^*K_s^o$ for Reaction (A.226) is sensitive to the value of the stability constant of $U(OH)_4$(aq), and the use of the stability constants for $U(OH)_4^{4-n}$ employed in a later work [2016SZE/MES] would make $\log_{10}{}^*K_s^o$ from [2013SZE/COS] by almost one $\log_{10}$ unit larger, *i.e.* close to – 5.1.

**[2015GUO/SZE]**

This is a determination of the enthalpy of formation of synthetic coffinite, $USiO_4$(cr). Two samples, labeled "coffinite-F" and "coffinite-G", were prepared by a method of hydrothermal synthesis in two independent laboratories, and were repeatedly purified from impurities of silica and $UO_2$ in $HNO_3$ and KOH solutions. The purified samples were characterised using TEM (transmission electron microscopy), IR infrared spectroscopy), powder X-ray diffraction (XRD), DSC-TG (differential scanning calorimetry and thermogravimetric analysis), and by EPMA (electron probe micro-analysis). The sample "coffinite-F" was pure and homogeneous, and had a practically exact $USiO_4$(cr) stoichiometry with a negligible amount of water and a crystallite size of 85 nm. The sample "coffinite-F" had a chemical composition identified as $USiO_4 \cdot 3.19SiO_2 \cdot 0.37H_2O$(cr) with a crystallite size of 65 nm. The authors noted that the particle size may affect measured thermodynamic properties.

High-temperature oxide melt solution calorimetry was conducted using a custom-built Tian-Calvet twin microcalorimeter. Two molten solvents were employed: a lead borate solvent ($2PbO \cdot B_2O_3$) at 802 °C, and a sodium molybdate solvent ($3Na_2O \cdot 4MoO_3$), both pre-saturated with $SiO_2$, at 703 °C. Oxygen gas was bubbled through the melt to ensure an oxidising environment and to facilitate dissolution. The

appropriate thermochemical cycles were used to determine the enthalpy of formation of coffinite from oxides, $UO_2$ (uraninite) and $SiO_2$ (quartz). The sample "coffinite-F" gave $\Delta_{f,\,oxide}H_m^o$ equal to (24.6 ± 3.1) kJ·mol$^{-1}$ from calorimetry in the sodium molybdate solvent, and (26.7 ± 4.7) kJ·mol$^{-1}$ in the lead borate solvent. The thermochemical results with "coffinite-G" required corrections for the excess silica and for excess water. The last correction presented difficulties, which were connected with the nature of the excess water: 1) whether it is liquid "free water", which, based on IR studies, is unlikely, with the resulting $\Delta_{f,\,oxide}H_m^o$ = – (5.5 ± 3.5) kJ·mol$^{-1}$; 2) if it is adsorbed on the surface, with $\Delta_{f,\,oxide}H_m^o$ = (24.1 ± 3.5) kJ·mol$^{-1}$; 3) or if it originated from the metashoepite ($UO_3 \cdot 2H_2O$) impurity, with $\Delta_{f,\,oxide}H_m^o$ = (23.9 ± 4.0) kJ·mol$^{-1}$. Judging by the abstract of the paper, the authors finally selected $\Delta_{f,\,oxide}H_m^o$ = (25.6 ± 3.9) kJ·mol$^{-1}$, apparently based on results for the pure and homogeneous sample "coffinite-F".

Using $\Delta_f H_m^o$ (298.15 K) = – (1085.0 ± 1.0) kJ·mol$^{-1}$ for $UO_2$(cr) and $\Delta_f H_m^o$ (298.15 K) = – (910.7 ± 1.0) kJ·mol$^{-1}$ for quartz (all from [2003GUI/FAN]), this review calculates for coffinite, $USiO_4$(cr), $\Delta_f H_m^o$ (298.15 K) = – (1970.1 ± 4.2) kJ·mol$^{-1}$ (the authors' value is – (1970.0 ± 4.2) kJ·mol$^{-1}$).

**[2016SZE/MES]**

This is a study of dissolution of coffinite, $USiO_4$(cr), in 0.1 M HCl solution. Coffinite was synthesised under hydrothermal conditions (250 °C, for 16 days) from aqueous solutions, containing $UCl_4$ and $Na_2SiO_3$ at alkaline pH (11.4). Samples were analysed by X-ray diffraction, the transmission and scanning electron microscopy. Coffinite (grains of the size of ~ 80 nm), cubic urania $UO_2$, and amorphous $SiO_2$ were detected. The resulting powder was purified in cycles in $HNO_3$ and KOH solutions, and after three cycles the average U/Si ratio was 1.01 ± 0.08, *i.e.* pure coffinite.

Dissolution experiments were performed in air or under Ar atmosphere in 0.1 M HCl at (298 ± 2) K and lasted up to several months (a plateau was reached within 30-50 days). Solutions were periodically sampled and analysed for U and Si by ICP-AES. Not more than 0.8 % of $UO_2^{2+}$ was formed by $O_2$(g) introduced into the system at sampling. It was found that in long-running experiments the elemental concentrations obtained for the as-prepared sample ($USiO_4$ + $UO_2$ + $SiO_2$), for the association ($USiO_4$ + $UO_2$) and for pure coffinite were very close, confirming that coffinite controlled the equilibrium. At the same time the concentrations of U and Si were much higher for the association ($SiO_2$ + $UO_2$). The dissolution is incongruent, except for the case of pure coffinite, where the U : Si ratio in the equilibrium solution is 0.74 ± 0.07, *i.e.* relatively close to 1. The X-ray diffraction pattern of coffinite after dissolution showed no evidence of additional secondary phases. The pH at equilibrium under Ar atmosphere ranged from 1.09 to 1.34.

Only experimental data obtained under Ar atmosphere were considered in the thermodynamic analysis to calculate the equilibrium constant for the reaction:

$$USiO_4(cr) + 4H^+ \rightleftharpoons U^{4+} + Si(OH)_4(aq) \qquad (A.227)$$

Speciation calculations were made with PHREEQC-2 program, using hydrolysis constants for $U^{4+}$ from [2003GUI/FAN] and [2001NEC/KIM], the activity coefficients were estimated using the SIT model. For Reaction (A.227) $\log_{10}{}^{*}K_s^o$ = – (5.25 ± 0.05), and this value was selected by the authors of [2016SZE/MES]. Close values of $\log_{10}{}^{*}K_s^o$ for Reaction (A.227) were obtained from equilirium concentrations over the phase associations $USiO_4 + UO_2 + SiO_2$, – (5.19 ± 0.08), – (5.34 ± 0.13), and $SiO_2 + USiO_4$ – (5.20 ± 0.07), – (4.63 ± 0.07). The major U species in equilibrium with coffinite are $U^{4+}$, $UOH^{3+}$, $U(OH)_2^{2+}$, and $UCl^{3+}$. The stability constants for the complexes $UOH^{3+}$ and $UCl^{3+}$ used by the authors of the study and selected in this review are identical, while the stability constant for $U(OH)_2^{2+}$ recommended in this reviews differs by 0.8 $\log_{10}$ units. Nevertheless, it was checked that the calculated values of the $\log_{10}{}^{*}K_s^o$ will change by less than 0.08 $\log_{10}$ units when employing stability constants for U(IV) complexes selected or retained in the current review.

The selected value of $\log_{10}{}^{*}K_s^o$, – (5.25 ± 0.05), is different from – (6.1 ± 0.2), estimated in [2013SZE/COS] from solubility studies of uranothorite solid solutions. This difference is explained by the authors by the different values of stability constants for $U(OH)_4^{4-n}$ used in the two studies. Adopting stability constants used in [2016SZE/MES] would make $\log_{10}{}^{*}K_s^o$ from [2013SZE/COS] by almost 1 $\log_{10}$ unit larger. In opinion of this review, the uncertainty of $\log_{10}{}^{*}K_s^o$ obtained in [2016SZE/MES] should be increased up to at least 0.3, because the calculated fractions of predominant species $U^{4+}$, $UCl^{3+}$, $UOH^{3+}$, $U(OH)_2^{2+}$ are close in magnitudes, and the stability constants for these species, especially for $U(OH)_2^{2+}$, are not very precise.

Correspondingly, for Reaction (A.227) $\Delta_r G_m^o$ = (30.0 ± 1.7) kJ·mol$^{-1}$ and $\Delta_f G_m^o$ ($USiO_4$, cr) = – (1869.0 ± 2.7) kJ·mol$^{-1}$, using auxiliary data from [2003GUI/FAN] for $U^{4+}$ and from [NEA TDB review on Ancillary Data – to be published] for $Si(OH)_4$(aq).

This means that coffinite is metastable with respect to the phase association $UO_2$(cr) + quartz and $UO_2$(cr) + amorphous silica: for the reaction $USiO_4(cr) \rightleftharpoons UO_2(cr) + SiO_2$(cr, quartz) the Gibbs energy change $\Delta_r G_m^o$ = – (19.06 ± 3.00) kJ·mol$^{-1}$, and for the reaction $USiO_4(cr) \rightleftharpoons UO_2(cr) + SiO_2(am)$ $\Delta_r G_m^o$ = – (13.08 ± 3.00) kJ·mol$^{-1}$. The auxiliary values used in this evaluation are: $\Delta_f G_m^o$ ($UO_2$, cr) = – (1031.833 ± 1.004) kJ·mol$^{-1}$ [2003GUI/FAN] $\Delta_f G_m^o$ ($SiO_2$, cr, quartz) = – (856.287 ± 1.002) kJ·mol$^{-1}$ [2003GUI/FAN], $\Delta_f G_m^o$ ($SiO_2$, am) = – (850.31 ± 1.002) kJ·mol$^{-1}$, calculated in this review from the Gibbs energy of formation of quartz, see above, and logarithms of aqueous solubility at 298.15 K of quartz and amorphous silica ($\log_{10}$m = – (3.743 ± 0.027) and – (2.696 ± 0.016), respectively, both values are from [NEA TDB

review on Ancillary Data – to be published]).

However, the conclusion that coffinite is metastable with respect to the phase association $UO_2(cr)$ + amorphous silica contradicts the direct experimental data obtained in [2016SZE/MES], as was already pointed out by the authors of [2016SZE/MES] themselves. Indeed, Table 4 of that work shows that equilibrium concentrations of U and Si are much higher for the association $UO_2(cr) + SiO_2(am)$ than for pure coffinite, indicating that coffinite should precipitate from this solution and is more thermodynamically stable compared with uraninite and amorphous silica (note that the complicating circumstance is a very small size of the uraninite crystals used, ~ 4 nm). From data in the last column of Table 4 in [2016SZE/MES] the current review calculated for Reaction (A.228)

$$UO_2(cr) + SiO_2(am) + 4H^+ \rightleftharpoons U^{4+} + Si(OH)_4(aq) \qquad (A.228)$$

$\log_{10}{}^{*}K_s^o$ (A.228) = – 2.54 (the average from two values, – 2.51 and – 2.57). Combining Reactions (A.227) and (A.228), one obtains Reaction (A.229):

$$USiO_4(cr) \rightleftharpoons UO_2(cr) + SiO_2(am) \qquad (A.229)$$

$\log_{10}{}^{*}K_s^o$ (A.229)= – 5.25 + 2.54 = – 2.71, or $\Delta_r G_m^o$ = + 15.47 kJ·mol$^{-1}$ as compared with – (13.08 ± 3.00) kJ·mol$^{-1}$ calculated using the Gibbs energy of coffinite evaluated in [2016SZE/MES] from the solubility of $USiO_4$(cr). Therefore, the current review concludes that experimental data of [2016SZE/MES] on equilibrium concentrations of Si and U over coffinite and the association $UO_2(cr) + SiO_2(am)$ are intrinsically contradicting and does not select any thermodynamic data from that study.

## A-1.7 Compounds and complexes in the uranium boron system

**[1988GAS]**

Gasparin [1988GAS] reported the synthesis and structural characterization of $Na[UO_2BO_3](cr)$. The structure consists of linked pentagonal bipyramids, "$UO_7$", borate ions, where two oxygen atoms are coordinated to the uranyl-ion and the third to $Na^+$, the latter is four-coordinated. The structure is not isomorphous with the corresponding Li-compound, $Li[UO_2BO_3](cr)$, [1990GAS].

**[2002CHE/KNY]**

Chernorukov *et al.* describe the preparation of $Li[UO_2(BO_3)]\cdot H_2O(cr)$ and $Li[UO_2(BO_3)]\cdot 0.5H_2O(cr)$ from the anhydrous compound by hydrothermal heating of $Li[UO_2(BO_3)](cr)$ at 200 °C; the compounds have been characterised by X-ray powder diffraction and IR spectroscopy and the water content by gravimetry. The mono-hydrate

loses water of crystallisation at 200 °C forming the hemi-hydrate, which is completely dehydrated at 540 °C. At higher temperature, 850-900 °C the anhydrous compound decomposes forming $Li_2U_2O_7$(cr) and liquid $B_2O_3$(l). Based on IR spectra Chernorukov *et al.* suggest that the layer structure can incorporate water, resulting in a hemihydrate $Li[UHBO_{5.5}] \equiv Li[UO_2BO_3 \cdot (H_2O)_{0.5}]$; the support for this is not convincing. The hydration of $Li[UO_2BO_3]$(cr) only takes place during hydrothermal treatment and the release of water of crystallisation requires high temperature. These observations suggest that the phase composition is retained both in the calorimetric and solubility experiments. The IR spectra, quite clearly suggest the presence of water resulting in absorption bands at ≈ 3200-3500 $cm^{-1}$ and 1600 $cm^{-1}$, which can be used as an analytical indicator for other anhydrous uranyl borates. There are no thermodynamic data in this study. An important observation is that the IR intensity in the anhydrous compound *decreases* above 1500 $cm^{-1}$.

**[2002KAR/CHE4]**

The standard enthalpy of formation of crystalline $Na[UO_2BO_3]$(cr) was determined at 298.15 K, $\Delta_f H^o = -(2257.5 \pm 4.0)$ kJ·mol$^{-1}$ using reaction calorimetry. The isobaric molar heat capacity was determined in the temperature range 10-300 K, $C_{p,m}$(298.15 K) = (145.8 ± 2.9) J·K$^{-1}$·mol$^{-1}$, where the uncertainty has been estimated by the present review. The extrapolation to 0 K was made using the expression, $C_{p,m} = 2.74 \times 10^{-3} T^{2.5}$; the authors claim that there are no noticeable anomalies in the temperature function. However, the recent study by Popova *et al.* [2018POP/BEN] reports a change in slope both in their data and those of Karyakin *et al.* [2002KAR/CHE4] at 174 K, indicating a thermal anomaly. From the heat capacity data Karyakin *et al.* obtain the corresponding molar entropy, $S^o_m$(298.15 K) = (167.2 ± 2.1) J·K$^{-1}$·mol$^{-1}$ and the thermal functions, $H$(298.15 K) – $H$(0) = 26.17 kJ·mol$^{-1}$ and – ($G$(298.15 K) – $H$(0)) = 23.69 kJ·mol$^{-1}$). The standard enthalpy, Gibbs energy and entropy of formation reported are:

$\Delta_f H^o = -(2257.5 \pm 4.0)$ kJ·mol$^{-1}$; $\Delta_f G^o = -(2122.5 \pm 4.5)$ kJ·mol$^{-1}$, and $\Delta_f S^o = -(452.7 \pm 2.1)$ J·K$^{-1}$·mol$^{-1}$. Recalculation by this review results in the values listed in the main text, Table 9-75.

The same system has also been discussed in [2003CHE/KNY3] where details about the calorimetric experiments are described.

**[2003CHE/KNY]** (This paper also contains information from [2002CHE/KNY])

In [2003CHE/KNY], Chernorukov *et al.* describe the synthesis, crystal structures, IR spectra and thermal properties of a number of hydrated alkali uranoborates, $M[UO_2(BO_3)] \cdot nH_2O$(cr), $Li[UO_2(BO_3)] \cdot nH_2O$(cr), $n$ = 0, 2, 1.5, 1, 0.5; $Na[UO_2(BO_3)] \cdot nH_2O$(cr), $n$ = 1.25, 1, 0.2; $K[UO_2(BO_3)] \cdot nH_2O$(cr), $n$ = 1.25, 1, 0.2;

$Rb[UO_2(BO_3)]\cdot nH_2O(cr)$, $n = 1,\ 0.25$; $Cs[UO_2(BO_3)]\cdot nH_2O(cr)$, $n = 1.5,\ 1,\ 0.5$. The syntheses started from the anhydrous phases that were prepared by solid state reactions between $UO_3$, $B_2O_3$ and $M_2CO_3/MNO_3$ at high temperature, followed by removal of excess $B_2O_3$ and $M_2CO_3/MNO_3$ by washing with boiling water. The monohydrates were prepared by hydrothermal reaction of the anhydrous compounds at 200 °C and the more hydrated phases by using a lower temperature, 130 °C in the hydrothermal reaction. The samples were analysed for boron and uranium but not for water. Additional characterisation was made using XRD. The IR spectra shown in their Figure 2 do not show information above 1550 $cm^{-1}$ (but indicate an increased absorption at higher wave-numbers), that provide information on the presence of water, *cf.* [2002CHE/KNY]. TGA analyses were used to identify a number of intermediates with different water content. As pointed out in [2002CHE/KNY], hydration and dehydration requires high temperatures, suggesting that changes in hydration at ambient temperatures do not take place in aqueous solution.

$Li[UO_2(BO_3)]\cdot 1.5H_2O(cr) \rightarrow Li[UO_2(BO_3)]\cdot H_2O(cr) \rightarrow Li[UO_2(BO_3)](cr)$, at 200 and 600 °C, respectively.

$Na[UO_2(BO_3)]\cdot H_2O(cr) \rightarrow Na[UO_2(BO_3)]\cdot 0.5H_2O(cr) \rightarrow Na[UO_2(BO_3)]\cdot 0.33H_2O(cr) \rightarrow Na[UO_2(BO_3)]\cdot 0.25H_2O(cr) \rightarrow Na[UO_2(BO_3)](cr)$, at 189, 320, 420 and 640 °C, respectively.

$K[UO_2(BO_3)]\cdot H_2O(cr) \rightarrow K[UO_2(BO_3)]\cdot 0.2H_2O(cr) \rightarrow K[UO_2(BO_3)](cr)$, at 140 and 720 °C, respectively.

$Rb[UO_2(BO_3)]\cdot H_2O(cr) \rightarrow Rb[UO_2(BO_3)]\cdot 0.25H_2O(cr) \rightarrow Rb[UO_2(BO_3)](cr)$, at 150 and 610 °C, respectively.

$Cs[UO_2(BO_3)]\cdot H_2O(cr) \rightarrow Cs[UO_2(BO_3)]\cdot 0.5H_2O(cr) \rightarrow Cs[UO_2(BO_3)](cr)$, at 130 and 430 °C, respectively.

Some of these compounds have been used to determine thermodynamic data. It is unfortunate that the authors have not made an analysis of the water content because this strongly affects the enthalpy of formation, the entropy and the heat capacity of the solid phases as will be discussed in the following.

**[2003CHE/KNY2]**

The authors describe the structure and thermal decomposition of anhydrous $M[UO_2BO_3](cr)$ phases, M = Li-Cs. Using dissolution calorimetry they have determined the enthalpy of formation of the different phases, these experiments are discussed in detail in their later study [2005KAR/CHE] that apparently uses the data from [2003CHE/KNY2] without a proper reference. Chernorukov *et al.* provide analytical data for the composition of the different phases but no specific analysis of the water content. They present IR data but these do not extend beyond 1550 $cm^{-1}$, where the

water bands may be found. However, the absorbtivity increases in this range while the opposite was found for the Li-compound in [2002CHE/KNY], which casts some doubts on the stoichiometry of the compounds used. The enthalpies of reaction are identical with the ones in [2005KAR/CHE] and are listed there.

**[2003CHE/KNY3]**

Chernorukov *et al.* have determined the standard enthalpy of formation of $M[UO_2(BO_3)](cr)$, M = Li, Na, K, Rb, Cs using dissolution calorimetry in HF (sln. 13.5 M), using the same thermodynamic cycle as in [2003CHE/KNY2]. The thermodynamic cycle used is:

$$UO_3(\gamma, cr) + HF(sln) \rightleftharpoons \text{solution 1} \quad \text{(A.230)}$$

$\Delta_r H$ (A.230)

$$NaBO_2(cr) + \text{solution 1} \rightleftharpoons \text{solution 2} \quad \text{(A.231)}$$

$\Delta_r H$ (A.231)

$$LiF(cr)/MCl(cr) + \text{solution 2} \rightleftharpoons \text{solution 3} \quad \text{(A.232)}$$

$\Delta_r H$ (A.232)

$$M[UO_2(BO_3)](cr) + HF(sln) \rightleftharpoons \text{solution 4} \quad \text{(A.233)}$$

$\Delta_r H$ (A.233)

$$NaF(cr)/MCl(cr) + \text{solution 4} \rightleftharpoons \text{solution 5} \quad \text{(A.234)}$$

$\Delta_r H$ (A.234)

The experimental enthalpies of dissolution are denoted $\Delta_r H\,(i)$, $i$ = (A.230)-(A.234); combination of Equations (A.230)-(A.234) gives:

$$UO_3(\gamma, cr) + NaBO_2(cr) \rightleftharpoons Na[UO_2(BO_3)](cr) \quad \text{(A.235)}$$

$$UO_3(\gamma, cr) + NaBO_2(cr) + LiF(cr) \rightleftharpoons Li[UO_2(BO_3)](cr) + NaF(cr) \quad \text{(A.236)}$$

$$UO_3(\gamma, cr) + NaBO_2(cr) + MCl(cr) \rightleftharpoons M[UO_2(BO_3)](cr) + NaCl(cr)\ ;\ M = K, Rb, Cs \quad \text{(A.237)}$$

$$\Delta_r H\,(A.235) = \Delta_r H\,(A.230) + \Delta_r H\,(A.231) - \Delta_r H\,(A.233); \quad \text{(A.238)}$$

$$\Delta_r H\,(A.236) = \Delta_r H\,(A.230) + \Delta_r H\,(A.231) + \Delta_r H\,(A.232) - \Delta_r H\,(A.233) - \Delta_r H\,((A.234), NaF); \quad \text{(A.239)}$$

$$\Delta_r H\,(A.237) = \Delta_r H\,(A.230) + \Delta_r H\,(A.231) + \Delta_r H\,(A.232) - \Delta_r H\,(A.233) - \Delta_r H\,((A.234), MCl); \quad \text{(A.240)}$$

The enthalpies of dissolution for Reactions (A.230) and (A.231) are $\Delta_r H$ (A.230) = – (113.1 ± 1.1) kJ·mol$^{-1}$ and $\Delta_r H$ (A.231) = – (136.4 ± 1.2) kJ·mol$^{-1}$, respectively; the other enthalpies of dissolution in Equation (A.239) are given in Table A-115.

Table A-115: Experimental heats of dissolution used in Equation (A.239).

| Compound | $\Delta_r H$ (A.233) /kJ·mol$^{-1}$ | MF /MCl | $\Delta_r H$ (A.232), $\Delta_r H$ (A.234) /kJ·mol$^{-1}$ |
|---|---|---|---|
| Li[$UO_2(BO_3)$](cr) | – (206.9 ± 0.8) | LiF | (6.64 ± 0.17) |
| Na[$UO_2(BO_3)$](cr) | – (191.9 ± 1.2) | NaF | – (5.23 ± 0.22) |
| | | NaCl | – (9.24 ± 0.11) |
| K[$UO_2(BO_3)$](cr) | – (172.6 ± 1.1) | KCl | (3.39 ± 0.24) |
| Rb[$UO_2(BO_3)$](cr) | – (175.4 ± 0.8) | RbCl | (1.14 ± 0.08) |
| Cs[$UO_2(BO_3)$](cr) | – (184.3 ± 2.2) | CsCl | (2.79 ± 0.24) |

In order to calculate the standard enthalpies of formation, $\Delta_f H^o$(M[$UO_2(BO_3)$], cr), Chernorukov *et al.* used the enthalpies of formation in Table A-116, these were taken from CODATA and the Glushko tables, issue 10, parts 1 and 2. These values were revised by the present review, using the NEA selected values (the value for $NaBO_2$(cr) is selected based on the information in [1982GLU/GUR], as discussed in the Auxiliary data section); the revised values are listed in bold in Table A-116.

Table A-116: Standard enthalpies of formation used to calculate the standard enthalpies of formation of M[$UO_2(BO_3)$](cr). The values selected by NEA from Chapter 14 are given in bold and have been used to recalculate the data from Cherorukov *et al.*

| Compound | $\Delta_f H$ /kJ·mol$^{-1}$ | Compound | $\Delta_f H$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $UO_3$(γ,cr) | **– (1223.800 ± 1.200)** | NaCl | – (411.4 ± 0.3) |
| | | | **– (411.260 ± 0.120)** |
| $NaBO_2$(cr) | – (976.1 ± 1.3)[(a)] | KCl | – (436.6 ± 0.3) |
| | **– (976.500 ± 2.500)** | | **– (436.460 ± 0.130)** |
| LiF | – (614.7 ± 3.3) | RbCl | – (435.2 ± 0.3) |
| | – (**618.300± 0.700**) | | **– (435.220 ± 0.160)** |
| NaF | – (572.8 ± 1.3) | CsCl | – (442.4 ± 0.3) |
| | – (**576.600 ± 0.700**) | | **– (442.310 ± 0.160)** |

(a) The value in bold is from the latest issue of *Thermodynamic properties of individual substances*, vol. 4 NAUKA, Moscow, 1982. The basis for the selection of this value is given in Auxiliary Information, [1982GLU/GUR].

The standard enthalpies of formation for the M[$UO_2(BO_3)$](cr) compounds recalculated using the NEA selected values are listed in Table A-117, but we have also accepted the Glushko value for the enthalpy of formation of $NaBO_2$(cr). The reason for this is that the thermodynamic data in the more recent Glushko tables are in good agreement with the CODATA/NEA selected values as exemplified by our review of the

enthalpy of formation of $CaB_2O_4$(cr) (Appendix A entries for [1947TOR/SHO] and [1948KEL/TOD]).

Table A-117: Standard enthalpies of formation, $\Delta_f H^o$(M[$UO_2(BO_3)$], cr), for the M[$UO_2(BO_3)$](cr) compounds, where the values recalculated by this review based on the NEA selected values are given in bold. The enthalpies of formation are identical with the ones in [2003CHE/KNY2] within the estimated uncertainties.

| Compound | $\Delta_f H^o$ (M[$UO_2(BO_3)$], cr) /kJ·mol$^{-1}$ |
|---|---|
| Li[$UO_2(BO_3)$](cr) | – (2272.5 ± 4.0) |
| | – **(2272.700 ± 3.500)**[(a)] |
| Na[$UO_2(BO_3)$](cr) | – (2257.5 ± 4.0) |
| | – **(2257.900 ± 3.400)** |
| K[$UO_2(BO_3)$](cr) | – (2289.5 ± 4.5) |
| | – **(2289.800 ± 3.400)** |
| Rb[$UO_2(BO_3)$](cr) | – (2287.5 ± 4.0) |
| | – **(2288.000 ± 3.300)** |
| Cs[$UO_2(BO_3)$](cr) | – (2284.0 ± 4.5) |
| | – **(2284.600 ± 3.900)** |

(a)Same as in [2003KAR/CHE]

The enthalpies of formation in this study are identical with the ones in [2003CHE/KNY2] and this review assumes that the same calorimetric data have been used.

Chernorukov *et al.* have also determined the enthalpies of formation of the hydrates M[$UO_2BO_3$]·$n$$H_2O$(cr) by dissolving the anhydrous compounds in aqueous 10 mol % HCl, according to the following scheme:

$$M[UO_2BO_3](cr) + HCl(sln) \rightleftharpoons sln \qquad (A.241)$$

$\Delta_r H$ (A.241);

$$nH_2O + HCl(sln) \rightleftharpoons sln \qquad (A.242)$$

$\Delta_r H$ (A.242) ≈ 0 kJ·mol$^{-1}$

$$M[UO_2BO_3]\cdot nH_2O(cr) + HCl(sln) \rightleftharpoons sln \qquad (A.243)$$

$\Delta_r H$ (A.243);

By combining Reactions (A.241)-(A.243) one obtains the enthalpy of reaction $\Delta_r H$ (A.244):

$$M[UO_2BO_3](cr) + nH_2O(l) \rightleftharpoons M[UO_2BO_3]\cdot nH_2O(cr) \qquad (A.244)$$

Chernorukov *et al.* have used the enthalpy of formation of pure liquid water, – 285.8 kJ·mol$^{-1}$ in their calculation instead of the enthalpy of formation of water in 11.6 M HCl, which is – 286.4 kJ·mol$^{-1}$.

The corresponding reaction enthalpies are reported in Table A-118. Based on these data, the enthalpies of formation of the hydrates are reported in Table A-119, where the data for $M[UO_2BO_3]\cdot nH_2O$(cr) compounds have been recalculated by the present review using the selected values of $\Delta_f H^\circ(M[UO_2BO_3], cr)$. The fact that the enthalpies of formation of the $M[UO_2BO_3]$(cr) and $M[UO_2BO_3]\cdot H_2O$(cr) are consistent (see the following text) suggests that the water analyses of the different phases are correct and the present review has therefore included these enthalpies of formation among the selected data.

Table A-118: Standard enthalpies of solution for $M[UO_2BO_3]\cdot nH_2O$(cr) in aqueous HCl in $kJ\cdot mol^{-1}$.

| $A^I$ | $n = 1.5$ | $n = 1$ | $n = 0.5$ | $n = 0.2$ | $n = 0$ |
|---|---|---|---|---|---|
| Li | (39.2 ± 0.4) | (52.1 ± 0.4) | (69.7 ± 0.4) | – | (90.0 ± 0.3) |
| Na | – | (49.0 ± 0.4) | (59.3 ± 0.4) | – | (86.3 ± 0.3) |
| K | – | (21.2 ± 0.3) | – | (46.9 ± 0.3) | (54.9 ± 0.3) |
| Rb | – | (40.1 ± 0.3) | – | (63.6 ± 0.3)[(a)] | (69.3 ± 0.3) |
| Cs | – | (39.6 ± 0.4) | (47.0 ± 0.4) | – | (65.7 ± 0.3) |

(a) $n = 0.25$

Table A-119: Standard enthalpies of formation of hydrated alkali uranoborates in $kJ\cdot mol^{-1}$, recalculated by this review using the enthalpies of solution of $M[UO_2BO_3]\cdot nH_2O$(cr), and the NEA selected auxiliary values for $M^+$, $UO_2^{2+}$ and $H_3BO_3$(aq). These data, corrected for the enthalpy of formation of water in 11.6 M HCl, – 286.4 $kJ\cdot mol^{-1}$, instead of the value – 285.83 $kJ\cdot mol^{-1}$ used by Chernorukov *et al.* are given in bold and are selected by this review.

| Compound | $\Delta_f H^\circ$ (298.15) /$kJ\cdot mol^{-1}$ | Compound | $\Delta_f H^\circ$ (298.15) /$kJ\cdot mol^{-1}$ |
|---|---|---|---|
| $Li[UO_2BO_3]\cdot 1.5H_2O$(cr) | – (2752.0 ± 4.0)[(a)] | $K[UO_2BO_3]\cdot H_2O$(cr) | – (2609.0 ± 4.5)[(a)] |
| | **– (2753.100 ± 3.500)** | | – (**2609.800 ± 3.400**) |
| $Li[UO_2BO_3]\cdot H_2O$(cr) | – (2596.0 ± 4.0)[(a)] | $K[UO_2BO_3]\cdot 0.2H_2O$(cr) | – (2355.0 ± 4.5)[(a)] |
| | **– (2597.000 ± 3.500)** | | **– (2355.000 ± 3.400)** |
| $Li[UO_2BO_3]\cdot 0.5H_2O$(cr) | – (2435.5 ± 4.0)[(a)] | $Rb[UO_2BO_3]\cdot H_2O$(cr) | – (2602.5 ± 4.0)[(a)] |
| | **– (2436.2 ± 3.500)** | | **– (2603.500 ± 3.300)** |
| $Na[UO_2BO_3]\cdot H_2O$(cr) | – (2580.5 ± 4.0)[(a)] | $Rb[UO_2BO_3]\cdot 0.25H_2O$(cr) | – (2364.0 ± 4.0)[(a)] |
| | – (2581.600 ± 3.500)[(b)] | | **– (2365.300 ± 3.300)** |
| $Na[UO_2BO_3]\cdot 0.5H_2O$(cr) | – (2427.5 ± 4.0)[(a)] | $Cs[UO_2BO_3]\cdot H_2O$(cr) | – (2596.0 ± 4.5)[(a)] |
| | **– (2428.100 ± 3.500)** | | **– (2597.000± 3.900)** |
| | | $Cs[UO_2BO_3]\cdot 0.5H_2O$(cr) | – (2445.5 ± 4.5)[(a)] |
| | | | **– (2446.400 ± 3.900)** |

(a) Data reported by [2003CHE/KNY3]

(b) The selected value of $\Delta_f H^\circ_m$ for the phase $Na[UO_2BO_3]\cdot H_2O$(cr) has been calculated from the Gibbs-Helmholtz relation, see main text.

Chernorukov *et al.* have also determined the entropy and heat capacity of $Na[UO_2BO_3]\cdot H_2O$(cr) using low-temperature calorimetry in the range 5-350 K and report $S_m^o$ (298.15 K) = (183.8 ± 2.1) $J\cdot K^{-1}\cdot mol^{-1}$ and $C_p^o$ (298.15 K) = (159.0 ± 1.6) $J\cdot K^{-1}\cdot mol^{-1}$. Using the NEA selected values of the molar entropies of the elements, we obtain $\Delta_f S_m^o$ ($Na[UO_2BO_3]\cdot H_2O$, cr, 298.15 K) = – (669.736 ± 3.014) $J\cdot K^{-1}\cdot mol^{-1}$ and $\Delta_f G_m^o$ ($Na[UO_2BO_3]\cdot H_2O$, cr, 298.15 K) = – (2381.918 ± 3.614) $kJ\cdot mol^{-1}$. The heat capacity in the temperature range 200-300 K could be described with the function $C_p = -0.0011T^2 + 0.8415T + 3.7869$, within the experimental uncertainty. The reported $S_m^o$ (298.15 K) = (**183.8 ± 3.0**) $J\cdot K^{-1}\cdot mol^{-1}$, and $C_p$ (298.15 K) = (**159.0 ± 1.6**) $J\cdot K^{-1}\cdot mol^{-1}$ are accepted by this review. The same experimental data is in this study are used in a following publication [2005KAR/CHE].

**[2003CHE/KNY4]**

Chernorukov *et al.* have determined the standard enthalpy of formation of the following uranyl(VI) borate compounds, $M[UO_2(BO_3)]_2\cdot nH_2O$(cr), M = Mg, Ca, Sr, Ba and $n$ = 0-7; there are two polymorphs denoted α and β for the Sr and Ba compounds. The anhydrous compounds were synthesised by hydrothermal ion-exchange at 200 °C in the reaction:

$$2K[UO_2(BO_3)](cr) + M^{2+}(sln) \rightleftharpoons M[UO_2(BO_3)]_2(cr) + 2K^+(sln) \quad \text{(A.245)}$$

No elemental analyses of the compounds are reported. The enthalpies of formation are based on dissolution calorimetry using the following thermochemical cycle for the anhydrous phases:

$$UO_3(\gamma, cr) + HCl(sln, 11.6\ M) \rightleftharpoons solution\,1 \quad \text{(A.246)}$$

$\Delta_r H$ (A.246) = – (70.2 ± 0.5) $kJ\cdot mol^{-1}$

$$CaB_2O_4(cr) + solution\,1 \rightleftharpoons solution\,2 \quad \text{(A.247)}$$

$\Delta_r H$ (A.247) = – (92.7 ± 0.9) $kJ\cdot mol^{-1}$

$$MCO_3(cr) + solution\,2 \rightleftharpoons solution\,3 \quad \text{(A.248)}$$

$\Delta_r H$ (A.248)

$$M[UO_2(BO_3)]_2(cr) + solution\,3 \rightleftharpoons solution\,4 \quad \text{(A.249)}$$

$\Delta_r H$ (A.249)

$$CaCO_3(cr) + solution\,4 \rightleftharpoons solution\,5 \quad \text{(A.250)}$$

$\Delta_r H$ (A.250)

Combination of Reactions (A.246)-(A.250) gives

$$2UO_3(\gamma, cr) + CaB_2O_4(cr) + MCO_3(cr) \rightleftharpoons M[UO_2(BO_3)]_2(cr) + CaCO_3(cr) \quad \text{(A.251)}$$

$$\Delta_r H \text{ (A.251)}$$

and

$$2UO_3(\gamma, cr) + CaB_2O_4(cr) \rightleftharpoons Ca[UO_2(BO_3)]_2(cr) \quad \text{(A.252)}$$

$$\Delta_r H \text{ (A.252)}$$

The standard enthalpies of formation are obtained as follows:

$$\Delta_f H^o(M[UO_2(BO_3)]_2, cr) = \Delta_r H \text{ (A.251)} + 2\,\Delta_f H^o(UO_3,\gamma, cr) + \Delta_f H^o(CaB_2O_4, cr) + \Delta_f H^o(MCO_3,cr) - \Delta_f H^o(CaCO_3,cr); \quad \text{(A.253)}$$

$$\Delta_f H^o(Ca[UO_2(BO_3)]_2, cr) = \Delta_r H \text{ (A.252)} + 2\,\Delta_f H^o(UO_3,\gamma, cr) + \Delta_f H^o(CaB_2O_4, cr) \quad \text{(A.254)}$$

The experimental heats of dissolution are given in Table A-120 and Table A-121.

Table A-120: Standard enthalpies of solution (kJ·mol$^{-1}$) for $M[UO_2BO_3]_2$(cr) in 11.6 M HCl ($T$ = 298.15 K).

| $A^{II}[UO_2(BO_3)]_2$(cr) | $\Delta_r H^o$ (A.249)/kJ·mol$^{-1}$ | $A^{II}CO_3$(cr) | $\Delta_r H^o$ (A.248)[ $\Delta_r H^o$ (A.250)]/kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2(BO_3)]_2$(cr) | – (272.4 ± 1.3) | $MgCO_3$(cr) | – (59.4 ± 0.9) |
| $Ca[UO_2(BO_3)]_2$(cr) | – (220.9 ± 1.2) | $CaCO_3$(cr) | – (40.3 ± 0.7) [– (30.1 ± 0.9)][(a)] |
| α-$Sr[UO_2(BO_3)]_2$ | – (215.4 ± 1.1) | $SrCO_3$(cr) | – (37.9 ± 0.8) |
| β-$Sr[UO_2(BO_3)]_2$ | – (224.6 ± 0.8) | | |
| α-$Ba[UO_2(BO_3)]_2$ | – (193.0 ± 0.1)[(a)] | $BaCO_3$(cr) | – (22.5 ± 0.8)[(a)] |
| β-$Ba[UO_2(BO_3)]_2$ | – (202.9 ± 0.4)[(a)] | | |

(a) Solvent mixture of 11.6 M HCl and 0.1 M $Na_2EDTA$

The heats of dissolution in 11.6 M HCl and 0.1 M $Na_2H_2EDTA$ include the enthalpy of protonation and the enthalpy of formation of the $MH_2EDTA$, and the effect is significant as indicated by the data for dissolution of $CaCO_3$. However, this does not have an effect on $\Delta_r H^o$ (A.251) and the related enthalpy of formation because the error is cancelled between $\Delta_r H^o$ (A.249) and $\Delta_r H^o$ (A.248). The present review has estimated uncertainties based on reported experimental data as described in Appendix C that differ significantly from those reported in [2003CHE/KNY4], where there is no information on the method used.

Table A-121: Standard enthalpies of solution (kJ·mol$^{-1}$) for $M[UO_2BO_3]_2{\cdot}nH_2O$(cr).

| $A^{II}$ | $n$ = 7 [4] | $n$ = 2 | $n$ = 1 [0.66] |
|---|---|---|---|
| Mg | – (95.6 ± 0.4) [– (199.5 ± 0.4)] | – | – (249.4 ± 0.4) |
| Ca | – | – | – (184.3 ± 0.4) [– (199.4 ± 0.2)] |
| Sr | – | – (178.1 ± 0.3) | – (190.0 ± 0.3) |
| Ba[(a)] | – | – (144.9 ± 0.3) | – (168.3 ± 0.3) |

(a) Solvent: mixture of 11.6 M HCl with 0.1 M $Na_2EDTA$

The following auxiliary data were taken from the Glushko tables, 1979, issue 9.

$\Delta_f H^o$ ($UO_3$,γ, cr) = – (1223.8 ± 1.2) kJ·mol$^{-1}$; same as selected by the NEA TDB.

$\Delta_f H^o$ ($CaB_2O_4$, cr) = – (2031.5 ± 1.5) kJ·mol$^{-1}$; same as selected by the NEA TDB, ([1947TOR/SHO], [1948KEL/TOD]).

$\Delta_f H^o$ ($MgCO_3$, cr) = – (1095.9 ± 1.3) kJ·mol$^{-1}$; the corresponding value selected by the NEA TDB is $\Delta_f H^o$ ($MgCO_3$, cr) = – (1112.4 ± 1.0) kJ·mol$^{-1}$.

$\Delta_f H^o$ ($CaCO_3$, cr) = – (1206.8 ± 0.8) kJ·mol$^{-1}$; the corresponding value selected by NEA is $\Delta_f H^o$ ($CaCO_3$, calcite) = – (1207.45 ± 1.20) kJ·mol$^{-1}$.

$\Delta_f H^o$ ($SrCO_3$, cr) = – (1225.5 ± 2.1) kJ·mol$^{-1}$;

$\Delta_f H^o$ ($BaCO_3$, cr) = – (1210.5 ± 2.5) kJ·mol$^{-1}$.

This review has recalculated the values reported by Chernorukov *et al.* using the NEA selected data in Chapter VI and the recalculated values are reported in Table A-122.

The enthalpy of formation of $M[UO_2(BO_3)]_2 \cdot nH_2O$(cr) was obtained using the following thermodynamic cycle:

$$M[UO_2(BO_3)]_2 \cdot nH_2O(cr) + HCl(11.6\ M) \rightleftharpoons \text{solution } 8 \qquad (A.255)$$

$$\Delta H(A.255)$$

$$nH_2O + \text{solution } 8 \rightleftharpoons \text{solution } 9 \qquad (A.256)$$

$$\Delta H(A.256) \approx 0\ \text{kJ}\cdot\text{mol}^{-1}$$

$$M[UO_2(BO_3)]_2(cr) + HCl(11.6\ M) \rightleftharpoons \text{solution } 9 \qquad (A.257)$$

$$\Delta H(A.257)$$

From Reactions (A.255)-(A.257) one obtains the enthalpy of reaction $\Delta H$(A.258) for reaction:

$$M[UO_2(BO_3)]_2(cr) + nH_2O(l) \rightleftharpoons M[UO_2(BO_3)]_2 \cdot nH_2O(cr) \qquad (A.258)$$

However, Chernorukov *et al.* have used the enthalpy of formation in pure liquid water, – 285.83 kJ·mol$^{-1}$, instead of the enthalpy of formation in 11.6 M HCl, – 286.3 kJ·mol$^{-1}$. Enthalpy data reported in [2003CHE/KNY4] and corrected by this review are summarised in Table A-122.

Chernorukov *et al.* have calculated the average increment in enthalpy for the different $M[UO_2BO_3]_2 \cdot nH_2O$(cr) compounds.

The enthalpies of reaction for the $M[UO_2BO_3]_2{\cdot}nH_2O$(cr) compounds are also reported in [2006CHE/SMI], [2006CHE/SMI2], [2007CHE/SMI] and [2008CHE/SMI], but these are the same data as in [2003CHE/KNY4].

Table A-122: Standard enthalpies of formation (kJ·mol$^{-1}$) of $M[UO_2(BO_3)]_2$(cr) and $M[UO_2(BO_3)]_2{\cdot}nH_2O$(cr) from Chernorukov *et al.* and those recalculated by the present review, including the correction for the change in the enthalpy of water. As the authors have not reported analytical data for the stoichiometry of the hydrates their thermodynamic data have not been accepted by this review and are included for information only.

| Compound | $\Delta_f H^\circ$ /kJ·mol$^{-1}$ | Compound | $\Delta_f H^\circ$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2(BO_3)]_2$(cr) | – (4347.5 ± 8.0) | $Mg[UO_2(BO_3)]_2{\cdot}7H_2O$(cr) | – (6525.0 ± 8.0) |
| | – (**4363.800 ± 4.000**)[(a)] | | – (6545.1 ± 8.4)[(a)] |
| | | $Mg[UO_2(BO_3)]_2{\cdot}4H_2O$(cr) | – (5563.5 ± 8.0) |
| | | | – (5582.1 ± 7.3)[(a)] |
| | | $Mg[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | – (4658.0 ± 8.0) |
| | | | – (4673.2 ± 5.9)[(a)] |
| $Ca[UO_2(BO_3)]_2$(cr) | – (4491.0 ± 8.0) | $Ca[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | – (4813.0 ± 8.0) |
| | – (**4491.300 ± 3.500**)[(a)] | | – (4814.3 ± 5.2) [(a)] |
| | | $Ca[UO_2(BO_3)]_2{\cdot}0.66H_2O$(cr) | – (4658.0 ± 8.0)[(b)] |
| | | | – (4701.8 ± 6.3)[(a)] |
| α-$Sr[UO_2(BO_3)]_2$(cr) | – (4512.5 ± 8.0) | $Sr[UO_2(BO_3)]_2{\cdot}2H_2O$(cr) | – (5047.0 ± 9.0)[(b)] |
| | – (**4512.900 ± 4.300**)[(a)] | | – (5122.9 ± 7.7)[(a)] |
| | | $Sr[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | – (4773.0 ± 8.0)[(b)] |
| β-$Sr[UO_2(BO_3)]_2$(cr) | – (4503.5 ± 8.0) | – | – (4824.7 ± 6.3)[(a)] |
| | – (**4503.700 ± 4.500**)[(a)] | – | |
| α-$Ba[UO_2(BO_3)]_2$(cr) | – (4507.5 ± 8.0) | $Ba[UO_2(BO_3)]_2{\cdot}2H_2O$(cr) | – (5031.0 ± 8.0)[(b)] |
| | – (**4509.000 ± 4.600**)[(a)] | | – (5129.9 ± 8.0)[(a)] |
| β-$Ba[UO_2(BO_3)]_2$(cr) | – (4498.0 ± 8.0) | $Ba[UO_2(BO_3)]_2{\cdot}H_2O$(cr) | – (4768.0 ± 8.0)[(b)] |
| | – (**4499.100 ± 4.600**)[(a)] | | – (4820.1 ± 6.5)[(a)] |

(a) Recalculated by this review;

(b) The present review has checked the calculations in the paper and noted that the reported values are erroneous; we have made a recalculation using the information in the paper and find the values reported in this table.

**[2003CHE/NIP]**

Chernorukov *et al.* report the solubility of $M[UO_2(BO_3)]{\cdot}nH_2O$(cr) phases for M = Li, $n$ = 1.5 and for M = Na, K, Rb, Cs, $n$ = 1, but provide no analytical information on the water content. Using these data, the Gibbs energy of reaction for the dissolution (A.259) and the Gibbs energy of formation, $\Delta_f G^\circ$ ($M[UO_2(BO_3)]$, cr) have been calculated and reported in Table A-123 and Table A-124. It should be noted that the solubility and the Gibbs energy of reaction in general do not vary much for small variations in the water content.

$$\begin{aligned} &M[UO_2(BO_3)]{\cdot}nH_2O + 3HCl(sln) \rightleftharpoons \\ &M^+(sln) + UO_2^{2+}(sln) + H_3BO_3(sln) + 3Cl^-(sln) + nH_2O \end{aligned} \qquad \text{(A.259)}$$

The dissolution is driven by the high initial acidity of HCl, 0.10 M and only a single solubility for each compound was reported. As a result of the dissolution the acidity decreases strongly to reach a final pH that varies from 3.6 to 4.1, the authors have not reported the uncertainty in pH but the present review has assumed a value of 0.05 pH-units. The solubility was measured using the total concentration of U and B, and the analyses demonstrated congruent dissolution. In order to calculate the concentration of $UO_2^{2+}$ (sln) and $H_3BO_3$(sln) at equilibrium, the speciation of uranium and borate was taken into account using data from Glushko, *Thermodynamic Constants of Substances*, 1961-1981, issues 1-10 and Naumov *et al. Handbook of Thermodynamic Quantities*, Moscow, Atomizdat., 1971. Activities were calculated using the Debye-Hückel approximation, which is reasonable at the low ionic strength $I$ = 0.14 M. Based on the solubility data Chernorukov *et al.* have calculated the solubility constant ${}^*K_s^o$ for Reaction (A.259). The present review has reanalysed the solubility data considering the following reaction:

$$M[UO_2BO_3]{\cdot}nH_2O(cr) + 2H^+ \rightleftharpoons M^+ + 1/2(UO_2)_2(OH)_2^{2+} + H_3BO_3(aq) + (n-1)H_2O(l) \quad \text{(A.260)}$$

The binuclear complex is predominant at pH ≈ 4 considering $[U]_{tot}$ = S ≈ 0.03 – 0.04 M (see Table A-123) and I ≈ 0.10 M, *cf.* Figure 9-5. The error in $[UO_2^{2+}]$ using (A.259) is therefore large, as can be seen from the mass balance $U_{tot} = [UO_2^{2+}] + 2[(UO_2)(OH)_2^{2+}]$. The predominant dissolution of $M[UO_2BO_3]{\cdot}nH_2O$(cr) is Reaction (A.260).

We have: ${}^*K_s = S^2 \times (S/2)^{1/2}/[H^+]^2$; $\log_{10}{}^*K_s = 2.5\log_{10}S - 1/2\log_{10}2 - 2\log_{10}[H^+]$, where $S$ is the measured solubility in Table A-123. Extrapolation to zero ionic strength using SIT gives $\log_{10}{}^*K_s^o = \log_{10}{}^*K_s - D$, where $D$ = 0.11, is the Debye-Hückel term at the experimental ionic strength ≈ 0.10 M. The values of $\log_{10}{}^*K_s$, $\log_{10}{}^*K_s^o$ and the corresponding Gibbs energies of reaction are given in Table A-123, together with the Gibbs energies of formation.

Using the procedure outlined above we have recalculated the data from Chernorukov *et al.* and report these values in Table A-123.

Table A-123: Experimental solubility, $S$, the solubility constant $\log_{10}{}^*K_s^o$(A.260) and $\Delta_r G$(A.260) reported in [2003CHE/NIP] and Gibbs energies of formation based on the latter. The corresponding quantities recalculated and selected by this review are given in bold. The number of water in $M[UO_2(BO_3)]{\cdot}nH_2O$(cr), given by Chernorukov *et al.* is $n$ = 1.5 for Li and $n$ = 1 for the other compounds.

| Parameter | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| pH/p[H$^+$] | 4.1/4.22 | 4.0/4.12 | 3.7/3.82 | 3.6/3.72 | 3.7/3.82 |
| $S$ (M) | 0.0363 | 0.0395 | 0.0405 | 0.0409 | 0.0413 |
| $\log_{10}{}^*K_s$ (A.260) | (4.69 ± 0.2) | (4.59 ± 0.2) | (4.01 ± 0.2) | (3.82 ± 0.2) | (4.03 ± 0.2) |
| $\log_{10}{}^*K_s^o$ (A.260) | **(4.58 ± 0.20)** | **(4.47 ± 0.20)** | **(3.90 ± 0.20)** | **(3.71 ± 0.20)** | **(3.92 ± 0.2)** |

(Continued on next page)

Table A-123 (continued)

| Parameter | Li | Na | K | Rb | Cs |
|---|---|---|---|---|---|
| $\Delta_r G^o$(A.259) | **– (26.142 ± 1.142)** | **– (25.515 ± 1.142)** | **– (22.261 ± 1.142)** | **– (21.177 ± 1.142)** | **– (22.376 ± 1.142)** |
| $\Delta_f G^o$(M[$UO_2(BO_3)$] ·$n H_2O$(cr) | **– (2528.265 ± 2.257)** | **– (2379.358 ± 2.256)** | **– (2403.168 ± 2.257)** | – (**2405.752 ± 2.260**) | – (**2412.000 ± 2.317**) |

The Gibbs energy of reaction for dissolution of $Na[UO_2BO_3]\cdot H_2O$(cr) obtained from the calorimetric value of $\Delta_f G^o_m$ ($Na[UO_2BO_3]\cdot H_2O$, cr) is in excellent agreement with $\Delta_r G°$(A.260) from the solubility data, and for this reason this review has accepted also the recalculated Gibbs energies of reaction and enthalpy of formation for the other alkali uranylborates. Using the Gibbs-Helmholtz equation, the recalculated values of the Gibbs energy of formation from Table A-123 and the selected enthalpy of formation from [2003CHE/KNY3], we have calculated the entropy of formation and the molar entropy for the $M[UO_2BO_3]\cdot nH_2O$(cr) compounds and the results are given in Table A-124. For $Na[UO_2BO_3]\cdot H_2O$(cr), three independent thermodynamic functions ($\log_{10}{}^* K^o_s$, $\Delta_f H^o_m$ and $S^o_m$) have been determined experimentally. As discussed in the main text, this review selects $\log_{10}{}^* K^o_s$ and $S^o_m$, whereas $\Delta_f H^o_m$ is calculated from the Gibbs-Helmholtz relation.

Table A-124: Standard thermodynamic functions for the $M[UO_2BO_3]\cdot nH_2O$(cr) compounds calculated from data in [2003CHE/NIP], [2003CHE/KNY3] and [2005KAR/CHE3]. These data have been recalculated using enthalpies and Gibbs energies of formation selected by the present review; these values are given in bold and selected by the present review. Using the Gibbs-Helmholtz equation, the entropy of formation and the molar entropy have been calculated from the enthalpies and Gibbs energies of formation, where our recalculated values are in bold.

| Compound | $\Delta_f G^o$ / kJ·mol$^{-1}$ | $\Delta_f H^o$ / kJ·mol$^{-1}$ | $\Delta_f S^o$ / J·K$^{-1}$·mol$^{-1}$ | $S^o(298)$ / J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|
| $Li[UO_2BO_3]\cdot 1.5H_2O$(cr) | – (2528 ± 4) | – (2752 ± 4) | – (751 ± 6) | 196 ± 6 |
| | **– (2528.265 ± 2.257)#** | **– (2753.100 ± 3.500)*** | **– (754.097 ± 13.968)#** | **193.887 ± 13.971#** |
| $Na[UO_2BO_3]\cdot H_2O$(cr) | – (2381 ± 4) | – (2580.5 ± 4) | – (669 ± 6) | 183 ± 6 |
| | – (2381.918 ± 3.614)* | – (2581.600 ± 3.500)* | **– (669.736 ± 3.014)*** | **183.800 ± 3.000*** |
| | **– (2379.358 ± 2.256)#** | **– (2579.039 ± 2.428)†** | | |
| $K[UO_2BO_3]\cdot H_2O$(cr) | – (2403.5 ± 5) | – (2609.0 ± 4.5) | – (689 ± 7) | 177 ± 7 |
| | **– (2403.168 ± 2.257)#** | – (**2609.800 ± 3.400**) | **– (693.045 ± 13.688)#** | **173.871 ± 13.691#** |
| $Rb[UO_2BO_3]\cdot H_2O$(cr) | – (2406 ± 5) | – (2602.5 ± 4.5) | – (659 ± 7) | 219 ± 7 |
| | **– (2405.752 ± 2.260)#** | **– (2603.500 ± 3.300)** | **– (663.252 ± 13.415)#** | **215.764 ± 13.420#** |
| $Cs[UO_2BO_3]\cdot H_2O$(cr) | – (2413 ± 5) | – (2596.0 ± 4.5) | – (614 ± 7) | 273 ± 7 |
| | **– (2412.000 ± 2.317)#** | **– (2597.000 ± 3.900)** | **– (620.495 ± 15.215)#** | **266.971 ± 15.222#** |

* Experimental value obtained by calorimetry from [2005KAR/CHE3].

# From solubility data; the entropy data have been calculated using the Gibbs-Helmholtz relation.

† Calculated using the Gibbs-Helmholtz relation.

This review has estimated the uncertainty in $\Delta_f S^o$ based on those in $\Delta_f G^o$ and $\Delta_f H^o$ which results in a somewhat larger uncertainty than reported by Karyakin *et*

The entropies in these structurally similar compounds are expected to increase in a regular fashion from Li to Cs, and we note that the entropy variation in the monohydrates does not follow the expected trend. The difference in entropy between the monohydrates and the corresponding anhydrous compounds is discussed in [2005KAR/CHE3], where one notes that the difference between $Na[UO_2BO_3]\cdot H_2O(cr)$ and $Na[UO_2BO_3])(cr)$ is 16.6 $J\cdot K\cdot mol^{-1}$, significantly smaller than the value from the Latimer method 44.7 $J\cdot K\cdot mol^{-1}$. The corresponding difference for the K, Rb and Cs-compounds are – 13, 30 and 52 $J\cdot K\cdot mol^{-1}$.

**[2003KAR/CHE]**

Karyakin *et al.* have determined the enthalpy, Gibbs energy and entropy of formation of $Li[UO_2(BO_3)](cr)$ and the corresponding values of the molar heat capacity, $C_p^o$ and entropy $S^o$, by using dissolution and low temperature calorimetry on a well-defined solid phase. The solid phase was prepared as described in a previous study [2002CHE/KNY], [2003CHE/KNY] and the authors state that X-ray diffraction pattern and elemental analyses (not reported) are consistent with those from the anhydrous compound. The calorimetry is described in detail and was based on dissolution in 13.5 M HF according to the following reactions:

$$UO_3(cr,\gamma) + HF(13.5\ M) \rightleftharpoons solution\,1 \qquad (A.261)$$

$$\Delta_r H^o\ (A.261) = -\ (113.1 \pm 1)\ kJ\cdot mol^{-1(*)}$$

$$NaBO_2(cr) + solution\,1 \rightleftharpoons solution\,2 \qquad (A.262)$$

$$\Delta_r H^o\ (A.262) = -\ (136.4 \pm 1.3)\ kJ\cdot mol^{-1\ (*)}$$

$$LiF(cr) + solution\,2 \rightleftharpoons solution\,3 \qquad (A.263)$$

$$\Delta_r H^o\ (A.263) = (6.64 \pm 0.17)\ kJ\cdot mol^{-1}$$

$$Li[UO_2(BO_3)]_2(cr) + solution\,3 \rightleftharpoons solution\,4 \qquad (A.264)$$

$$\Delta_r H^o\ (A.264) = -\ (206.9 \pm 0.9)\ kJ\cdot mol^{-1\ (*)}$$

$$NaF(cr) + solution\,4 \rightleftharpoons solution\,5 \qquad (A.265)$$

$$\Delta_r H^o\ (A.265) = -\ (5.23 \pm 0.22)\ kJ\cdot mol^{-1}$$

(*)The uncertainties are slightly different in [2005KAR/CHE]

These data are the same as discussed in [2003CHE/KNY]. All of these reactions go to completion which means that they can be combined by using equivalent amounts of the solid reactants, resulting in the net reaction:

$$UO_3(cr,\gamma) + NaBO_2(cr) + LiF(cr) \rightleftharpoons Li[UO_2(BO_3)](cr) + NaF(cr) \qquad (A.266)$$

$\Delta_r H^o$ (A.266) = $\Delta_r H^o$ (A.261) + $\Delta_r H^o$ (A.262) + $\Delta_r H^o$ (A.263) – $\Delta_r H^o$ (A.264) – $\Delta_r H^o$ (A.265) = – (30.7 ± 1.8) kJ·mol$^{-1}$.

The following enthalpies of formation from Glushko, *Thermal Constants of Substances*, 1981, issue 10, part 1 and 2 were used:

$\Delta_f H^o$ ($UO_3$, cr, γ) = – (1223.8 ± 1.2) kJ·mol$^{-1}$, consistent with NEA TDB.

$\Delta_f H^o$ ($NaBO_2$, cr) = – (976.5 ± 2.5) kJ·mol$^{-1}$, accepted by NEA TDB, *cf.* Supporting Inf. Table 14-3.

$\Delta_f H^o$ (LiF, cr) = – (618.3 ± 0.7) kJ·mol$^{-1}$, accepted by NEA TDB.

$\Delta_f H^o$ (NaF, cr) = – (572.83 ± 1.26) kJ·mol$^{-1}$, the value selected by NEA TDB is – (576.600 ± 0.700) kJ·mol$^{-1}$.

[2003CHE/KNY3] *et al.* report the enthalpy of formation, $\Delta_f H^o$ (Li[$UO_2(BO_3)$], cr, γ) = – (2272.5 ± 4.0) kJ·mol$^{-1}$, recalculated by the present review to $\Delta_f H^o$ (Li[$UO_2(BO_3)$], cr, γ) = **– (2272.700 ± 3.500)** kJ·mol$^{-1}$ using the NEA selected values for NaF(cr). The molar heat capacity $C_p^o$ (Li[$UO_2(BO_3)$], cr, γ) = **(176.3 ± 1.0)** J·K$^{-1}$·mol$^{-1}$ and entropy $S^o$ (Li[$UO_2(BO_3)$], cr, γ) = **(178.7 ± 3.0)** J·K$^{-1}$·mol$^{-1}$ have been included among the selected values together with the entropy of formation $\Delta_f S^o$ (Li[$UO_2(BO_3)$], cr, γ) = **– (419.400 ± 3.014)** J·K$^{-1}$·mol$^{-1}$ and the Gibbs energy of formation, $\Delta_f G^o$ (Li[$UO_2(BO_3)$], cr, γ) = **– (2147.656 ± 3.614)** kJ·mol$^{-1}$.

**[2004CHE/KNY]**

Chernorukov *et al.* have determined the enthalpy of formation of uranyl(VI) silicate, germanate and borate phases using dissolution calorimetry. Here we will only discuss the enthalpy of formation of $UO_2(BO_2)_2$(cr). The authors report the synthesis and the analysis of the solid where the latter are in excellent agreement with the stoichiometric formula. Based on calorimetric heats of dilution of $UO_3$(γ, cr), $B(OH)_3$(cr) and $UO_2(BO_2)_2$(cr) they have calculated the enthalpy of reaction $\Delta_r H^o$(A.267) and from the enthalpies of formation of $UO_3$(γ, cr), $B(OH)_3$(cr) and $H_2O$(l) the enthalpy of formation, $\Delta_f H^o(UO_2(BO_2)_2$, cr).

$$UO_3(\gamma, cr) + 2B(OH)_3(cr) \rightleftharpoons UO_2(BO_2)_2(cr) + 3H_2O(l) \qquad (A.267)$$

Chernorukov *et al.* report $\Delta_r H^o$(A.267) = (12.8 ± 1.1) kJ·mol$^{-1}$, based on the measured heats of dissolution. The same experimental data have been used in a later study [2006CHE/SMI4], with the same heats of dilution and uncertainties, except for the dissolution of $UO_2(BO_2)_2$(cr) for which the uncertainty has been increased from 0.5 to 2.5 kJ·mol$^{-1}$. This review assumes that the lower value is a misprint, and has accepted the higher value. From $\Delta_r H^o$(A.267) = (12.8 ± 2.7) kJ·mol$^{-1}$ and the NEA accepted enthalpies of formation $\Delta_f H^o(UO_3$, γ, cr) = – (1223.8 ± 1.2) kJ·mol$^{-1}$; $\Delta_f H^o(B(OH)_3$, cr)

= – (1094.8 ± 0.8) kJ·mol$^{-1}$ (a slightly different value – (1094.2 ± 0.8) kJ·mol$^{-1}$, was used in [2004CHE/KNY]); $\Delta_f H^o(H_2O, l)$ = – (286.14 ± 0.04) kJ·mol$^{-1}$, based on $L_1$ = – 0.31 kJ·mol$^{-1}$, this review obtains $\Delta_f H^o(UO_2(BO_2)_2, cr)$ = **– (2541.400 ± 3.400)** kJ·mol$^{-1}$, identical with the value reported by Chernorukov *et al.*

**[2005KAR/CHE3]**

Karyakin *et al.* have reported enthalpy of formation of uranyl(VI) borate compounds, M[$UO_2(BO_3)$]·$nH_2O$(cr), M = Li, Na, K, Rb, Cs, where the data for the Li-compound has been described in [2003CHE/KNY3]. The solid phases are well characterised using X-ray powder diffraction and elemental analyses. The authors conducted low temperature heat capacity measurements and determined the molar heat capacity, $C_p^o$ and entropy $S^o$ of the anhydrous M[$UO_2BO_3$](cr) phases with results listed in Table A-125. The enthalpy of formation was determined using dissolution calorimetry and a thermodynamic cycle similar to the one in [2003CHE/KNY3] as follows, the experimental enthalpies of formation are identical with the ones in [2003CHE/KNY3] and the only new information is obtained from low-temperature determinations of the isobaric heat capacity, $C_p^o$ and the molar entropy, $S_m^o$ (298.15 K) and the corresponding molar entropy of formation.

The isobaric heat capacity and the molar entropy from Karyakin *et al.* are given in Table A-125; they report an uncertainty in the measured heat capacities of 1-3 % between 10 and 40 K, 0.5 %, between 40 and 80 K, and 0.2-0.3 % between 80 and 330 K. The uncertainty in the molar entropy was reported as 2.1 J·K$^{-1}$·mol$^{-1}$, which was increased to 3 J·K$^{-1}$·mol$^{-1}$ by this review.

Table A-125: Entropy and heat capacity for the M[$UO_2BO_3$](cr) compounds.

| Compound | $S^{o(a)}$ /J·K$^{-1}$·mol$^{-1}$ | $C_p^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|
| Li[$UO_2BO_3$](cr) | (178.7 ± 3) | (176.3 ± 1) |
| Na[$UO_2BO_3$](cr) | (167.2 ± 3) | (145.8 ± 1) |
| Na[$UO_2BO_3$]·$H_2O$(cr) | (183.8 ± 3) | (159.0 ± 1) |
| K[$UO_2BO_3$](cr) | (187.2 ± 3) | (157.6 ± 1) |
| Rb[$UO_2BO_3$](cr) | (185.5 ± 3) | (148.8 ± 1) |
| Cs[$UO_2BO_3$](cr) | (214.5 ± 3) | (179.8 ± 1) |

(a) The uncertainty in the standard molar entropy and heat capacity is estimated by this review.

The values for Li[$UO_2BO_3$](cr) and Na[$UO_2BO_3$]·$H_2O$(cr) are identical with those reported in [2003KAR/CHE] and [2003CHE/KNY3]. Using these data, they report the thermodynamic functions, which have been included among the selected values after recalculation with the NEA-approved auxiliary data. For these structurally similar compounds we expect the molar entropy to increase in a regular fashion from Li to Cs; it is obvious that the entropy for Li[$UO_2BO_3$](cr) deviates from this trend.

Based on the enthalpies of formation and the molar entropies, this review has calculated the entropy and Gibbs energy of formation reported in Table A-126. The present review has selected the following thermodynamic data for the anhydrous $M[UO_2BO_3](cr)$, M = Li-Cs, compounds.

Table A-126: Heat capacity, entropy and enthalpy, entropy and Gibbs energy of formation for $M[UO_2BO_3]$ phases, M = Li-Cs; all values accepted by this review (except for $\Delta_f H^o_m$ and $\Delta_f G^o_m$ of $Na[UO_2BO_3]\cdot H_2O(cr)$, see main text).

| Compound | $\Delta_f H^o$ /kJ·mol$^{-1}$ | $\Delta_f S^o$ /J·K$^{-1}$mol$^{-1}$ | $S^o(298.15)$ | $\Delta_f G^o$ /kJ·mol$^{-1}$ | $C_p^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Li[UO_2BO_3](cr)$ | **– (2272.7 ± 3.5)** | **– (419.400 ± 3.014)** | **178.7 ± 3** | **– (2147.656 ± 3.614)** | **176.3 ± 1** |
| $Na[UO_2BO_3](cr)$ | **– (2257.9 ± 3.4)** | **– (453.080 ± 3.014)** | **167.2 ± 3** | **– (2122.814 ± 3.517)** | **145.8 ± 1** |
| $Na[UO_2BO_3]\cdot H_2O(cr)$ | **– (2581.6 ± 3.5)** | **– (669.736 ± 3.014)** | **183.8 ± 3** | **– (2381.918 ± 3.614)** | **159.0 ± 1** |
| $K[UO_2BO_3](cr)$ | **– (2289.8 ± 3.4)** | **– (446.460 ± 3.014)** | **187.2 ± 3** | **– (2156.688 ± 3.517)** | **157.6 ± 1** |
| $Rb[UO_2BO_3](cr)$ | **– (2288.0 ± 3.3)** | **– (460.260 ± 3.023)** | **185.5 ± 3** | **– (2150.773 ± 3.421)** | **148.8 ± 1** |
| $Cs[UO_2BO_3](cr)$ | **– (2284.6 ± 3.9)** | **– (439.710 ± 3.034)** | **214.5 ± 3** | **– (2153.500 ± 4.004)** | **179.8 ± 1** |

The entropy values vary in an unexpected way, the entropy difference between $Na[UO_2BO_3]\cdot H_2O(cr)$ and $Na[UO_2BO_3](cr)$ is 16.6 J·K$^{-1}$·mol$^{-1}$, significantly lower than the estimated value using the Latimer method (Appendix D), 44.7 J·K$^{-1}$·mol$^{-1}$. In the same way the entropy of $Na[UO_2BO_3](cr)$ is lower than that of $Li[UO_2BO_3](cr)$, however these compounds are not isomorphic, [1988GAS], [1990GAS], and the same may be true for the Rb and Cs compounds. The present review notes that both the enthalpy of formation, the entropy and the heat capacity are strongly dependent on the water content in these compound, which makes the accuracy of the water analysis important and more details could have been added in the publications ($Na[UO_2BO_3]\cdot H_2O(cr)$ has been prepared from the anhydrous compounds and then treated hydrothermally).

Karyakin *et al.* have determined the enthalpies of formation of the hydrated alkali uraniumborates using heats of dissolution in HCl solution, also these data are identical with the ones reported in [2003CHE/KNY3].

**[2005CHE/NIP]**

Chernorukov *et al.* have measured the solubility of $M^m[UO_2(BO_3)]_m\cdot nH_2O(cr)$ solids, where M = Li-Cs and Mg-Ba. There is no information on the analytical composition of the solid phases. The solubility data for the alkali compounds seem to be the same as in [2003CHE/NIP], *cf.* this review in Appendix A. We have therefore only reanalysed the experimental data for the $M[UO_2BO_3]_2\cdot nH_2O(cr)$ compounds from 0.100 M HCl, using the same procedure as in the analysis of [2003CHE/NIP]. As reported there the predominant uranyl species is $(UO_2)_2(OH)_2^{2+}$ and the concentration $[UO_2^{2+}]$ was calculated from the equilibrium constant $\log_{10} {}^*\beta^o_{2,2}$ selected by the NEA TDB.

The solubility reaction studied is:

$$\begin{aligned} &M^{m}[UO_2(BO_3)]_m \cdot nH_2O(cr) + 3mHCl(sln) \rightleftharpoons \\ &M^{m+}(Cl^-, sln) + UO_2^{2+}(Cl^-, sln) + mH_3BO_3(Cl^-, sln) + nH_2O(Cl^-, sln) \end{aligned} \quad \text{(A.268)}$$

At the pH of around 4 where the experiments were made and considering the total concentration of uranium ($C_U$ in Table A-127) the predominant uranyl species is $(UO_2)_2(OH)_2^{2+}$ and not $UO_2Cl^+$, and the concentration of free uranyl-ion is very strongly dependent on the pH. The authors do not report any uncertainty value for pH, but it is most likely at least 0.1 pH unit.

The predominant reaction in the dissolution is:

$$\begin{aligned} &M[UO_2BO_3]_2 \cdot nH_2O(cr) + 4H^+ \rightleftharpoons \\ &M^{2+} + (UO_2)_2(OH)_2^{2+} + 2H_3BO_3(Cl^-, sln) + (n-2)H_2O \end{aligned} \quad \text{(A.269)}$$

Denoting the experimental solubility, *S,* based on $[M^{2+}]$ from Table I in [2005CHE/NIP] we obtain:

${}^*K_s = S(S)(2S)^2/[H^+]^4$ and $\log_{10}{}^*K_s = 4\log_{10}S + \log_{10}4 - 4\log_{10}[H^+]$; $\log_{10}{}^*K_s^o = \log_{10}{}^*K_s - 4D$. The ionic strength is approximately 0.1 m and the Debye-Hückel term $D$ is 0.11.

The experiments were made by equilibrating the various solids with HCl solutions with different initial concentrations, $10^{-1}$, $10^{-2}$, $10^{-3}$, $10^{-4}$ M, and pure water; the solubility was measured using the total concentrations U(VI) and borate. The analytical data indicate that the dissolution was congruent only in the test solutions with initial concentrations of HCl equal to 0.100 M. The analysis of the solubility data in order to obtain solubility constants and the corresponding Gibbs energy of reaction is not straight-forward and the authors have used equilibrium constants from the Glushko tables for speciation of U(VI) and borate and corrected for activity coefficients using the D.-H. model. These data have been used with the auxiliary data to give the Gibbs energy of formation that are listed in their Table 2 in [2005CHE/NIP], where the headings in columns 3 and 4 have been interchanged, column 3 reports values of $S^o$ and column 4 values of $\Delta_f S^o$. The reported Gibbs energy of formation is very different from the value obtained by calorimetry, as also found in our re-calculation. This review does not consider the solubility data reliable and they are reported for information only in Table A-127. It should be noted that the Gibbs energies of formation in Table 2 of [2005CHE/NIP] have been calculated from calorimetric data and not from their measured solubilities.

Chernorukov *et al.* also report the solubility at higher pH, but the analyses of borate and uranium clearly show that the dissolution is then non-congruent and cannot be used to obtain thermodynamic information; the solubility curve shown in Figure 1b

in [2005CHE/NIP] is meaningless. For resons discussed in the main text, these solubility data have not been accepted by the present review.

Table A-127: Experimental solubility ($S$) as reported in [2005CHE/NIP], and corresponding solubility constant, ${}^{*}K_s$(A.269), Gibbs energy of reaction, $\Delta_r G^o$(A.269) and Gibbs energy of formation $\Delta_f G^o_m$ ($M[UO_2(BO_3)]_2{\cdot}nH_2O$, cr), as recalculated in this review, $n$ = 4 for Mg, 1 for Ca and 2 for Sr and Ba. Only the solubility at the lowest pH/p$C_{H+}$ have been used but the values at the higher values are available in the original paper.

| | Mg | | Ca | | Sr | | Ba | |
|---|---|---|---|---|---|---|---|---|
| pH / p$C_{H+}$ | 3.9 / 4.02 | | 4.0 / 4.12 | | 4.0 / 4.12 | | 3.9 / 4.02 | |
| | $C_B \times 10^2$ | $C_U \times 10^2$ | $C_B \times 10^2$ | $C_U \times 10^2$ | $C_B \times 10^2$ | $C_U \times 10^2$ | $C_B \times 10^2$ | $C_U \times 10^2$ |
| | 2.9 | 3.2 | 2.6 | 3.1 | 1.0 | 1.1 | 2.6 | 3.0 |
| $\log_{10}{}^{*}K_s$ (A.269) | (9.42 ± 0.50) | | (9.70 ± 0.50) | | (7.96 ± 0.50) | | (9.27 ± 0.50) | |
| $\log_{10}{}^{*}K^o_s$ (A.269) | (8.98 ± 0.500) | | (9.26 ± 0.500) | | (7.52 ± 0.500) | | (8.83 ± 0.500) | |
| $\Delta_r G^o$(A.269) | – (51.258 ± 2.854) | | – (52.856 ± 2.854) | | – (42.924 ± 2.854) | | – (50.402 ± 2.854) | |
| $\Delta_f G^o$(A.269) | – (5164.236 ± 4.989) | | – (4548.649 ± 4.920) | | – (4806.779 ± 4.870) | | – (4793.093 ± 5.456) | |

**[2006CHE/KNY3]**

Chernorukov *et al.* studied the solubility of $M[UO_2(BO_3)]_2{\cdot}nH_2O$(cr) phases, M = Mn, Co, Ni, Zn, in hydrochloric acid of different total concentrations (0.1, 0.01, $10^{-3}$ and $10^{-4}$ M), water and $5 \times 10^{-3}$ M $H_3BO_3$ with the aim of estimating the solubility constants for Reactions (A.270) and (A.271). The solid phases were prepared by ion-exchange between $K[UO_2BO_3]$(cr) and $MCl_2$ in aqueous solution at 200 °C as described in [2003CHE/KNY]. The phases were characterised by XRD and elemental analyses, but no analysis was made of the water content.

$$M[UO_2BO_3]_2{\cdot}nH_2O(cr) + 6H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2H_3BO_3(aq) + nH_2O(l) \qquad (A.270)$$

$$M[UO_2BO_3]_2{\cdot}nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2BO_3^{3-} + nH_2O(l) \qquad (A.271)$$

A pre-requisite for determination of solubility constants is that the dissolution is congruent and this can be judged by the analytical total concentrations of M, borate and U(VI) after equilibrium has been attained. The analytical data presented in [2006CHE/KNY3], Table 1 of the publication, suggest that congruent dissolution only takes place at pH > 7 and not as claimed by the authors in the range 5.5 < pH < 7.5; in measurements with added $H_3BO_3$ ($5 \times 10^{-3}$ M) the solubility seems to be congruent but it is not clear if the analysis of borate is accurate enough to support this claim. In addition, this review notes that the analytical errors are often several percent. Chernorukov *et al.* have used the measured solubility and literature information on the speciation in the equilibrium solutions and estimates of activity coefficients to calculate

the solubility product for Reaction (A.270) and Reaction (A.271) reported in Table A-128.

Table A-128: Equilibrium constants for the solubility reactions, $\log_{10}{}^{*}K_s$(A.270) and $\log_{10}{}^{*}K_s$(A.271) for $M[UO_2(BO_3)]_2{\cdot}nH_2O$(cr) phases, M = Mn, Co, Ni, Zn, as reported in [2006CHE/KNY3].

| Compound $M[UO_2(BO_3)]_2{\cdot}nH_2O$(cr) | Mn | Co | Ni | Zn |
|---|---|---|---|---|
| p$K_s$(A.271) | (58.4 ± 0.5) | (56.9 ± 0.6) | (56.1 ± 0.5) | (57.1 ± 0.6) |
| p*$K_s$(A.270) | – (26.3 ± 0.5) | – (27.7 ± 0.6) | – (28.5 ± 0.5) | – (27.6 ± 0.6) |

There is no information on the equilibrium constants used to calculate the speciation of M(II), U(VI) and borate in the equilibrated test solutions, where in particular the hydrolysis of M(II) is important but experimental data are scarce. In particular, there is no information on the dissociation constant resulting in formation of $BO_3^{3-}$. This review does not have information on the auxiliary data used in [2006CHE/KNY] and it is also not clear which experimental solubility the authors have used to calculate solubility constants, and for this reason the reported solubility products and Gibbs energies of formation have not been accepted.

**[2006CHE/NIP]**

This is a review article mainly based on studies from the Nizhny Novgorod groups that summarises their studies on U(VI)- $VO_4^{3-}$, $PO_4^{3-}$, $AsO_4^{3-}$, $HSiO_4^{3-}$ and $BO_3^{3-}$ systems. There is no new thermodynamic data in this paper but it contains a table of stoichiometric compositions of the aqueous species that they have used. This paper is discussed in the phosphate, arsenate and silicate sections.

**[2006CHE/SMI]**

Chernorukov *et al.* have reported the enthalpy, Gibbs energy and entropy of formation for $Ca[UO_2(BO_3)]_2$(cr) using dissolution calorimetry and low temperature calorimetry to determine the heat capacity and entropy of $Ca[UO_2BO_3]_2$(cr). The solid phase has been characterised by X-ray analysis and elemental analysis using X-ray fluorescence with an accuracy of 2-5 %. The compound is consistent with the known structure described by Gasparin, [1986GAS].

The enthalpy for Reaction (A.272) is identical with the one in [2003CHE/KNY4] and discussed there.

$$2UO_3(cr,\gamma) + CaB_2O_4(cr) \rightleftharpoons Ca[UO_2(BO_3)]_2(cr) \qquad (A.272)$$

The molar heat capacity and entropy, $C_p^o(Ca[UO_2(BO_3)]_2, cr) = 252.9$ $J \cdot K^{-1} \cdot mol^{-1}$ and $S^o(Ca[UO_2(BO_3)]_2, cr) = (291.8 \pm 2.1)$ $J \cdot K^{-1} \cdot mol^{-1}$, have been obtained from low-temperature calorimetry in the range 7-304 K where the uncertainty in the heat capacity is 2 % below 12 K, 0.5 % between 12 and 40 K and 0.2 % at T > 40 K. Based on this, the present review has estimated an accuracy in $C_p^o(Ca[UO_2(BO_3)]_2, cr, 298.15\ K) = 1.5$ $J \cdot K^{-1} \cdot mol^{-1}$. The entropy of formation $\Delta_f S_m^o(Ca[UO_2(BO_3)]_2, cr) = -(887.750 \pm 2.181)$ $J \cdot K^{-1} \cdot mol^{-1}$ is obtained using NEA consistent values of the molar entropies of the elements. The Gibbs energy of formation, $\Delta_f G_m^o(Ca[UO_2(BO_3)]_2, cr) = -(4226.6 \pm 2.4)$ $kJ \cdot mol^{-1}$ is calculated based on the enthalpy of formation in [2003CHE/KNY4] and the entropy of formation in the present study. This value has been recalculated using our selected value for the enthalpy of formation, recalculated here as $-(4491.3 \pm 3.5)$ $kJ \cdot mol^{-1}$, *cf.*, review of [2003CHE/KNY4] to give, $\Delta_f G_m^o(Ca[UO_2(BO_3)]_2, cr) = -(4226.617 \pm 3.560)$ $kJ \cdot mol^{-1}$.

Based on their own studies and literature information Chernorukov *et al.* have calculated the standard thermodynamic functions for the formation of crystalline calcium uranoborate according to:

$$Ca(NO_3)_2(cr) + 2UO_3(cr) + B_2O_3(cr) \rightleftharpoons Ca[UO_2(BO_3)]_2(cr) + 2NO_2(g) + 1/2O_2(g) \quad \text{(A.273)}$$

This reaction may be of interest for waste glass processing.

**[2006CHE/SMI2]**

Chernorukov *et al.* report the standard thermodynamic functions for $Mg[UO_2(BO_3)]_2 \cdot 4H_2O(cr)$ based on dissolution reaction and low temperature calorimetry. The sample used was prepared by hydro-thermal ion-exchange using $K[UO_2BO_3](cr)$ and 0.3 M $Mg[NO_3]_2$ solution. The analytical data in percent, reported for the compound are: MgO, 5.3 (5.34); $UO_3$, 75.7 (75.87); $B_2O_3$, 9.5, (0.23); $H_2O$, 0.5, (9.56), the theoretical values are given within parenthesis. The values for $B_2O_3$ and $H_2O$ are obviously not correct. However, the analyses of U and B are consistent with a tetra-hydrate and we have accepted this.

The dissolution calorimetry is the same as in [2003CHE/KNY4] and is discussed there. The new experimental information is data on isobaric heat capacity, molar entropy and entropy of formation obtained from calorimetric data in the temperature range 3-340 K. The molar heat capacity and entropy of $Mg[UO_2(BO_3)]_2 \cdot 4H_2O(cr)$ are $C_p^o = (389.3 \pm 1.5)$ and $S^o = (410.2 \pm 3.4)$ $J \cdot K^{-1} \cdot mol^{-1}$, respectively. Chernorukov *et al.* obtain $\Delta_f S_m^o(Mg[UO_2(BO_3)]_2 \cdot 4H_2O, cr) = -(1693.454 \pm 3.429)$ $J \cdot K^{-1} \cdot mol^{-1}$. Combining this value with the recalculated enthalpy of formation from [2003CHE/KNY4], $\Delta_f H_m^o(Mg[UO_2(BO_3)]_2 \cdot 4H_2O, cr) = -(5582.1 \pm 7.3)$ $kJ \cdot mol^{-1}$, this review finds $\Delta_f G_m^o(Mg[UO_2(BO_3)]_2 \cdot 4H_2O, cr) =$

– (5077.197 ± 7.371) kJ·mol$^{-1}$, as compared to – (5059 ± 11) kJ·mol$^{-1}$, reported by Chernorukov *et al.*; the difference is due to the different values of the enthalpy of formation of $MgCO_3$(cr) used. The entropy of $Mg[UO_2BO_3]_2$(cr) from [2007CHE/SMI] is $S^o$ = (267.0 ± 2.1) J·K$^{-1}$·mol$^{-1}$ and the difference in entropy between this value and the one for the tetra-hydrate is 35.8 J·K$^{-1}$·mol$^{-1}$ per water, as compared to 45 J·K$^{-1}$·mol$^{-1}$ estimated by the Latimer method.

**[2006CHE/SMI4]**

Chernorukov *et al.* have prepared and characterised $UO_2(BO_2)_2$(cr) using elemental analyses and XRD; these data confirm the composition of the phase used. The enthalpy of formation of uranium metaborate, $UO_2(BO_2)_2$(cr) is based on dissolution reaction calorimetry in 13.5 M HF (~ 16.5 m, HF, $\overline{L}_1$ = – 0.56 kJ·mol$^{-1}$, [1965PAR]) but the experimental data are the same as in [2004CHE/KNY], where they are discussed in detail. The new data in the present study refers to heat capacity measurement in the temperature range 6-302 K, from which the authors report the molar heat capacity, entropy and thermal functions, $C_p^o(UO_2(BO_2)_2, cr)$ = 159.9 and $S^o(UO_2(BO_2)_2, cr)$ = (174.2 ± 2.1) J·K$^{-1}$·mol$^{-1}$, respectively. From the latter and the entropy of the elements we have $\Delta_f S_m^o(UO_2(BO_2)_2, cr)$ = – (503.256 ± 2.116) J·K$^{-1}$·mol$^{-1}$ and $\Delta_f G_m^o(UO_2(BO_2)_2, cr)$ = – (2391.354 ± 3.458) kJ·mol$^{-1}$, recalculated with $\Delta_f H_m^o(UO_2(BO_2)_2, cr)$ = – (2541.400 ± 3.400) kJ·mol$^{-1}$. All these values have been included among the selected values. Using the data from the present and previous studies, Chernorukov *et al.* report data of interest for the synthesis of uranyl borate phases according to:

$$UO_3(cr,\gamma) + B_2O_3(cr) \rightleftharpoons UO_2(BO_2)_2(cr) \quad \text{(A.274)}$$

$$UO_2(BO_2)_2(cr) \rightleftharpoons 1/3U_3O_8(cr) + B_2O_3(cr) + 1/6O_2 \quad \text{(A.275)}$$

$\Delta_r H^o$(A.274) = – (46.0 ± 4.0) kJ·mol$^{-1}$; $\Delta_r G^o$(A.274) = – (52.0 ± 4.5) kJ·mol$^{-1}$; $\Delta_r S^o$(A.274) = (21.6 ± 2.2) J·K$^{-1}$·mol$^{-1}$.

$\Delta_r H^o$(A.275) = (81.5 ± 4.0) kJ·mol$^{-1}$; $\Delta_r G^o$(A.275) = (75.5 ± 4.5) kJ·mol$^{-1}$; $\Delta_r S^o$(A.275) = – (8.1 ± 2.2) J·K$^{-1}$·mol$^{-1}$.

Phase equilibria are important in systems that use glasses for fixation of radioactive waste and the following data have been reported by Chernorukov *et al.* using known thermodynamic data.

$$1/2UO_2(BO_2)_2(cr) + 1/2M_2UO_4(cr) \rightleftharpoons M[UO_2(BO_3)](cr)\ ;\ M = Li\text{-}Cs; \quad \text{(A.276)}$$

$$1/2UO_2(BO_2)_2(cr) + 1/2MUO_4(cr) \rightleftharpoons 1/2M[UO_2(BO_3)]_2(cr)\ ;\ M = Mg\text{-}Ba; \quad \text{(A.277)}$$

$$1/3UO_2(BO_2)_2(cr) + 1/3M_2U_2O_7(cr) + 1/3MBO_2(cr) \rightleftharpoons M[UO_2(BO_3)](cr)\ ;$$

$$M = Li\text{-}Cs; \quad \text{(A.278)}$$

$$1/3UO_2(BO_2)_2(cr) + 1/3MU_2O_7(cr) + 1/3M_{0.5}BO_2(cr) \rightleftharpoons 1/2M[UO_2(BO_3)]_2(cr) ;$$

M = Mg-Ba; (A.279)

Chernorukov *et al.* report the following data that are given for information only.

Table A-129: Thermodynamic functions for Reactions (A.276)-(A.277) and (A.278)-(A.279) in kJ·mol$^{-1}$ from Chernorukov *et al.*.

| | $\Delta_r H^o$(A.276)/(A.277) /kJ·mol$^{-1}$ | $\Delta_r G^o$(A.276)/(A.277) /kJ·mol$^{-1}$ | $\Delta_r H^o$(A.278)/(A.279) /kJ·mol$^{-1}$ | $\Delta_r G^o$(A.278)/(A.279) /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| Li | – (18.0 ± 5.0) | – (24.5 ± 6.0) | – (13.0 ± 5.0) | – |
| Na | – (40.0 ± 5.0) | – (38.5 ± 6.0) | – (19.0 ± 5.0) | – (17.0 ± 6.0) |
| K | – (60.0 ± 5.0) | – | – (31.0 ± 5.0) | – |
| Rb | – (57.0 ± 5.5) | – (52.5 ± 6.0) | – (38.0 ± 5.5) | – |
| Cs | – (50.5 ± 5.5) | – (55.5 ± 6.0) | – (47.0 ± 5.5) | – (51.5 ± 7.0) |
| Mg | (26.0 ± 7.0) | – | – | – |
| Ca | (26.5 ± 7.0) | (30.5 ± 8.0) | – | – |
| Sr | (7.5 ± 7.0) | – | – | – |
| Ba | (16.0 ± 7.0) | – | – | – |

**[2006CHE/SMI5]**

Chernorukin *et al.* reports the enthalpy of formation of $Ca[UO_2BO_3]_2$(cr) based on dissolution calorimetry in 11.6 M HCl and heat capacity measurements in the temperature range 6.6-304.8 K to obtain the isobaric heat capacity, molar entropy, and the entropy and Gibbs energy of formation. The information on the calorimetry of dissolution is identical with the one reported in [2003CHE/KNY4] and does not represent new experimental data. The calorimetric studies have been made using well characterised crystalline calcium uranoborate and the reported isobaric heat capacity, $C_p^o$ (298.15 K) = (252.9 ± 1.5) J·K$^{-1}$·mol$^{-1}$, molar entropy, $S_m^o$ (298.15 K) = (291.8 ± 2.1) J·K$^{-1}$·mol$^{-1}$, and entropy of formation, $\Delta_f S_m^o$ (298.15 K) = – (887.750 ± 2.181) J·K$^{-1}$·mol$^{-1}$ have been accepted by the present review. Using our selected value $\Delta_f H_m^o$ ($Ca[UO_2BO_3]_2$, cr) = – (4491.300 ± 3.500) kJ·mol$^{-1}$ from [2003CHE/KNY4], we have calculated the Gibbs energy of formation, $\Delta_f G_m^o$ ($Ca[UO_2BO_3]_2$, cr) = – (4226.617 ± 3.560) kJ·mol$^{-1}$, using the Gibbs-Helmholtz equation.

**[2007CHE/SMI]**

Chernorukov *et al.* have determined the enthalpy of formation of $Mg[UO_2BO_3]_2$(cr) using dissolution calorimetry with a method similar to the one in [2003CHE/KNY4]. By calorimetric measurement of the heats of dissolution of $UO_3$(γ, cr), $CaB_2O_4$(cr), $CaCO_3$(cr), $MgCO_3$(cr) and $Mg[UO_2BO_3]_2$(cr) they obtain the enthalpy of reaction, $\Delta_r H^o$(A.280) = (20.2 ± 1.0) kJ·mol$^{-1}$.

$$2UO_3(\gamma, cr) + CaB_2O_4(cr) + MgCO_3(cr) \rightleftharpoons Mg[UO_2BO_3]_2(cr) + CaCO_3(cr) \quad (A.280)$$

Using the following enthalpies of formation: $\Delta_f H^o_m(UO_3, \gamma, cr) = -(1223.8 \pm 1.2)$ kJ·mol$^{-1}$, $\Delta_f H^o_m(CaB_2O_4, cr) = -(2031.1 \pm 1.5)$ kJ·mol$^{-1}$, $\Delta_f H^o_m(MgCO_3, cr) = -(1095.9 \pm 1.3)$ kJ·mol$^{-1}$ and $\Delta_f H^o_m(CaCO_3, cr) = -(1206.8 \pm 0.8)$ kJ·mol$^{-1}$, they obtain $\Delta_f H^o_m(Mg[UO_2BO_3]_2, cr) = -(4347.5 \pm 8.0)$ kJ·mol$^{-1}$. This value has been recalculated using the NEA selected values $\Delta_f H^o_m(CaB_2O_4, cr) = -(2031.5 \pm 1.7)$ kJ·mol$^{-1}$, $\Delta_f H^o_m(MgCO_3, cr) = -(1112.4 \pm 1.0)$ kJ·mol$^{-1}$ and $\Delta_f H^o_m(CaCO_3, cr) = -(1207.4 \pm 1.5)$ kJ·mol$^{-1}$ to give, $\Delta_f H^o_m(Mg[UO_2BO_3]_2, cr) = -(4363.8 \pm 4.0)$ kJ·mol$^{-1}$, where the uncertainty is based on the reported uncertainty in the individual enthalpies of formation. Chernorukov *et al.* have used low temperature calorimetry from 8.0 to 334 K to calculate the isobaric heat capacity, $C^o_p(298.15\ K) = (242.2 \pm 1.5)$ J·K$^{-1}$·mol$^{-1}$ and $S^o(298.15\ K) = (267.0 \pm 2.1)$ J·K$^{-1}$·mol$^{-1}$. The entropy of formation calculated from the measured molar entropy of $Mg[UO_2BO_3]_2$(cr) and the molar entropies of the elements, reported by Chernorukov *et al.*, $\Delta_f S^o_m(Mg[UO_2BO_3]_2, cr) = -(903.0 \pm 2.1)$ J·K$^{-1}$·mol$^{-1}$, revised by this review to $-(903.630 \pm 2.146)$ J·K$^{-1}$·mol$^{-1}$, is accepted by this review and used together with our selected enthalpy of formation, $\Delta_f H^o_m(Mg[UO_2BO_3]_2, cr) = -(4363.8 \pm 4.0)$ kJ·mol$^{-1}$, to give the selected Gibbs energy of formation, $\Delta_f G^o(Mg[UO_2BO_3]_2, cr) = -(4094.383 \pm 4.052)$ kJ·mol$^{-1}$.

**[2008CHE/SMI]**

The standard enthalpies of formation of $Ba[UO_2BO_3]_2$(cr) and $Ba[UO_2BO_3]_2 \cdot 2H_2O$(cr) have been determined using dissolution calorimetry with a method described in [2003CHE/KNY4], [2006CHE/SMI2] and [2007CHE/SMI]. The reported data are identical with the ones in [2003CHE/KNY4]. From these data Chernorukov *et al.* obtain the enthalpy of reaction, $\Delta_r H^o$(A.281):

$$2UO_3(cr, \gamma) + CaB_2O_4(cr) + BaCO_3(cr) + nH_2O(l) \rightleftharpoons Ba[UO_2BO_3]_2 \cdot nH_2O(cr) + CaCO_3(cr) \quad (A.281)$$

Elemental analyses of both solid phases are in excellent agreement with the given stoichiometry.

To calculate the enthalpies of formation of $Ba[UO_2BO_3]_2$(cr) and $Ba[UO_2BO_3]_2 \cdot 2H_2O$(cr), the following auxiliary data were used: $\Delta_f H^o_m(UO_3, cr, \gamma) = -(1223.8 \pm 1.2)$ kJ·mol$^{-1}$; $\Delta_f H^o_m(CaB_2O_4, cr) = -(2031.1 \pm 1.5)$ kJ·mol$^{-1}$, $\Delta_f H^o_m(BaCO_3, cr) = -(1210.9 \pm 2.5)$ kJ·mol$^{-1}$, $\Delta_f H^o_m(CaCO_3, cr) = -(1206.8 \pm 0.8)$ kJ·mol$^{-1}$ and $\Delta_f H^o_m(H_2O, l) = -(285.83 \pm 0.04)$ kJ·mol$^{-1}$. The following enthalpies of formation were reported, $\Delta_f H^o_m(Ba[UO_2BO_3]_2, cr, \alpha) = -(4507.5 \pm 8.0)$ kJ·mol$^{-1}$, and $\Delta_f H^o_m(Ba[UO_2BO_3 \cdot 2H_2O, cr) = -(5031.0 \pm 8.0)$ kJ·mol$^{-1}$, these are the same as in [2003CHE/KNY4]. These values have been recalculated by the present review using our selected values

$\Delta_f H_m^o$ ($CaB_2O_4$, cr) = – (2031.5 ± 1.7) kJ·mol$^{-1}$, $\Delta_f H_m^o$ ($BaCO_3$, cr) = – (1213.0 ± 2.0) kJ·mol$^{-1}$, $\Delta_f H_m^o$ ($CaCO_3$, cr) = – (1207.5 ± 1.2) kJ·mol$^{-1}$ and the enthalpy of formation in 11.6 M HCl, $\Delta_f H_m^o$ ($H_2O$, 11.6 M HCl) = – 286.4 kJ·mol$^{-1}$; we find $\Delta_f H_m^o$ (α-$Ba[UO_2BO_3]$, cr, α) = – (4509.0 ± 4.6) kJ·mol$^{-1}$, and $\Delta_f H_m^o$ ($Ba[UO_2BO_3]_2$·$2H_2O$, cr) = – (5129.9 ± 8.0) kJ·mol$^{-1}$. Chernorukov *et al.* [2008CHE/SMI] used adiabatic vacuum calorimetry at 7-340 K and reported $C_{p,m}^o$ ($Ba[UO_2BO_3]_2$, cr, 298.15 K) = 229.7 J·K$^{-1}$·mol$^{-1}$ and $C_{p,m}^o$ ($Ba[UO_2BO_3]_2$·$2H_2O$, cr, 298.15 K) = 311.8 J·K$^{-1}$·mol$^{-1}$. The corresponding molar entropies are, $S^o$($Ba[UO_2BO_3]_2$, cr, 298.15 K) = (282.0 ± 1.8) J·K$^{-1}$·mol$^{-1}$ and $S^o$($Ba[UO_2BO_3]_2$·$2H_2O$, cr, 298.15 K) = (360.7 ± 2.6) J·K$^{-1}$·mol$^{-1}$. The entropy contribution from two water of crystallisation is 80.6 J·K$^{-1}$·mol$^{-1}$, in good agreement with the estimate 90 J·K$^{-1}$·mol$^{-1}$ using the Latimer method. The isobaric heat capacity and molar entropy for the compounds are included among the selected values, as are the entropies of formation, $\Delta_f S_m^o$ ($Ba[UO_2BO_3]_2$, cr) = – (918.380 ± 2.033) J·K$^{-1}$·mol$^{-1}$, and $\Delta_f S_m^o$ ($Ba[UO_2BO_3]_2$·$2H_2O$,cr) = – (1306.192 ± 2.766) J·K$^{-1}$·mol$^{-1}$. The Gibbs energy of formation reported by Chernorukov *et al.* are $\Delta_f G_m^o$ ($Ba[UO_2BO_3]_2$, cr) = – (4234.0 ± 8.5) kJ·mol$^{-1}$, and $\Delta_f G_m^o$ ($Ba[UO_2BO_3]_2$·$2H_2O$, cr) = – (4642.0 ± 8.5) kJ·mol$^{-1}$, these values have been recalculated by the present review using the enthalpies of formation recalculated by this review and we find $\Delta_f G_m^o$ ($Ba[UO_2BO_3]_2$, cr, α) = – (4235.185 ± 4.640) kJ·mol$^{-1}$, and $\Delta_f G_m^o$ ($Ba[UO_2BO_3]_2$·$2H_2O$, cr) = – (4740.459 ± 8.042) kJ·mol$^{-1}$. The recalculated values have been accepted by this review.

This is an accurate study where all necessary information to allow a quality assessment is provided.

**[2008MAR/SMI]**

Marochkina *et al.* discuss their previous low-temperature heat capacity data of alkali- and alkaline-earth uranoborates at $T < 50$ K, using Debye-theory and its fractal generalisation for extrapolation to 0 K. They suggest that the function $C_p^o(T)$ is dependent on $T$ in chain structures, on $T^2$ in layer structures and on $T^3$ in framework structures, this information is of interest for the extrapolation of heat capacity data to 0 K. Marochkina *et al.* report the isobaric heat capacities and entropies in Table A-130, but this is a summary of published data. In the last column the present review has added the entropy of water estimated by the Latimer method and notes that the entropy of $Li[UO_2BO_3]$(cr) is significantly lower than that of $Na[UO_2BO_3]$(cr), where the opposite is expected, while the trend in entropy for $M[UO_2BO_3]_2$(cr) is the expected one. The difference between the experimental entropy for the hydrated and anhydrous compounds corresponds to (36 ± 4), (31 ± 4) and (40 ± 4) J·K$^{-1}$·mol$^{-1}$ per water for the Mg- Sr- and Ba-compounds respectively, as compared to 45 J·K$^{-1}$·mol$^{-1}$ estimated by the

Latimer method. This review suggests that this agreement is reasonably good, but that a small uncertainty in the water content cannot be excluded.

Table A-130: Isobaric heat capacity, $C_p^o$(298.15 K) and $S^o$(298.15 K) in J·K$^{-1}$·mol$^{-1}$ for M[$UO_2BO_3$](cr), M = Li, Na, K, Rb, and M[$UO_2BO_3$]$_2$·$n$$H_2O$(cr), M = Mg, Ca, Sr, Ba. These data are included among the selected values except for Sr[$UO_2BO_3$]$_2$(cr), as the form (α or β) is not indicated for this phase.

| Compound | $C_p^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $S^o$(298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $S^o$(298.15 K) /J·K$^{-1}$·mol$^{-1}$ Estimate based on Latimer |
|---|---|---|---|
| Li[$UO_2BO_3$](cr) | **176.3** | **178.7** | |
| Na[$UO_2BO_3$](cr) | **145.8** | **167.2** | |
| K[$UO_2BO_3$](cr) | **157.6** | **187.2** | |
| Rb[$UO_2BO_3$](cr) | **148.8** | **185.5** | |
| Mg[$UO_2BO_3$]$_2$(cr) | **242.2** | **267.0** | |
| Mg[$UO_2BO_3$]$_2$·4$H_2O$(cr) | **389.3** | **410.2** | 447 |
| Ca[$UO_2BO_3$]$_2$(cr) | **252.9** | **291.8** | |
| Sr[$UO_2BO_3$]$_2$(cr) | 262.2 | 289.2 | |
| Sr[$UO_2BO_3$]$_2$·2$H_2O$(cr) | **316.4** | **351.5** | 379 |
| Ba[$UO_2BO_3$]$_2$(cr) | **229.7** | **282.0** | |
| Ba[$UO_2BO_3$]$_2$·2$H_2O$(cr) | **311.8** | **360.7** | 372 |

**[2011KNY/BUL]**

Knyazev and Bulanova have studied phase-transition using high-temperature X-ray diffraction in the range 298-1100 K and DTA to identify two polymorphs, α and β, for the Li-compound that interchanges reversibly at around 1050 K. There is no thermodynamic information.

**[2012KNY/KUZ]**

The authors have used a list of thermodynamic data, mainly from their own studies to model phase diagrams of interest for preparation of nuclear waste glass. There are no new thermodynamic data presented and the paper is for this reason mainly of interest in waste-glass applications.

**[2018POP/BEN]**

The thermal properties of Na[$UO_2BO_3$](cr) have been investigated using Powder X-ray data, Raman spectroscopy and calorimetric determination of isobaric heat capacities in the temperature range 293.40-1.822 K. Based on these data the authors report $C_{p,m}^o$ (298.15 K) = (143.2 ± 2.9) J·K$^{-1}$·mol$^{-1}$, and $S^o$(298.15 K) = (174.9 ± 3.5) J·K$^{-1}$·mol$^{-1}$ and $H^o$(298.15 K) – $H^o$(0 K) = (26.37 ± 0.53) kJ·mol$^{-1}$. The errors were estimated from the accuracy of the measurement equipment used, about 2 %. The thermal data indicate an anomaly in the slope around 175 K, similar observation was

also reported by Karyakin *et al.* [2002KAR/CHE], but not identified as an anomaly by them. The heat capacity as a function of temperature was described by the following expression:

$$C^{o}_{p,m}/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = (188.3 \pm 27.8) + (11.20 \pm 3.97) \times 10^{-3}\,(T/\mathrm{K}) - (4.308 \pm 1.431) \times 10^{-6}\,(T/\mathrm{K})^{-2}.$$

We note that the molar heat capacity and entropy are in good agreement with the values reported in [2002KAR/CHE].

## A-1.8 Compounds and complexes in the uranium vanadium system

**[1982ZHI/SHM]**

Zhil'tsova *et al.* have made a careful review of previous studies of the thermodynamics of carnotite, $K_2[UO_2VO_4]_2{\cdot}3H_2O$(cr), pointing out several flaws in the experimental methods used. They report in detail the methods used to prepare and analyse the synthetic carnotite phase that they used in their experiments. The composition was analysed before and after equilibrium to ensure that no phase transformation took place. The equilibrium solutions were analysed for U and K and their ratio was found to be constant and equal to 1.00 with an uncertainty of at most 1 %. The solubility was measured in a 0.010 M HCl solution, with an initial pH = 2.05, which after equilibrium is increased to 2.15.

The authors propose that the following reaction takes place:

$$K_2[UO_2VO_4]_2 \cdot 3H_2O(cr) + 4H^+ \rightleftharpoons 2K^+ + 2UO_2^{2+} + 2H_2VO_4^- + 3H_2O(l) \qquad (A.282)$$

However, the predominance diagram for vanadium in Mesmer and Baes [1976BAE/MES] and the one reported by Zhil'tsova *et al.* in their Figure 3, suggest that the predominant form of vanadium(V) at pH = 2.15 is $VO_2^+(aq)$ and the reaction studied is accordingly:

$$K_2[UO_2VO_4]_2 \cdot 3H_2O(cr) + 8H^+ \rightleftharpoons 2K^+ + 2UO_2^{2+} + 2VO_2^+ + 7H_2O(l) \qquad (A.283)$$

${}^{*}K_s$ (A.283) = $[S]^6/[H^+]^8$, or $\log_{10}{}^{*}K_s = 6(-3.02) + 8(2.15) = -0.92$.

The ionic strength correction is very small and accordingly the value of $\log_{10}{}^{*}K^{o}_{s}$ (A.283) = – (1.10 ± 0.40), where the uncertainty is determined by the pH measurements, assumed to be ± 0.05 pH units. The Gibbs energy of reaction is $\Delta_r G^o_m = (6.279 \pm 2.283)$ kJ·mol$^{-1}$. Using the NEA selected Gibbs energies of formation, $\Delta_f G^o_m(UO_2^{2+})$, $\Delta_f G^o_m(K^+)$ and $\Delta_f G^o_m(H_2O, l)$, we obtain, $\Delta_f G^o_m(K_2[UO_2VO_4]_2{\cdot}3H_2O, cr) = -(6.279 \pm 2.283) - 2\{(952.551 \pm 1.747) + (590.280 \pm 1.530) + (282.510 \pm 0.116)\} - 7(237.14 \pm 0.04) = -(5316.941 \pm 5.188)$

kJ·mol$^{-1}$. This review notes that our recalculated value is significantly different from the value – 5280 kJ·mol$^{-1}$ reported by Langmuir, [1978LAN].

**[1986MER]**

The structure of the mineral francevillite, $Ba_{0.96}Pb_{0.04}[UO_2VO_4]_2{\cdot}5H_2O$(cr), is isomorphous with the corresponding Ca-compound and has the same layer and interlayer structure.

**[1988FOT/SLO]**

The [1988FOT/SLO] book devotes only 10 pages out of a total of 243 to thermodynamic properties. They report a Table of $\Delta_f H_m^o$, $S_m^o$ and $C_{p,m}^o$, with some references to their own papers. The present review has not considered these data because of lack of experimental details.

**[1989ZHI/PER]**

Zhil'tsova *et al.* studied the solubility of synthetic tyuamunite, a uranyl vanadate of the idealised formula $Ca[UO_2VO_4]_2{\cdot}(5\text{-}8)H_2O$(cr). The synthesised sample had a composition $Ca_{0.9}(UO_2)_2(V_2O_8)_{0.9}{\cdot}13.8H_2O$(cr) and $Ca_{1.1}(UO_2)_2(V_2O_8)_{0.9}{\cdot}8.8H_2O$(cr) after dissolution. The phase was characterised by X-ray diffraction and chemical analysis. Solubility studies were conducted at 25 °C in HCl solutions at two pH values (2.10 and 2.80) with periodic manual shaking of the test solutions. Concentrations of U, V, and Ca were measured: U by titration; V by the colorimetric phosphorus-tungsten method; Ca – by atomic absorption spectroscopy (AAS), pH (the activity scale) was also determined. Steady-state concentrations were reached in 7-8 days. The reported equilibrium concentration of Ca, U and V deviate significantly from the expected ratio 1:2:2, demonstrating that the dissolution was not congruent, with the possible exception at pH = 2.10. The reaction taking place in the test solutions is not the one proposed in Reaction (A.284), but the one in Reaction (A.285):

$$Ca[UO_2VO_4]_2(cr) \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 2VO_4^{3-} \quad \text{(A.284)}$$

$$Ca[UO_2VO_4]_2(cr) + 8H^+ \rightleftharpoons Ca^{2+} + 2UO_2^{2+} + 2VO_2^+ + 4H_2O(l) \quad \text{(A.285)}$$

Based on the measured solubility, the solubility product of Reaction (A.284), for synthetic tyuamunite was determined. Activity coefficients were calculated using the extended Debye-Hückel equation. The corrections for hydrolysis and formation of the chloride complex of uranyl ion were taken into account, for vanadium the species $H_3VO_4$(aq) and $H_2VO_4^-$ were considered. The authors report the solubility product and Gibbs energy of formation for Reaction (A.284):

$$\log_{10} K_s^o = -(51.48 \pm 0.09)$$

Based on this, Zhil'tsova *et al.* report $\Delta_f G_m^o$ ($Ca[UO_2VO_4]_2$, cr) = – (4557.2 ± 0.5) kJ·mol$^{-1}$, which recalculated using our selected values results in $\Delta_f G_m^o$ ($Ca[UO_2VO_4]_2$, cr) = – (4537.3 ± 5.3) kJ·mol$^{-1}$. Zhil'tsova *et al.* also report the equilibrium constant for the ion-exchange Reaction (A.286), $\log_{10} K$(A.286) = 5.89 at a ionic strength about 0.1 M.

$$Ca[UO_2VO_4]_2(cr) + 2K^+ \rightleftharpoons K_2[UO_2VO_4]_2(cr) + Ca^{2+} \quad \text{(A.286)}$$

Because of experimental shortcomings, the present review has not accepted the solubility constants and Gibbs energies of formation proposed by Zhil'tsova *et al.*

**[1992KAR/CHE]**

Chernorukov *et al.* report enthalpies of formation of $M[UO_2VO_4]$(cr), M = Na-Cs, from dissolution calorimetry in HF(aq) resulting in enthalpies of reaction for the following reactions, but with no experimental details:

$$MVO_3(cr) + UO_3(cr) \rightleftharpoons M[UO_2VO_4](cr) \quad \text{(A.287)}$$

$$0.5\{M_2UO_4(cr) + V_2O_5(cr) + UO_3(cr)\} \rightleftharpoons M[UO_2VO_4](cr) \quad \text{(A.288)}$$

$$0.5M_2O(cr) + 0.5V_2O_5(cr) + UO_3(cr) \rightleftharpoons M[UO_2VO_4](cr) \quad \text{(A.289)}$$

The authors have moreover measured the enthalpy of dissolution of $\{Na_2U_2O_7 + V_2O_5\}$ to obtain a second value for the enthalpy of formation of $Na[UO_2VO_4]$(cr). In this review, we have recalculated the enthalpy of formation of $Na[UO_2VO_4]$(cr) using the following thermodynamic cycle, with the notation used in [1992KAR/CHE]:

$$0.5\{Na_2U_2O_7(cr) + V_2O_5(cr)\} + 6HF(sln) \rightleftharpoons NaF(sln) + UO_2F_2(sln) + VOF_3(sln) + 3H_2O(sln) \quad \text{(A.290)}$$

$\Delta H_r$(A.290) = – (190.8 ± 1.10) kJ·mol$^{-1}$;

$$Na[UO_2VO_4](cr) + 6HF(sln) \rightleftharpoons NaF(sln) + UO_2F_2(sln) + VOF_3(sln) + 3H_2O(sln) \quad \text{(A.291)}$$

$\Delta H_r$(A.291) = – (153.1 ± 0.90) kJ·mol$^{-1}$;

$$2V(cr) + 5/2O_2(g) \rightleftharpoons V_2O_5(cr) \quad \text{(A.292)}$$

$\Delta H_r$(A.292) = – (1556.0 ± 3.0) kJ·mol$^{-1}$;

$$2Na(cr) + 2U(cr) + 7/2O_2(g) \rightleftharpoons Na_2U_2O_7(cr) \quad \text{(A.293)}$$

$\Delta H_r$(A.293) = – (3203.8 ± 4.00) kJ·mol$^{-1}$;

$$Na(cr) + U(cr) + V(cr) + 3O_2(g) \rightleftharpoons Na[UO_2VO_4](cr) \quad (A.294)$$

$\Delta H_r$(A.294) = – (2413 ± 6) kJ·mol$^{-1}$;

this value was recalculated by the present review to $\Delta H_r$(A.294) = – (2417.6 ± 2.9) kJ·mol$^{-1}$, which differs significantly from the value obtained using the first thermodynamic cycle ($\Delta_f H^o$($NaUO_2VO_4$, cr) = – (2404.0 ± 2.4) kJ·mol$^{-1}$, recalculated in this review). The enthalpy of formation has been redetermined in a later study, [1998KAR/CHE5], with a significantly different value for the enthalpy of formation and the authors point out that this might be due to the presence of some water impurity in the samples used in the first experiments and for this reason they prefer the one reported in [1998KAR/CHE5]. The present review accepts their argument and only considers the data from the second study that reports $\Delta_f H^o_m$ = – (2429.6 ± 6) kJ·mol$^{-1}$, recalculated to this review $\Delta_f H^o_m$ = – (2430.3 ± 4.2) kJ·mol$^{-1}$.

Karyakin *et al.* report also the enthalpy of formation of K[$UO_2VO_4$](cr), $\Delta_f H^o_m$ $\Delta_f H^o_m$ (K[$UO_2VO_4$], cr) = – (2453.8 ± 5.3) kJ·mol$^{-1}$. This value has been recalculated by the present review using NEA TDB auxiliary data to $\Delta_f H^o_m$ (K[$UO_2VO_4$], cr) = – (2446.700 ± 6.000) kJ·mol$^{-1}$, which is our selected value; Chernorukov *et al.* report from another solubility study, $\Delta_f H^o_m$ (K[$UO_2VO_4$], cr) = – (2467.000 ± 2.300) kJ·mol$^{-1}$; these values have been calculated from the Gibbs energy of formation from the solubility data and the calorimetric value of the entropy of formation. The values from calorimetry and from solubility data are in disagreement, and the present review has preferred the calorimetric one.

The calorimetric enthalpies of formation of Rb[$UO_2VO_4$](cr) and Cs[$UO_2VO_4$](cr) have been recalculated and selected by this review, but we note that they differ significantly from the values obtained from the Gibbs energy of formation based on solubility experiments in [2001CHE/SUL] and the entropy of formation in [1996KAR/CHE2].

Table A-131: Enthalpies of formation of M[$UO_2VO_4$](cr) in kJ·mol$^{-1}$ from [1992KAR/CHE] using the auxiliary data from the Glushko tables. In column 3 we report our recalculated data in bold, which are included among the selected values.

| Compound | $\Delta_f H^o$(A.289)/kJ·mol$^{-1}$ [1992KAR/CHE] | $\Delta_f H^o$ /kJ·mol$^{-1}$ Recalculated by this review | Reference |
|---|---|---|---|
| Na[$UO_2VO_4$](cr) | – (2407 ± 8), – (2413 ± 6) | – (2404.0 ± 2.4) | [1992KAR/CHE] |
| | Based on two cycles | – (2417.6 ± 2.9) | |
| | | **– (2430.300 ± 4.200)**[(a)] | [1998KAR/CHE5] |
| K[$UO_2VO_4$](cr) | – (2451 ± 9) | **– (2446.700 ± 6.000)**[(a)] | [1992KAR/CHE] |
| | | – (2466.7 ± 6.0)[(b)] | [2001CHE/SUL] |
| Rb[$UO_2VO_4$](cr) | – (2460 ± 14) | **– (2430.800 ± 1.900)**[(a)] | [1992KAR/CHE] |
| | | – (2477.1 ± 6.0)[(b)] | [2001CHE/SUL] |
| Cs[$UO_2VO_4$](cr) | – (2480 ± 14) | **– (2436.400 ± 2.800)**[(a)] | [1992KAR/CHE] |
| | | – (2493.8 ± 6.0)[(b)] | [2001CHE/SUL] |

(a) Recalculated by this review
(b) From solubility and entropy data

**[1995KAR/CHE2]**

Standard enthalpies of formation of $Li[UO_2VO_4](cr)$, $Na[UO_2NbO_4](cr)$ and $Rb[UO_2TaO_4](cr)$ have been determined by dissolution calorimetry in 3 M $H_2SO_4$ and 26 M HF. From the dissolution enthalpies they have obtained the enthalpies of Reactions (A.295)-(A.297):

$$LiNO_3(cr) + NaVO_3(cr) + UO_3(cr) \rightleftharpoons Li[UO_2VO_4](cr) + NaNO_3(cr) \quad (A.295)$$

$\Delta_r H(A.295) = -(19.2 \pm 2.8)$ kJ·mol$^{-1}$.

$$NaNO_3(cr) + KNbO_3(cr) + UO_3(cr) \rightleftharpoons Na[UO_2NbO_4](cr) + KNO_3(cr) \quad (A.296)$$

$$RbNO_3(cr) + KTaO_3(cr) + UO_3(cr) \rightleftharpoons Rb[UO_2TaO_4](cr) + KNO_3(cr) \quad (A.297)$$

The enthalpies of formation reported by the authors are:

$\Delta_f H^o_m$ ($Li[UO_2VO_4]$, cr) = $-(2401 \pm 11)$ kJ·mol$^{-1}$;

$\Delta_f H^o_m$ ($Na[UO_2NbO_4]$, cr) = $-(2552 \pm 17)$ kJ·mol$^{-1}$;

$\Delta_f H^o_m$ ($Rb[UO_2TaO_4]$, cr) = $-(2632 \pm 19)$ kJ·mol$^{-1}$.

The enthalpies of formation were based on auxiliary data from the Glushko Tables, Issue 10, Parts 1 and 2, Moscow 1981, where the value for $UO_3$(cr, γ) = $-(1228.3 \pm 3)$ kJ·mol$^{-1}$, significantly different from the CODATA value selected by NEA, $-1223.8$ kJ·mol$^{-1}$, we suggest that this is a printing error. The authors do not report the enthalpy of formation of $KNbO_3$(cr) and the present review has used $\Delta_f H^o_m$ ($KNbO_3$, s) = $-1346.8$ kJ·mol$^{-1}$ from [1971NAU/RYZ], which is only an estimate based on poorly constrained Gibbs energies of formation and estimated entropies. The data from Karyakin *et al.* were re-analysed by the present review, using the NEA auxiliary data, and we find:

$\Delta_f H^o_m$ ($Li[UO_2VO_4]$, cr) = $-(2398.3 \pm 3.5)$ kJ·mol$^{-1}$;
$\Delta_f H^o_m$ ($Na[UO_2NbO_4]$, cr) = $-(2547.9 \pm 5.8)$ kJ·mol$^{-1}$; where the uncertainty does not take the one in $KNbO_3$ into account.

$\Delta_f H^o_m$ ($Rb[UO_2TaO_4]$, cr) = $-(2627.5 \pm 7.2)$ kJ·mol$^{-1}$.

The enthalpy of formation of $Li[UO_2VO_4](cr)$ is selected in the present review, $\Delta_f H^o_m$ ($Li[UO_2VO_4]$, cr) = $-(2398.3 \pm 3.5)$ kJ·mol$^{-1}$. The values for the other two compounds are given for information only.

The synthesis of the compounds is well described. However, there are no details on the chemical analyses, although it seems clear that all are anhydrous.

**[1996KAR/CHE2]**

The isobaric heat capacity of $Rb[UO_2VO_4](cr)$ and $Cs[UO_2VO_4](cr)$ compounds were determined between 60 and 320 K and extrapolated to 0 K using an empirical method. The accuracy of this procedure was established by comparison of corresponding data for the isostructural $K[UO_2VO_4](cr)$, for which heat capacity was measured down to 5 K. The authors report the isobaric heat capacity, $C_p^o$ (298.15 K), the molar entropy $S_m^o$ (298.15 K) and the entropy of formation, $\Delta_f S_m^o$ (298.15 K). By using these data and the enthalpy of formation of the compounds from [1992KAR/CHE], they calculate the corresponding Gibbs energy of formation, $\Delta_f G_m^o$ (298.15 K), these data are listed in Table A-132. This review notes that the Gibbs energies of formation calculated from the calorimetric data are not consistent with those obtained from solubility experiments [2003CHE/SUL4].

Table A-132: Thermodynamic data for $Rb[UO_2VO_4](cr)$ and $Cs[UO_2VO_4](cr)$ from [1992KAR/CHE] and [1996KAR/CHE2].

| Compound | $C_p^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $S^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f H^o$ (298.15 K) /kJ·mol$^{-1}$ | $\Delta_f G^o$ (298.15 K) /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| $Rb[UO_2VO_4](cr)$ | **181.900 ± 0.900** | **224.000 ± 0.900** | **– (547.106 ± 1.015)** | – (2460 ± 14)<br>**– (2430.8 ± 1.9)**[(a)] | – (2296.9 ± 14)<br>**– (2267.680 ± 1.924)**<br>Recalc. |
| $Cs[UO_2VO_4](cr)$ | **179.800 ± 0.9** | **226.700 ± 1.000** | **– (552.856 ± 1.136)** | – (2480 ± 14)<br>**– (2436.4 ± 2.8)**[(a)] | – (2315 ± 14)<br>**– (2271.566 ± 2.820)**<br>Recalc. |

(a) Recalculated values from [1992KAR/CHE].

**[1996KAR/CHE3]**

Carnotite $K[UO_2VO_4]\cdot nH_2O(cr)$, or $K_2[UO_2VO_4]_2\cdot nH_2O(cr)$ is one of the most abundant minerals in vanadium-uranium ore deposits and its thermodynamics is therefore important.

Karyakin *et al.* have commented on the previous literature ([1962HOS/GAR], [1978LAN], [1982ZHI/SHM], [1992KAR/CHE]) and report $\Delta_f G_m^o$ ($K[UO_2VO_4]\cdot 1.5H_2O$, 298.15 K) = – 2707 kJ·mol$^{-1}$, [1962HOS/GAR]; $\Delta_f G_m^o$ ($K[UO_2VO_4]\cdot 1.5H_2O$, 298.15 K) = – 2651 kJ·mol$^{-1}$, $\Delta_f G_m^o$ ($K[UO_2VO_4]$, 298.15 K) = – 2295 kJ·mol$^{-1}$ [1978LAN]; Zhil'tsova *et al.* find $\Delta_f G_m^o$ (298.15 K) = – 2657 kJ·mol$^{-1}$ for $K[UO_2VO_4]_2\cdot 1.5H_2O(cr)$, all these studies are based on solubility measurements; by adding the Gibbs energy of formation for 1.5 water to the Gibbs energy of formation of $K[UO_2VO_4](cr)$ obtained from calorimetry, we find $\Delta_f G_m^o$ (298.15 K) = (2645.972 ± 2.59) kJ·mol$^{-1}$ for $K_2[UO_2VO_4]_2\cdot 3H_2O(cr)$, which demonstrates the consistence of the different experimental observations

[1996KAR/CHE3] used enthalpies of formation from their previous study, [1992KAR/CHE], $\Delta_f H_m^o$ ($K[UO_2VO_4]$, cr, 298.15 K) = – (2451 ± 9), and new

experimental determinations of the molar entropy and entropy of formation from the anhydrous $K[UO_2VO_4](cr)$, based on isobaric heat capacity measurements between 5 and 320 K. They report $C_p^o(298.15\ K) = (177.0 \pm 1.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, $S_m^o(298.15\ K) = (216.400 \pm 0.900)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, $\Delta_f S_m^o(298.15\ K) = -(542.5 \pm 0.9)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, values that are selected, although $\Delta_f S_m^o(298.15\ K) = -(542.606 \pm 0.990)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ has been recalculated in this review. The corresponding Gibbs energy of formation is $\Delta_f G^o(K[UO_2VO_4], cr, 298.15\ K) = -(2289 \pm 9)\ kJ{\cdot}mol^{-1}$. Using our selected enthalpy of formation, we find $\Delta_f G^o(K[UO_2VO_4], cr, 298.15\ K) = -(2284.922 \pm 6.007)\ kJ{\cdot}mol^{-1}$.

Chernorukov *et al.* have also determined the solubility product for Reaction (A.298) at pH 2.15:

$$K[UO_2VO_4](cr) + 2.5H^+ \rightleftharpoons K^+ + UO_2^{2+} + 0.5H_3V_2O_7^- + 0.5H_2O(l) \qquad (A.298)$$

Their discussion is not correct because vanadium is mainly present as $VO_2^+$ at this pH and not as $H_3V_2O_7^-$. In addition they have included the concentration of water, instead of its activity when calculating the solubility constant for the reaction. The experimental solubility at this pH is $1 \times 10^{-3}$ M and the agreement with the calculated solubility in [1996KAR/CHE3], $3 \times 10^{-3}$ M, is coincidental. The present review has reanalysed the solubility data in [2001CHE/SUL] using only the data at the lowest pH where the hydrolysis of $UO_2^{2+}$ and $VO_2^+$ is negligible and finds $\Delta_f G_m^o(K[UO_2VO_4], 298.15\ K) = -(2308.982 \pm 3.260)\ kJ{\cdot}mol^{-1}$. This value is significantly different from the value obtained by calorimetry, $-(2284.922 \pm 6.007)\ kJ{\cdot}mol^{-1}$, possibly indicating that the anhydrous phase became partially hydrated in the course of the solubility experiments.

**[1998CHE/SUL]**

The uranovanadate compounds investigated in this contribution were prepared by refluxing a solution of $V_2U_2O_7$ and the corresponding metal nitrates at pH = 3. The solids were analysed using energy dispersive X-ray fluorescence, EDAX and the water content by calcination at 450 °C. The stoichiometries reported are $Ni[UO_2VO_4]_2{\cdot}4H_2O(cr)$, $Zn[UO_2VO_4]_2{\cdot}(4\text{-}5)H_2O(cr)$ and $Cd[UO_2VO_4]_2{\cdot}(8\text{-}4)H_2O(cr)$. The authors note that samples with different water content display very near the same X-ray powder pattern, indicating similar structures and weak coordination of water. This is confirmed by the structures that are composed of infinite layers of $[UO_2VO_4]_{2\infty}$ consisting of linked pentagonal $U_7$ bipyramids and $V_2O_8$ dimers. The hydrated M(II) ions are located between the layers; in addition the structures contain large cavities that can accommodate additional crystal water. As a result the water content can be highly variable, with some water strongly bonded to M(II) and the rest weakly bonded similar to water in zeolites. A figure of the isostructural $Ca[UO_2VO_4]_2{\cdot}4H_2O(cr)$ is shown in the

Appendix A entry of [2010BUR/REY]. Thermodynamic data based on these samples must be looked upon with suspicion.

**[1998KAR/CHE5]**

$Na[UO_2VO_4](cr)$ and $Na[UO_2VO_4]\cdot 2H_2O(cr)$ are analogues to the mineral strelkinite and the thermodynamic data in this paper are relevant for the properties of this mineral. Karyakin *et al.* have characterised the phases by XRD and found them to be compatible with the mineral (a detailed discussion of these structures is given in [2012SUL/SOM]). Karyakin *et al.* have determined the molar heat capacity and entropy by low temperature calorimetry between 80 and 320 K, data that were extrapolated to 0 K. The reported entropies are in excellent agreement with the Latimer estimate of the entropy contribution for water, 45 $J\cdot K^{-1}\cdot mol^{-1}$(Appendix D), suggesting that the water content of the two phases is correct. The authors have used reaction calorimetry based on the following thermodynamic cycle to calculate the enthalpy of formation of the two phases.

$$NaVO_3(cr) + UO_3(cr) + (847HF + 2354H_2O) \rightleftharpoons \text{solution 1} \qquad \text{(A.299)}$$

$\Delta_r H$(A.299)

$$Na[UO_2VO_4](cr) + (847HF + 2354H_2O) \rightleftharpoons \text{solution 2} \qquad \text{(A.300)}$$

$\Delta_r H$(A.300)

$$NaVO_3(cr) + UO_3(cr) \rightleftharpoons Na[UO_2VO_4](cr) \qquad \text{(A.301)}$$

$\Delta_r H$(A.301) = $\Delta_r H$(A.299) – $\Delta_r H$(A.300) = $\Delta_f H^o(NaVUO_6, cr)$ – $\Delta_f H^o(NaVO_3, cr)$ – $\Delta_f H^o(UO_3, cr)$;

$\Delta_f H^o_m(NaVO_3, cr) = -(1148.1 \pm 5.0)$ $kJ\cdot mol^{-1}$ was taken from the compilation of Glushko, issue X, Part 1, Moscow, 1981. This value has been replaced by the selected value in the present review $\Delta_f H^o_m(NaVO_3, cr) = -(1149.1 \pm 1.5)$ $kJ\cdot mol^{-1}$; $\Delta_f H^o_m(UO_3, cr)$ is the value selected by NEA TDB.

From this thermodynamic cycle, Karyakin *et al.* report $\Delta_f H^o_m(Na[UO_2VO_4], cr) = -(2429.6 \pm 6.0)$ $kJ\cdot mol^{-1}$, recalculated by this review to, $\Delta_f H^o_m(Na[UO_2VO_4], cr) = -(2430.3 \pm 4.2)$ $kJ\cdot mol^{-1}$; these values are significantly different from the values, $\Delta_f H^o_m(Na[UO_2VO_4], cr) = -(2407 \pm 8)$ $kJ\cdot mol^{-1}$ and $-(2413.0 \pm 6)$ $kJ\cdot mol^{-1}$, based on two other thermodynamic cycles in the work of [1992KAR/CHE]. The enthalpy of reaction, $\Delta_r H$(A.301), reported in [1992KAR/CHE], is $-(31.2 \pm 2.6)$ $kJ\cdot mol^{-1}$, as compared to $-(57.4 \pm 2.6)$ $kJ\cdot mol^{-1}$ in [1998KAR/CHE5] and this discrepancy is suggested to be a result of the hygroscopic properties of $Na[UO_2VO_4](cr)$. However, both the IR spectra and the low-temperature data indicate that the $Na[UO_2VO_4](cr)$ used in [1998KAR/CHE5] is anhydrous. Since the same batch

was used in the calorimetric study, this suggests that their revised value is the more accurate one.

Thermodynamic data for $Na[UO_2VO_4]\cdot 2H_2O$(cr) were obtained from the enthalpy of formation obtained using calorimetry and the entropy data. The following cycle was used:

$$Na[UO_2VO_4]\cdot 2H_2O(cr) + (847HF + 2354H_2O) \rightleftharpoons \text{solution 4} \quad \text{(A.302)}$$

$\Delta_r H$(A.302)

$$2H_2O + (847HF + 2352H_2O) \rightleftharpoons (847HF + 2354H_2O) \quad \text{(A.303)}$$

$\Delta_r H$(A.303)

$$NaVO_3(cr) + UO_3(cr, \gamma) \rightleftharpoons Na[UO_2VO_4](cr) \quad \text{(A.304)}$$

$\Delta_r H$(A.304)

$$NaVO_3(cr) + UO_3(cr) + 2H_2O \rightleftharpoons Na[UO_2VO_4]\cdot 2H_2O(cr) \quad \text{(A.305)}$$

$\Delta_r H$(A.305)

From the experimental values and the enthalpies of formation of $NaVO_3$(cr), $UO_3$(cr) and $H_2O$, Karyakin *et al.* obtain, $\Delta_f H^o_m$ ($Na[UO_2VO_4]\cdot 2H_2O$, cr) = – (3030 ± 6) kJ·mol$^{-1}$ and $\Delta_f G^o_m$ ($Na[UO_2VO_4]\cdot 2H_2O$, cr) = – (2758 ± 7) kJ·mol$^{-1}$; they have, however, used the enthalpy of formation of pure water and not in the aqueous HF solvent which is – 286.5 kJ·mol$^{-1}$ based on $L_1$ = – 0.71 kJ·mol$^{-1}$, calculated from the 1965 Parker tables [1965PAR]. The corrected enthalpy of formation, $\Delta_f H^o_m$ ($Na[UO_2VO_4]\cdot 2H_2O$, cr) = – (3032.9 ± 5.1) kJ·mol$^{-1}$ has been accepted by the present review.

The molar entropy and isobaric heat capacity of $Na[UO_2VO_4]$(cr) and $Na[UO_2VO_4]\cdot 2H_2O$(cr) have been determined by calorimetric heat capacity measurements in the temperature range 5-310 K, resulting in $C^o_p$ ($Na[UO_2VO_4]$, cr, 298.15 K) = (180.2 ± 1.5) J·K$^{-1}$·mol$^{-1}$, $S^o_m$ ($Na[UO_2VO_4]$, cr, 298.15 K) = (209.1 ± 3.0) J·K$^{-1}$·mol$^{-1}$, and $\Delta_f S^o$($Na[UO_2VO_4]$, cr) = – (536.526 ± 3.028) J·K$^{-1}$·mol$^{-1}$. The uncertainty in the isobaric heat capacity has been estimated by the present review. When calculating the entropy of formation, Karyakin *et al.* used $S^o$(V, s) = (28.90 ± 0.30) J·K$^{-1}$·mol$^{-1}$ from Glushko, issue VIII, part 1, 1978, a value that is based on the Bureau of Mines report [1961MAH/KEL], the present review has selected a slightly different value, $S^o$(V, s) = (28.91 ± 0.33) J·K$^{-1}$·mol$^{-1}$; the other entropies for the elements are the same as used by the NEA TDB. The selected Gibbs energy of formation, $\Delta_f G^o_m$ ($Na[UO_2VO_4]$, cr) = – (2270.335 ± 4.296) kJ·mol$^{-1}$ has been calculated from the Gibbs-Helmholtz equation.

For the $Na[UO_2VO_4]\cdot 2H_2O$(cr) compound, the present review has selected the isobaric heat capacity, $C^o_p$ ($Na[UO_2VO_4]\cdot 2H_2O$, cr, 298.15 K) = (267.7 ± 1.5) J·K$^{-1}$·mol$^{-1}$,

the molar entropy, $S_m^o$ (Na[$UO_2VO_4$]·2$H_2O$, cr, 298.15 K) = (298.4 ± 3.0) J·K$^{-1}$·mol$^{-1}$ and $\Delta_f S_m^o$ (Na[$UO_2VO_4$]·2$H_2O$, cr) = – (913.738 ± 3.028) J·K$^{-1}$·mol$^{-1}$. These data has been used to calculate the selected Gibbs energy of formation, $\Delta_f G_m^o$ (Na[$UO_2VO_4$]·2$H_2O$, cr) = – (2760.469 ± 5.179) kJ·mol$^{-1}$ from the Gibbs-Helmholtz equation. The difference in entropy between the dihydrate and the anhydrous compound is 89.3 J·K$^{-1}$·mol$^{-1}$, which corresponds to 44.7 J·K$^{-1}$·mol$^{-1}$, identical with the Latimer estimate 45 J·K$^{-1}$·mol$^{-1}$.

The difference in Gibbs energy of formation between Na[$UO_2VO_4$]·2$H_2O$(cr) and $NaUO_2VO_4$(cr) is (490 ± 8) kJ·mol$^{-1}$, that is 245 kJ·mol$^{-1}$ for each water, suggesting a rather weak bonding.

Karyakin *et al.* have calculated the solubility constants for Reaction (A.306) using the known Gibbs energies of formation and $\Delta_f G^o(H_2VO_4^-)$ = – 1021 kJ·mol$^{-1}$ from the Glushko tables.

$$Na[UO_2VO_4]\cdot 2H_2O(cr) + 2H^+ \rightleftharpoons Na^+ + UO_2^{2+} + H_2VO_4^- + 2H_2O(l) \qquad (A.306)$$

They report a solubility of $7.2 \times 10^{-9}$ M at pH = 7, calculated from the equilibrium constant (A.306) for congruent dissolution.

$$^*K_s^o\,(A.306) = [Na^+][\,UO_2^{2+}\,][\,H_2VO_4^-\,][H_2O]^2/[H^+]^2 = s^3[55.4]^2/[H^+]^2;$$

This equation is not correct because in the standard state the activity of water is unity and not 55.4. As a result of this they find a much lower solubility than they report for dissolution of $NaUO_2VO_4$(cr), $s = 2 \times 10^{-6}$ M also at pH = 7. This review has calculated the solubility constant of Na[$UO_2VO_4$](cr), Reaction (A.307) and finds, $\log_{10} {}^*K_s^o$ = – 5.85, from which we find a solubility, $s = 2.5 \times 10^{-7}$ M.

$$Na[UO_2VO_4](cr) + 2H^+ \rightleftharpoons Na^+ + UO_2^{2+} + H_2VO_4^- \qquad (A.307)$$

However, the experimental data reported by Karyakin *et al.* demonstrate that the dissolution is not congruent and the solubility data can therefore not be used to calculate the solubility constant and the Gibbs energy of reaction and formation.

**[1999CHE/SUL]**

M[$UO_2VO_4$]$_2$·4$H_2O$(cr), M = Fe, Mn, Co and, Cu[$UO_2VO_4$]$_2$·9$H_2O$(cr) were prepared hydrothermally by reaction of $V_2U_2O_{11}$(cr) with a saturated solution of M($NO_3$)$_2$. The solids were characterised by elemental analyses that confirmed the reported stoichiometry, but no details were given. M[$UO_2VO_4$]$_2$·2$H_2O$(cr), M = Fe, Mn, Co, Cu were identified and characterised by X-ray powder diffraction. In addition M[$UO_2VO_4$]$_2$·$H_2O$(cr), M = Mn, Co and Mn[$UO_2VO_4$]$_2$(cr) were observed. The compounds are orthorhombic and composed of layers of $(UO_2VO_4)_\infty$ with crystal water and $M^{2+}$-ions located in between. DTA analyses reveal that the thermal decomposition proceeds in several stages to produce lower crystal hydrates and anhydrous compounds.

**[1999KAR/CHE2]**

Karyakin *et al.*, have used dissolution calorimetry in approximately 5.5 M HCl (850 HCl + 8490 $H_2O$), as described in their previous publication [1999KAR/CHE]. The synthesis, purification and phase identification has been described in more detail in [1998KAR/CHE5]. More experimental details are given in the review of [2003KAR/CHE4]. The experimental method is satisfactory and the thermodynamic cycles are described in detail in their paper. The enthalpies of formation used in the thermodynamic cyces are taken from the Glushko tables, where the data for $Mg_2V_2O_7$(cr), $Mg_3(VO_4)_2$(cr), $Ca(VO_3)_2$(cr) and $Ba_2V_2O_7$(cr) are reported. Only the enthalpies of formation for $Mg_2V_2O_7$(cr) and $Ca(VO_3)_2$(cr) have been scrutinised by the present review. Enthalpies of formation of $Mg_3(VO_4)_2$(cr) and $Ba_2V_2O_7$(cr) from [1988FOT/SLO] are used for scoping calculations as they are the only ones available, *cf.* Table 14-3. The enthalpy of formation of the Mg- and Ba-compounds depend on the enthalpies of formation of $Mg_3(VO_4)_2$(cr) and $Ba_2V_2O_7$(cr), respectively, and as these values are not accepted by this review, the enthalpies of formation of the Mg- and Ba-uranyl vanadates are given for information only. The enthalpies of formation of the hydrates have been calculated using the enthalpy of formation of pure water and not of water in the aqueous HCl solution and have to be corrected by using the relative partial molar enthalpy of water in the HCl solution, $L_1 = -0.53$ kJ·mol$^{-1}$, calculated from the data in the 1965 Parker tables. The enthalpies of formation for the $A^{II}[UO_2VO_4]_2$(cr) compounds and their crystal hydrates are listed in Table A-133 together with enthalpies of formation from a following study by the same group discussed in [2003KAR/CHE4]. The authors do not explain the difference in enthalpy of formation of $Ca[UO_2VO_4]_2$(cr) in the two studies. Slight differences appear also for other compounds, and this review has preferred the values recalculated from data in [2003KAR/CHE4]. These hydrates are layer-structures, *cf.* [2010BUR/REY], where different amounts of water can be located between the layers and as a result, one may expect a variable water content. The water is also weakly bonded as shown by the difference in enthalpy of formation between $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr) and $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr), which is 293 kJ·mol$^{-1}$ per water, close to the molar enthalpy of formation of liquid water, 285.3 kJ·mol$^{-1}$. The difference in enthalpy per water for the Sr-compounds is 303 kJ·mol$^{-1}$ and for the Ba-compounds 296 kJ·mol$^{-1}$. We note, however, that there is a significant difference between the calorimetric enthalpies of formation and those obtained from Gibbs energies and entropies of formation obtained from solubility data and experimental molar entropies.

Table A-133: Enthalpies of formation for $A^{II}[VUO_6]_2$(cr) compounds and their crystal hydrates as reported in [1999KAR/CHE2] and corrected in this review for the enthalpy of formation of water in the HCl solution used.

| Compound | $\Delta_f H^\circ$ /kJ·mol$^{-1}$ | Compound | $\Delta_f H^\circ$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2VO_4]_2$(cr) | – (4667.5 ± 9.0) | $Mg[UO_2VO_4]_2{\cdot}5H_2O$(cr) | – (6243.5 ± 9.0) |
| | – (4678.8 ± 10.3)[(a)] | | – (6257.2 ± 10.4)[(a)] |
| $Ca[UO_2VO_4]_2$(cr) | – (4822.0 ± 11.5) | $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr) | – (7193.0 ± 11.0) |
| | – (4828.7 ± 7.0)[(a)] | | – (7203.7± 6.9)[(a)] |
| | | $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr) | – (6318.0 ± 11.0) |
| | | | – (6327.3 ± 7.5)[(a)] |
| $Sr[UO_2VO_4]_2$(cr) | – (4852.0 ± 16.0) | $Sr[UO_2VO_4]_2{\cdot}5H_2O$(cr) | – (6363.0 ± 16.0) |
| | – (4858.2 ± 17.7)[(a)] | | – (6372.0 ± 16.6)[(a)] |
| $Ba[UO_2VO_4]_2$(cr) | – (4906.5 ± 20.0) | $Ba[UO_2VO_4]_2{\cdot}4H_2O$(cr) | – (6092.0 ± 20.0) |
| | – (4914.6 ± 10.4)[(a)] | | – (6102.7 ± 10.4)[(a)] |

(a) Recalculated by this review

**[1999KAR/CHE3]**

Karyakin *et al.* have determined the isobaric heat capacity of $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr), $Ba[UO_2VO_4]_2{\cdot}4H_2O$(cr) between 10-300 K and for $Mg[UO_2VO_4]_2{\cdot}5H_2O$(cr), $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr), $Sr[UO_2VO_4]_2{\cdot}5H_2O$(cr), $Pb[UO_2VO_4]_2{\cdot}5H_2O$(cr) and $Ba[UO_2VO_4]_2$(cr) in the temperature range 80-300 K. The Ca, Ba and Pb compounds are synthetic analogs of the minerals tyuyaminite, francevillite and curite, respectively. All heat capacity functions are normal with no indications of phase transitions or magnetic/electronic contributions, the exception is $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr), which has a S-shape in the range 160-230 K that the authors explain as result of hindered rotations of weakly bound water. They report $H^\circ(T) - H^\circ(0)$, $S^\circ(T)$ and $G^\circ(T) - H^\circ(T)$ in the temperature range 0-300 K and the standard entropy and Gibbs energy of formation for the compounds at 298.15 K. Using the calorimetric enthalpies of formation from [1999KAR/CHE2] they determined the standard Gibbs energy of formation of the compound. The enthalpy of formation, $\Delta_f H^\circ(Ca[UO_2VO_4]_2{\cdot}5H_2O, cr) = -(6318.0 \pm 11.0)$ kJ·mol$^{-1}$ recalculated by this review to $-(6327.3 \pm 7.1)$ was determined in a new experiment using the same experimental method as in [1999KAR/CHE2]. The thermodynamic data are listed in Table A-134. We note that the calculated Gibbs energies of formation are very different from the ones obtained by solubility measurement in [2001CHE/SUL2].

The difference in entropy between $Ba[UO_2VO_4]_2{\cdot}4H_2O$(cr) and $Ba[UO_2VO_4]_2$(cr) is 199.6 J·K·mol$^{-1}$, or 49.9 J·K·mol$^{-1}$ per water, very close to the Latimer estimate, 44.7 J·K·mol$^{-1}$, which is a good indication of consistency in the calorimetric data and for this reason we have included the thermodynamic data for $Ba[UO_2VO_4]_2{\cdot}4H_2O$(cr) among the selected values.

Table A-134: Heat capacities and entropies of the uranovanadates $M^{II}[UO_2VO_4]_2{\cdot}nH_2O$(cr), ($M^{II}$ = Mg, Ca, Sr, Ba) from [1999KAR/CHE3] and [2003KAR/CHE4].

| Compound | $C^{o}_{p,m}$ (298.15K) /J·K$^{-1}$·mol$^{-1}$[a] | $S^{o}$ (298.15K) /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f S^{o}$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2VO_4]_2{\cdot}5H_2O$(cr) | **627.5 ± 3.0** | **631.6 ± 4.0** | **– (1956.002 ± 4.066)** |
| $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr) | **777.5 ± 3.0** | **786.6 ± 2.0** | **– (2509.690 ± 2.164)** |
| $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr) | **589.6 ± 3.0** | **639.4 ± 4.0** | **– (1957.122 ± 4.084)** |
| $Sr[UO_2VO_4]_2{\cdot}5H_2O$(cr) | **650.0 ± 3.0** | **684.8 ± 4.0** | **– (1925.832 ± 4.070)** |
| $Ba[UO_2VO_4]_2{\cdot}4H_2O$(cr) | **564.9 ± 3.0** | **631.8 ± 2.0** | **– (1752.296 ± 2.286)** |
| $Ba[UO_2VO_4]_2$(cr) | **365.0 ± 3.0** | **432.1 ± 4.0** | **– (1018.972 ± 4.150)** |
| $Pb[UO_2VO_4]_2{\cdot}5H_2O$(cr) | 637.8 ± 3 | 655.8 ± 4.0 | – (1963.0 ± 4.0) |

(a) The uncertainty is estimated by this review based on the values reported by Karyakin *et al.* 1.5 % below 10 K, 0.5 % below 40 K and 0.2-0.3 % above 40 K.

The molar entropies in Table A-134 are used to calculate the corresponding entropies of reaction and the Gibbs energies of formation. The present review has noted a significant difference between these values and the ones obtained by dissolution calorimetry and we have interpreted this as a result of non-stoichiometric water content. The heat capacity between 80 and 0 K was calculated using the Kelley-Parks procedure as:

$$C_p(T) = (0.798 + 0.358 \times 10^{-3}T) \times C^{o}_p(298.15\ \text{K})\ \text{for}\ Mg[UO_2VO_4]_2{\cdot}5H_2O\text{(cr)};$$

$$C_p(T) = (0.985 + 1.484 \times 10^{-3}T) \times C^{o}_p(298.15\ \text{K})\ \text{for}\ Ca[UO_2VO_4]_2{\cdot}5H_2O\text{(cr)};$$

$$C_p(T) = (0.889 + 0.252 \times 10^{-3}T) \times C^{o}_p(298.15\ \text{K})\ \text{for}\ Sr[UO_2VO_4]_2{\cdot}5H_2O\text{(cr)};$$

$$C_p(T) = (1.916 + 1.150 \times 10^{-3}T) \times C^{o}_p(298.15\ \text{K})\ \text{for}\ Ba[UO_2VO_4]_2{\cdot}4H_2O\text{(cr)};$$

$$C_p(T) = (0.860 + 0.168 \times 10^{-3}T) \times C^{o}_p(298.15\ \text{K})\ \text{for}\ Pb[UO_2VO_4]_2{\cdot}5H_2O\text{(cr)};$$

**[2000KAR/CHE2]**

The range of existence of the crystal hydrates of $Na[UO_2VO_4]$(cr) and the enthalpy and entropy of dehydration is reported, based on isopiestic and static vapor pressure data of the Reactions (A.308) and (A.309). The enthalpy of reaction was calculated from the temperature dependence of the equilibrium constant, $K = p(H_2O)$.

$$Na[UO_2VO_4]{\cdot}2H_2O\text{(cr)} \rightleftharpoons Na[UO_2VO_4]{\cdot}H_2O\text{(cr)} + H_2O\text{(g)} \quad \text{(A.308)}$$

$\Delta_r H$(A.308) = (53.2 ± 0.4) kJ·mol$^{-1}$.

$$Na[UO_2VO_4]\cdot H_2O(cr) \rightleftharpoons Na[UO_2VO_4](cr) + H_2O(g) \quad (A.309)$$

$\Delta_r H$(A.309) = (58.1 ± 0.8) kJ·mol$^{-1}$.

The corresponding entropies of reaction are, $\Delta_r S$(A.308) = (127.0 ± 0.1) J·K$^{-1}$·mol$^{-1}$ and $\Delta_r S$(A.309) = (128.0 ± 2.0) J·K$^{-1}$·mol$^{-1}$. The enthalpy of reaction for:

$$Na[UO_2VO_4]\cdot 2H_2O(cr) \rightleftharpoons Na[UO_2VO_4](cr) + 2H_2O(g) \quad (A.310)$$

$\Delta_r H$(A.310) = (111.3 ± 1.2) kJ·mol$^{-1}$.

The latter is in reasonable agreement with $\Delta_r H$(A.310) ≈ (118.9 ± 6.6) kJ·mol$^{-1}$, obtained from the enthalpies of formation $\Delta_f H^o$(Na[$UO_2VO_4$]·2$H_2O$, cr) = – (3032.9 ± 5.1) kJ·mol$^{-1}$ and $\Delta_f H^o$(Na[$UO_2VO_4$], cr) = – (2430.3 ± 4.2) kJ·mol$^{-1}$ from [1998KAR/CHE5], revised and selected by this review.

The enthalpy of formation $\Delta_f H^o$(Na[$UO_2VO_4$·$H_2O$], cr), was determined as follows:

$\Delta_f H^o$(Na[$UO_2VO_4$·$H_2O$], cr) = 0.5{$\Delta_r H$(A.308) – $\Delta_r H$(A.309) +$\Delta_f H^o$(Na[$UO_2VO_4$·2$H_2O$, cr) + $\Delta_f H^o$(Na[$UO_2VO_4$], cr). The present review has included our recalculated $\Delta_f H^o$(Na[$UO_2VO_4$·$H_2O$], cr) = **– (2734.100 ± 3.300)** kJ·mol$^{-1}$ among the selected values.

The values of $\Delta_f S^o$(Na[$UO_2VO_4$]·$H_2O$, cr) = – (724.882 ± 5.017) J·K$^{-1}$·mol$^{-1}$ and $S^o$(Na[$UO_2VO_4$]·$H_2O$, cr) = (254.000 ± 5.000) J·K$^{-1}$·mol$^{-1}$ were calculated from the corresponding values for Na[$UO_2VO_4$](cr) by adding the entropy contribution from water estimated using the Latimer method. Using these entropy data, the obtained Gibbs energies of formation is $\Delta_f G^o$(Na$UO_2VO_4$·$H_2O$, cr) = – (2517.976 ± 3.623) kJ·mol$^{-1}$. These values are given for information only.

**[2000KAR/CHE3]**

The enthalpy of formation of uranyl pyrovanadate, $(UO_2)_2V_2O_7$(cr) and uranovanadic acid, H[$UO_2VO_4$]·2$H_2O$(cr) have been determined using dissolution calorimetry based on the following set of reactions:

$$V_2O_5(cr) + 2UO_3(cr) + (847HF + 2354H_2O) \rightleftharpoons \text{solution 1} \quad (A.311)$$

$\Delta_r H$(A.311);

$$(UO_2)_2V_2O_7(cr) + (847HF + 2354H_2O) \rightleftharpoons \text{solution 2} \quad (A.312)$$

$\Delta_r H$(A.312);

$$2H[UO_2VO_4]\cdot 2H_2O(cr) + (847HF + 2350H_2O) \rightleftharpoons \text{solution 3} \quad (A.313)$$

$\Delta_r H$(A.313);

$$V_2O_5(cr) + 2UO_3(cr) + (847HF + 2356H_2O) \rightleftharpoons \text{solution 4} \quad (A.314)$$

$\Delta_r H$(A.314)

Subtraction of Reaction (A.312) from Reaction (A.311) gives:

$V_2O_5(cr) + 2UO_3(cr) \rightleftharpoons (UO_2)_2V_2O_7(cr)$ ; $\Delta_r H$(A.313) = $\Delta_r H$(A.311) – $\Delta_r H$(A.312);

The experiment is arranged so that the concentrations of solution 1 and solution 2 are identical.

Using the data for the enthalpy of formation of $V_2O_5$(cr) and $UO_3$(cr), $\Delta_f H^o_m(V_2O_5, cr) = -(1551.0 \pm 5.5)$ kJ·mol$^{-1}$ and $\Delta_f H^o_m(UO_3, cr) = -(1223.8 \pm 1.2)$ kJ·mol$^{-1}$ from Glushko, Thermal Constants of Substances, issue 10, Part 1, 1981, the authors obtain $\Delta_f H^o_m((UO_2)_2V_2O_7, cr) = -(3935.5 \pm 12.0)$ kJ·mol$^{-1}$. The present review finds $\Delta_f H^o_m((UO_2)_2V_2O_7, cr) =$ **– (3939.200 ± 6.100)** kJ·mol$^{-1}$ based on the recommended auxiliary data, and this value has been included among the selected values.

The enthalpy of formation of $H[UO_2VO_4]\cdot 2H_2O$(cr) has been obtained from the enthalpy of Reaction (A.315):

$$V_2O_5(cr) + 2UO_3(cr) + 5H_2O(l) \rightleftharpoons 2H[UO_2VO_4]\cdot 2H_2O(cr) \quad \text{(A.315)}$$

$\Delta_r H$(A.315) = $\Delta_r H$(A.314) – $\Delta_r H$(A.313);

The authors report $\Delta_f H^o_m(H[UO_2VO_4]\cdot 2H_2O, cr) = -(2754.0 \pm 5.5)$ kJ·mol$^{-1}$, which has been recalculated to $\Delta_f H^o_m(H[UO_2VO_4]\cdot 2H_2O, cr) =$ **– (2757.6 ± 3.2)** kJ·mol$^{-1}$ using our selected value for the enthalpy of formation of $V_2O_5$(cr), and correcting for the enthalpy of formation of water in the HF solvent used, as calculated from the value of $L_1(H_2O, HF\ soln.) = -0.71$ kJ·mol$^{-1}$ from [1965PAR].

The molar heat capacity and entropy have been obtained using low temperature calorimetry data in the range 5-300 K, where the heat capacities below 5 K were estimated by the function $C_p(T) = 1.438 \times 10^{-3} T^3$. The following heat capacity and entropy values were reported and have been selected by this review:

$C^o_p((UO_2)_2V_2O_7, cr, 298.15\ K) =$ **(296.7 ± 2.1)** J·K$^{-1}$·mol$^{-1}$,
$S^o((UO_2)_2V_2O_7, cr, 298.15\ K) =$ **(356.0 ± 2.1)** J·K$^{-1}$·mol$^{-1}$,
$C^o_p(H[UO_2VO_4]\cdot 2H_2O, cr, 298.15\ K) =$ **(324.9 ± 1.5)** J·K$^{-1}$·mol$^{-1}$,
$S^o(H[UO_2VO_4]\cdot 2H_2O, cr, 298.15\ K) =$ **(295.4 ± 2.1)** J·K$^{-1}$·mol$^{-1}$.

The reported entropies of formation, $\Delta_f S^o((UO_2)_2V_2O_7, cr, 298.15\ K) = -(930.0 \pm 2.1)$ J·K$^{-1}$·mol$^{-1}$ and $\Delta_f S^o(H[UO_2VO_4]\cdot 2H_2O, cr, 298.15\ K) = -(930.5 \pm 2.1)$ J·K$^{-1}$·mol$^{-1}$ have been obtained using the entropies of the elements from the Glushko tables. This review finds $\Delta_f S^o((UO_2)_2V_2O_7, cr, 298.15\ K) =$ **– (930.076 ± 2.221)** J·K$^{-1}$·mol$^{-1}$ and $\Delta_f S^o(H[UO_2VO_4]\cdot 2H_2O, cr, 298.15\ K) =$ **– (930.778 ± 2.131)** J·K$^{-1}$·mol$^{-1}$; these values have been accepted by this review. From the enthalpies of formation and entropies given above this review recalculates $\Delta_f G^o((UO_2)_2V_2O_7, cr, 298.15\ K) =$

**– (3661.898 ± 6.136)** kJ·mol$^{-1}$ and $\Delta_f G^o$(H[$UO_2VO_4$]·2$H_2O$, cr, 298.15 K) = **– (2480.089 ± 3.262)** kJ·mol$^{-1}$. These values have also been selected.

The heat capacity data indicate a phase transition in H[$UO_2VO_4$]·2$H_2O$(cr) around 125 K, with $\Delta_{tr}H$ = 210 kJ·mol$^{-1}$ and $\Delta_{tr}S$ = 1.6 J·K$^{-1}$·mol$^{-1}$.

**[2001CHE/SUL]**

The solubility of uranovanadates of the series $A^I[UO_2VO_4]\cdot nH_2O$(cr) (with $A^I$ = H, Na, K, Rb, Cs, Tl) was investigated by Chernorukov *et al.* [2001CHE/SUL]. These data are discussed in more detail in [2003CHE/SUL4]. The authors report the solubility of the solids at different pH, after an equilibration time of 7-10 days with constant stirring. They report analyses of the concentrations of U and V that are used to decide if the dissolution is congruent, or not. The data in Table 1 of the publication suggests that congruent dissolution takes place at pH < 3.95 for the anhydrous K, Rb and Cs compounds. The dissolution of Na[$UO_2VO_4$]·2$H_2O$(cr) is not congruent and H[$UO_2VO_4$]·2$H_2O$(cr) only dissolves congruently at pH = 1.4. The only solubility data accepted by this review are the ones where congruent dissolution takes place and for these only experimental data at two different pH values can be used. Chernorukov *et al.* report more data but for these only the uranium concentration was analysed and there is then no proof of congruent dissolution, these data have been rejected. The solubility is about $10^{-4}$ M in the measured pH range.

The solubility reaction taking place is:

$$M[UO_2VO_4]\cdot nH_2O(cr) + 4H^+ \rightleftharpoons M^+ + UO_2^{2+} + VO_2^+ + (2+n)H_2O(l) \qquad (A.316)$$

In the pH range studied one can neglect the hydrolysis of uranium and vanadium [1976BAE/MES] and chloride complex formation, making the modeling much simpler than suggested in the paper. As the dissolution is congruent the concentrations of the cations are the same. The ionic strength of the test solutions are approximately 0.040 M and the activity coefficients for all solutes have been calculated by the present review using SIT, while the activity of water is 1.00. These data have been re-analysed in [2003CHE/SUL4] and the resulting equilibrium constants are listed there.

Chernorukov have also made calculations of the solubility of the alkali uranylvanadates in aqueous solutions containing chloride, sulfate and carbonate, but these provide no new thermodynamic information.

**[2001CHE/SUL2]**

The data reported in this publication are nearly identical to that reported in [2003CHE/SUL4], although the data are discussed in more detail in the latter

publication. We note however that no analytical data on the water content has been presented in any of these two studies. Chernorukov *et al.* have studied the solubility of uranovanadates $A^{II}[UO_2VO_4)_2]\cdot nH_2O$(cr) ($A^{II}$ = Mg, Ca, Sr, Ba, Co, Ni, Cu, Pb) in water and aqueous solutions using the same methodology as in [2001CHE/SUL]. A scrutiny of the reported solubility data reveals that congruent dissolution takes place only at pH ≈ 1.4; at higher pH the dissolution is not congruent. Chernorukov *et al.* report solubility products for Reaction (A.317) and the corresponding Gibbs energy of reaction and these are listed in Table A-135. The authors have estimated the equilibrium constants and speciation of the reaction products taking a number of species into account. However, hydrolysis and chloride complex formation can be neglected in the pH range studied and it is difficult to understand their rather complicated procedure to estimate the activity coefficients needed to determine the equilibrium constants at zero ionic strength and therefore the accuracy of the reported Gibbs energies of formation is not accepted by this review. We have recalculated the solubility data from [2001CHE/SUL2] so that they refer to Reaction (A.318), because this is the reaction taking place in the test solutions used. We have calculated the concentration solubility constants $\log_{10}{}^{*}K_s^o$ from the reported concentration in the various test solutions. These constants have then been extrapolated to zero ionic strength using SIT. The experimental equilibrium constants refer to an ionic medium with an ionic strength of (0.100 ± 0.005) M. In the SIT calculation we have estimated the value of $\Delta\varepsilon = -(0.14 \pm 0.1)$ kg·mol$^{-1}$ using published or estimated interaction coefficients for chloride media. The small value means that the extrapolation to zero ionic strength can be made using the Debye-Hückel term only, $-6D = -0.656$.

$$M[UO_2VO_4]_2 \cdot nH_2O(cr) \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_4^{3-} + nH_2O(l) \qquad (A.317)$$

$$M[UO_2VO_4]_2 \cdot nH_2O(cr) + 8H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_2^{+} + (n+4)H_2O(l) \qquad (A.318)$$

The experimental solubility, $s = [M^{2+}]$, is the average concentration of dissolved total concentrations of uranium and vanadium. Hence, $\log_{10}{}^{*}K_s$ (A.318) = $5\log_{10}s + 4\log_{10}2 - 8\log_{10}[H^+]$ and $\log_{10}{}^{*}K_s^o$ (A.318) = $\log_{10}{}^{*}K_s$ (A.318) – 6*D*. It is not possible to use the experimental pH values that have large errors in the acid solutions. The proton concentration is instead calculated from the mass balance in Reaction (A.318).

The calculations are shown in Table A-136, using NEA selected values for the reaction products, except for $Co^{2+}$, $\Delta_f G^o(Co^{2+}) = -(53.64 \pm 0.38)$ kJ·mol$^{-1}$, taken from [1972GLU/MED], vol. 6.

Table A-135: Gibbs energies of formation and solubility products for $M[UO_2VO_4]\cdot nH_2O$(cr), (M = Mg, Ca, Sr, Ba, Ci, Ni, Cu, Pb) as reported in [2001CHE/SUL2], which refer to Reaction (A.317). The value $\Delta_f G^o(VO_4^{3-}) = -(889.5 \pm 5.0)$ kJ·mol$^{-1}$ from [1974GLU/MED], is different from the selected value in Chapter 14, $\Delta_f G^o(VO_4^{3-}) = -(892.75 \pm 1.91)$ kJ·mol$^{-1}$. These values are given for information only.

| Compound | $\Delta_f G^o$ (298.15 K) /kJ·mol$^{-1}$ | $\log_{10} K_s^o$ | $\Delta_r G^o$ (298.15 K) /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2VO_4]_2\cdot 5H_2O$(cr) | – 5660 | – 57.46 | 328.0 |
| $Ca[UO_2VO_4]_2\cdot 8H_2O$(cr) | – 6472 | – 58.34 | 333.1 |
| $Sr[UO_2VO_4]_2\cdot 5H_2O$(cr) | – 5777 | – 59.0 | 336.8 |
| $Ba[UO_2VO_4]_2\cdot 5H_2O$(cr) | – 5764 | – 57.89 | 330.5 |
| $Co[UO_2VO_4]_2\cdot 4H_2O$(cr) | –5023 | – 57.52 | 328.4 |
| $Ni[UO_2VO_4]_2\cdot 4H_2O$(cr) | – 5006 | – 56.23 | 321.0 |
| $Cu[UO_2VO_4]_2\cdot 9H_2O$(cr) | – 6090 | – 57.77 | 329.8 |
| $Pb[UO_2VO_4]_2\cdot 5H_2O$(cr) | – 5228 | – 57.27 | 327.0 |

The estimated uncertainty by Chernorukov *et al.* is ± 20 kJ·mol$^{-1}$, which is probably based on the fact that they have used solubility data in regions where the solubility is not congruent.

The Gibbs energy of formation is calculated from Reaction (A.317), as:

$$\Delta_f G^o(M[UO_2VO_4]_2\cdot nH_2O) = -\Delta_r G^o(A.317) + \Delta_f G^o(M^{2+}) + 2\,\Delta_f G^o(VO_4^{3-}) + 2\Delta_f G^o(UO_2^{2+}) + n\Delta_f G^o(H_2O);$$

The solubility product, $\log_{10} K_s^o$ (A.317) = – 58.34 and the Gibbs energy of formation $\Delta_f G^o(Ca[UO_2VO_4]_2\cdot 8H_2O, cr) = -6462$ kJ·mol$^{-1}$, reported by Chernorukov *et al.* are very different from the ones reported by Zhil'tsova *et al.* $\log_{10} K_s^o$ (A.317) = – (51.48 ± 0.09) and $\Delta_f G^o(Ca[UO_2VO_4]_2, cr) = -(4557.2 \pm 0.5)$ kJ·mol$^{-1}$.

The large difference in the Gibbs energies of formation for the Mg, Ca, Sr and Ba compounds in Table A-136 and the ones calculated from calorimetric data in [1999KAR/CHE3], and [2002CHE/KAR2] is probably due to difference in the water content between the samples used and their ideal stoichiometry. Chernorukov *et al.* have not presented analytical data for the water content of their samples and the present review for this reason provides for information only our recalculated solubility constants and the corresponding Gibbs energies of reaction.

Table A-136: Experimental solubility data re-analysed by the present review, where the hydrogen ion concentrations, [$H^+$] are calculated from the stoichiometry of the reaction, because the experimental pH values are inaccurate. The Gibbs energies of formation have been calculated using the reported composition of the solid phases. As no analyses have been made on the solid after equilibrium only the solubility constants, $\log_{10}{}^{*}K_s^o$(A.318) and Gibbs energies of reaction, $\Delta_r G^o$(A.318), for "watersaturated" phases of unknown water content have been reported, but these values are for information only.

| | [$H^+$] mM | $S \times 10^{-3}$ | $\log_{10}$[$H^+$] | $\log_{10}{}^{*}K_s$ | $\log_{10}{}^{*}K_s^o$ | $\Delta_r G^o$ /kJ·mol$^{-1}$ | $\Delta_f G^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $Mg[UO_2VO_4]_2{\cdot}5H_2O$(cr) | 65.8 | (4.28 ± 0.5) | – 1.18 | – (1.21 ± 0.4) | – (1.870 ± 0.400) | (10.674 ± 2.283) | – (5685.971 ± 5.358) |
| $Ca[UO_2VO_4]_2{\cdot}8H_2O$(cr) | 83.4 | (2.08 ± 0.5) | – 1.08 | – (3.57 ± 0.4) | – (4.220 ± 0.400) | (24.088 ± 2.283) | – (6508.236 ± 5.304) |
| $Sr[UO_2VO_4]_2{\cdot}5H_2O$(cr) | 82.0 | (2.25 ± 0.5) | – 1.09 | – (3.32 ± 0.4) | – (3.980 ± 0.400) | (22.718 ± 2.283) | – (5806.504 ± 5.247) |
| $Ba[UO_2VO_4]_2{\cdot}5H_2O$(cr) | 81.6 | (2.30 ± 0.5) | – 1.09 | – (3.28 ± 0.4) | – (3.940 ± 0.400) | (22.490 ± 2.283) | – (5800.068 ± 5.795) |
| $Co[UO_2VO_4]_2{\cdot}4H_2O$(cr) | 72.8 | (3.4 ± 0.5) | – 1.14 | – (2.03 ± 0.4) | – (2.690 ± 0.400) | (15.354 ± 2.283) | – (5051.776 ± 5.200) |
| $Ni[UO_2VO_4]_2{\cdot}4H_2O$(cr) | 69.6 | (3.8 ± 0.5) | – 1.16 | – (1.16 ± 0.4) | – (2.280 ± 0.400) | (13.014 ± 2.283) | – (5041.569 ± 5.243) |
| $Cu[UO_2VO_4]_2{\cdot}9H_2O$(cr) | 74.4 | (3.25 ± 0.5) | – 1.13 | – (2.21 ± 0.4) | – (2.870 ± 0.400) | (16.382 ± 2.283) | – (6119.824 ± 5.431) |
| $Pb[UO_2VO_4]_2{\cdot}5H_2O$(cr) | 77.4 | (2.28 ± 0.55) | – 1.11 | – (3.13 ± 0.4) | – (3.790 ± 0.400) | (21.633 ± 2.283) | – (5265.793 ± 5.204) |

**[2001KAR/CHE]**

This is a review article of data in previous publications from the Chernorukin, Karyakin group at University of Nizhny Novgorod.

**[2002CHE/KAR2]**

The enthalpy of formation of the $A^{II}[UO_2VO_4)_2]\cdot nH_2O(cr)$ compounds were determined using dissolution calorimetry with the following thermodynamic cycle:

$$KUO_2VO_4(cr) + HCl(sln\,1{:}10) \rightleftharpoons solution\,1 \quad (A.319)$$

$\Delta_r H(A.319) = -(25.3 \pm 2.3)$ kJ·mol$^{-1}$

$$(n-k)H_2O(l) + solution\,1 \rightleftharpoons solution\,2 \text{ ; if } n > k \quad (A.320)$$

$\Delta_r H(A.320) \approx 0$ kJ·mol$^{-1}$

$$A^{II}SO_4 \cdot nH_2O(cr) + solution\,2 \rightleftharpoons solution\,3 \quad (A.321)$$

$\Delta_r H(A.321)$ in Table A-137

$$K_2SO_4(cr) + HCl(sln) \rightleftharpoons solution\,4 \quad (A.322)$$

$\Delta_r H(A.322) = (13.52 \pm 0.85)$ kJ·mol$^{-1}$

$$(k-n)H_2O(l) + solution\,4 \rightleftharpoons solution\,5 \text{ ; if } n < k \quad (A.323)$$

$\Delta_r H(A.323) \approx 0$ kJ·mol$^{-1}$

$$A^{II}(UO_2VO_4)_2 \cdot nH_2O(cr) + solution\,5 \rightleftharpoons solution\,6 \quad (A.324)$$

$\Delta_r H(A.324)$

The experimental heats of dissolution are listed in Table A-137.

Table A-137: Standard enthalpies of solution of sulfates and uranovanadates of *d* transition metals in kJ·mol$^{-1}$ at 298.15 K.

| $A^{II}SO_4\cdot nH_2O(cr)$ | $\Delta_r H^\circ$ (A.321) | $A^{II}[UO_2VO_4]_2\cdot nH_2O(cr)$ | $-\Delta_r H^\circ$ (A.324) ($n > 4$) | $-\Delta_r H^\circ$ (A.324) ($n = 4$) | $-\Delta_r H^\circ$ (A.324) ($n = 0$) |
|---|---|---|---|---|---|
| $MnSO_4\cdot H_2O(cr)$ | (9.7 ± 0.9) | $Mn[UO_2VO_4]_2\cdot nH_2O(cr)$ | – | (81.1 ± 3.1) | (197.1 ± 2.9) |
| $FeSO_4\cdot 7H_2O(cr)$ | (38.5 ± 1.4) | $Fe[UO_2VO_4]_2\cdot nH_2O(cr)$ | – | (126.7 ± 2.4) | (230.5 ± 5.1) |
| $CoSO_4\cdot 6H_2O(cr)$ | (53.6 ± 1.3) | $Co[UO_2VO_4]_2\cdot nH_2O(cr)$ | – | (71.7 ± 2.2) | (174.9 ± 2.3) |
| $NiSO_4\cdot 6H_2O(cr)$ | (38.7 ± 0.7) | $Ni[UO_2VO_4]_2\cdot nH_2O(cr)$ | – | (83.8 ± 1.8) | (208.9 ± 1.7) |
| $CuSO_4\cdot 5H_2O(cr)$ | (53.0 ± 0.7) | $Cu[UO_2VO_4]_2\cdot nH_2O(cr)$ | (122.8 ± 1.6) ($n = 9$) | (176.8 ± 5.4) | (279.8 ± 2.4) |
| $ZnSO_4\cdot 7H_2O(cr)$ | (36.7 ± 1.0) | $Zn[UO_2VO_4]_2\cdot nH_2O(cr)$ | (131.8 ± 1.7) ($n = 5$) | (135.1 ± 4.9) | (237.4 ± 6.0) |
| $CdSO_4\cdot 8/3H_2O(cr)$ | – (25.2 ± 0.5) | $Cd[UO_2VO_4]_2\cdot nH_2O(cr)$ | (168.8 ± 0.7) ($n = 8$) | (176.6 ± 3.1) | (256.5 ± 4.7) |

By combining Reactions (A.319)-(A.324) one obtains a reaction whose enthalpy is:

$\Delta_r H(\text{A.325}) = 2\Delta_r H(\text{A.319}) + \Delta_r H(\text{A.321}) - \Delta_r H(\text{A.322}) - \Delta_r H(\text{A.324})$;

$$2K[UO_2VO_4](cr) + A^{II}SO_4 \cdot nH_2O(cr) \rightleftharpoons A^{II}[UO_2VO_4]_2 \cdot nH_2O(cr) + K_2SO_4(s) + (n-k)H_2O \qquad \text{(A.325)}$$

The enthalpies of formation of $A^{II}[UO_2VO_4]_2 \cdot nH_2O$(cr) are based on the enthalpy of formation of $K[UO_2VO_4]$(cr), $\Delta_f H^o(K[UO_2VO_4], cr) = -(2451 \pm 5)$ kJ·mol$^{-1}$ (recalculated by this review to $-(2446.7 \pm 6.0)$ kJ·mol$^{-1}$), the same as in [1992KAR/CHE], presumably using the same data but reporting a lower uncertainty. In addition Chernorukov *et al.* have used enthalpies of formation for the sulfates in Reaction (A.325) from the Glushko tables 1972, issue 6, 1974, issue 7 and 1974, issue 7, part 2.

Chernorukov *et al.* used the enthalpy of reaction, $\Delta_r H$(A.326), to calculate the enthalpy of formation for the anhydrous compounds.

$$M[UO_2VO_4]_2 \cdot nH_2O(cr) \rightleftharpoons M[UO_2VO_4]_2(cr) + nH_2O(l) \qquad \text{(A.326)}$$

The authors have used $\Delta_f H^o(H_2O, l) = -285.83$ kJ·mol$^{-1}$, instead of the value in the approximately 5.5 M hydrochloric acid solution used. The present review has corrected this value to $\Delta_f H^o(H_2O, HCl) = -286.36$ kJ·mol$^{-1}$, based on the relative partial molar entropy $L_1 = -0.53$ kJ·mol$^{-1}$ obtained using the data in [1965PAR]. The experimental enthalpies of formation in Table A-138 have been corrected accordingly. The reported uncertainty in Gibbs enthalpy of formation is very large because it is a result in accumulated errors in the different auxiliary data used (enthalpies of reaction, enthalpy of formation of $KUO_2VO_4$(cr)).

In order to calculate the enthalpy of reaction, $\Delta_f H^o(A^{II}(UO_2VO_4)_2 \cdot nH_2O, cr)$ the auxiliary data from Chapter 14 have been used.

The entropy and isobaric heat capacity of $Co[UO_2VO_4]_2 \cdot 4H_2O$(cr) were determined using low-temperature calorimetry between 80 and 300 K and extrapolated to 0 K using the function: $C_p(T) = (1.106 + 0.770 \times 10^{-3}T)\, C_p^o$, resulting in $C_p^o(298.15\text{ K}) = (655.2 \pm 7.0)$ J·K$^{-1}$·mol$^{-1}$ and $S^o(298.15\text{ K}) = (680.700 \pm 10.000)$ J·K$^{-1}$·mol$^{-1}$, where the uncertainties have been estimated by this review. Note that the difference in the entropy values between $Co[UO_2VO_4]_2 \cdot 4H_2O$(cr) and $Ba[UO_2O_4]_2 \cdot 4H_2O$(cr) is about + 49 J·K$^{-1}$·mol$^{-1}$, while the Latimer method gives the difference between similar Co and Ba compounds of about – 13 J·K$^{-1}$·mol$^{-1}$, therefore, the uncertainty in $S^o(298.15\text{ K})$ for $Co[UO_2VO_4]_2 \cdot 4H_2O$(cr) may be largely underestimated. The entropies for the other compounds were calculated from the entropy contribution of the "$UO_2VO_4^-$" structure estimated from $Co(UO_2VO_4)_2 \cdot 4H_2O$(cr) and the entropy contribution of crystal water, estimated to

47.8 $J \cdot K^{-1} \cdot mol^{-1}$ for each water, using the Latimer method. The resulting entropy contribution is:

$$S^o(UO_2VO_4^-) = \{S^o(Co(UO_2VO_4)_2 \cdot 4H_2O) - S^o(Co^{2+}) - 4 \times 47.8\}/2 \quad \text{(A.327)}$$

The entropies of the other compounds are then:

$$M(UO_2VO_4)_2 \cdot nH_2O \rightleftharpoons 2S^o(UO_2VO_4^-) + S^o(M^{2+}) + n \times 47.8 \quad \text{(A.328)}$$

These entropy values and the corresponding entropies of formation are listed in Table A-138. The Gibbs energy of formation for the different solids has been calculated from the Gibbs-Helmholtz relation using the entropy and enthalpy of formation. The data reported in [2002CHE/KAR2] are listed in Table A-138 and in view of the large uncertainties, they have been given for information only.

Table A-138: Thermodynamic data for $M[UO_2(VO_4)_2] \cdot nH_2O$(cr), M = Mn, Fe, Co, Ni, Cu, Zn, Cd and corresponding anhydrous compounds, $M[UO_2(VO_4)_2]$(cr). The values in italics have been recalculated from the data in [2002CHE/KAR2] by the present review and are reported for information only.

| Compound | $-\Delta_f H^o$ /kJ·mol$^{-1}$ | $S^o$ /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f S^o$ /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f G^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $Mn[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5681 ± 19) | 679.4 | 1673.2 | 5182 |
| | *(5675.4 ± 12.2)* | *(679.4 ± 15.0)* | *(1674.286 ± 15.018)* | *(5176.212 ± 12.996)* |
| $Fe[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5520 ± 18) | 679.9 | 1667.9 | 5023 |
| | *(5508.0 ± 12.3)* | *(679.9 ± 15.0)* | *(1668.861 ± 15.018)* | *(5010.29 ± 13.090)* |
| $Co[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5515 ± 19) | (680.7 ± 0.4) | (1670.0 ± 1.8) | (5018 ± 21) |
| | *(5506.9 ± 12.2)* | *(680.7 ± 10.0)* | *(1671.016 ± 10.027)* | *(5008.687 ± 12.561)* |
| $Ni[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5517 ± 19) | 680.3 | 1670.2 | 5019 |
| | *(5508.3 ± 12.1)* | *(680.3 ± 15.0)* | *(1671.246 ± 15.019)* | *(5010.018 ± 12.902)* |
| $Cu[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5291 ± 19) | 681.1 | 1672.9 | 4798 |
| | *(5283.9 ± 12.1)* | *(681.1 ± 15.0)* | *(1673.726 ± 15.017)* | *(4784.879 ± 12.902)* |
| $Cu[UO_2(VO_4)]_2 \cdot 9H_2O$(cr) | (6774 ± 19) | 920.1 | 2599.1 | 5999 |
| | *(6769.7 ± 12.1)* | *(920.1 ± 15.0)* | *(2601.006 ± 15.018)* | *(5994.210 ± 12.902)* |
| $Zn[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5576 ± 19) | 681.6 | 1680.6 | 5075 |
| | *(5565.7 ± 12.1)* | *(681.6 ± 15.0)* | *(1681.706 ± 15.017)* | *(5064.299 ± 12.902)* |
| $Zn[UO_2(VO_4)]_2 \cdot 5H_2O$(cr) | (5865 ± 19) | 729.4 | 1865.9 | 5309 |
| | *(5855.4 ± 12.1)* | *(729.4 ± 15.0)* | *(1867.162 ± 15.017)* | *(5298.706 ± 12.902)* |
| $Cd[UO_2(VO_4)]_2 \cdot 4H_2O$(cr) | (5486 ± 19) | 690.3 | 1682.1 | 4984 |
| | *(5479.4 ± 12.1)* | *(690.3 ± 15.0)* | *(1683.176 ± 15.018)* | *(4977.561 ± 12.902)* |
| $Cd[UO_2(VO_4)]_2 \cdot 8H_2O$(cr) | (6637 ± 19) | 881.5 | 2423.0 | 5915 |
| | *(6632.7 ± 12.1)* | *(881.5 ± 15.0)* | *(2425.000 ± 15.018)* | *(5909.686 ± 12.902)* |
| $Mn[UO_2(VO_4)]_2$(cr) | (4422 ± 19) | 488.2 | 933.2 | 4144 |
| | *(4414.0 ± 12.3)* | *(488.2 ± 15.0)* | *(932.462 ± 15.018)* | *(4135.986 ± 13.090)* |
| $Fe[UO_2(VO_4)_2]_2$(cr) | (4273 ± 19) | 488.7 | 926.9 | 3996 |
| | *(4258.7 ± 12.1)* | *(488.7 ± 15.0)* | *(927.037 ± 15.018)* | *(3982.304 ± 12.902)* |
| $Co[UO_2(VO_4)]_2$(cr) | (4269 ± 19) | 489.5 | 929.0 | 3992 |
| | *(4258.2 ± 12.2)* | *(489.5 ± 15.0)* | *(929.192 ± 15.018)* | *(3981.161 ± 12.996)* |
| $Ni[UO_2(VO_4)]_2$(cr) | (4248 ± 19) | 489.1 | 929.2 | 3971 |
| | *(4655.6 ± 12.1)* | *(489.1 ± 15.0)* | *(929.422 ± 15.019)* | (4378.493 ± 12.902) |

(Continued on next page)

Table A-138 (continued)

| Compound | $-\Delta_f H^o$ /kJ·mol$^{-1}$ | $S^o$ /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f S^o$ /J·K$^{-1}$·mol$^{-1}$ | $-\Delta_f G^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $Cu[UO_2(VO_4)]_2$(cr) | (4044 ± 19) | 489.9 | 931.9 | 3766 |
| | *(4035.5 ± 12.1)* | *(489.9 ± 15.0)* | *(931.902 ± 15.017)* | *(3757.653 ± 12.902)* |
| $Zn[UO_2(VO_4)]_2$(cr) | (4330 ± 20) | 490.4 | 939.7 | 4049 |
| | *(4318.0 ± 12.1)* | *(490.4 ± 15.0)* | *(939.882 ± 15.017)* | *(4037.774 ± 12.902)* |
| $Cd[UO_2(VO_4)]_2$(cr) | (4264 ± 19) | 499.1 | 941.1 | 3983 |
| | *(4254.1 ± 13.3)* | *(499.1 ± 15.0)* | *(941.352 ± 15.018)* | *(3973.436 ± 14.034)* |

No thermodynamic properties have been included among the selected values and they are given for information only.

**[2003CHE/SUL4]**

The solubility study reported in this publication refers to Reaction (A.329), from which the solubility products in Table A-139 have been obtained. We note that the reported data for the alkali and alkaline-earth compounds seem to be the same as in [2001CHE/SUL] and [2001CHE/SUL2], from which the reported data have been revised by this review. The authors have not reported analytical data for the water content of the solid phases, which means that these Gibbs energies of reaction for the solubility reactions cannot be used to deduce Gibbs energies of formation for the different solids.

$$A^k[UO_2VO_4]_k \cdot nH_2O(cr) \rightleftharpoons M^{k+} + kUO_2^{2+} + kVO_4^{3-} + nH_2O(l) \qquad (A.329)$$

The solubility has been measured (Reactions (A.330) and (A.331)) in HCl solutions with the initial concentration of 0.100 M and then varied the pH; the total concentrations of the cations and their ratio provides information if the dissolution is congruent, or not, but this point is not discussed by the authors. The reported pH values are not very accurate and the present review has therefore preferred to use the total concentration of $[H^+] = 0.100 - 4S$, where $S$ denotes the solubility, from which the listed values in Table A-139 have been obtained. This review finds reasonable evidence for congruent dissolution at pH ≈ 1.4 for K, Rb, Cs, Mg, Ca, Sr, Ba, Co, Ni, Cu and Pb, but not at higher pH. The reported solubility data have been reinterpreted in this review with the solubility reactions (A.330) and (A.331). The resulting solubility constants are listed in Table A-139, together with the corresponding Gibbs energy of formation of the compounds; there is also a comparison of these values with those obtained by calorimetry in previous publications from the same authors. Based on the Gibbs energy of formation and speciation of the cations, they have calculated the solubility of the different compounds over the pH range 1-8, but these data are useless as the phases are not stable at higher pH.

$$M[UO_2VO_4] \cdot nH_2O(cr) + 4H^+ \rightleftharpoons M^+ + UO_2^{2+} + VO_2^+ + (n+2)H_2O(l) \qquad (A.330)$$

$$M[UO_2VO_4]_2 \cdot nH_2O(cr) + 8H^+ \rightleftharpoons M^{2+} + 2UO_2^{2+} + 2VO_2^+ + (n+4)H_2O(l) \quad \text{(A.331)}$$

The conditional equilibrium constants are

$$^*K_s\,(A.330) = \{[M^+][UO_2^{2+}][VO_2^+]\}/[H^+]^4; \quad \text{(A.332)}$$

$$^*K_s\,(A.331) = \{[M^{2+}][UO_2^{2+}]^2[VO_2^+]^2\}/[H^+]^8; \quad \text{(A.333)}$$

The solubility constants $-\log_{10}{}^*K_s^o$ for Reactions (A.330) and (A.331) have been determined from the conditional values in approx. 0.10 M HCl by using SIT but only including the Debye-Hückel term. The Gibbs energies of formation have been calculated using the Gibbs energies of reaction and the Gibbs energies of formation of the reaction products selected by NEA, with the exception of $Co^{2+}$ for which the Glushko value has been used. Details of our solubility analysis are given in Table A-139.

It is not clear to the reviewers if the solubility data are a result of new experiments or if they are taken from previous studies, [2001CHE/SUL] and [2001KAR/CHE] for the alkali compounds, and [1999KAR/CHE3], [2001CHE/SUL2] and [2003KAR/CHE4], for the alkaline-earth compounds and [2002CHE/KAR] for the Co compound. The auxiliary data used are from the Glushko tables. The agreement between the Gibbs energies of formation obtained from solubility data and calorimetry is very poor. We find the calorimetric data reliable and have not accepted the solubility data. The corresponding $\log_{10}{}^*K_s^o$ and Gibbs energies of reaction are given for information only.

Table A-139: Solubility products, Gibbs energy of reaction and formation for $M^k[UO_2VO_4]_k \cdot nH_2O$(cr) compounds, $M^k$ = (H, Na, K, Rb, Cs, Ca, Sr, Ba, Co, Ni, Cu, Pb). The Gibbs energy of formation are recalculated in this review from the Gibbs energy of Reactions (A.329) and (A.330) using the Gibbs energy of formation $\Delta_f G^o(VO_2^+) = -(589.13 \pm 3.45)$ kJ·mol$^{-1}$.

| Compound | pH meas. | pH calc | $\log_{10}S$ | $\log_{10}{}^*K_s$ | $\log_{10}{}^*K_s^o$ | $\Delta_r G^o$ /kJ·mol$^{-1}$ | $\Delta_f G^o$ /kJ·mol$^{-1}$ From literature (recalculated) | Reference |
|---|---|---|---|---|---|---|---|---|
| $K[UO_2VO_4]$(cr) | 1.4 | 1.19 | – 2.06 | – (1.42 ± 0.4) | – (1.64 ± 0.4) | (9.361 ± 2.283) | – (2308.982 ± 3.260)[a] | [2001CHE/SUL], [2003CHE/SUL4] |
| $Rb[UO_2VO_4]$(cr) | 1.25 | 1.07 | – 2.41 | – (2.95 ± 0.4) | – (3.17 ± 0.4) | (18.094 ± 2.283) | – (2319.214 ± 3.261)[a] | [2001CHE/SUL], [2003CHE/SUL4] |
| $Cs[UO_2VO_4]$(cr) | 1.3 | 1.02 | – 2.96 | – (4.80 ± 0.4) | – (5.02 ± 0.4) | (28.654 ± 2.283) | – (2337.211 ± 3.301)[a] | [2001CHE/SUL], [2003CHE/SUL4] |
| $Mg(UO_2VO_4)_2 \cdot 5H_2O$(cr) | 1.4 | 1.18 | – 2.37 | – (1.21 ± 0.4) | – (1.87 ± 0.4) | (10.674 ± 2.283) | – (5654 ± 18)<br>– (5685.971 ± 5.358)[a] | [2001CHE/SUL2], [2003CHE/SUL4] |
| $Ca(UO_2VO_4)_2 \cdot 8H_2O$(cr) | 1.35 | 1.08 | – 2.68 | – (3.57 ± 0.4) | – (4.22 ± 0.4) | (24.088 ± 2.283) | – (6508.236 ± 5.304)[a] | [2001CHE/SUL2], [2003CHE/SUL4] |
| $Sr(UO_2VO_4)_2 \cdot 5H_2O$(cr) | 1.35 | 1.09 | – 2.65 | – (3.32 ± 0.4) | – (3.98 ± 0.4) | (22.718 ± 2.283) | – (5770 ± 19)<br>– (5806.504 ± 5.247)[a] | [2001CHE/SUL2], [2003CHE/SUL4] |
| $Ba(UO_2VO_4)_2 \cdot 5H_2O$(cr) | 1.4 | 1.09 | – 2.64 | – (3.28 ± 0.4) | – (3.94 ± 0.4) | (22.490 ± 2.283) | – (5749 ± 20)<br>– (5800.068 ± 5.795)[a] | [2001CHE/SUL2], [2003CHE/SUL4] |
| $Co(UO_2VO_4)_2 \cdot 4H_2O$(cr) | 1.4 | 1.14 | – 2.47 | – (2.03 ± 0.4) | – (2.69 ± 0.4) | (15.354 ± 2.283) | – (5014 ± 12)<br>– (5051.776 ± 5.200)[a] | [2001CHE/SUL2], [2003CHE/SUL4] |
| $Ni(UO_2VO_4)_2 \cdot 4H_2O$(cr) | 1.4 | 1.16 | – 2.42 | – (1.16 ± 0.4) | – (2.28 ± 0.4) | (13.014 ± 2.283) | – (5041.569 ± 5.243)[a] | [2001CHE/SUL2], [2003CHE/SUL4] |
| $Cu(UO_2VO_4)_2 \cdot 9H_2O$(cr) | 1.4 | 1.13 | – 2.49 | – (2.21 ± 0.4) | – (2.87 ± 0.4) | (16.382 ± 2.283) | – (6119.824 ± 5.431)[a] | [2001CHE/SUL2], [2003CHE/SUL4] |
| $Pb(UO_2VO_4)_2 \cdot 5H_2O$(cr) | 1.5 | 1.11 | – 2.64 | – (3.13 ± 0.4) | – (3.79 ± 0.4) | (21.633 ± 2.283) | – (5265.793 ± 5.204)[a] | [2001CHE/SUL2], [2003CHE/SUL4] |

(a) Recalculated by this review

**[2003KAR/CHE4]**

This is a review of the previous studies by this group ([1998KAR/CHE], [1999KAR/CHE2], and [1999KAR/CHE3]), which repeats the information obtained there. It includes details of the synthesis and characterisation of alkaline-earth uranovanadates, $M[UO_2VO_4]_2 \cdot nH_2O(cr)$, where $n$ = 5 for Mg and Sr, $n$ = 8 for Ca and $n$ = 4 for Ba. The elemental analyses and the water content are in good agreement with the given stoichiometry. The enthalpy of formation is determined by dissolution calorimetry as exemplified by the following sets of reactions for the Mg-compounds

$$2MgV_2O_7(cr) + 2UO_3(cr) + 5H_2O(l) \rightleftharpoons \text{solution 1} \qquad \text{(A.334)}$$

$$\Delta_r H(\text{A.334}) = -(556.6 \pm 2.2)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$Mg[UO_2VO_4]_2 \cdot 5H_2O(cr) + Mg_3(VO_4)_2(cr) \rightleftharpoons \text{solution 2} \qquad \text{(A.335)}$$

$$\Delta_r H(\text{A.335}) = -(396.5 \pm 1.9)\ \text{kJ}\cdot\text{mol}^{-1}.$$

Reactions (A.334) and (A.335) go to completion which means that the experiment can be arranged in such a way that solutions 1 and 2 have the same composition. Subtraction of Eqn. (A.335) from Eqn. (A.334) gives the enthalpy of reaction, $\Delta_r H(\text{A.336}) = -(160.1 \pm 2.7)\ \text{kJ}\cdot\text{mol}^{-1}$.

$$2Mg_2V_2O_7(cr) + 2UO_3(cr) + 5H_2O(l) \rightleftharpoons Mg[UO_2VO_4]_2 \cdot 5H_2O(cr) + Mg_3(VO_4)_2(cr) \qquad \text{(A.336)}$$

In order to calculate the enthalpy of formation of $Mg[UO_2VO_4]_2 \cdot 5H_2O(cr)$ one needs, in addition to $\Delta_r H(\text{A.336})$, the enthalpies of formation of $UO_3(cr)$ and $H_2O(l)$ from the NEA-TDB database; $Mg_2V_2O_7(cr)$, $\Delta_f H^o_m = -(2841.0 \pm 3.2)\ \text{kJ}\cdot\text{mol}^{-1}$, selected in this review, see Chapter 14; and of $Mg_3(VO_4)_2(cr)$, $\Delta_f H^o_m = -(3464.3 \pm 7.1)\ \text{kJ}\cdot\text{mol}^{-1}$ based on [1988FOT/SLO]. However, as the Fotiev *et al.* paper was not available to this review, results obtained with $Mg_3(VO_4)_2(cr)$ were not selected. As the auxiliary value of $\Delta_f H^o_m$ for $Ba_2V_2O_7(cr)$ is not selected in this review, the enthalpy of formation of $Ba[UO_2VO_4]_2 \cdot 4H_2O(cr)$ is given for information only. Generally, data are close to those in [1999KAR/CHE2], only for anhydrous $Ca[UO_2VO_4]_2(cr)$ the reported value of the enthalpy of formation is for ~ 30 $\text{kJ}\cdot\text{mol}^{-1}$ more positive.

Karyakin *et al.* [2003KAR/CHE4], also report results from low-temperature calorimetry in the temperature range 80-300K, with extrapolation to 0 K. The isobaric heat capacity and the molar entropy of the compounds at 298.15 K are listed in Table A-140 with uncertainties of 1 % in the heat capacity and 4-6 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in the entropy, estimated by the present review.

Table A-140: Isobaric heat capacity and standard thermodynamic functions of alkaline-earth uranovanadates at 298.15 K from [2003KAR/CHE4].

| Compound | $C_p$(298) /J·K$^{-1}$·mol$^{-1}$ | $S^o$(298) /J·K$^{-1}$·mol$^{-1}$ | $H^o(298) - H^o(0)$ /kJ·mol$^{-1}$ | $-[G^o(298) - H^o(0)]$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| $Ba[UO_2VO_4]_2$(cr) | **365.0** | **432.1** | 64.31 | 64.53 |
| $Mg[UO_2VO_4]_2 \cdot 5H_2O$(cr) | **627.5** | **631.6** | 100.6 | 87.67 |
| $Ca[UO_2VO_4]_2 \cdot 5H_2O$(cr) | **589.6** | **639.4** | 99.20 | 91.49 |
| $Ca[UO_2VO_4]_2 \cdot 8H_2O$(cr) | **777.5** | **786.6** | 126.2 | 108.3 |
| $Sr[UO_2VO_4]_2 \cdot 5H_2O$(cr) | **650.0** | **684.8** | 108.0 | 96.16 |
| $Ba[UO_2VO_4]_2 \cdot 4H_2O$(cr) | **564.9** | **631.8** | 98.33 | 90.05 |

Table A-141: Standard thermodynamic functions for the formation of alkaline-earth uranovanadates and their crystal hydrates at 298.15 K. The values in bold are included among the selected values.

| Compound | $\Delta_f H^o$ /kJ·mol$^{-1}$ | $\Delta_f S^o$ /J·K$^{-1}$·mol$^{-1}$ | $\Delta_f G^o$ /kJ·mol$^{-1}$ |
|---|---|---|---|
| $Mg[UO_2VO_4]_2$(cr) | – (4667.5 ± 9.0) | | |
| | – (4678.8 ± 10.3)[(a)] | | |
| $Ca[UO_2VO_4]_2$(cr) | – (4792.0 ± 11.0) | | |
| | **– (4798.7 ± 7.1)[(a)]** | | |
| $Sr[UO_2VO_4]_2$(cr) | – (4852.0 ± 16.0) | | |
| | **– (4858.200 ± 17.8)[(a)]** | | |
| $Ba[UO_2VO_4]_2$(cr) | – (4906.5 ± 20.0) | **– (1018.972 ± 4.150)** | – (4610.893 ± 14.752) |
| | – (4914.7 ± 14.7)[(a)] | | |
| $Mg[UO_2VO_4]_2 \cdot 5H_2O$(cr) | – (6243.5 ± 9.0) | | |
| | – (6257.2 ± 10.3)[(a)] | **– (1956.002 ± 4.066)** | – (5674.018 ± 10.371) |
| $Ca[UO_2VO_4]_2 \cdot 5H_2O$(cr) | – (6318.0 ± 11) | | |
| | **– (6327.3 ± 7.1)[(a)]** | **– (1957.122 ± 4.084)** | **– (5743.784 ± 7.204)** |
| $Ca[UO_2VO_4]_2 \cdot 8H_2O$(cr) | – (7193 ± 11.0) | | |
| | **– (7203.7 ± 7.0)[(a)]** | **– (2509.690 ± 2.164)** | **– (6455.436 ± 7.030)** |
| $Sr[UO_2VO_4]_2 \cdot 5H_2O$(cr) | – (6363.0 ± 16) | | |
| | **– (6372.1 ± 16.7)[(a)]** | **– (1925.832 ± 4.070)** | **– (5797.913 ± 16.744)** |
| $Ba[UO_2VO_4]_2 \cdot 4H_2O$(cr) | – (6092.5 ±19.5) | | |
| | – (6102.8 ± 14.7)[(a)] | **– (1752.296 ± 2.286)** | – (5580.353 ± 14.716) |

(a) Recalculated in this review.

Karyakin *et al.* also report thermodynamic data useful for planning of synthesis of alkaline-earth uranovanadates from oxides. This information is of less interest for the NEA reviews and when needed the original publication [2003KAR/CHE4] should be consulted.

Using the thermodynamic data in Table A-141 and the Gibbs energy of formation of $M^{2+}$, $UO_2^{2+}$ and $VO_4^{3-}$, Karyakin *et al.* estimated the solubility of the alkaline-earth uranovanadates and their solubility products and the latter are given in Table A-142. These data are not included among the selected values and are provided for information only.

$$M[UO_2VO_4]_2 \cdot nH_2O(cr) \rightleftharpoons M^+ + UO_2^{2+} + VO_4^{3-} + nH_2O(l) \qquad (A.337)$$

Table A-142: Solubility products and estimated solubilities at pH 7 for alkaline-earth uranovanadates.

| Compound | $K_s$ ($M^3$) | Estimated solubility in M at pH 7 |
|---|---|---|
| $Mg[UO_2VO_4]_2 \cdot 5H_2O$(cr) | $1 \times 10^{-54}$ | $1 \times 10^{-8}$ |
| $Ca[UO_2VO_4]_2 \cdot 5H_2O$(cr) | $4.5 \times 10^{-51}$ | $7.5 \times 10^{-8}$ |
| $Sr[UO_2VO_4]_2 \cdot 5H_2O$(cr) | $1.5 \times 10^{-58}$ | $2 \times 10^{-9}$ |
| $Ba[UO_2VO_4]_2 \cdot 4H_2O$(cr) | $9.0 \times 10^{-65}$ | $1.5 \times 10^{-10}$ |
| $Ca[UO_2VO_4]_2$(cr) | $9.5 \times 10^{-51}$ | $8.5 \times 10^{-8}$ |

These data indicate that the alkaline-earth uranovanadates have a low solubility in the pH range encountered in many surface and ground water systems.

**[2004SUL/CHE]**

This study reports the enthalpies of formation of synthetic samples of $Pb[(UO_2)(PO_4)]_2 \cdot 6H_2O$(cr), $Pb[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr), and $Pb[(UO_2)(VO_4)]_2 \cdot 5H_2O$(cr). The purity of phases was confirmed with X-ray diffractometry, the elemental composition was determined with an electron microscope equipped with an EDAX energy-dispersive analyser (accuracy 2-5 at. %). However, the exact stoichiometry of studied samples was not reported.

This part of the review is concerned only with results for $Pb[(UO_2)(VO_4)]_2 \cdot 6H_2O$(cr) and the experimental details are discussed in the review of the corresponding phosphate and arsenate phases. Calorimetric runs were made in an adiabatic calorimeter at 298.15 K by measuring enthalpies of reactions of a series of compounds $(Pb(NO_3)_2$(cr), $KUO_2PO_4 \cdot 3H_2O$(cr), $KUO_2VO_4 \cdot 3H_2O$(cr), $KUO_2AsO_4 \cdot 3H_2O$(cr), $KNO_3$(cr), $H_2O$(l), $Pb[(UO_2)(PO_4)]_2 \cdot 6H_2O$(cr), $Pb[(UO_2)(AsO_4)]_2 \cdot 8H_2O$(cr)) in 4 M (~ 4.57 m) aqueous $HNO_3$ solution. The thermochemical cycle employed resulted in the following $\Delta_r H_m$ values (in kJ·mol$^{-1}$):

$$Pb(NO_3)_2(cr) + 2KUO_2VO_4 \cdot 3H_2O(cr) + 2H_2O(l) \rightleftharpoons Pb[(UO_2)(VO_4)]_2 \cdot 5H_2O(cr) + 2KNO_3(cr) \quad \text{(A.338)}$$

The authors calculated:

$\Delta_f H^o_m$ ($Pb[(UO_2)(VO_4)]_2 \cdot 5H_2O$, cr) = – (5811 ± 7) kJ·mol$^{-1}$

and $\Delta_f H^o_m$ ($Pb[(UO_2)(AsO_4)]_2 \cdot 8H_2O$, cr) = – (6126 ± 5) kJ·mol$^{-1}$ (recalculated in this work as – (6131.8 ± 8.2) kJ·mol$^{-1}$). For $Pb[(UO_2)(VO_4)]_2 \cdot 5H_2O$(cr), combining $\Delta_f H^o_m$ with the entropy value for this phase from [1999KAR/CHE3], Suleimanov *et al.* [2004SUL/CHE] calculated $\Delta_f G^o_m$ = – (5226 ± 6) kJ·mol$^{-1}$. It is not clear from the paper how the authors obtained a value for the enthalpy of formation of $KUO_2AsO_4 \cdot 3H_2O$(cr) = – (3047 ± 4) kJ·mol$^{-1}$. In addition, the enthalpy of formation value they have used for $KUO_2VO_4 \cdot 3H_2O$(cr) is also not listed. There are no NEA-

endorsed values of $\Delta_f H_m^\circ$ for some compounds and the reported enthalpies of formation are therefore given for information only.

**[2006CHE/NIP]**

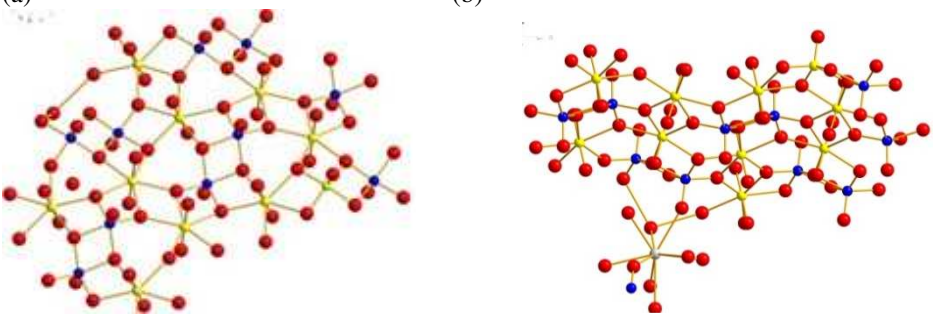
This is a review article based on studies of the Nizhny Novgorod group on the chemistry of U(VI), $VO_4^{3-}$, $PO_4^{3-}$, $AsO_4^{3-}$, $HSiO_4^{3-}$ and $BO_3^{3-}$ systems. There is no new thermodynamic information in this paper, but it contains a list of the constitution of the soluble complexes that are present in the solutions studied. The list is far from complete and the present review questions the proposed $H_xBO_3^{x-3}$ species.

**[2010BUR/REY]**

The orthorhombic layer structure of $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr) is illustrated in Figure A-10a and the coordination of $Ca^{2+}$ in the interlayer in Figure A-10b.

Figure A-10: Structure of $Ca[UO_2VO_4]_2{\cdot}5H_2O$(cr) reported in [2010BUR/REY]: (a) Structure of the uranylvanadate layer, colour code: V, blue, U, yellow, oxygen red, calcium, silver. (b) Structure of the interlayer and coordination around $Ca^{2+}$ that consists of $5H_2O$, three vanadyl oxygen and two uranyl oxygen. This layer structure is different from the one found in the corresponding phosphate compounds.

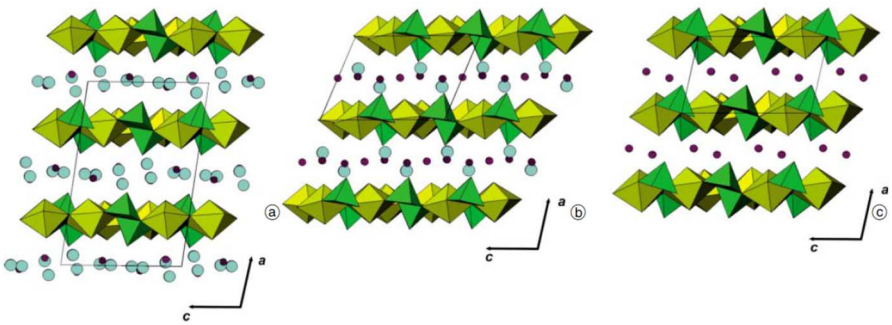
(a) (b)



**[2012SUL/SOM]**

Suleimanov *et al.* describe a possible mechanism for the structural transformation during dehydration of $Na[UO_2VO_4]{\cdot}2H_2O$(cr) by using X-ray diffraction data from the same single crystal during the dehydration. Figure A-11 shows fragments of the layers and interlayer content in the structures $Na[UO_2VO_4]{\cdot}2H_2O$(cr), $Na[UO_2VO_4]{\cdot}H_2O$(cr) and $Na[UO_2VO_4]$(cr) as reported in [2012SUL/SOM].

Figure A-11: Fragments of the crystal structures of (a) $Na[UO_2VO_4]\cdot 2H_2O$(cr); (b) $Na[UO_2VO_4]\cdot H_2O$(cr) and (c) $Na[UO_2VO_4]$(cr), demonstrating the layer structure and the positions of the $Na^+$-ions (black circles) and water, light blue circles. The structure change is smaller in the first dehydration step and larger in the second, consistent with the changes in energies of reaction. (Reprinted with permission from *Z. Kristallogr.*, **2012**, *227*, 522. Copyright (2012) De Gruyter).




**[2012TOK/KIM]**

Tokumaya *et al.* discuss the solubility of uranium(VI) in equilibrium with different minerals, becquerelite, Ca-autunite, uranophane and tyuyamunite, $Ca(UO_2)_2V_2O_8\cdot 8H_2O$(cr). There are two parts in this study, in the first the authors study different chemical models by using available thermodynamic data for soluble complexes and the solid phases and they then use these to calculate the concentration of U(VI) as a function of pH; this information indicates that the minimum solubility is obtained around pH 6-7 for all minerals and that the lowest solubility, $\approx 10^{-7}$ M, is obtained in equilibrium with becquerelite and tyuyamunite. In the second part the authors have made an experimental study where solid phases were formed in solutions with initial concentrations of $Ca^{2+}$, U(VI) and V(V) equal to $6 \times 10^{-5}$ M, $2 \times 10^{-5}$ M and $2 \times 10^{-5}$ M, respectively; these experiments were made by varying the pH in the range 3-9 and analysing the concentrations of Ca, U and V. The solubility varied with time at the different values of pH and it is not clear if equilibrium was attained, or not. The U analyses of the solutions suggest that tyuyamunite is the solubility determining solid phase but the vanadium analyses demonstrate that this is only the case in the pH range 3-5. The solubility data provide no new thermodynamic information.

**[2013NIP/CHE]**

The transformation of $(UO_2)_3(VO_4)_2\cdot 4H_2O$(cr) in aqueous solution has been studied using chemical analysis, X-ray diffraction and IR spectroscopy and Nipruk *et al.* have identified several phase-transformations:

$$\text{at pH} < 2,\ (UO_2)_3(VO_4)_2\cdot 4H_2O(cr) + 6H^+ \rightleftharpoons V_2O_5(cr) + 3UO_2^{2+} + 7H_2O(l) \qquad \text{(A.339)}$$

at pH > 7,

$$(UO_2)_3(VO_4)_2 \cdot 4H_2O(cr) + 2NaOH + H_2O(l) \rightleftharpoons$$
$$2Na[UO_2VO_4] \cdot 2H_2O(cr) + UO_3 \cdot 2H_2O(cr) \quad (A.340)$$

at pH > 12,

$$2(UO_2)_3(VO_4)_2 \cdot 4H_2O(cr) + 18NaOH \rightleftharpoons 3Na_2U_2O_7(cr) + 4Na_3VO_4(cr) + 17H_2O(l) \quad (A.341)$$

The solubility reported by the authors is based on analyses of the total concentrations of uranium and vanadium, which the authors claim should be 3:2, by referring to the reaction:

$$(UO_2)_3(VO_4)_2 \cdot 4H_2O(cr) \rightleftharpoons 3UO_2^{2+} + 2VO_4^{3-} + 4H_2O(l) \quad (A.342)$$

It is clear that this is not the reaction taking place in the different test solutions and the data reported are therefore not accepted by the present review, but their reported solubilities are provided in Table A-143 for information.

Table A-143: Experimental solubilities of $(UO_2)_3(VO_4)_2 \cdot 4H_2O(cr)$ as function of pH.

| pH | *S* in M | Ratio U/V |
|---|---|---|
| 2.39 | $(8.78 \pm 1.26) \times 10^{-4}$ | 6.37 |
| 2.84 | $(1.48 \pm 0.24) \times 10^{-4}$ | 1.85 |
| 3.39 | $(3.56 \pm 0.66) \times 10^{-5}$ | 1.69 |
| 3.51 | $(2.35 \pm 0.52) \times 10^{-5}$ | 1.63 |
| 3.62 | $(1.60 \pm 0.38) \times 10^{-5}$ | 1.85 |
| 3.78 | $(1.10 \pm 0.22) \times 10^{-5}$ | 2.06 |
| 4.21 | $(4.00 \pm 1.08) \times 10^{-6}$ | 2.25 |
| 4.33 | $(2.68 \pm 0.86) \times 10^{-6}$ | 1.30 |
| 4.35 | $(3.41 \pm 0.90) \times 10^{-6}$ | 2.22 |
| 5.50 | $(6.11 \pm 2.92) \times 10^{-7}$ | 1.41 |

## A-1.9 Uranium polyoxometallates

**[2007YUS/SHI2]**

See review in Chapter 17 (Appendix A, Pu).

**[2007YUS/SHI4]**

See review in Chapter 17 (Appendix A, Pu).

**[2007YUS/SHI3]**

See review in Chapter 17 (Appendix A, Pu).

# A-1.10 Uranium molybdate compounds

# A-1.11 Uranium compounds and complexes with group 2 elements

**[2001MAT/YAM]**

The heat capacity of "$BaUO_3$" is reported in the temperature range 373-873 K using Differential Scanning Calorimetry. The "$BaUO_3$" material was prepared from $BaCO_3$ and $UO_2$ mixed in stoichiometric amounts and heated in air at 1227 K. In a second step, the mixture was pelletised and sintered in a reducing atmosphere at 1773 K. Previous work has stressed the difficulty of obtaining non-oxidised stoichiometric $BaUO_3$ [2003GUI/FAN]. The lowest oxygen content Hinatsu [1993HIN], [1993HIN2] could reach by reduction of $BaUO_4$ under a flow of hydrogen was $BaUO_{3.023}$ according to the Ce(IV)-Fe(II) back-titration. $BaUO_{3.023}$ showed a single cubic perovskite phase (in space group *Pm3m*) with cell parameter $a = 4.4075(10)$ Å [1993HIN]. The lattice parameter found in the work of Matsuda *et al.* [2001MAT/YAM], *i.e.* 4.404 Å, suggests an oxygen content greater than O/U=3, namely $BaUO_{3.023}$ ($x > 0.023$), and hence greater than for pure $BaUO_3$. The authors did not perform any chemical analysis of their sample.

The DSC measurements were performed under high-purity argon flow. The heat capacity data were estimated both using an enthalpy method applied to limited temperature intervals and a scanning method applied to individual temperatures on large temperature intervals. The results from both methods are in good agreement, and close to the values obtained with the rule of Neumann-Kopp (NK) using the auxiliary data recommended in this review for $UO_2$(cr) [2014KON/BEN] and BaO(cr) [1994COR/LAA]. The corresponding temperature dependence of the heat capacity function is:

$$C^{\circ}_{p,\mathrm{m}}(BaUO_3, \mathrm{cr}, T) = 126.6 + 1.61\times10^{-2}T - 1.42\times10^{6}T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

It should be noted that the third coefficient was not reported correctly in the work of [2001MAT/YAM]. The value obtained at 298.15 K by extrapolation of the aforementioned equation is $C^{\circ}_{p,\mathrm{m}}(BaUO_3, \mathrm{cr}, 298.15\ \mathrm{K}) = 115.4\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, in reasonable agreement with that obtained with NK's rule, *i.e.*, 110.7 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

The authors subsequently derived the heat capacity, entropy, enthalpy increment, and free energy functions between 298.15 and 1000 K, using the aforementioned equation and the entropy estimation by Cordfunke and IJdo [1988COR/IJD], [1990COR/KON], *i.e.*, $S^{\circ}_{\mathrm{m}}(BaUO_3, \mathrm{cr}, 298.15\ \mathrm{K}) = (142.0 \pm 2.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. The enthalpy and Gibbs energy of formation at 298.15 K were calculated using the measured heat capacity data together with the thermodynamic functions of BaO(cr) and $UO_2$(cr) tabulated by Cordfunke and Konings [1990COR/KON]. Applying the third law method with the data recommended in this

review for BaO(cr) [1994COR/LAA] and $UO_2$(cr) [2014KON/BEN], we have recalculated $\Delta_f H_m^o$ ($BaUO_3$, cr, 298.15 K) = – (1641.0 ± 10.0) kJ·mol$^{-1}$, which is much higher than the value found by [2001MAT/YAM], *i.e.*, – (1725.0 ± 10.0) kJ·mol$^{-1}$, but in reasonable agreement with the data recommended by [1992GRE/FUG], [2003GUI/FAN] derived from the solution calorimetry studies of Williams *et al.* [1984WIL/MOR], *i.e.*, – (1690.0 ± 10.0) kJ·mol$^{-1}$. The reason for the discrepancy between the present calculation and that of [2001MAT/YAM] could not be identified, however.

**[2004BAN/DAS]**

The standard Gibbs energies of formation of $Ba_2U_3O_{11}$ and $BaU_2O_7$ were determined in the temperature ranges 1009-1178.5 K and 1001-1206 K, respectively, using a calcia stabilised zirconia (CSZ) solid state electrochemical cell. $Ba_2U_3O_{11}$ and $BaU_2O_7$ were prepared from $BaCO_3$ and $U_3O_8$ mixed in stoichiometric amounts, and heated at 1025 K for 340 hours, and 1125 K for 400 hours, respectively, with intermediate regrinding steps. The prepared samples were characterised using X-ray diffraction, but were not analysed chemically. The three phases mixtures {$Ba_2U_3O_{11}$(cr) + $BaUO_4$(cr) + $U_3O_8$(cr)} and {$Ba_2U_3O_{11}$(cr) + $BaU_2O_7$(cr) + $U_3O_8$(cr)} were pressed into pellets for the electromotive force (emf) measurements and sintered in purified argon atmosphere at 800 K. X-ray diffraction patterns collected after the experiment confirmed the absence of reaction with the electrolyte tube or platinum electrode.

The two cells are represented as follows:

Cell (I): (-)Pt/{$Ba_2U_3O_{11}$(cr)+$BaUO_4$(cr)+$U_3O_8$(cr)}//CSZ//$O_2${p($O_2$)=21.21 kPa}/Pt

Cell (II): (-)Pt/{$Ba_2U_3O_{11}$(cr)+$BaU_2O_7$(cr)+$U_3O_8$(cr)}//CSZ//$O_2${p($O_2$)=21.21 kPa}/Pt

The emf of both cells were measured after equilibration over the temperature ranges (1009-1178.5 K) and (1001-1206 K), respectively.

The equilibrium reaction for Cell (I) is written as follows:

$$6BaO_4(cr) + U_3O_8(cr) + 1/2O_2(g) \rightleftharpoons 3Ba_2U_3O_{11}(cr)$$

Combining the Gibbs energy of formation of $BaUO_4$(s) and $U_3O_8$(s) reported by Matsui [1995MAT] and Barin [1995BAR] together with the measured variation of emf of Cell (I), [2004BAN/DAS] derived the Gibbs energy of formation of $Ba_2U_3O_{11}$(cr) in the temperature range (1009-1178.5 K). The latter data were recalculated in this review using the recommended thermodynamic functions for $U_3O_8$(cr) [2014KON/BEN] and $BaUO_4$(cr) [2003GUI/FAN], yielding the following function with an uncertainty of ± 6 kJ·mol$^{-1}$:

$\Delta_f G_m^o$ ($Ba_2U_3O_{11}$, cr, *T*) (kJ·mol$^{-1}$) = – 5218.0395 + 0.96508 *T* (K)(1009-1178.5 K).

The extrapolation of the aforementioned equation at 298.15 K using the heat capacity and entropy data recommended in this review yields $\Delta_f G_m^o$ ($Ba_2U_3O_{11}$, cr, 298.15 K) = – (4920.2 ± 6) kJ·mol$^{-1}$, in reasonable agreement with the value estimated using the method of Chen *et al.* [1999CHE/EWI] which sums polyhedral contributions for uranyl phases, *i.e.*, – (4938.4) kJ·mol$^{-1}$ [2004BAN/DAS]. The slope and intercept of the aforementioned function correspond to the standard molar enthalpy and entropy of formation at the average temperature $T_{ave}$ = 1093.8 K. [2004BAN/DAS] could not derive the enthalpy of formation at 298.15 K, however, due to the lack of heat capacity data at the time they reported this work.

The heat capacity and enthalpy increments of $Ba_2U_3O_{11}$(cr) were later measured by [2010DAS/SIN] using DSC in continuous mode and a high temperature Calvet calorimeter, respectively. Using the heat capacity coefficients recalculated in this review, the enthalpy of formation was derived at 298.15 K by second law analysis of the data as $\Delta_f H_m^o$ ($Ba_2U_3O_{11}$, cr, 298.15 K) = – (5208.1 ± 6.0) kJ·mol$^{-1}$. Moreover, a third law analysis based on the recommended entropy value for $Ba_2U_3O_{11}$(cr) yielded $\Delta_f H_m^o$ ($Ba_2U_3O_{11}$, cr, 298.15 K) = – (5212.8 ± 0.2) kJ·mol$^{-1}$. The latter uncertainty corresponds to the standard deviation along the temperature interval only. The second and third law values are in very good agreement with each other, and in reasonable agreement with the value estimated using the method suggested by Morss [2002MOR] based on acidity parameters, *i.e.*, – (5187.9) kJ·mol$^{-1}$, and with the method suggested by Chen *et al.* [1999CHE/EWI] based on the summation of polyhedral contributions, *i.e.* – (5237.2) kJ·mol$^{-1}$ [2004BAN/DAS]. The present review retains the average of the second and third law values for the enthalpy of formation of $Ba_2U_3O_{11}$(cr) at 298.15 K, *i.e.*:

$\Delta_f H_m^o$ ($Ba_2U_3O_{11}$, cr, 298.15 K) = – (5210.5 ± 6.0) kJ·mol$^{-1}$.

The equilibrium reaction for Cell (II) is as written as follows:

$$3Ba_2U_3O_{11}(cr) + U_3O_8(cr) + 1/2O_2(g) \rightleftharpoons 6BaU_2O_7(cr)$$

Combining the derived Gibbs energy of formation for $Ba_2U_3O_{11}$(s) together with that reported by Matsui [1995MAT] for $U_3O_8$(s) and the measured variation of emf of the Cell (II), the Gibbs energy of formation of $BaU_2O_7$(cr) was derived in the temperature range (1001-1206 K). The latter data were recalculated in the present review using the recommended thermodynamic functions for $U_3O_8$(cr) [2014KON/BEN] and $Ba_2U_3O_{11}$(cr), yielding the following function with an uncertainty of ± 6 kJ·mol$^{-1}$:

$\Delta_f G_m^o$ ($BaU_2O_7$, cr, *T*) (kJ·mol$^{-1}$) = – 3220.5410 + 0.60192 *T* (K)(1001-1206 K).

There again, the heat capacity function and entropy value at 298.15 K were not available at the time of the work of [2004BAN/DAS]. Using the data retained in this review for $BaU_2O_7$(cr), the Gibbs energy of formation was extrapolated from the aforementioned equation at 298.15 K as $\Delta_f G_m^o$ ($BaU_2O_7$, cr, 298.15 K) =

– (3052.7 ± 6.0) kJ·mol$^{-1}$, in very good agreement with the estimation using the method suggested by Chen *et al.* [1999CHE/EWI], *i.e.*, – (3052.1 ± 6.7) kJ·mol$^{-1}$. A second and third law analyses of the data yielded $\Delta_f H^o_m$ ($BaU_2O_7$, cr, 298.15 K) = – (3212.3 ± 6.0) kJ·mol$^{-1}$ and – (3240.7 ± 1.4) kJ·mol$^{-1}$, respectively. The agreement between those two values is rather poor. Moreover, the third law analysis shows a slight drift with temperature. The value recommended by [1992GRE/FUG], [2003GUI/FAN], *i.e.*, – (3237.2 ± 5.0) kJ·mol$^{-1}$ based on the solution calorimetry studies of Cordfunke and Ouweltjes [1988COR/OUW], are considered more reliable than the results obtained here. This review therefore retains:

$$\Delta_f H^o_m (BaU_2O_7, \text{cr}, 298.15\ \text{K}) = -(3237.2 \pm 5.0)\ \text{kJ·mol}^{-1}.$$

**[2006CHE/SMI3]**

The standard enthalpy of formation of $Ba_2SrUO_6$ was determined at 298.15 K using solution calorimetry in 1 mol·dm$^{-3}$ HCl(aq) medium, while the standard heat capacity and entropy at 298.15 K were measured with an adiabatic vacuum calorimeter. $Ba_2SrUO_6$ was synthesised by solid-state reaction between the metal nitrates and $UO_3$ mixed in stoichiometric amounts, and heated at 1073 K for three hours, 1373 K for three hours, and 1553 K for 20 hours, with intermediate regrinding steps. The prepared sample was characterised using X-ray diffraction, but was not analysed chemically. $Ba_2SrUO_6$ shows a monoclinic $GdFeO_3$-type perovskite structure in space group $P2_1/n$ according to the neutron diffraction studies of Groen and IJdo [1987GRO/IJD] and synchrotron X-ray powder diffraction data of Reynolds *et al.* [2013REY/KEN]. Previous studies by Gens *et al.* [1985GEN/FUG] had assigned it an orthorhombic symmetry based on Debye-Scherrer X-ray powder data. The unit cell parameters of [2006CHE/SMI3] are in good agreement with those of [1987GRO/IJD] and [2013REY/KEN].

The solution calorimetry studies were performed in 1 mol·dm$^{-3}$ hydrochloric acid medium. The error on the experimental enthalpies was estimated by the authors not to exceed 1.5-2.0 %. The standard enthalpy of solution of $Ba_2SrUO_6$ in 1 mol·dm$^{-3}$ HCl(aq) was found as – (531.7 ± 4.7) kJ·mol$^{-1}$. Gens *et al.* performed a very similar study in 1985 [1985GEN/FUG]. They found – (524.6 ± 1.1) kJ·mol$^{-1}$ when dissolving $Ba_2SrUO_6$ in 1 mol·dm$^{-3}$ HCl(aq) [1985GEN/FUG], in reasonable agreement with the result of [2006CHE/SMI3], and derived a standard enthalpy of formation as $\Delta_f H^o_m$ ($Ba_2SrUO_6$, cr, 298.15 K) = – (3257.3 ± 4.4) kJ·mol$^{-1}$. The value recalculated by [1992GRE/FUG], [2003GUI/FAN] using the recommended auxiliary data is – (3257.3 ± 5.7) kJ·mol$^{-1}$. [2006CHE/SMI3] found a very different result, however, *i.e.* $\Delta_f H^o_m$ ($Ba_2SrUO_6$, cr, 298.15 K) = – (2940.0 ± 8.5) kJ·mol$^{-1}$. The thermochemical cycles employed by both sets of authors are different. [2006CHE/SMI3] used the following scheme:

$$UO_3(cr) + solvent \rightleftharpoons solution\,1 \quad (A.343)$$

$$BaO(cr) + 1/2\,solution\,1 \rightleftharpoons 1/2\,solution\,2 \quad (A.344)$$

$$SrO(cr) + solution\,2 \rightleftharpoons solution\,3 \quad (A.345)$$

$$Ba_2SrUO_6 + solvent \rightleftharpoons solution\,4 \quad (A.346)$$

[2006CHE/SMI3] makes the assumption that the solutions formed from reactions (A.345) and (A.346) are identical, and derive the standard enthalpy of formation from the equilibrium Reaction (A.347):

$$UO_3(cr) + 2BaO(cr) + SrO(cr) \rightleftharpoons Ba_2SrUO_6(cr) \quad (A.347)$$

whose reaction enthalpy is given by $\Delta_r H^o$ (A.347) = $\Delta_r H^o$ (A.343) + 2 $\Delta_r H^o$ (A.344) + $\Delta_r H^o$ (A.345) – $\Delta_r H^o$ (A.346) (derived from the experimentally determined enthalpies of solutions (A.343)-(A.346)).

We suggest in the present review that solution (A.345) and (A.346) should correspond to {$2BaCl_2 + SrCl_2 + UO_2Cl_2 + 4H_2O$ (in 1 mol·dm$^{-3}$ HCl)} after the reaction of $Ba_2SrUO_6$(cr) with 8 HCl (in 1 mol·dm$^{-3}$ HCl(aq)), corresponding to the following dissolution reactions:

$$UO_3(cr) + 8HCl(sln) \rightleftharpoons (UO_2Cl_2 + H_2O + 6HCl)(sln) \quad (A.348)$$

$$BaO(cr) + 0.5(UO_2Cl_2 + H_2O + 6HCl)(sln) \rightleftharpoons (BaCl_2 + 0.5UO_2Cl_2 + 1.5H_2O + HCl)(sln) \quad (A.349)$$

$$Sr^{II}O(cr) + 2(BaCl_2 + 0.5UO_2Cl_2 + 1.5H_2O + HCl)(sln) \rightleftharpoons (Sr^{II}Cl_2 + 2BaCl_2 + UO_2Cl_2 + 4H_2O)(sln) \quad (A.350)$$

$$Ba_2Sr^{I}UO_6 + 8HCl(sln) \rightleftharpoons (2BaCl_2 + Sr^{II}Cl_2 + UO_2Cl_2 + 4H_2O)(sln) \quad (A.351)$$

Based on the aforementioned reaction scheme, we derived in the present review a very similar result to that of [2006CHE/SMI3] using the recommended auxiliary data, *i.e.* $\Delta_f H^o_m$ ($Ba_2SrUO_6$, cr, 298.15 K) = – (2940.2 ± 8.2) kJ·mol$^{-1}$. An alternative calculation is based on the following thermochemical cycle in Table A-144, with $\Delta_f H^o_m$ ($Ba_2SrUO_6$, cr, 298.15 K) = $\Delta_r H^o_8 = -\Delta_r H^o_1 + \Delta_r H^o_2 + \Delta_r H^o_3 + \Delta_r H^o_4 + \Delta_r H^o_5 + \Delta_r H^o_6 + \Delta_r H^o_7$.

Table A-144: Thermochemical cycle used in this review to assess the standard enthalpy of formation of $Ba_2SrUO_6$ based on the results of [2006CHE/SMI3].

| | Reaction | $\Delta_r H^o$(298.15 K) in 1M HCl(aq) | Reference |
|---|---|---|---|
| 1 | $Ba_2SrUO_6 + sln \rightleftharpoons 2BaCl_2 + SrCl_2 + UO_2Cl_2 + 4H_2O(sln)$ | – (531.7 ± 4.7) | [2006CHE/SMI3] |
| 2 | $2BaO + sln \rightleftharpoons 2BaCl_2 + 2H_2O(sln)$ | – (387.6 ± 5.6) | [2006CHE/SMI3] |
| 3 | $SrO + sln \rightleftharpoons SrCl_2 + H_2O(sln)$ | – (112.0 ± 1.4) | [2006CHE/SMI3] |
| 4 | $UO_3 + sln \rightleftharpoons UO_2Cl_2 + H_2O(sln)$ | – (61.7 ± 0.8) | [2006CHE/SMI3] |
| 5 | $2Ba + O_2 \rightleftharpoons 2BaO$ | – (1096.2 ± 5.0) | [2003GUI/FAN] |
| 6 | $Sr + 0.5O_2 \rightleftharpoons SrO$ | – (590.6 ± 0.9) | [2003GUI/FAN] |
| 7 | $U + 1.5O_2 \rightleftharpoons UO_3$ | – (1223.8 ± 1.2) | [2003GUI/FAN] |
| 8 | $2Ba + Sr + U + 3O_2 \rightleftharpoons Ba_2SrUO_6$ | **– (2940.2 ± 9.1)** | **This review** |

The latter analysis yields a very similar result, *i.e.*, $\Delta_f H^o_m$ ($Ba_2SrUO_6$, cr, 298.15 K) = – (2940.2 ± 9.1) kJ·mol$^{-1}$. The difference with the result of [1985GEN/FUG] probably originates from the values of the dissolution enthalpies of BaO(cr) and SrO(cr) measured by [2006CHE/SMI3], which are in strong disagreement with those reported by [1990COR/KON2] in 1 mol·dm$^{-3}$ HCl(aq) medium. The BaO(cr) and SrO(cr) samples used by [2006CHE/SMI3] might have contained some carbonate and/or hydroxide impurities. Using corrected values for the dissolution enthalpies of BaO(cr) and SrO(cr) [1990COR/KON2], one derives $\Delta_f H^o_m$ ($Ba_2SrUO_6$, cr, 298.15 K) = – (3230.6 ± 7.1) kJ·mol$^{-1}$ (see Table A-145), in better agreement with the selected value [2003GUI/FAN]. The final result is still 26.7 kJ·mol$^{-1}$ higher than expected, however. The dissolution enthalpy of $UO_3$ in 1 mol·dm$^{-3}$ HCl(aq) medium reported by [2006CHE/SMI3] seems reasonable, and is in good agreement with that reported by Cordfunke *et al.* [1976COR/OUW] in 4.98 mol·dm$^{-3}$ HCl(aq) medium, *i.e.*, – (64.98 ± 0.3) kJ·mol$^{-1}$. The disagreement could therefore also originate from the value of the dissolution enthalpy of $Ba_2SrUO_6$(cr) measured in the work of [2006CHE/SMI3]. Moreover, since the authors [2006CHE/SMI3] do not report the quantities of material dissolved, one cannot judge if all solutions had a similar final concentration.

Table A-145: Thermochemical cycle used in this review to assess the standard enthalpy of formation of $Ba_2SrUO_6$ based on the results of [2006CHE/SMI3] and [1990COR/KON2].

| | Reaction | $\Delta_r H^o$(298.15 K) in 1 M HCl(aq) | Reference |
|---|---|---|---|
| 1 | $Ba_2SrUO_6 + sln \rightleftharpoons 2BaCl_2 + SrCl_2 + UO_2Cl_2 + 4H_2O(sln)$ | – (531.7 ± 4.7) | [2006CHE/SMI3] |
| 2 | $2BaO + sln \rightleftharpoons 2BaCl_2 + 2H_2O(sln)$ | – (546.038 ± 0.48) | [1990COR/KON2] |
| 3 | $SrO + sln \rightleftharpoons SrCl_2 + H_2O(sln)$ | – (243.93 ± 0.33) | [1990COR/KON2] |

(Continued on next page)

Table A-145 (continued)

| | Reaction | $\Delta_r H^o$(298.15 K) in 1 M HCl(aq) | Reference |
|---|---|---|---|
| 4 | $UO_3 + sln \rightleftharpoons UO_2Cl_2 + H_2O(sln)$ | – (61.7 ± 0.8) | [2006CHE/SMI3] |
| 5 | $2Ba + O_2 \rightleftharpoons 2BaO$ | – (1096.2 ± 5.0) | [2003GUI/FAN] |
| 6 | $Sr + 0.5O_2 \rightleftharpoons SrO$ | – (590.6 ± 0.9) | [2003GUI/FAN] |
| 7 | $U + 1.5O_2 \rightleftharpoons UO_3$ | – (1223.8 ± 1.2) | [2003GUI/FAN] |
| 8 | $2Ba + Sr + U + 3O_2 \rightleftharpoons Ba_2SrUO_6$ | – **(3230.6 ± 7.1)** | **This review** |

In view of the apparent discrepancies in the work of [2006CHE/SMI3], we prefer in this review to retain the assessment of [1985GEN/FUG] and the enthalpy of formation selected by [1992GRE/FUG], [2003GUI/FAN]:

$$\Delta_f H^o_m (Ba_2SrUO_6, cr, 298.15\ K) = – (3257.3 \pm 5.7)\ kJ{\cdot}mol^{-1}.$$

[2006CHE/SMI3] also measured the low temperature heat capacity of $Ba_2SrUO_6$ in the temperature range 8-331 K using adiabatic vacuum calorimetry. The error on the measurements was estimated within 2 % at helium temperatures, 0.5 % up to 40 K, and 0.2 % above 40 K. The present review agrees with the derived standard heat capacity and entropy values, but assigns larger uncertainties to the final results as the authors report very limited experimental details to assess the purity of their sample:

$$C^o_{p,m} (Ba_2SrUO_6, cr, 298.15\ K) = (223.7 \pm 1.3)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$S^o_m (Ba_2SrUO_6, cr, 298.15\ K) = (287.4 \pm 2.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

**[2006KNY/CHE]**

The authors report high temperature X-ray diffraction studies of $Ba_2SrUO_6$, and the determination of the standard enthalpies of formation of $Ba_2SrUO_6$, $Ba_2CaUO_6$, $Ba_2MgUO_6$, and $Ba_3UO_6$ using solution calorimetry in a 1 $mol{\cdot}dm^{-3}$ HCl(aq) medium. The $Ba_2MUO_6$ compounds (M = Mg, Ca, Sr, Ba) were prepared by solid state reaction between the alkaline-earth metal oxides and uranium oxide heated at successively 1073 K (3 hours), 1373 K (3 hours) and 1473 K (20 hours). They were characterised using X-ray diffraction, but were not analysed chemically. $Ba_2MgUO_6$ is reported to be a cubic perovskite, $Ba_2CaUO_6$ and $Ba_2SrUO_6$ monoclinic perovskites, and $Ba_3UO_6$ a rhombohedral perovskite. High temperature X-ray diffraction measurements were performed on the $Ba_2SrUO_6$ sample from room temperature up to 1273 K. The authors identified the occurrence of a reversible phase transition around 869-932 K associated with a break in the temperature dependence of the unit cell parameters. They suggested 896 K as the transition temperature. These results match those of [2013REY/KEN], who found a first order phase transition between monoclinic α-$Ba_2SrUO_6$ (in space group *P21/n*) and rhombohedral β-$Ba_2SrUO_6$ (in space group *R-3*) around 900 K.

[2006KNY/CHE] moreover report coefficients of thermal expansion for this compound, with an isotropic expansion along all three directions for the α-phase.

The solution calorimetry studies of the $Ba_2M^{II}UO_6$ (M = Mg, Ca, Sr, Ba) compounds were performed in 1 mol·dm$^{-3}$ hydrochloric acid medium. The error on the experimental enthalpies was estimated not to exceed 1.5-2.0 %. The measured standard enthalpies of solution of $Ba_2M^{II}UO_6$ in 1 mol·dm$^{-3}$ HCl(aq), reported in Table A-146, are compared with literature data. The enthalpies of dissolution of $Ba_2CaUO_6$(cr) and $Ba_2SrUO_6$(cr) in 1 mol·dm$^{-3}$ HCl(aq) were already measured by Gens *et al.* [1985GEN/FUG] on well-characterised samples [1992GRE/FUG]. The enthalpies of reaction of $Ba_2MgUO_6$(cr) and $Ba_3UO_6$(cr) with 1 mol·dm$^{-3}$ HCl(aq) were assessed by Morss *et al.* [1982MOR/FUG], [1983MOR/WIL2]. The results of [2006KNY/CHE] are in rather poor agreement with the past studies. The authors use the following thermochemical cycle:

$$UO_3(cr) + \text{solvent} \rightarrow \text{solution 1} \quad \text{(A.352)}$$

$$BaO(cr) + 1/2\,\text{solution 1} \rightarrow 1/2\,\text{solution 2} \quad \text{(A.353)}$$

$$M^{II}O(cr) + \text{solution 2} \rightarrow \text{solution 3} \quad \text{(A.354)}$$

$$Ba_2M^{II}UO_6 + \text{solvent} \rightarrow \text{solution 4} \quad \text{(A.355)}$$

[2006KNY/CHE] make the assumption that the solutions formed from Reactions (A.354) and (A.355) are identical, and derive the standard enthalpy of formation from the equilibrium Reaction (A.356):

$$UO_3(cr) + 2BaO(cr) + M^{II}O(cr) \rightleftharpoons Ba_2M^{II}UO_6(cr) \quad \text{(A.356)}$$

whose reaction enthalpy is given by $\Delta_r H°(\text{A.356}) = \Delta_r H°(\text{A.352}) + 2\Delta_r H°(\text{A.353}) + \Delta_r H°(\text{A.354}) - \Delta_r H°(\text{A.355})$ (known from the experimentally determined enthalpies of solutions (A.352)-(A.355)).

It is suggested in this review that solutions (A.354) and (A.355) should correspond to $\{2BaCl_2 + M^{II}Cl_2 + UO_2Cl_2 + 4H_2O$ (in 1 mol·dm$^{-3}$ HCl)$\}$ after the reaction of $Ba_2M^{II}UO_6$(cr) with 8HCl (in 1 mol·dm$^{-3}$ HCl(aq)). The thermochemical cycle as written above corresponds to the following dissolution reactions:

$$UO_3(cr) + 8HCl(sln) \rightleftharpoons (UO_2Cl_2 + H_2O + 6HCl)(sln) \quad \text{(A.357)}$$

$$BaO(cr) + 0.5(UO_2Cl_2 + H_2O + 6HCl)(sln) \rightleftharpoons (BaCl_2 + 0.5UO_2Cl_2 + 1.5H_2O + HCl)(sln) \quad \text{(A.358)}$$

$$M^{II}O(cr) + 2(BaCl_2 + 0.5UO_2Cl_2 + 1.5H_2O + HCl)(sln) \rightleftharpoons (M^{II}Cl_2 + 2BaCl_2 + UO_2Cl_2 + 4H_2O)(sln) \quad \text{(A.359)}$$

$$Ba_2M^{II}UO_6 + 8HCl(sln) \rightleftharpoons (2BaCl_2 + M^{II}Cl_2 + UO_2Cl_2 + 4H_2O)(sln) \quad \text{(A.360)}$$

Based on the aforementioned reaction scheme, we have recalculated in this review the standard enthalpies of formation of the $Ba_2M^{II}UO_6$(cr) compounds using the recommended auxiliary data (see Table A-145). The values derived agree with those of [2006CHE/SMI3], but are in strong disagreement with the data previously reported in the literature [1982MOR/FUG], [1983MOR/WIL2], [1985GEN/FUG].

Table A-146: Dissolution enthalpies in 1 mol·dm$^{-3}$ HCl(aq) medium and derived standard enthalpies of formation reported in the work of [2006KNY/CHE] and comparison with those measured by [1982MOR/FUG], [1985GEN/FUG], [1983MOR/WIL2].

| Sample | $\Delta_r H^\circ_{diss}$ (298 K) in 1 mol·dm$^{-3}$ HCl(aq)[(a)] | $\Delta_r H^\circ_{diss}$ (298 K) in 1 mol·dm$^{-3}$ HCl(aq)[(b)] | **$\Delta_f H^\circ$($Ba_2MUO_6$, cr, 298 K)**[(c)] | $\Delta_f H^\circ$($Ba_2MUO_6$, cr, 298 K)[(d)] |
|---|---|---|---|---|
| $Ba_2MgUO_6$ | – (418.6 ± 0.5) | – (451.2 ± 3.9) [1982MOR/FUG] | – **(3082.9 ± 7.8)** | – (3245.9 ± 6.5) |
| $Ba_2CaUO_6$ | – (406.7 ± 0.8) | – (477.6 ± 2.0) [1985GEN/FUG] | – **(3031.8 ± 7.9)** | – (3295.8 ± 5.9) |
| $Ba_2SrUO_6$ | – (531.7 ± 4.7) | – (524.6 ± 1.1) [1985GEN/FUG] | – **(2940.2 ± 8.2)** | – (3257.3 ± 5.7) |
| $Ba_3UO_6$ | – (468.0 ± 2.2) | – (555.4 ± 1.5) [1983MOR/WIL2] | – **(3043.2 ± 10.5)** | – (3210.4 ± 8.0) |

(a) Dissolution enthalpies reported by [2006KNY/CHE]
(b) Dissolution enthalpies reported by [1982MOR/FUG], [1985GEN/FUG], [1983MOR/WIL2]
(c) Enthalpies of formation recalculated in this review based on the experimental data of [2006KNY/CHE]
(d) Enthalpies of formation reported by [1982MOR/FUG], [1985GEN/FUG], [1983MOR/WIL2]

An alternative calculation is based on the following thermochemical cycle (Table A-147), with (M = Mg, Ca, Sr, Ba), and $\Delta_f H^\circ_m(Ba_2MUO_6, cr, 298.15\ K) = \Delta_r H^\circ_8 = -\Delta_r H^\circ_1 + \Delta_r H^\circ_2 + \Delta_r H^\circ_3 + \Delta_r H^\circ_4 + \Delta_r H^\circ_5 + \Delta_r H^\circ_6 + \Delta_r H^\circ_7$.

Table A-147: Thermochemical cycle used in this review to assess the standard enthalpy of formation of $Ba_2MUO_6$ based on the results of [2006KNY/CHE].

| | Reaction |
|---|---|
| 1 | $Ba_2MUO_6 + sln \rightleftharpoons 2BaCl_2 + MCl_2 + UO_2Cl_2 + 4H_2O(sln)$ |
| 2 | $2BaO + sln \rightleftharpoons 2BaCl_2 + 2H_2O(sln)$ |
| 3 | $MO + sln \rightleftharpoons MCl_2 + H_2O(sln)$ |
| 4 | $UO_3 + sln \rightleftharpoons UO_2Cl_2 + H_2O(sln)$ |
| 5 | $2Ba + O_2 \rightleftharpoons 2BaO$ |
| 6 | $M + 0.5O_2 \rightleftharpoons MO$ |
| 7 | $U + 1.5O_2 \rightleftharpoons UO_3$ |
| 8 | $2Ba + M + U + 3O_2 \rightleftharpoons Ba_2MUO_6$ |

The latter analysis yields very similar results. As mentioned already in [2006CHE/SMI3], the disagreement with the results of [1985GEN/FUG], [1982MOR/FUG], [1983MOR/WIL2] probably partly originates from the values of the dissolution enthalpies of BaO(cr) and SrO(cr) measured by [2006CHE/SMI3], which are in strong disagreement with those reported by [1990COR/KON2] in 1 mol·dm$^{-3}$ HCl(aq) medium. The BaO(cr) and SrO(cr) samples used by [2006CHE/SMI3] might have contained some carbonate and/or hydroxide impurities. The dissolution enthalpy of $UO_3$ in 1 mol·dm$^{-3}$ HCl(aq) medium reported by [2006CHE/SMI3] seems reasonable, and is in good agreement with that reported by Cordfunke *et al.* [1976COR/OUW] in 4.98 mol·dm$^{-3}$ HCl(aq) medium, *i.e.*, – (64.98 ± 0.3) kJ·mol$^{-1}$. We could not find any reference data for the dissolution enthalpies of CaO(cr) and MgO(cr) in 1 mol·dm$^{-3}$ HCl(aq) medium. Using corrected values for the dissolution enthalpies of BaO(cr) and SrO(cr) [1990COR/KON2], the standard enthalpies of formation listed in Table A-148 are derived, which are in better agreement with the selected values in [2003GUI/FAN]. The final results are still not satisfactory, however. [2006KNY/CHE] do not report the quantities of material dissolved, so that one cannot judge if all solutions had a similar final concentration.

Table A-148: Re-assessment of the standard enthalpies of formation of $Ba_2MUO_6$ based on the dissolution enthalpies measured by [2006KNY/CHE] and dissolution enthalpies of BaO(cr) and SrO(cr) reported by [1990COR/KON2].

| Sample | $\Delta_r H^\circ_{diss}$ (298 K) in 1 mol·dm$^{-3}$ HCl(aq)[(a)] | $\Delta_r H^\circ_{diss}$ (298 K) in 1 mol·dm$^{-3}$ HCl(aq)[(b)] | **$\Delta_f H^\circ$($Ba_2MUO_6$, cr, 298 K)**[(c)] | $\Delta_f H^\circ$($Ba_2MUO_6$, cr, 298 K)[(d)] |
|---|---|---|---|---|
| $Ba_2MgUO_6$ | – (418.6 ± 0.5) | – (451.2 ± 3.9) [1982MOR/FUG] | – **(3241.3 ± 5.3)** | – (3245.9 ± 6.5) |
| $Ba_2CaUO_6$ | – (406.7 ± 0.8) | – (477.6 ± 2.0) [1985GEN/FUG] | – **(3190.3 ± 5.4)** | – (3295.8 ± 5.9) |
| $Ba_2SrUO_6$ | – (531.7 ± 4.7) | – (524.6 ± 1.1) [1985GEN/FUG] | – **(3230.6 ± 7.1)** | – (3257.3 ± 5.7) |
| $Ba_3UO_6$ | – (468.0 ± 2.2) | – (555.4 ± 1.5) [1983MOR/WIL2] | – **(3280.9 ± 6.2)** | – (3210.4 ± 8.0) |

(a) Dissolution enthalpies reported by [2006KNY/CHE]
(b) Dissolution enthalpies reported by [1982MOR/FUG], [1985GEN/FUG], [1983MOR/WIL2]
(c) Enthalpies of formation recalculated in this review based on the dissolution enthalpies of [2006KNY/CHE] for $Ba_2MUO_6$, and corrected values of the dissolution enthalpies of SrO(cr) and BaO(cr) [1990COR/KON2].
(d) Enthalpies of formation reported by [1982MOR/FUG], [1985GEN/FUG], [1983MOR/WIL2]

In view of the apparent discrepancies in the work of [2006CHE/KNY], we prefer in this review to retain the assessments of [1982MOR/FUG], [1983MOR/WIL2], [1985GEN/FUG] and the enthalpies of formation recommended by [1992GRE/FUG], [2003GUI/FAN]:

$$\Delta_f H^\circ_m (Ba_2MgUO_6, \text{cr}, 298.15\ \text{K}) = -(3245.9 \pm 6.5)\ \text{kJ·mol}^{-1}$$

$$\Delta_f H^o_m (Ba_2CaUO_6, cr, 298.15\ K) = -(3295.8 \pm 5.9)\ kJ \cdot mol^{-1}$$

$$\Delta_f H^o_m (Ba_2SrUO_6, cr, 298.15\ K) = -(3257.3 \pm 5.7)\ kJ \cdot mol^{-1}$$

$$\Delta_f H^o_m (Ba_3UO_6, cr, 298.15\ K) = -(3210.4 \pm 8.0)\ kJ \cdot mol^{-1}.$$

**[2006KNY/CHE2]**

The authors report the measurement of the enthalpy of formation at 298.15 K of $Ba_2Sm_{2/3}UO_6$ by reaction calorimetry as well as low temperature heat capacity in the temperature range 80-300 K by adiabatic vacuum calorimetry. $Ba_2Sm_{2/3}UO_6$ was prepared by solid state synthesis from $UO_3$(cr), BaO(cr) and $Sm_2O_3$(cr) mixed in stoichiometric amounts, and heated at 1073 K (3 hours), 1373 K (3 hours) and 1553 K (20 hours). The samples were characterised at room temperature using X-ray diffraction, but were not analysed chemically. $Ba_2Sm_{2/3}UO_6$ adopts a perovskite structure [1972KEM/HOF].

The enthalpy of formation was measured in 1 $mol \cdot dm^{-3}$ hydrochloric acid medium. The calorimeter used a 40 $cm^3$ Teflon calorimetric ampule. The temperature was monitored with a Pt resistance thermometer accurate to ± 0.001 K. The error on the reaction enthalpies was estimated not to exceed 1.5-1.8 %. The thermochemical cycle used to derive the standard formation enthalpy is the following:

$$UO_3(cr) + \text{solvent} \rightarrow \text{solution 1} \qquad (A.361)$$

$$BaO(cr) + 1/2\,\text{solution 1} \rightarrow 1/2\,\text{solution 2} \qquad (A.362)$$

$$Sm_2O_3(cr) + \text{solution 2} \rightarrow \text{solution 3} \qquad (A.363)$$

$$Ba_2Sm_{2/3}UO_6 + \text{solvent} \rightarrow \text{solution 4} \qquad (A.364)$$

The authors assume that the solutions formed from Reactions (A.363) and (A.364) are identical, and derive the standard enthalpy of formation from the equilibrium Reaction (A.365):

$$UO_3(cr) + 2BaO(cr) + 1/3Sm_2O_3(cr) \rightleftharpoons Ba_2Sm_{2/3}UO_6(cr) \qquad (A.365)$$

whose reaction enthalpy is given by $\Delta_r H°(A.365) = \Delta_r H°(A.361) + 2\Delta_r H°(A.362) + 1/3\Delta_r H°(A.363) - \Delta_r H°(A.364)$ (known from the experimentally determined enthalpies of solutions (A.361)-(A.364)).

The same method was applied for the determination of the enthalpies of formation of $Ba_2M^{II}UO_6$(cr) ($M^{II}$ = Mg, Ca, Sr, Ba) [2006KNY/CHE], [2006CHE/SMI3]. The derived values were found in strong disagreement with those reported in the literature, however, as detailed in Appendix A: see [2006KNY/CHE], [2006CHE/SMI3].

The dissolution enthalpy of $UO_3$ in 1 mol·dm$^{-3}$ HCl(aq) medium reported by [2006CHE/KNY2], *i.e.*, – (61.7 ± 0.8) kJ·mol$^{-1}$, seems reasonable, and is in good agreement with that reported by Cordfunke *et al.* [1976COR/OUW] in 4.98 mol·dm$^{-3}$ HCl(aq) medium, *i.e.*, – (64.98 ± 0.3) kJ·mol$^{-1}$. The dissolution enthalpy of BaO(cr) measured by [2006CHE/KNY2] in 1 mol·dm$^{-3}$ HCl(aq), *i.e.*, – (193.8 ± 2.8) kJ·mol$^{-1}$, is in strong disagreement with that reported by [1990COR/KON2] in the same medium, *i.e.*, – (273.08 ± 0.24) kJ·mol$^{-1}$), however. The BaO(cr) sample used by [2006CHE/KNY2] might have contained some carbonate and/or hydroxide impurities. This discrepancy might be the reason for the poor agreement between the results of [2006KNY/CHE], [2006CHE/SMI3] and those selected by [2003GUI/FAN] for the series $Ba_2M^{II}UO_6$(cr) ($M^{II}$ = Mg, Ca, Sr, Ba) (See Appendix A [2006KNY/CHE], [2006CHE/SMI3]). The enthalpy of dissolution of $Sm_2O_3$(cr) reported by [2006CHE/KNY2] in 1 mol·dm$^{-3}$ HCl(aq), *i.e.*, – (364.2 ± 0.3) kJ·mol$^{-1}$, seems again in rather poor agreement with the data available in the literature [2014KON/BEN]: Montgomery and Hubert reported – (408.8 ± 1.4) kJ·mol$^{-1}$ in 0.48 mol·dm$^{-3}$ HCl(aq) [1959MON/HUB], Baker *et al.* found – (417.1 ± 1.2) kJ·mol$^{-1}$ in 2 mol·dm$^{-3}$ HCl(aq) [1972BAK/FIT] and – (406.7 ± 4.6) kJ·mol$^{-1}$ in 3.99 mol·dm$^{-3}$ HCl(aq) [1972BAK/FIT], Hennig and Oppermann found – (412.8 ± 0.5) kJ·mol$^{-1}$ in 4 mol·dm$^{-3}$ HCl(aq) [1997HEN/OPP]. In addition, [2006CHE/KNY2] do not report the quantities of material dissolved, so that one cannot judge if all solutions had a similar final concentration. In view of the aforementioned discrepancies, the present review cannot select the reported enthalpy of formation for $Ba_2Sm_{2/3}UO_6$(cr).

The heat capacity in the temperature range 80-300 K was measured using adiabatic vacuum calorimetry. The authors unfortunately did not report their experimental data, but only the standard thermodynamic functions (standard heat capacity, entropy, enthalpy increment and free energy) calculated every 10 K between 80 and 300 K after analysis of their data. The derived heat capacity at 298.15 K, *i.e.*, (186.4 J·K$^{-1}$·mol$^{-1}$) is much lower (14.8 %) than the estimated value using Neumann Kopp's rule applied to BaO(cr) [1994COR/LAA], $UO_3$(cr) [2014KON/BEN], and $Sm_2O_3$(cr) [2014KON/BEN], *i.e.*, (214.0 J·K$^{-1}$·mol$^{-1}$). This review accepts the derived standard heat capacity at 298.15 K, but assigns a high uncertainty (3 %) given the poor agreement with NK's rule and since the $Ba_2Sm_{2/3}UO_6$ material was only characterised using X-ray diffraction:

$$C^{\circ}_{p,\mathrm{m}}(Ba_2Sm_{2/3}UO_6, \mathrm{cr}, 298.15\ \mathrm{K}) = (186.4 \pm 5.6)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

[2006CHE/KNY2] used the method of Kelley-Parks [1929KEL/PAR] to estimate the heat capacity values below 80 K, and thereafter the standard entropy at 298.15 K by integration of the curve ($C^{\circ}_{p,\mathrm{m}}/T$) = f($T$). The values below 80 K were calculated from the equation $C^{\circ}_{p,\mathrm{m}}(Ba_2Sm_{2/3}UO_6) = (0.6849 + 0.0019T) \times C^{\circ}_{p,\mathrm{m}}(Ba_2SrUO_6, \mathrm{cr}, T)$ where the heat capacity of $Ba_2SrUO_6$(cr) was chosen as reference compound [2006CHE/SMI3]. This review assigns a rather large uncertainty (3 %) to the derived standard entropy as the method employed relies on an

approximation below 80 K. The measurement needs to be completed below 80 K to yield a more reliable final result:

$$S^{o}_{m}(Ba_2Sm_{2/3}UO_6, cr, 298.15\ K) = (244.1 \pm 7.3)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

**[2007CHE/KNY]**

The authors report the measurement of the low temperature heat capacity of $Ba(Sc_{2/3}U_{1/3})O_3$ and $Ba(Y_{2/3}U_{1/3})O_3$ in the temperature range 80-350 K using adiabatic vacuum calorimetry. $Ba(Sc_{2/3}U_{1/3})O_3$ and $Ba(Y_{2/3}U_{1/3})O_3$ were prepared by solid state synthesis from $UO_3$, $BaCO_3$, $Sc_2O_3$ and $Y_2O_3$ mixed in stoichiometric amounts, and heated at 1373 K (two hours) and 1573 K (two hours). The samples were characterised at room temperature using X-ray diffraction, but were not analysed chemically. Both structures were reported isostructural and were indexed with a cubic cell ($a$ = 8.419(2) and $a$ = 8.661(6) Å, respectively).

The error on the heat capacity measurements collected with a BKT-3 adiabatic vacuum calorimeter were estimated not to exceed 0.2 %. The authors unfortunately did not report their experimental data, but only the standard thermodynamic functions (standard heat capacity, entropy, enthalpy increment and free energy) calculated every 10 K between 0 and 340 K after analysis of their data.

The derived heat capacities at 298.15 K are in good agreement with Neumann Kopp's rule applied to BaO(cr) [1994COR/LAA], $UO_3$(cr) [2014KON/BEN], $Sc_2O_3$(cr) [1995BAR], and $Y_2O_3$(cr) [1995BAR] as reported in Table A-149.

Table A-149: Experimental heat capacity values at 298.15 K measured by [2007CHE/KNY] and comparison with those predicted from NK's rule.

| Compound | $C^{o}_{p,m}$ (298.15 K)[(a)] /J·K$^{-1}$·mol$^{-1}$ | $C^{o}_{p,m}$ (298.15 K)[(b)] /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|
| $Ba_3Sc_2UO_9$ | (313.5 ± 0.6) | 317.1 |
| $Ba_3Y_2UO_9$ | (330.6 ± 0.6) | 325.5 |

(a) Experimental data from [2007CHE/KNY]
(b) Estimated using NK's rule applied to BaO(cr) [1994COR/LAA], $UO_3$(cr) [2014KON/BEN], $Sc_2O_3$(cr) [1995BAR], and $Y_2O_3$(cr) [1995BAR].

This review accepts the derived standard heat capacities at 298.15 K, but assigns higher uncertainties since the materials were only characterised using X-ray diffraction:

$$C^{o}_{p,m}(Ba_3Sc_2UO_9, cr, 298.15\ K) = (313.5 \pm 1.9)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$C^{o}_{p,m}(Ba_3Y_2UO_9, cr, 298.15\ K) = (330.6 \pm 2.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

[2007CHE/KNY] used the method of Kelley-Parks [1929KEL/PAR] to estimate the heat capacity values below 80 K, and thereafter the standard entropy at 298.15 K by integration of the curve ( $C^{o}_{p,m}/T$) = f($T$)). This review assigns a rather large uncertainty (3 %) to the derived standard entropies as the method employed relies on an approximation below 80 K. The measurements need to be updated below 80 K to yield a more reliable final result:

$$S^{o}_{m}(Ba_3Sc_2UO_9, cr, 298.15\ K) = (383.1 \pm 11.5)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}(Ba_3Y_2UO_9, cr, 298.15\ K) = (416.4 \pm 12.5)\ J\cdot K^{-1}\cdot mol^{-1}.$$

**[2007POP/COL]**

The low temperature heat capacity of $BaUO_4$ was measured over the temperature range 1.911 to 292.58 K using thermal relaxation calorimetry with a Physical Property Measurement System (PPMS, Quantum Design). The enthalpy increments were furthermore measured in the temperature range 484.2 to 1566.4 K using drop calorimetry. $BaUO_4$ was prepared from $BaCO_3$ and $U_3O_8$ mixed in stoichiometric amounts. The X-ray diffraction analysis did not show any secondary phases. However, the authors did not perform any further chemical analysis of their sample. The authors derived the following thermodynamic functions at 298.15 K: $C^{o}_{p,m}(BaUO_4, cr, 298.15\ K) = (123.11 \pm 3.7)\ J\cdot K^{-1}\cdot mol^{-1}$ and $S^{o}_{m}(BaUO_4, cr, 298.15\ K) = (151.9 \pm 4.6)\ J\cdot K^{-1}\cdot mol^{-1}$.

These results are in very good agreement with those of [1980OHA/FLO] obtained on a well-characterised sample using adiabatic calorimetry, *i.e.*, $C^{o}_{p,m}(298.15\ K) = (125.27 \pm 0.25)\ J\cdot K^{-1}\cdot mol^{-1}$ and $S^{o}_{m}(298.15\ K) = (153.97 \pm 0.31)\ J\cdot K^{-1}\cdot mol^{-1}$. They are in strong disagreement with those of [1980WES/ZAI], who found $C^{o}_{p,m}(298.15\ K) = 143.84\ J\cdot K^{-1}\cdot mol^{-1}$ and $S^{o}_{m}(298.15\ K) = (177.84 \pm 0.33)\ J\cdot K^{-1}\cdot mol^{-1}$. The material in the latter study was not characterised chemically, however, and [1980OHA/FLO] questioned its purity. In addition, the results of [2007POP/COL] and [1980OHA/FLO] are in better agreement with the trend followed by the alkali and alkaline-earth uranates $Na_2UO_4$, $Cs_2UO_4$, $MgUO_4$, $CaUO_4$, and α-$SrUO_4$ as shown by [2008KON/POP].

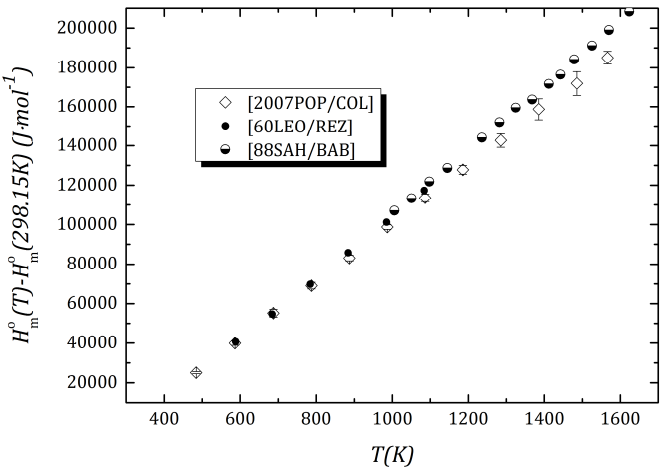
[2003GUI/FAN] accepted the heat capacity and entropy values of [1980OHA/FLO], but increased both uncertainties to ± 2.5 $J\cdot K^{-1}\cdot mol^{-1}$. This review retains the values of [2003GUI/FAN], [1980OHA/FLO] and assigned uncertainties since they were derived on a well-characterised material (chemical and spectrochemical analyses).

$$C^{o}_{p,m}(BaUO_4, cr, 298.15\ K) = (125.3 \pm 2.5)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}(BaUO_4, cr, 298.15\ K) = (154.0 \pm 2.5)\ J\cdot K^{-1}\cdot mol^{-1}.$$

The enthalpy increments as measured by drop calorimetry by [2007POP/COL] are compared in Figure A-12 to the results of Saha *et al.* from 1006 to 1667 K [1988SAH/BAB], and Leonidov *et al.* from 589 to 1084 K [1960LEO/REZ] as recalculated by O'Hare *et al.* [1980OHA/FLO]. The results of [2007POP/COL] are in good agreement with those of [1960LEO/REZ], but about 5-7 % lower than [1988SAH/BAB]. The measurements of [1988SAH/BAB] merge smoothly with those of [1960LEO/REZ].

Figure A-12: Enthalpy increment measurements of [1960LEO/REZ], [1988SAH/BAB] and [2007POP/COL] reported for $BaUO_4$.

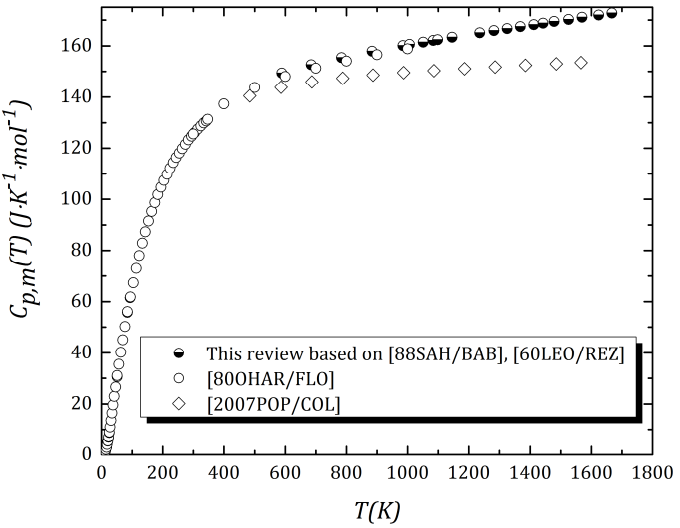



In this review, the enthalpy increment data of Saha *et al.* [1988SAH/BAB] were fitted together with those of Leonidov *et al.* [1960LEO/REZ]. The fitting equation was constrained with the selected value $C_{p,\mathrm{m}}^{\mathrm{o}}(BaUO_4, \mathrm{cr}, 298.15\ \mathrm{K}) = 125.3\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and imposing the condition $H_{\mathrm{m}}(T) - H_{\mathrm{m}}^{\mathrm{o}}(298.15\,\mathrm{K}) = 0$ at 298.15 K. The derived heat capacity equation merges smoothly with the low temperature results of O'Hare *et al.* [1980OHA/FLO]. The heat capacity equation determined in the work of Popa *et al.* gives lower values than derived herein. Moreover, their results do not fit well with those of [1980OHA/FLO] in the range 300-350 K. Therefore, the enthalpy and heat capacity functions from 298.15 to 1667 K are best represented using the data of Saha *et al.* [1988SAH/BAB] and Leonidov *et al.* [1960LEO/REZ]:

$$H_{\mathrm{m}}(T) - H_{\mathrm{m}}^{\mathrm{o}}(298.15\,\mathrm{K}) = 146.43\ T + 8.1350 \times 10^{-3}\ T^2 + 2.30987 \times 10^{6}\ T^{-1} - 5.2130 \times 10^{4}\ \mathrm{J{\cdot}mol^{-1}}$$

$$C_{p,\mathrm{m}}^{\mathrm{o}}(BaUO_4, \mathrm{cr}, T) = 146.43 + 1.6270 \times 10^{-2}\ T - 2.30987 \times 10^{6}\ T^{-2}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

Figure A-13: Comparison between the heat capacity equations derived in this review and in the work of [2007POP/COL] and [1980OHA/FLO].




**[2008CHE/KNY]**

[2008CHE/KNY] report the solid state synthesis, X-ray diffraction characterisation, infrared spectroscopy, and determination of the enthalpies of formation of the series $Ba_2A^{II}UO_6$ ($A^{II}$ = Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb) using solution calorimetry. The compounds were synthesised by solid state reaction between $UO_3$(cr), $M^{II}O$(cr) and BaO(cr) at 1173 K. The series $A^{II}$ = (Mn, Fe, Co) was prepared in evacuated quartz ampules for 50 hours with intermediate regrinding steps every five hours. The series $A^{II}$ = (Zn, Cd, Pb) was heated in alundum crucibles for 1.5-2 hours with intermediate regrinding steps every 0.3 hours. $Ba_2NiUO_6$ and $Ba_2CuUO_6$ were also synthesised in alundum crucibles by heating for 50 hours with intermediate regrinding steps every five hours. The $Ba_2A^{II}UO_6$ ($A^{II}$ = Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb) series shows a perovskite structure. $Ba_2A^{II}UO_6$ compounds with $A^{II}$ = (Mn,Fe,Co,Ni,Zn) have cubic symmetry, in space group *Fm3m* [2008CHE/KNY]. $Ba_2CuUO_6$, $Ba_2CdUO_6$, and $Ba_2CdUO_6$ crystallise in the tetragonal, orthorhombic and cubic systems, respectively.

The solution calorimetry studies were performed with an upgraded calorimeter (designed by Skuratov) in 2 mol·dm$^{-3}$ hydrochloric acid medium for $Ba_2A^{II}UO_6$ ($A^{II}$ = Mn, Fe, Cu, Zn, and Cd) (see Scheme 1); and in a 4 mol·dm$^{-3}$ HCl(aq) + 0.1 mol·dm$^{-3}$ $Na_2EDTA$ medium in 7.5:1 ratio for $Ba_2A^{II}UO_6$ ($A^{II}$ = Co, Ni, Pb) (see scheme 2). The thermochemical cycles used to derive the standard formation enthalpies are the following:

Scheme 1:

$$UO_3(cr) + \text{solvent}\,1 \rightarrow \text{solution}\,1 \quad \text{(A.366)}$$

$$BaO(cr) + 1/2\,\text{solution}\,1 \rightarrow 1/2\,\text{solution}\,2 \quad \text{(A.367)}$$

$$A^{II}O(cr) + \text{solution}\,2 \rightarrow \text{solution}\,3 \quad \text{(A.368)}$$

$$Ba_2A^{II}UO_6 + \text{solvent}\,1 \rightarrow \text{solution}\,4 \quad \text{(A.369)}$$

Scheme 2:

$$Ba_3UO_6(cr) + \text{solvent}\ 2 \rightarrow \text{solution}\ 5 \quad \text{(A.370)}$$

$$A^{II}(NO_3)_2 \cdot nH_2O(cr) + \text{solution}\,5 \rightarrow \text{solution}\,6 \quad \text{(A.371)}$$

$$Ba_2A^{II}UO_6 + \text{solvent}\ 2 \rightarrow \text{solution}\ 7 \quad \text{(A.372)}$$

$$Ba(NO_3)_2(cr) + \text{solution}\ 7 \rightarrow \text{solution}\ 8 \quad \text{(A.373)}$$

$$nH_2O(liq) + \text{solution}\ 8 \rightarrow \text{solution}\ 9 \quad \text{(A.374)}$$

($n$ = 0 for Pb; $n$ = 6 for Co, Ni)

The authors assume that the solutions formed from Reactions (A.368) and (A.369) are identical, and derive the standard enthalpy of formation for the series ($A^{II}$ = Mn, Fe, Cu, Zn, and Cd) from the equilibrium Reaction (A.375):

$$UO_3(cr) + 2BaO(cr) + A^{II}O(cr) \rightleftharpoons Ba_2A^{II}UO_6(cr) \quad \text{(A.375)}$$

whose reaction enthalpy is given by $\Delta_r H°(\text{A.375}) = \Delta_r H°(\text{A.366}) + 2\Delta_r H°(\text{A.367}) + \Delta_r H°(\text{A.368}) - \Delta_r H°(\text{A.369})$ (known from the experimentally determined enthalpies of solutions (A.366)-(A.369)).

The same method was applied for the determination of the enthalpies of formation of $Ba_2M^{II}UO_6(cr)$ ($M^{II}$ = Mg, Ca, Sr, Ba) [2006KNY/CHE], [2006CHE/SMI3]. The derived values were found in strong disagreement with those reported in the literature, however, as detailed in Appendix A: see [2006KNY/CHE], [2006CHE/SMI3].

In this review, it is suggested that solutions (A.368) and (A.369) should correspond to {$2BaCl_2 + A^{II}Cl_2 + UO_2Cl_2 + 4H_2O$ (in 2 mol·dm$^{-3}$ HCl)} after the reaction of $Ba_2A^{II}UO_6(cr)$ with 8HCl (in 2 mol·dm$^{-3}$ HCl(aq)). The thermochemical cycle (Scheme 1) as written corresponds to the following dissolution reactions:

$$UO_3(cr) + 8HCl(sln) \rightleftharpoons (UO_2Cl_2 + H_2O + 6HCl)(sln) \quad \text{(A.376)}$$

$$BaO(cr) + 1/2(UO_2Cl_2 + H_2O + 6HCl)(sln) \rightleftharpoons (BaCl_2 + 1/2\,UO_2Cl_2 + 3/2\,H_2O + HCl)(sln) \quad \text{(A.377)}$$

$$A^{II}O(cr) + 2(BaCl_2 + 1/2\,UO_2Cl_2 + 3/2\,H_2O + HCl)(sln) \rightleftharpoons (A^{II}Cl_2 + 2BaCl_2 + UO_2Cl_2 + 4H_2O)(sln) \quad (A.378)$$

$$Ba_2A^{II}UO_6 + 8HCl(sln) \rightleftharpoons (A^{II}Cl_2 + 2BaCl_2 + UO_2Cl_2 + 4H_2O)(sln) \quad (A.379)$$

The dissolution enthalpy of $UO_3$ in 2 mol·dm$^{-3}$ HCl(aq) medium reported by [2008CHE/KNY], *i.e.*, – (64.2 ± 1.3) kJ·mol$^{-1}$, seems reasonable, and is in good agreement with that reported by Cordfunke *et al.* [1976COR/OUW] in 4.98 mol·dm$^{-3}$ HCl(aq) medium, *i.e.*, – (64.98 ± 0.3) kJ·mol$^{-1}$. The dissolution enthalpy of BaO(cr) measured by [2008CHE/KNY] in 2 mol·dm$^{-3}$ HCl(aq), *i.e.*, – (188.7 ± 1.5) kJ·mol$^{-1}$, is in strong disagreement with that reported by [1990COR/KON2] in 1 mol·dm$^{-3}$ HCl(aq) medium, *i.e.*, – (273.08 ± 0.24) kJ·mol$^{-1}$, however. The BaO(cr) sample used by [2008CHE/KNY] might have contained some carbonate and/or hydroxide impurities. This discrepancy might be the reason for the poor agreement between the results of [2006KNY/CHE], [2006CHE/SMI3] and those selected by [2003GUI/FAN] for the series $Ba_2M^{II}UO_6$(cr) ($M^{II}$ = Mg, Ca, Sr, Ba) (See Appendix A [2006KNY/CHE], [2006CHE/SMI3]). [2008CHE/KNY] do not report the quantities of material dissolved, so that one cannot judge if all solutions had a similar final concentration. In view of the aforementioned discrepancies, the present review cannot select the reported enthalpies of formation for the series $Ba_2A^{II}UO_6$(cr) ($A^{II}$ = Mn, Fe, Cu, Zn, and Cd).

In addition, the authors suppose for the Scheme 2 that the solutions formed from Reactions (A.371) and (A.374) are identical, and derive the standard enthalpy of formation for the series ($A^{II}$ = Pb, Co, Ni) from the equilibrium Reaction (A.380):

$$Ba_3UO_6(cr) + A^{II}(NO_3)_2 \cdot nH_2O(cr) \rightleftharpoons Ba_2A^{II}UO_6 + Ba(NO_3)_2(cr) + nH_2O(liq) \quad (A.380)$$

whose reaction enthalpy is given by $\Delta_r H°(A.375) = \Delta_r H°(A.370) + \Delta_r H°(A.371) - \Delta_r H°(A.372) - \Delta_r H°(A.373) - \Delta_r H°(A.374)$ (known from the experimentally determined enthalpies of solutions (A.370)-(A.374)).

The dissolution enthalpy of $Ba_3UO_6$ measured by [2008CHE/KNY] in 4 mol·dm$^{-3}$ HCl(aq) + 0.1 mol·dm$^{-3}$ $Na_2EDTA$ medium, *i.e.*, – (454.8 ± 1.9) kJ·mol$^{-1}$, is in strong disagreement with that reported [1983MOR/WIL2] in 1 mol·dm$^{-3}$ HCl(aq) medium and selected by [2003GUI/FAN], *i.e.*, – (555.4 ± 1.5) kJ·mol$^{-1}$. In view of this discrepancy, the derived standard formation enthapies for the series $Ba_2A^{II}UO_6$(cr) ($A^{II}$ = Pd, Co, Ni) cannot be selected in the present review.

**[2008FU/AU]**

[2008FU/AU] report the crystal structure characterisation of the double perovskites $Ba_2M(II)M'(VI)O_6$ (M = Ca, Sr, M' = Te, W, U) using X-ray diffraction. In addition, non-ambient XRD data were collected for $Ba_2SrWO_6$ and $Ba_2CaWO_6$ in the temperature range 80 to 723 K. Neutron diffraction data were obtained at room temperature for $Ba_2CaUO_6$ and $Ba_2SrWO_6$ at the High-Flux Reactor (NRG, Petten). The structure of

$Ba_2SrWO_6$ was shown to be monoclinic in space group *I2/m*, in accordance with previous studies by Cox *et al.* [1984COX/HAS] and Kovba *et al.* [1971KOV/LYK]. $Ba_2SrTeO_6$ is rhombohedral in space group *R-3*, and not tetragonal as reported by [1984KUL/TRO]. The structure of $Ba_2CaUO_6$ was found monoclinic, in space group *P21/n*, isostructural with $Sr_2CaUO_6$ and $Ba_2SrUO_6$ [1987GRO/IJD]. Previous studies by Kemmler-Sack and Seeman [1975KEM/SAC] had assigned it an orthorhombic cell, while Gens *et al.* had described it with a slightly distorted cubic perovskite structure [1985GEN/FUG]. $Ba_2CaWO_6$ and $Ba_2CaTeO_6$ were shown to be cubic, in space group *Fm-3m*. In addition, $Ba_2SrWO_6$ was found to exhibit a *I2/m->R-3* phase transition around 598-623 K. As for $Ba_2CaWO_6$, a structural phase change from cubic *Fm-3m* to tetragonal *I4/m* was identified when cooling below about 240 K. [2008FU/AU] discuss in this paper the relationships between the tilt systems, tolerance factors, and covalency of the M/M' cations.

**[2008KON/POP]**

The low temperature heat capacities of $CaUO_4$ (rhombohedral in space group $R\bar{3}m$) and $SrUO_4$ (orthorhombic in space group *Pbcm)* were measured over the temperature range 2.0 to 305.1 K using thermal relaxation calorimetry with a Physical Property Measurement System (PPMS, Quantum Design). The $SrUO_4$ phase was incorrectly attributed to the low temperature α modification of the compound (α-$SrUO_{4-x}$ being rhombohedral, isostructural with $CaUO_4$, with a wide range of oxygen non-stoichiometries). In fact the measurement refers to the β form, isostructural with $BaUO_4$ (orthorhombic in space group *Pbcm*), according to the X-ray diffraction data. $CaUO_4$ and β-$SrUO_4$ were prepared from $CaCO_3$, $SrCO_3$ and $U_3O_8$ mixed in stoichiometric amounts. The X-ray diffraction analysis did not show any secondary phases. The authors did not perform any further chemical analysis of their sample.

The heat capacity and entropy values adopted in the reviews of [1992GRE/FUG], [2003GUI/FAN] for these two compounds at 298.15 K were based on the measurements of Westrum *et al.* [1980WES/ZAI], who reported thermodynamic functions for the series $MgUO_4$, $CaUO_4$, $SrUO_4$, and $BaUO_4$ using adiabatic calorimetry. Their results for $BaUO_4$ were in strong disagreement with those of [1980OHA/FLO] and [2007POP/COL], however. This stimulated [2008KON/POP] to re-assess the thermodynamic functions of $CaUO_4$ and $SrUO_4$. It should be noted that the low temperature heat capacity measurements of Westrum *et al.* [1980WES/ZAI] also refer to the orthorhombic modification of $SrUO_4$, *i.e.*, to the β phase, and not to α as suggested by [1992GRE/FUG], [2003GUI/FAN]. There is a confusion in the literature with respect to the assignment of the α and β polymorphs, as illustrated by the work of [1972SAW], assigning the α form to the orthorhombic structure.

[2008KON/POP] derived the following thermodynamic functions at 298.15 K: $C^{o}_{p,m}$ ($CaUO_4$, cr, 298.15 K) = (115.4 ± 2.4) J·K$^{-1}$·mol$^{-1}$, $S^{o}_{m}$ ($CaUO_4$, cr, 298.15 K) =

(114.7 ± 1.6) J·K$^{-1}$·mol$^{-1}$, $C^{o}_{p,m}$ (β-$SrUO_4$, cr, 298.15 K) = (119.7 ± 2.4) J·K$^{-1}$·mol$^{-1}$, and $S^{o}_{m}$ (β-$SrUO_4$, cr, 298.15 K) = (147.2 ± 1.8) J·K$^{-1}$·mol$^{-1}$. This review agrees with this derivation of the thermodynamic functions.

The results obtained are significantly lower than those of Westrum *et al.* [1980WES/ZAI], *i.e.*, $C^{o}_{p,m}$ ($CaUO_4$, cr, 298.15 K) = 123.8 J·K$^{-1}$·mol$^{-1}$ and $C^{o}_{p,m}$ (β-$SrUO_4$, cr, 298.15 K) = 130.62 J·K$^{-1}$·mol$^{-1}$, as was the case for $BaUO_4$. The entropy value of β-$SrUO_4$ measured by [2008KON/POP] is moreover in good agreement with the trend followed by the alkali and alkaline-earth uranates $Na_2UO_4$, $Cs_2UO_4$ [1992GRE/FUG], $BaUO_4$ [2007POP/COL], and $MgUO_4$ [1980WES/ZAI]. $CaUO_4$ is found outside of the trend, but this is expected given that uranium is 8-fold coordinated in the latter phase, while it is 6-fold coordinated in $UO_3$ and along the series (Mg, Na, β-Sr, Ba, Cs).

In this review, the newly determined heat capacity and entropy values of [2008KON/POP] are retained since both studies [2007POP/COL] and [2008KON/POP] indicate that the measurements by Westrum *et al.* are probably in error [1980WES/ZAI]. The uncertainty on the results has been increased, however. The present review recommends:

$$C^{o}_{p,m}\ (CaUO_4, cr, 298.15K) = (115.4 \pm 3.5)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}\ (CaUO_4, cr, 298.15\ K) = (114.7 \pm 2.3)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$C^{o}_{p,m}\ (SrUO_4, \beta, 298.15K) = (119.7 \pm 3.6)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}\ (SrUO_4, \beta, 298.15K) = (147.2 \pm 2.9)\ J\cdot K^{-1}\cdot mol^{-1}.$$

[2008KON/POP] pointed out that the error between their results and those of Westrum *et al.* increased regularly with temperature for β-$SrUO_4$ (up to 9 %), while they remained quasi constant for $CaUO_4$ (5 % to 7 %), suggesting that the cause for discrepancy could be different for the two compounds, although the exact reason for the discrepancy could not be identified.

Combining the retained entropy values together with the enthalpies of formation recommended by [2003GUI/FAN], the Gibbs energies of formation of $CaUO_4$ and β-$SrUO_4$ were recalculated at 298.15 K in the present review:

$$\Delta_f G^{o}_{m}\ (CaUO_4, cr, 298.15\ K) = -\ (1886.798 \pm 2.404)\ kJ\cdot mol^{-1}$$

$$\Delta_f G^{o}_{m}\ (SrUO_4, \beta, 298.15\ K) = -\ (1878.381 \pm 5.469)\ kJ\cdot mol^{-1}.$$

**[2009CHE/KNY2]**

The authors report the measurement of the low temperature heat capacities of $Ba(In_{2/3}U_{1/3})O_3$ and $Sr(In_{2/3}U_{1/3})O_3$ in the temperature range 80-350 K using a BKT-3 adiabatic vacuum calorimeter. $Ba(In_{2/3}U_{1/3})O_3$ and $Sr(In_{2/3}U_{1/3})O_3$ were prepared by solid

state synthesis from $UO_3$, $BaCO_3$, $SrCO_3$, and $In_2O_3$ mixed in stoichiometric amounts, and heated at 1543 K for 70 hours. The samples were characterised at room temperature using X-ray diffraction, but were not analysed chemically. Both structures adopt a cubic perovskite type of structure with cell parameters $a$ = 8.496(2) Å [1979BER/GRE] and $a$ = 8.3363(3) Å [2009CHE/KNY2] for $Ba(In_{2/3}U_{1/3})O_3$ and $Sr(In_{2/3}U_{1/3})O_3$, respectively. The error on the heat capacity measurements were estimated not to exceed 0.2 % from 80 to 350 K. The authors unfortunately did not report their experimental data, but only the standard thermodynamic functions (standard heat capacity, entropy, enthalpy increment and free energy) calculated every 10 K between 0 and 340 K after analysis of their data.

The derived heat capacities at 298.15 K are in good agreement with Neumann Kopp's rule applied to BaO(cr) [1994COR/LAA], SrO(cr) [1994COR/LAA], $UO_3$(cr) [2003GUI/FAN], and $In_2O_3$(cr) [1995BAR] as reported in Table A-150.

Table A-150: Comparison between with the heat capacity values at 298.15 K measured by [2009CHE/KNY2] and those predicted from NK's rule.

| Compound | $C^{o}_{p,m}$ (298.15 K)[(a)] /J·K$^{-1}$·mol$^{-1}$ | $C^{o}_{p,m}$ (298.15 K)[(b)] /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|
| $Ba_3In_2UO_9$ | (329.1 ± 0.6) | 323.4 |
| $Sr_3In_2UO_9$ | (321.3 ± 0.6) | 317.4 |

(a) Experimental results of [2009CHE/KNY2]

(b) Estimation based on Neumann Kopp's rule (this review) from the data of BaO(cr) [1994COR/LAA], SrO(cr) [1994COR/LAA], $UO_3$(cr) [2003GUI/FAN], and $In_2O_3$(cr) [1995BAR].

This review accepts the derived standard heat capacities at 298.15 K, but assigns higher uncertainties since the materials were only characterised using X-ray diffraction:

$$C^{o}_{p,m}(Ba_3In_2UO_9, cr, 298.15\ K) = (329.1 \pm 2.0)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$C^{o}_{p,m}(Sr_3In_2UO_9, cr, 298.15\ K) = (321.3 \pm 1.9)\ J\cdot K^{-1}\cdot mol^{-1}.$$

[2009CHE/KNY2] used the method of Kelley-Parks [1929KEL/PAR] to estimate the heat capacity values below 80 K, and thereafter the standard entropy at 298.15 K by integration of the curve ( $C^{o}_{p,m}/T$) = f($T$) ). This review assigns a rather large uncertainty (3 %) to the derived standard entropies as the method employed relies on an approximation below 80 K. The measurements need to be completed below 80 K to yield a more reliable final result:

$$S^{o}_{m}(Ba_3In_2UO_9, cr, 298.15\ K) = (417.9 \pm 12.5)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}(Sr_3In_2UO_9, cr, 298.15\ K) = (384.6 \pm 11.5)\ J\cdot K^{-1}\cdot mol^{-1}.$$

**[2010CHE/KNY]**

[2010CHE/KNY] report the solid state synthesis, X-ray diffraction characterisation, infrared spectroscopy measurement, and determination of the enthalpies of formation of the series $Sr_2A^{II}UO_6$ ($A^{II}$ = Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Zn, and Cd) using solution calorimetry. The compounds were synthesised by reaction between $UO_3$(cr), $M^{II}O$(cr), $Sr_2O$(cr) or $Sr_2CO_3$(cr) in the temperature range 1173-1423 K. The $Sr_2A^{II}UO_6$ phases are reported isotructural, with a distorted monoclinic perovskite structure, in space group $P2_1/n$. The $Sr_2Mg^{II}UO_6$, $Sr_2Ba^{II}UO_6$ and $Sr_2Cd^{II}UO_6$ compounds were synthesised for the first time, and their crystal structures refined by the Rietveld method. In addition, IR spectra were collected in the range 4000-400 $cm^{-1}$, which revealed four type of absorption bands as for $Ba_2A^{II}UO_6$ [2008CHE/KNY].

The enthalpies of formation were estimated using solution calorimetry in a HCl(aq) (1 $mol \cdot dm^{-3}$ or 2 $mol \cdot dm^{-3}$) medium for $Sr_2A^{II}UO_6$ ($A^{II}$ = Mg, Ca, Sr, Ba, Mn, Fe, Zn, Cd) (see Scheme 1); and in a 4 $mol \cdot dm^{-3}$ HCl(aq) medium with 0.1 $mol \cdot dm^{-3}$ solution of Trilon B (in ratio 7.5:1) for $Sr_2Co^{II}UO_6$ and $Sr_2Ni^{II}UO_6$ (see Scheme 2). The thermochemical cycles used to derive the standard formation enthalpies are the followings:

Scheme 1:

$$UO_3(cr) + \text{solvent } 1 \rightarrow \text{solution } 1 \quad \text{(A.381)}$$

$$SrO(cr) + 1/2\,\text{solution } 1 \rightarrow 1/2\,\text{solution } 1 \quad \text{(A.382)}$$

$$A^{II}O(cr) + \text{solution } 2 \rightarrow \text{solution } 3 \quad \text{(A.383)}$$

$$Sr_2A^{II}UO_6 + \text{solvent } 1 \rightarrow \text{solution } 4 \quad \text{(A.384)}$$

Scheme 2:

$$Sr_3UO_6(cr) + \text{solvent } 2 \rightarrow \text{solution } 5 \quad \text{(A.385)}$$

$$A^{II}(NO_3)_2 \cdot nH_2O(cr) + \text{solution } 5 \rightarrow \text{solution } 6 \quad \text{(A.386)}$$

$$Sr_2A^{II}UO_6 + \text{solvent } 2 \rightarrow \text{solution } 7 \quad \text{(A.387)}$$

$$Sr(NO_3)_2(cr) + \text{solution } 7 \rightarrow \text{solution } 8 \quad \text{(A.388)}$$

$$nH_2O(liq) + \text{solution } 8 \rightarrow \text{solution } 9 \quad \text{(A.389)}$$

The authors assume that the solutions formed from Reactions (A.383) and (A.384) are identical, and derive the standard enthalpy of formation for the series ($A^{II}$ = Mg, Ca, Sr, Ba, Mn, Fe, Zn, Cd) from the equilibrium Reaction (A.390):

$$UO_3(cr) + 2SrO(cr) + A^{II}O(cr) \rightleftharpoons Sr_2A^{II}UO_6(cr) \quad \text{(A.390)}$$

whose reaction enthalpy is given by $\Delta_r H°(A.390) = \Delta_r H°(A.381) + 2\Delta_r H°(A.382) + \Delta_r H°(A.383) - \Delta_r H°(A.384)$ (known from the experimentally determined enthalpies of solutions (A.381)-(A.384)).

The same method was already applied to determine the enthalpies of formation of $Ba_2M^{II}UO_6$(cr) ($M^{II}$ = Mg, Ca, Sr, Ba) [2006KNY/CHE], [2006CHE/SMI3]. The derived values were found in strong disagreement with those reported in the literature, however, as detailed in Appendix A: see [2006KNY/CHE], [2006CHE/SMI3].

In this review, it is suggested that solutions (A.383) and (A.384) should correspond to {$2SrCl_2+A^{II}Cl_2+UO_2Cl_2+4H_2O$(in 1 mol·dm$^{-3}$ HCl)} after the reaction of $Sr_2A^{II}UO_6$(cr) with 8HCl (in 1 mol·dm$^{-3}$ HCl(aq)). The thermochemical cycle (Scheme 1) as written above corresponds to the following dissolution reactions:

$$UO_3(cr) + 8HCl(sln) \rightleftharpoons (UO_2Cl_2 + H_2O + 6HCl)(sln) \quad \text{(A.391)}$$

$$SrO(cr) + 1/2(UO_2Cl_2 + H_2O + 6HCl)(sln) \rightleftharpoons (SrCl_2 + 1/2UO_2Cl_2 + 3/2H_2O + HCl)(sln) \quad \text{(A.392)}$$

$$A^{II}O(cr) + 2(SrCl_2 + 1/2UO_2Cl_2 + 3/2H_2O + HCl)(sln) \rightleftharpoons (A^{II}Cl_2 + 2SrCl_2 + UO_2Cl_2 + 4H_2O)(sln) \quad \text{(A.393)}$$

$$Sr_2A^{II}UO_6 + 8HCl(sln) \rightleftharpoons (A^{II}Cl_2 + 2SrCl_2 + UO_2Cl_2 + 4H_2O)(sln) \quad \text{(A.394)}$$

Among the derived values, only $Sr_3UO_6$(cr) was reported already in the literature. The value found in the study of [2010CHE/KNY], *i.e.*, $\Delta_f H^o_m$ ($Sr_3UO_6$, cr, 298.15 K) = – (2995.0 ± 6.0) kJ·mol$^{-1}$, is in strong disagreement with that reported by [1999COR/BOO], [1967COR/LOO], [1983MOR/WIL2] and with the value recommended by [2003GUI/FAN], *i.e.*, $\Delta_f H^o_m$ ($Sr_3UO_6$, cr, 298.15 K) = – (3263.5 ± 3.0) kJ·mol$^{-1}$. A similar discrepancy was already noted for the enthalpies of formation of $Ba_2SrUO_6$, $Ba_2CaUO_6$, $Ba_2MgUO_6$, and $Ba_3UO_6$ determined by [2006KNY/CHE], [2006CHE/SMI3] with the same method.

The standard enthalpy of formation of $Sr_3UO_6$ can be derived with the following thermochemical cycle (Table A-151), with $\Delta_f H^o_m$ ($Sr_3UO_6$, cr, 298.15 K) = $\Delta_r H^o_8 = \Delta_r H^o_1 + \Delta_r H^o_2 + \Delta_r H^o_3 + \Delta_r H^o_4 + \Delta_r H^o_5 + \Delta_r H^o_6 + \Delta_r H^o_7$.

Table A-151: Thermochemical cycle used in this review to assess the standard enthalpy of formation of $Sr_3UO_6$ based on the results of [2006CHE/SMI3].

| | Reaction | $\Delta_rH^o$(298.15 K) in 1 M HCl(aq) | Reference |
|---|---|---|---|
| 1 | $Sr_3UO_6 + sln \rightleftharpoons \{2SrCl_2 + SrCl_2 + UO_2Cl_2 + 4H_2O\}(sln)$ | – (473.8 ± 2.0) | [2010CHE/KNY] |
| 2 | $2SrO + sln \rightleftharpoons \{SrCl_2 + 2H_2O\}(sln)$ | – (224.0 ± 3.0) | [2010CHE/KNY] |
| 3 | $SrO + sln \rightleftharpoons \{SrCl_2 + H_2O\}(sln)$ | – (112.0 ± 1.4) | [2010CHE/KNY] |
| 4 | $UO_3 + sln \rightleftharpoons \{UO_2Cl_2 + H_2O\}(sln)$ | – (61.7 ± 0.8) | [2010CHE/KNY] |
| 5 | $2Sr + O_2 \rightleftharpoons 2SrO$ | – (1181.2 ± 1.8) | [2003GUI/FAN] |
| 6 | $Sr + 0.5O_2 \rightleftharpoons SrO$ | – (590.6 ± 0.9) | [2003GUI/FAN] |
| 7 | $U + 1.5O_2 \rightleftharpoons UO_3$ | – (1223.8 ± 1.2) | [2003GUI/FAN] |
| 8 | $2Sr + Sr + U + 3O_2 \rightleftharpoons Sr_3UO_6$ | – **(2919.5 ± 4.6)** | **This review** |

The latter analysis yields $\Delta_f H_m^o(Sr_3UO_6, cr, 298.15\ K) = -(2919.5 \pm 4.6)$ kJ·mol$^{-1}$. The difference with the selected value [2003GUI/FAN] probably originates from the values of the dissolution enthalpy of SrO(cr) measured by [2010CHE/KNY], which is in strong disagreement with that reported by [1990COR/KON2] in 1 mol·dm$^{-3}$ HCl(aq) medium. The SrO(cr) sample used by [2010CHE/KNY] might have contained some carbonate and/or hydroxide impurities. Using the corrected value for the dissolution enthalpy of SrO(cr) [1990COR/KON2], one derives $\Delta_f H_m^o(Sr_3UO_6, cr, 298.15\ K) = -(3315.3 \pm 3.3)$ kJ·mol$^{-1}$. The latter value is 51.8 kJ·mol$^{-1}$ lower than selected in [2003GUI/FAN], however. The dissolution enthalpy of $UO_3$ in 1 mol·dm$^{-3}$ HCl(aq) medium reported by [2006CHE/SMI3] seems reasonable, and is in good agreement with that reported by Cordfunke *et al.* [1976COR/OUW] in 4.98 mol·dm$^{-3}$ HCl(aq) medium, *i.e.*, $-(64.98 \pm 0.3)$ kJ·mol$^{-1}$. The disagreement is also related to the value of the dissolution enthalpy of $Sr_3UO_6$(cr) measured in the work of [2010CHE/KNY]. Using the data of [1983MOR/WIL2] for the dissolution enthalpy of $Sr_3UO_6$(cr), and that of [1990COR/KON2] for the dissolution enthalpy of SrO(cr), one derives $\Delta_f H_m^o(Sr_3UO_6, cr, 298.15\ K) = -(3239.0 \pm 3.7)$ kJ·mol$^{-1}$, in better agreement with [2003GUI/FAN].

The present review disregards the result of [2010CHE/KNY] in view of the aforementioned discrepancies, and prefers that of [1983MOR/WIL2] since the associated standard enthalpy of formation, $-(3263.95 \pm 4.39)$ kJ·mol$^{-1}$, is in good agreement with that determined by [1999COR/BOO] in 5.075 mol·dm$^{-3}$ HCl(aq) medium, $-(3255.39 \pm 2.92)$ kJ·mol$^{-1}$, and that determined by [1967COR/LOO] in 6 mol·dm$^{-3}$ $HNO_3$(aq) medium, $-(3263.08 \pm 4.24)$ kJ·mol$^{-1}$. The standard enthalpy of formation of $Sr_3UO_6$(cr) recommended by [2003GUI/FAN] based on the mean of the values of [1967COR/LOO] and [1983MOR/WIL2] is retained:

$$\Delta_f H_m^o(Sr_3UO_6, cr, 298.15\ K) = -(3263.5 \pm 3.0)\ kJ \cdot mol^{-1}.$$

Given the discrepancy found for $Sr_3UO_6$, as well as $Ba_2SrUO_6$, $Ba_2CaUO_6$, $Ba_2MgUO_6$, and $Ba_3UO_6$ [2006KNY/CHE], [2006CHE/SMI3] measured with the same method, the values reported for the other $Sr_2A^{II}UO_6$ ($A^{II}$ = Mg, Ca, Ba, Mn, Fe, Zn, Cd) compounds cannot be selected in this review.

In addition, the authors suppose that the solutions formed from Reactions (A.386) and (A.389) are identical, and derive the standard enthalpy of formation for $Sr_2Co^{II}UO_6$ and $Sr_2Ni^{II}UO_6$ from the equilibrium Reaction (A.395):

$$Sr_3UO_6(cr) + A^{II}(NO_3)_2 \cdot nH_2O(cr) \rightleftharpoons Sr_2A^{II}UO_6 + Sr(NO_3)_2(cr) + nH_2O(liq) \quad (A.395)$$

whose reaction enthalpy is given by $\Delta_r H°(A.395) = \Delta_r H°(A.385) + \Delta_r H°(A.386) - \Delta_r H°(A.387) - \Delta_r H°(A.388) - \Delta_r H°(A.389)$ (known from the experimentally determined enthalpies of solutions (A.385)-(A.389)).

The dissolution enthalpy of $Sr_3UO_6$ measured by [2010CHE/KNY] in 4 mol·dm$^{-3}$ HCl(aq) medium with 0.1 mol·dm$^{-3}$ solution of Trilon B (in ratio 7.5:1), *i.e.*,

– (476.8 ± 2.0) kJ·mol$^{-1}$, is in strong disagreement with that reported [1983MOR/WIL2] in 1 mol·dm$^{-3}$ HCl(aq) medium and selected by [2003GUI/FAN], *i.e.*, – (550.1 ± 2.6) kJ·mol$^{-1}$. In view of this discrepancy, the derived standard formation enthalpies for the series $Sr_2A^{II}UO_6$(cr) ($A^{II}$ = Co, Ni) cannot be selected in the present review.

**[2010DAS/SIN]**

The heat capacities and enthalpy increments of $BaU_2O_7$, $Ba_2U_3O_{11}$, $Ba_{2.875}UO_{5.875}$ and $Ba_3UO_6$ were measured using Differential Scanning Calorimetry in continuous mode and a high-temperature Calvet calorimeter in the temperature ranges 126-304 K and 299-1011 K, respectively. $BaU_2O_7$, $Ba_2U_3O_{11}$, $Ba_{2.875}UO_{5.875}$ and $Ba_3UO_6$ were prepared from $BaCO_3$ and $U_3O_8$ mixed in stoichiometric amounts. The prepared samples were analysed using X-ray diffraction. The corresponding X-ray diffraction patterns showed rather poorly crystalline materials. The authors did not report any chemical analysis of their samples.

Heat capacity values at 298.15 K were obtained by least-squares analysis of the DSC data. These results are compared in Table A-152 to the values predicted from Neumann-Kopp's (NK) rule using the data of $BaUO_4$, $UO_3$ [2003GUI/FAN], BaO [1994COR/LAA]; and using the data of $UO_3$ [2003GUI/FAN] and BaO [1994COR/LAA], respectively.

Table A-152: Comparison between the DSC results of [2010DAS/SIN] and the values predicted by Neumann-Kopp's (NK) rule.

| Compound | Ba/U ratio | $C^{o}_{p,m}$ (298.15 K)[(a)] | $C^{o}_{p,m}$ (298.15 K)[(b)] | $C^{o}_{p,m}$ (298.15 K)[(c)] |
|---|---|---|---|---|
| **$BaU_2O_7$** | 0.5 | (190.4 ± 5.7) | 206.9[(b)] | 210.4[(c)] |
| **$Ba_2U_3O_{11}$** | 0.667 | (325.84 ± 9.8) | 335.7[(b)] | 339.1[(c)] |
| **$Ba_{2.875}UO_{5.875}$** | 2.875 | (215.04 ± 6.5) | 213.5[(b)] | 217.0[(c)] |
| **$Ba_3UO_6$** | 3 | (216.27 ± 6.5) | 219.4[(b)] | 222.9[(c)] |

(a) Experimental data recalculated from [2010DAS/SIN]
(b) Values obtained when applying Neumann-Kopp's rule to $BaUO_4$, $UO_3$, and BaO, *i.e.*, $C^{o}_{p,m}$ (298.15 K) = $x\,C^{o}_{p,m}$ ($BaUO_4$) + $y\,C^{o}_{p,m}$ ($UO_3$) + $z\,C^{o}_{p,m}$ (BaO)
(c) Values obtained when applying Neumann-Kopp's rule to $UO_3$ and BaO, *i.e.*, $C^{o}_{p,m}$ (298.15 K) = $y\,C^{o}_{p,m}$ ($UO_3$) + $z\,C^{o}_{p,m}$ (BaO)

The experimental value for $BaU_2O_7$ is much lower (8.0 to 9.5 %) than predicted by Neumann-Kopp's rule, which is rather unexpected. The same situation is observed for $Ba_2U_3O_{11}$, although less critical (2.9 to 3.9 %). The heat capacity values of $Ba_{2.875}UO_{5.875}$ and $Ba_3UO_6$ are in good agreement with NK considering the experimental uncertainties. This review recommends the following functions:

$$C^{o}_{p,m}(BaU_2O_7, cr, 298.15\ K) = (206.9 \pm 17.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$C^{o}_{p,m}\ (Ba_2U_3O_{11},\ cr,\ 298.15\ K) = (325.8 \pm 9.8)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$C^{o}_{p,m}\ (Ba_{2.875}UO_{5.875},\ cr,\ 298.15\ K) = (215.1 \pm 6.5)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

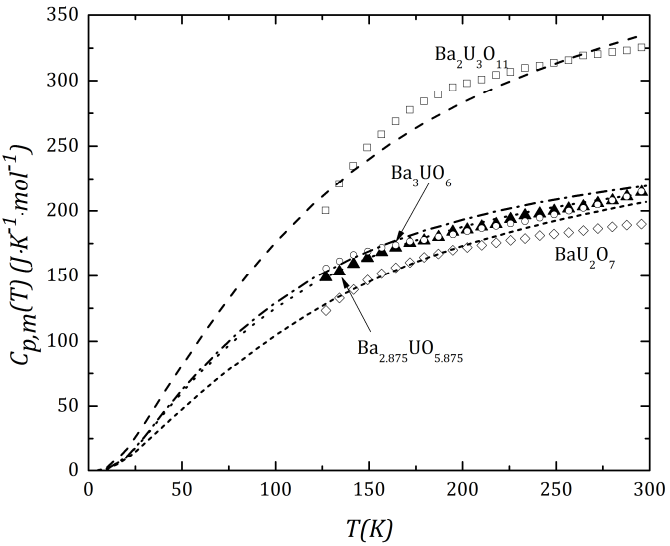
$$C^{o}_{p,m}\ (Ba_3UO_6,\ cr,\ 298.15\ K) = (216.3 \pm 6.5)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

The value in bracket is an estimation using NK. The data for $Ba_2U_3O_{11}$, $Ba_{2.875}UO_{5.875}$ and $Ba_3UO_6$ [2010DAS/SIN] are selected in this review. The heat capacity for $BaU_2O_7$ is listed in the table of data for scoping calculations. Complementary measurements using another technique such as adiabatic or relaxation calorimetry would be needed to confirm the values for $BaU_2O_7$ and $Ba_2U_3O_{11}$.

As their heat capacity data covered only the temperature range 127-298.15 K, the authors used approximations to estimate the heat capacity values below 127 K, and therefore derive the standard entropies at 298.15 K. In the temperature range 10-127 K, they used the additive rule based on the data of $BaUO_4$ [1980OHA/FLO], $UO_3$ [1988COR/WES], and BaO [1969GME2]. In the temperature range 0-10 K, the heat capacity was determined as $C^{o}_{p,m} = \alpha{\cdot}T^3$ by extrapolation of the previous functions in the range 5-25 K.

We have found a number of errors in the derivation of the entropy functions at 298.15 K. The entropy functions have been recalculated using the updated data for $BaUO_4$ [1980OHA/FLO], $UO_3$ [2014KON/BEN], and BaO [1994COR/LAA] in the temperature range 0-127 K, and the experimental data of [2010DAS/SIN] in the temperature range 127-298.15 K.

Figure A-14: Comparison between the experimental DSC results of [2010DAS/SIN] and the prediction based on Neumann-Kopp's rule in the temperature range 0-304 K (dotted lines).



The results are listed in Table A-153, and compared to previous estimations in the literature by [1988COR/IJD] based on phase diagrams calculations combined with experimental evidence. They are also compared to an estimation based on the additive contributions of $BaUO_4$ [1980OHA/FLO], $UO_3$ [2014KON/BEN], and BaO [1994COR/LAA], and based on the additive contributions of $UO_3$ [2014KON/BEN] and BaO [1994COR/LAA], considering the mixing configurational entropy to be 0 at 298.15 K. The data are also compared to the method of Latimer [1951LAT] as detailed in Appendix D.

Table A-153: Comparison of the standard entropies recalculated in this review from the data of [2010DAS/SIN] with estimations based on the additivity rule, and on the method of Latimer [1951LAT].

| Compound | Ba/U ratio | $S^o_m$ (298.15 K)[(a)] | $S^o_m$ (298.15 K)[(b)] | $S^o_m$ (298.15 K)[(c)] | $S^o_m$ (298.15 K)[(d)] | $S^o_m$ (298.15 K) [1988COR/IJD] |
|---|---|---|---|---|---|---|
| $BaU_2O_7$ | 0.5 | (246.7 ± 10.0) | 250.1 | 262.2 | 254.2 | (260 ± 5) |
| $Ba_2U_3O_{11}$ | 0.667 | **(421.9 ± 10.0)** | 416.2 | 428.4 | 411.2 | (405 ± 5) |
| $Ba_{2.875}UO_{5.875}$ | 2.875 | **(283.6 ± 5.0)** | 285.2 | 297.4 | 269.1 | |
| $Ba_3UO_6$ | 3 | **(288.6 ± 5.0)** | 294.0 | 306.1 | 276.6 | 298 |

(a) Value recalculated in this review based on the experimental data of [2010DAS/SIN];
(b) Values calculated with the additive rule applied to $BaUO_4$, $UO_3$, and BaO, *i.e.*, $S^o_m$ (298.15 K) = $x\ S^o_m$ ($BaUO_4$)+ $y\ S^o_m$ ($UO_3$)+ $z\ S^o_m$ (BaO);
(c) Values calculated with the additive rule applied to $UO_3$ and BaO, *i.e.*, $S^o_m$ (298.15 K) = $y\ S^o_m$ ($UO_3$)+z $S^o_m$ (BaO);
(d) Values calculated using the method of Latimer (see Appendix D).

The standard entropies at 298.15 K re-calculated in this review are:

$$S^o_m(Ba_2U_3O_{11}, cr, 298.15\ K) = (421.9 \pm 10.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$S^o_m(Ba_{2.875}UO_{5.875}, cr, 298.15\ K) = (283.6 \pm 5.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$S^o_m(Ba_3UO_6, cr, 298.15\ K) = (288.6 \pm 5.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

In the case of $BaU_2O_7$, the recalculated standard entropy was not retained since the corresponding heat capacity data showed rather unexpected results. The value estimated by [1988COR/IJD], [2003GUI/FAN] is retained for scoping calculations. As for $Ba_{2.875}UO_{5.875}$, the aforementioned value is in rather poor agreement with the experimental data of [2011DAS/SIN]. As detailed in Appendix A (section [2011DAS/SIN]), the entropy value derived from the latter study is preferred in this review. Complementary measurements using adiabatic or relaxation calorimetry are required over the full temperature range (0-298 K) to confirm the entropy functions for all four compositions.

Finally, the high temperature enthalpy increment data of [2010DAS/SIN] were fitted to simple polynomials in $T$ in this review, constraining the equation with the selected values for $C^o_{p,m}$ (298.15 K) and imposing the condition

$H_m(T) - H_m^o(298.15\,K) = 0$ at 298.15 K, yielding the following equations for the enthalpy increments and the heat capacity functions in Table A-154:

$BaU_2O_7$: $H_m(T) - H_m^o(298.15\,K) = 208.95\,T + 2.6510 \times 10^{-2}\,T^2 + 1.58738 \times 10^6\,T^{-1} - 6.9979 \times 10^4$ J·mol$^{-1}$

$Ba_2U_3O_{11}$ (i): $H_m(T) - H_m^o(298.15\,K) = 401.27\,T + 1.1945 \times 10^{-2}\,T^2 + 7.34208 \times 10^6\,T^{-1} - 1.4533 \times 10^5$ J·mol$^{-1}$

$Ba_2U_3O_{11}$ (ii): $H_m(T) - H_m^o(298.15\,K) = 373.94\,T + 2.6785 \times 10^{-2}\,T^2 + 4.81909 \times 10^6\,T^{-1} - 1.3003 \times 10^5$ J·mol$^{-1}$

$Ba_{2.875}UO_{5.875}$: $H_m(T) - H_m^o(298.15\,K) = 288.76\,T + 2.5550 \times 10^{-3}T^2 + 6.68314 \times 10^6\,T^{-1} - 1.0874 \times 10^5$ J·mol$^{-1}$

$Ba_3UO_6$: $H_m(T) - H_m^o(298.15\,K) = 309.94\,T + 1.5350 \times 10^{-3}T^2 + 8.40557 \times 10^6\,T^{-1} - 1.2074 \times 10^5$ J·mol$^{-1}$.

In the case of $Ba_2U_3O_{11}$, two cases were envisaged: (i) $C_{p,m}^o$ ($Ba_2U_3O_{11}$, cr, 298.15 K) = (325.8 ± 9.8) J·K$^{-1}$·mol$^{-1}$; and (ii) $C_{p,m}^o$ ($Ba_2U_3O_{11}$, cr, 298.15 K) = (335.7 ± 9.8) J·K$^{-1}$·mol$^{-1}$ to account for the discrepancy with the expected value from Neumann-Kopp's rule.

Table A-154: Selected heat capacity coefficients for $BaU_2O_7$, $Ba_2U_3O_{11}$, $Ba_{2.875}UO_{5.875}$ and $Ba_3UO_6$ (shown in bold) based on the results of [2010DAS/SIN].

| Phase | | *T* range /K | Heat capacity coefficients $C_{p,m}^o = a + bT + eT^{-2}$ /J·K$^{-1}$·mol$^{-1}$ | | | $C_{p,m}^o$, 298.15 K /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | | a | b | e | |
| $BaU_2O_7$(cr) | | 298.9-1000 | **208.95** | **$5.3020 \times 10^{-2}$** | **$-1.58738 \times 10^6$** | (206.9 ± 17.0) |
| $Ba_2U_3O_{11}$(cr) | (i) | 323.4-999.9 | **401.27** | **$2.3890 \times 10^{-2}$** | **$-7.34208 \times 10^6$** | (325.8 ± 9.8) |
| $Ba_2U_3O_{11}$(cr) | (ii) | 323.4-999.9 | 373.94 | $5.3570 \times 10^{-2}$ | $-4.81909 \times 10^6$ | (335.7 ± 9.8) |
| $Ba_{2.875}UO_{5.875}$(cr) | | 306.1-1010.6 | **288.76** | **$5.1100 \times 10^{-3}$** | **$-6.68314 \times 10^6$** | (215.1 ± 6.5) |
| $Ba_3UO_6$(cr) | | 302-1011.6 | **309.94** | **$3.0700 \times 10^{-3}$** | **$-8.40557 \times 10^6$** | (216.3 ± 6.5) |

The derived heat capacity functions for $BaU_2O_7$ and $Ba_2U_3O_{11}$ are in good agreement with the rule of Neumann-Kopp (based on the heat capacity functions for $UO_3$ [2014KON/BEN], [2003GUI/FAN] and BaO [1994COR/LAA]) over the temperature range 0-1100 K. The derived functions for $Ba_{2.875}UO_{5.875}$ and $Ba_3UO_6$ are higher than predicted by this rule, however. The difference amounts at 1000 K to about

11 and 15 %, respectively. The deviation from the additive rule seems to increase with the Ba/U ratio.

**[2011DAS/SIN]**

[2011DAS/SIN] determined the Gibbs energy of formation of $Ba_{2.875}UO_{5.875}$ in the temperature range 1030-1220 K using a manometric technique, by measuring the equilibrium $CO_2$(g) pressure over the ternary phase field $Ba_{2.875}UO_{5.875}$(cr)-$Ba_3UO_6$(cr)-$BaCO_3$(cr) with an absolute pressure transducer. The enthalpy of formation and entropy at 298.15 K of $Ba_{2.875}UO_{5.875}$ were subsequently derived by second and third law treatment of the data. $Ba_{2.875}UO_{5.875}$ was prepared from $BaCO_3$ and $U_3O_8$ mixed in stoichiometric amounts, and heated under air at 1273 K for 300 hours. The prepared sample was characterised using X-ray diffraction, but was not analysed chemically. The three phases mixtures {$Ba_{2.875}UO_{5.875}$(cr)+$Ba_3UO_6$(cr)+$BaCO_3$(cr)} were pressed into pellets for the manometric measurements. Equilibrium times of about 200-400 hours were allowed at each measured temperature point between 1030 and 1220 K. The corresponding equilibrium reaction is written as:

$$8Ba_{2.875}UO_{5.875}(cr) + BaCO_3(cr) \rightleftharpoons 8Ba_3UO_6(cr) + CO_2(g) \qquad (A.396)$$

X-ray diffraction patterns collected after the experiment confirmed that no new phase had formed, and therefore the co-existence of the three-phases mixture. The variation of the equilibrium $CO_2$(g) pressure with respect to temperature was fitted by least-squares regression, yielding:

$$\ln(P_{CO2})/\text{bar} = 7.67283 - 12787/(T/\text{K})$$

The Gibbs energy of Reaction (A.396) in the temperature range 1030-1220 K was subsequently derived as:

$$\Delta_r G_m^o(T)\ /\text{kJ}\cdot\text{mol}^{-1} \pm 0.3 = 106.3 - 0.0637\ (T/\text{K}).$$

The Gibbs energy of formation of $Ba_{2.875}UO_{5.875}$ (cr) was then calculated from the data of the Gibbs energies of formation of $BaCO_3$(cr) [1995PAR2], [1995BAR], $CO_2$(g) [2003GUI/FAN], [1998CHA], and $Ba_3UO_6$(cr) [2010DAS/SIN], [2003GUI/FAN]. Using the auxiliary data recommended in this review for $BaCO_3$(cr) and $CO_2$(g), as well as the thermodynamic functions retained for $Ba_3UO_6$(cr), the Gibbs energy of formation was recalculated as:

$$\Delta_f G_m^o(Ba_{2.875}UO_{5.875}, \text{cr}, T)\ /\text{kJ}\cdot\text{mol}^{-1} \pm 0.3 = -3114.8 + 0.5096\ (T/\text{K}).$$

The second and third law calculations of [2011DAS/SIN] were found to be in error. A second law treatment of the data using the recommended auxiliary functions yields the following values for the reaction enthalpy at 298.15 K, enthalpy of formation and entropy at 298.15 K: $\Delta_r H_m^o$ (298.15 K) = (86.0 ± 2.0) kJ·mol$^{-1}$, $\Delta_f H_m^o$ ($Ba_{2.875}UO_{5.875}$, cr, 298.15 K) =

– (3118.7 ± 8.0) kJ·mol$^{-1}$, and $S_m^o$ ($Ba_{2.875}UO_{5.875}$, cr, 298.15 K) = (297.7 ± 5.0) J·K$^{-1}$·mol$^{-1}$. The latter entropy value is in very good agreement with the additive rule based on the selected data for $UO_3$ [2003GUI/FAN], and BaO [1994COR/LAA] (*i.e.* 297.4 J·K$^{-1}$·mol$^{-1}$), considering the mixing configurational entropy to be 0 at 298.15 K. The accordance with the additivity rule based on the selected data for $BaUO_4$, $UO_3$ [2003GUI/FAN], and BaO [1994COR/LAA] is not as good, however (*i.e.* 285.2 J·K$^{-1}$·mol$^{-1}$).

The third law treatment of the data yields: $\Delta_r H_m^o$ (298.15 K) = (211.4 ± 6.5) kJ·mol$^{-1}$ and $\Delta_f H_m^o$ ($Ba_{2.875}UO_{5.875}$, cr, 298.15 K) = – (3134.4 ± 8.0) kJ·mol$^{-1}$. The latter results are in strong disagreement with the second law values. Moreover, the reaction enthalpy changes linearly with temperature, which indicates that one of the entropy functions involved in Reaction (A.396) is ill-defined. The aforementioned calculation is based on the entropy value for $Ba_{2.875}UO_{5.875}$ derived from the work of [2010DAS/SIN], *i.e.* $S_m^o$ ($Ba_{2.875}UO_{5.875}$, cr, 298.15 K) = (283.6 ± 5.0) J·K$^{-1}$·mol$^{-1}$. The second law treatment shows the entropy value should be higher, however. When using the value obtained by second law, *i.e.* $S_m^o$ ($Ba_{2.875}UO_{5.875}$, cr, 298.15 K) = (297.7 ± 5.0) J·K$^{-1}$·mol$^{-1}$, the enthalpy of reaction and enthalpy of formation are derived as $\Delta_r H_m^o$ (298.15 K) = (85.7 ± 0.4) kJ·mol$^{-1}$ and $\Delta_f H_m^o$ ($Ba_{2.875}UO_{5.875}$, cr, 298.15 K) = – (3118.7 ± 8.0) kJ·mol$^{-1}$, in very good agreement with the second law results. Moreover, the linear derivation of the reaction enthalpy with respect to temperature disappears. Therefore the values selected in this review are the following:

$$\Delta_f H_m^o (Ba_{2.875}UO_{5.875}, \text{cr}, 298.15\ \text{K}) = -(3118.7 \pm 8.0)\ \text{kJ·mol}^{-1}$$

$$S_m^o (Ba_{2.875}UO_{5.875}, \text{cr}, 298.15\ \text{K}) = (297.7 \pm 5.0)\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

This review points to the need to repeat the low temperature heat capacity measurements of $Ba_{2.875}UO_{5.875}$ [2010DAS/SIN] to confirm the suggested entropy value.

**[2013KES/DAS]**

The authors investigated the phase relationships in the SrO-$UO_3$-$MoO_3$ system at 1023 K in air, and reported a sketch of the stable phase boundaries based on their XRD analyses. Using $UO_3$, $MoO_3$ and $SrCO_3$ starting materials, [2013KES/DAS] prepared twenty two phases mixtures of various compositions so as to identify coexisting phases in the Sr-Mo-U-O system. Moreover, the authors reported for the first time the measurement of the melting point, thermal expansion coefficients and heat capacity of the quaternary phase $SrUMo_4O_{16}$(cr) in the temperature range 310 to 759 K. $UO_3$, $MoO_3$ and $SrCO_3$ were mixed in different molar proportions and heated at 673 K for six hours plus 1023 K for 30 hours. Among the many phases reported in the literature for the Sr-U-O system, the well-characterised phases $Sr_5U_3O_{14}$, $Sr_3U_{11}O_{36}$, $Sr_2U_3O_{11}$, $SrUO_4$, $Sr_2UO_5$, $Sr_3UO_6$, were included in the drawing of the SrO-$UO_3$ pseudo-binary

sub-system. $SrU_4O_{13}$ was not included. As for the SrO-$MoO_3$- pseudo-binary sub-system at 1023 K, the phases considered were: $SrMoO_4$ and $Sr_3MoO_6$. $Sr_2MoO_5$ was identified as a mixture of $SrMoO_4$ and $Sr_3MoO_6$. Only $UMoO_6$ was considered for the $UO_3$-$MoO_3$ sub-system.

$SrUMo_4O_{16}$(cr) was prepared by mixing $UO_3$, $SrCO_3$ and $MoO_3$ in the molar ratio (1:1:4) and heating in an alumina boat at 673 K for four hours plus 1023 K for 30 hours. $SrUMo_4O_{16}$(cr) crystallises in the monoclinic system with lattice parameters $a$ = 11.474(5) Å, $b$ = 6.772(2) Å, $c$ = 8.480(2) Å and β = 90.93 ° [1988MAR2]. The prepared samples were analysed by X-ray diffraction, but no further chemical analysis was performed. The thermal stability of the $SrUMo_4O_{16}$(cr) phase was studied by Thermogravimetry and Differential Thermal Analysis by heating in a alumina cup up to 1073 K and 773 K in dry air at 10 K·min$^{-1}$. The melting point of the material was identified at 1043 K. The heat capacity of the material was measured in the temperature range 310 to 759 K using a Differential Scanning Calorimeter in the step mode. The measurement was done under argon flow at a rate of 5 K·min$^{-1}$. The fitted heat capacity equation for the range 310-759 K is:

$C^{\circ}_{p,m}$ ($SrUMo_4O_{16}$, cr, 298.15 K) = 405.709 + 0.00263 × $T$ /K – 17.532 × 10$^6$ ($T$/K)$^{-2}$ J·K$^{-1}$·mol$^{-1}$.

It should be noted that these coefficients were not all reported correctly in the paper of [2013KES/DAS]. The heat capacity values were found to be less than those calculated from the Neumann Kopp rule. This review points to the need to repeat the measurement on a well-characterised material to confirm the results of [2013KES/DAS]. In addition, the authors estimated the enthalpy of formation and standard entropy at 298.15 K based on the methods of Kubashewski *et al.* [1993KUB/ALC], and finally the Gibbs energy of formation as a function of temperature. However, we have not pursued this approach since the data at 298.15 K are estimated, and therefore the derived Gibbs energy function has appreciable uncertainties.

**[2013REY/KEN]**

The authors report a structural investigation of the double perovskite $Ba_2SrUO_6$ using synchrotron X-ray powder diffraction at the beamline BL-10 of the Australian synchrotron in the temperature range 313-1200 K. $Ba_2SrUO_6$ was prepared by solid state reaction from $UO_2(NO_3)_2.6H_2O$, $BaCO_3$, and $SrCO_3$ heated at 1673 K. [2013REY/KEN] confirmed that $Ba_2SrUO_6$ adopts a monoclinic structure in space group $P2_1/n$ at room temperature, as reported by [1987GRO/IJD] who performed neutron diffraction measurements on the same compound. The refinement yielded lattice parameters as $a$ = 6.24163(3) Å, $b$ = 6.26392(3) Å, $c$ = 8.82472(4) Å, β = 89.7892(3) °, in good agreement with the neutron data of [1987GRO/IJD], and X-ray data of

[2006CHE/SMI3], [2006KNY/CHE]. The latter structure is fully ordered with the larger $Ba^{2+}$ cations on the perovskite-A sites, and no anti-site mixing between the $Sr^{2+}$ and $U^{6+}$ cations. [2013REY/KEN] also showed that $Ba_2SrUO_6$ undergoes a first order transition around 900 K to a rhombohedral structure in space group $R\bar{3}$, and a continuous transition above 1200 K to a cubic structure in space group $Fm\bar{3}m$. The authors discuss the sequence of transitions in terms of local structure within the perovskites.

**[2016GUO/TIF]**

The authors reported the structural and thermodynamic investigations of the uranate compounds $MgUO_4$, $CrUO_4$, and $FeUO_4$ using powder X-ray diffraction, X-ray Absorption Spectroscopy, X-ray photoelectron spectroscopy, $^{57}Fe$ Mössbauer spectroscopy and high temperature oxide melt solution calorimetry. In addition, DFT calculations of the structural and energetic properties were performed, and used to discuss the trends in stability. $MgUO_4$ and $CrUO_4$, were synthesised using a co-precipitation method from uranyl acetate ($UO_2(CH_3COO)_2{\cdot}2H_2O$) and Mg acetate ($Mg(CH_3COO)_2$) or Cr acetate ($C_8H_{16}Cr_2O_{10}$). $FeUO_4$ was obtained from a mixture of $U_3O_8$ and $Fe_3O_4$. The X-ray diffraction analysis of the sample did not show any impurities, while the EPMA analysis confirmed that the compounds were stoichiometric within analytical uncertainties. $MgUO_4$ has orthorhombic symmetry in space group *Imam* [1954ZAC], while $CrUO_4$ and $FeUO_4$ are isostructural, orthorhombic in space group *Pbcn* [1961SMI/CLI], [1965BAC/BER]. The combined XANES and XPS data confirmed the hexavalence of uranium in $MgUO_4$, and suggested the formation of pentavalent uranium in $CrUO_4$ and $FeUO_4$. The XPS data moreover showed that Cr and Fe were both trivalent, which means that uranium can occur either as $U^{5+}$ or a mixture of $U^{6+}$ and $U^{4+}$ to achieve charge neutrality. The $^{57}Fe$ Mössbauer spectra suggested Fe to be a high spin Fe(III). In addition, the authors performed DFT calculations of the projected density of states using the GCA+U approximation, which confirmed the experimental valence states determinations, *i.e.*, the presence of $U^{6+}$ in $MgUO_4$, and $U^{5+}$, $Fe^{3+}$ and $Cr^{3+}$ in $CrUO_4$ and $FeUO_4$.

The high temperature oxide melt solution calorimetry measurements were performed using a custom built Tian-Calvet twin calorimeter as described in [1977NAV], [1997NAV]. The powdered samples were dropped in the form of pellets from room temperature to a molten sodium molybdate ($3Na_2O{\cdot}4MoO_3$) at 702 °C for $MgUO_4$ and 802 °C for $CrUO_4$, and a molten lead borate solution ($2PbO{\cdot}B_2O_3$) at 802 °C for $FeUO_4$. Using appropriate thermochemical cycles, the enthalpies of formation of the ternary uranate compounds were derived at 298.15 K, as well as the enthalpies of formation from the binary oxides $\Delta_{f,ox}H(MUO_4, cr, 298.15\ K)$ (M = Mg, Cr, Fe) corresponding to the following reactions:

$$\gamma\text{-}UO_3(cr, 298.15\,K) + MgO(cr, 298.15\,K) \rightarrow MgUO_4(cr, 298.15\,K) \quad \text{(A.397)}$$

$$1/2\,\gamma\text{-}UO_3(cr, 298.15\,K) + 1/2UO_2(cr, 298.15\,K) + 1/2Cr_2O_3(cr, 298.15\,K) \rightarrow CrUO_4(cr, 298.15\,K) \quad (A.398)$$

$$1/2\,\gamma\text{-}UO_3(cr, 298.15\,K) + 1/2UO_2(cr, 298.15\,K) + 1/2Fe_2O_3(cr, 298.15\,K) \rightarrow FeUO_4(cr, 298.15\,K) \quad (A.399)$$

$$1/3U_3O_8(cr, 298.15\,K) + 1/3Fe_3O_4(cr, 298.15\,K) \rightarrow FeUO_4(cr, 298.15\,K) \quad (A.400)$$

The calculation was repeated in this review, using the recommended auxiliary data, yielding:

$$\Delta_f H^\circ_m (MgUO_4, cr, 298.15\ K) = -(1859.2 \pm 2.6)\ kJ{\cdot}mol^{-1}$$

$$\Delta_f H^\circ_m (CrUO_4, cr, 298.15\ K) = -(1753.6 \pm 4.8)\ kJ{\cdot}mol^{-1}$$

$$\Delta_f H^\circ_m\ FeUO_4, cr, 298.15\ K) = -(1599.7 \pm 3.1)\ kJ{\cdot}mol^{-1}.$$

The results for $MgUO_4$ and $FeUO_4$ are in very good agreement with that of [2016GUO/TIF], but with slightly increased uncertainties. Those results are also in good accordance with previous measurements reported in the literature, namely $\Delta_f H^\circ_m (MgUO_4, cr, 298.15\ K) = -(1857.3 \pm 1.5)\ kJ{\cdot}mol^{-1}$ [2003GUI/FAN] obtained by solution calorimetry in $HNO_3$ and $HNO_3$/HF mixtures [1977OHA/BOE], and $\Delta_f H^\circ_m (FeUO_4, cr, 298.15\ K) = -(1588.7 \pm 1.2)\ kJ{\cdot}mol^{-1}$ obtained using $2PbO{\cdot}B_2O_3$ solvent at 715 °C in air for a $FeUO_4$ sample containing $U_3O_8$ as impurity phase [2016GUO/TIF]. The thermochemical cycle used for $CrUO_4$ was found to contain an error. The derived formation enthalpy is therefore 71 $kJ{\cdot}mol^{-1}$ higher than reported by [2016GUO/TIF].

The re-calculated enthalpies of formation from the binary oxides corresponding to Equations (A.397)-(A.400) are $\Delta_{f,ox}H(MUO_4, cr, 298.15\ K) = -(33.8 \pm 1.7)\ kJ{\cdot}mol^{-1}$, $\Delta_{f,ox}H(CrUO_4, cr, 298.15\ K) = -(32.1 \pm 1.0)\ kJ{\cdot}mol^{-1}$ and $\Delta_{f,ox}H(FeUO_4, cr, 298.15\ K) = -(32.2 \pm 2.8)\ kJ{\cdot}mol^{-1}$ or $-(34.6 \pm 4.7)\ kJ{\cdot}mol^{-1}$, respectively, in good agreement with the data reported by [2016GUO/TIF]. Those experimental values were plotted against the ionic radius of the metal cation and compared with the results reported in the literature for $CaUO_4$, $SrUO_4$ and $BaUO_4$. $\Delta_{f,ox}H$ showed a negative linear trend, becoming more exothermic with increasing ionic radius of the metal cation. The trend of thermodynamic stability was related to the acid-base chemistry: a higher energetic stability is obtained when the $M^{2+}$ cation becomes more basic ($Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$) along the series $MUO_4$ and the U-O bonds become more covalent.

# A-1.12 Uranium compounds and complexes with group 1 elements

**[2002BER/LAV]**

[2002BER/LAV] solved for the first time the crystal structure of α-$Cs_2U_4O_{12}$ by simultaneous refinement of X-ray and neutron diffraction data. α-$Cs_2U_4O_{12}$ was prepared by heating a stoichiometric mixture of cesium carbonate and $U_3O_8$ during 24 hours at 1373 K under $CO_2$ flow. The structure was shown to be rhombohedral in space group *R*-3 (and not *R*3*m* as reported in the literature [1976EGM]) with hexagonal cell parameters as $a$ = 15.4232(1) Å and $c$ = 19.1816(2) Å. The structure is derived from the "modified pyrochlore" $RbNiCrF_6$ type with a three-dimensional framework of $UO_6$ octahedra and $UO_7$ distorted pentagonal bipyramids sharing corners or edges.

**[2002BER/VER]**

[2002BER/VER] investigated the local uranium environment in four cesium uranates, namely $Cs_2UO_4$, $Cs_2U_2O_7$, $Cs_4U_5O_{17}$ and $Cs_2U_4O_{12}$ using X-ray diffraction (XRD), neutron diffraction, X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS). The cesium uranates were prepared from $Cs_2CO_3$ and $U_3O_8$ mixed in stoichiometric amounts and heated under air (1073 K) or $CO_2$ (1373 K) atmosphere. In addition ICP-MS analysis was performed which showed that the total impurity level of the synthesised samples was below 1000 ppm. The crystal structures of $Cs_2UO_4$ and $Cs_4U_5O_{17}$ were refined by the Rietveld method using the structural models of Van Egmond as starting point [1976EGM]. The model for $Cs_2U_2O_7$ was based on the neutron diffraction study of [1993MIJ/IJD]. The structure of $Cs_2U_4O_{12}$ was solved by ab-initio. $Cs_2UO_4$ crystallises in the tetragonal system, in space group *I4/mmm* ($a$ = 4.391(1) Å, $c$ = 14.823(1) Å); $Cs_2U_2O_7$ in the monoclinic system, in space group *C2/m* ($a$ = 14.5293(9) Å, $b$ = 4.3233(3) Å, $c$ = 7.4899(5) Å, β = 113.852(1) °); $Cs_4U_5O_{17}$ in the orthorhombic system, in space group *Pbcn* ($a$ = 18.7599(10) Å, $b$ = 7.0638(4) Å, $c$ = 14.9548(7) Å); $Cs_2U_4O_{12}$ has trigonal symmetry, in space group *R-3* ($a$ = 15.4207(6) Å, $c$ = 19.1762(11) Å). The monovalent cesium uranates ($Cs_2UO_4$, $Cs_2U_2O_7$, $Cs_4U_5O_{17}$) were shown to have uranyl-type of environments based on the crystal structure determinations and XANES data. The hexavalence of the uranium was moreover confirmed based on Bond Valence Sum calculations using the formalism of Zachariasen [1978ZAC] and XPS results [2000BER/LAV]. $Cs_2U_4O_{12}$ was shown to be a mixed valence state compound based on the XRD, XPS and XANES data. An ordered distribution of $U^{5+}$ was suggested for the U1 and U4 sites, of $U^{6+}$ on the U2 site, and an average distribution of one $U^{5+}$ and two $U^{6+}$ on the U3 site. The uranium environment in this case is moreover much more symmetric as found by XANES and EXAFS.

**[2002KES/AGA]**

The authors investigated the Rb-Sr-U-O quaternary phase diagram at 1173 K and reported the stable phase boundaries based on their XRD analyses. Using $UO_3$, $Rb_2CO_3$ and $SrCO_3$ starting materials, [2002KES/AGA] prepared twenty two phases mixtures of various compositions to identify coexisting phases in the Rb-Sr-U-O system. $UO_3$, $Rb_2CO_3$ and $SrCO_3$ were first dissolved in 1-2M $HNO_3$ and the three solutions mixed in different molar ratios of $UO_3$, $Rb_2O$ and SrO. A few drops of glycerol were added to homogenise the amorphous powders, and the solutions were evaporated to dryness. The mixtures were subsequently heated in platinum boats in air at 1173 K with intermediate grinding steps and finally quenched in air.

Among the many phases reported in the literature for the Sr-U-O system, namely $Sr_3UO_6$, $Sr_2UO_5$, $Sr_3U_2O_9$, $SrUO_4$, $Sr_3U_{11}O_{36}$, $SrU_4O_{13}$, $SrU_2O_7$ and $Sr_2U_3O_{11}$, only the first six well-characterised phases were included in the drawing of the SrO-$UO_3$ pseudo-binary sub-system at 1173 K. $SrU_2O_7$ and $Sr_2U_3O_{11}$ were excluded. As for the $Rb_2O$-$UO_3$ pseudo-binary sub-system at 1173 K, the phases considered were: $Rb_2U_7O_{22}$, $Rb_2U_4O_{13}$, $Rb_2U_2O_7$, $Rb_2UO_4$. $Rb_4UO_5$ was excluded because not well characterised. No phases were reported for the SrO-$Rb_2O$ sub-system. [2006KES/AGA] could finally identify two novel quaternary phases, namely $Rb_2Sr_2U_4O_{15}$, with monoclinic symmetry (Z = 2) and cell parameters as $a$ = 7.875(4) Å, $b$ = 13.199(4) Å, $c$ = 6.667(5) Å, and β = 104.93(8) °; and $Rb_8Sr_2U_6O_{24}$ with cubic symmetry in space group *Im3m* and cell parameter as $a$ = 8.743(1) Å. The structural parameters of $Rb_8Sr_2U_6O_{24}$ were refined. The crystal structure of $Rb_2Sr_2U_4O_{15}$ could not be solved, however.

**[2002MOR]**

Morss estimated in this work, based on acid-base interactions, the enthalpies of formation and stability of various ternary oxides of the actinides with alkali and alkaline-earth elements. The stability of ternary oxides with respect to the binary constituent oxides is expressed by the free energy of the reaction:

$$AO(cr) + BO_2(cr) \rightleftharpoons ABO_3(cr) \qquad (A.401)$$

But in fact the entropy of such reaction is nearly zero, so that the stability of the ternary oxide is directly reflected by the value of the reaction enthalpy (or enthalpy of complexation).

Using the approach developed by Smith [1987SMI2], Morss calculated a quantitative scale of oxide acidity parameters $a$ for the following binary actinide oxides: $ThO_2$, $PaO_2$, $UO_2$, $UO_3$, $NpO_2$, $NpO_3$, $Pu_2O_3$, $PuO_2$, $Am_2O_3$, $Cm_2O_3$, $CmO_2$, $Bk_2O_3$, $Cf_2O_3$, $CfO_2$. The method of Smith [1987SMI2] is based on the empirical expression (A.402), which is derived from Pauli's electronegativity scale:

$$a(\text{acid}) - a(\text{base}) = [-\Delta_r H^o(\text{reaction})]^{1/2} \quad \text{(A.402)}$$

where $a$(acid) and $a$(base) are the acidity parameters of the acid and base involved in a reaction such as Reaction (A.403)[1987SMI2]:

$$Na_2O(cr) + N_2O_5(cr) \rightleftharpoons 2NaNO_3(cr) \quad \text{(A.403)}$$

To normalise his approach for the different equation stoichiometries, Smith used the convention that the basic oxide transfers one mole of oxide ion to the acidic oxide. The best values for the different acidity parameters were subsequently estimated based on a least-squares analysis of 250 oxoacid salts involving 70 binary oxides [1987SMI2], taking for reference the acidity parameter of water to be zero, *i.e.*, $a(H_2O,l) = 0$.

Morss derived the acidity parameters of the binary actinide oxides using Reactions such as (A.404) and (A.405):

$$BaO(cr) + UO_2(cr) \rightleftharpoons BaUO_3(cr) \quad \text{(A.404)}$$

$$BaO(cr) + UO_3(cr) \rightleftharpoons BaUO_4(cr) \quad \text{(A.405)}$$

Using the enthalpies of formation of $BaUO_3$(cr), $BaUO_4$(cr), BaO(cr), $UO_2$(cr) and $UO_3$(cr) determined experimentally, the reaction enthalpies of (A.404) and (A.405) were first calculated. The acidity parameters for $UO_2$(cr) and $UO_3$(cr) were subsequently estimated with the relations (A.406) and (A.407) taking for the acidity parameter of BaO(cr) the value reported by Smith [1987SMI2]:

$$a(UO_2) - a(BaO) = [-\Delta_r H^o(A.404)]^{1/2} \quad \text{(A.406)}$$

$$a(UO_3) - a(BaO) = [-\Delta_r H^o(A.405)]^{1/2} \quad \text{(A.407)}$$

The latter calculation was performed for various alkali and alkaline-earth ternary uranium oxides, and the mean values derived as $a(UO_2) = -3.3$ and $a(UO_3) = 3.7$, respectively. Unfortunately, [2002MOR] did not report the detail of the compositions used to derived those mean values, so that we cannot re-assess the calculation of the acidity parameters. We have carried out in this review the calculation for $MUO_4$ (M = Mg, Ca, Sr, Ba), $M_3UO_6$ (M = Ca, Sr, Ba) and $M_2U_2O_7$ (M = Li, Na, K, Rb, Cs), which yielded a mean acidity parameter $a(UO_3)$=3.96, in good agreement with the result of [2002MOR].

Using for the acidity parameter of $UO_3$ $a(UO_3) = 3.7$, [2002MOR] calculated the expected enthalpies for $MUO_4$ (M = Mg, Ca, Sr, Ba), $M_3UO_6$ (M = Ca, Sr, Ba) and $M_2U_2O_7$ (M = Li, Na, K, Rb, Cs), and compared them to the values determined experimentally with solution calorimetry. We have repeated the calculation in this review using the recommended auxiliary data (Table A-155). The results, listed in Table A-156 below, are very close to those of [2002MOR].

Table A-155: Enthalpies of formation and acidity parameters used in this review to estimate the standard enthalpies of formation of various alkali and alkaline-earth uranates based on acid-base interactions.

| Base | $\Delta_f H_m^\circ$ (Base, 298.15 K) /kJ·mol$^{-1}$ | Reference | a(Base) [1987SMI2] |
|---|---|---|---|
| MgO | – (601.6 ± 0.3) | [2003GUI/FAN] | – (4.5 ± 1.0) |
| CaO | – (634.92 ± 0.90) | [2003GUI/FAN] | – (7.5 ± 0.4) |
| SrO | – (590.6 ± 0.9) | [2003GUI/FAN] | – (9.4 ± 0.4) |
| BaO | – (548.1 ± 2.5) | [2003GUI/FAN] | – (10.8 ± 0.3) |
| $Li_2O$ | – (598.73) | [1998CHA] | – (9.2 ± 0.5) |
| $Na_2O$ | – (415.1 ± 4.2) | [1991KNA/KUB] | – (12.5 ± 0.4) |
| $K_2O$ | – (363.171) | [1998CHA] | – (14.6 ± 0.5) |
| $Rb_2O$ | – (339.0) | [1995BAR] | – (15.0 ± 0.6) |
| $Cs_2O$ | – (345.975) | [1995BAR] | – (15.2 ± 0.7) |

Table A-156: Comparison between experimental and calculated standard enthalpies of formation of various alkali and alkaline-earth uranates based on acid-base interactions.

| Ternary oxide | $\Delta_f H_m^\circ$ (calc, 298.15 K) /kJ·mol$^{-1}$(a) | $\Delta_f H_m^\circ$ (calc, 298.15 K) /kJ·mol$^{-1}$(b) | $\Delta_f H_m^\circ$ (exp, 298.15 K)(c) | Deviation (%) |
|---|---|---|---|---|
| $MgUO_4$ | – 1892.64 | – 1892.7 | – (1857.3 ± 1.5) | 1.90 |
| $CaUO_4$ | – 1984.16 | – 1984.3 | – (2002.3 ± 2.3) | 0.91 |
| β-$SrUO_4$ | – 1986.01 | – 1987.6 | – (1988.4 ± 5.4) | 0.24 |
| $BaUO_4$ | – 1982.15 | – 1982.1 | – (1993.8 ± 3.3) | 0.58 |
| $Ca_3UO_6$ | – 3379.44 | – 3380 | – (3305.4 ± 4.1) | 2.24 |
| $Sr_3UO_6$ | – 3338.82 | – 3343.5 | – (3263.5 ± 3.0) | 2.31 |
| $Ba_3UO_6$ | – 3288.6 | – 3288.4 | – (3210.4 ± 8.0) | 2.44 |
| $Li_2U_2O_7$ | – 3212.74 | – 3212 | – (3213.6 ± 5.3) | 0.03 |
| $Na_2U_2O_7$ | – 3125.14 | – 3124.3 | – (3203.8 ± 4.0) | 2.46 |
| $K_2U_2O_7$ | – 3145.661 | – 3144 | – (3250.5 ± 4.5) | 3.23 |
| $Rb_2U_2O_7$ | – 3136.29 | – 3136.3 | – (3232.0 ± 4.3) | 2.96 |
| $Cs_2U_2O_7$ | – 3150.785 | – 3150.6 | – (3220.0 ± 10.0) | 2.15 |

(a) Enthalpy of formation re-calculated in this review.
(b) Enthalpy of formation calculated by [2002MOR].
(c) Experimental data

The deviation between experimental and calculated value is listed in the last column of Table A-156. The overall agreement is good, which shows that such approach based on the acidities of the binary oxides can be particularly appealing to estimate the enthalpies of formation of new compositions, and to predict their stabilities. Morss points to the fact that the acidity parameter needs to be carefully calculated taking into account the local structural coordination geometry, however. The assessment made by Morss concerns only hexavalent uranium phases. It would be particularly

interesting to assess his acidity parameters for Np, Pu, Am, Ac, Cf and Cm ternary oxide phases.

**[2005YAG/OBB]**

The authors report the synthesis at high temperatures of $Rb_2U_2O_7$ and $Rb_8U_9O_{31}$ by solid state reaction and crystal structure determination using single crystal X-ray diffraction data, the measurement of their densities using pycnometry, as well as differential thermal analysis (DTA) in the temperature range 293-1573 K, conductivity, and infrared spectroscopy measurements. $Rb_2U_2O_7$ and $Rb_8U_9O_{31}$ polycrystalline materials were prepared by reaction between $RbNO_3$ and $U_3O_8$ mixed in stoichiometric amounts and heated in air with intermediate regrinding steps. $Rb_2U_2O_7$ was heated for two days at 1023 K. $Rb_8U_9O_{31}$ was heated at 1173 K for three weeks. The single crystals were obtained while mixing $Rb_2O$-$U_3O_8$-$MoO_3$ in an excess of rubidium carbonate $Rb_2CO_3$. The first mixture corresponded to a molar ratio Mo/U=2/1 with 10 mole of $Rb_2CO_3$ for 2 mole of $MoO_3$. It was heated in a platinum crucible at 1213 K for three hours and then slowly cooled down at 0.2 $K \cdot min^{-1}$. The second mixture corresponded to the same molar ratio, and was heated at 1473 K before being cooled down (0.3 $K \cdot min^{-1}$). The products of reaction were washed with water to remove $Rb_2CO_3$ excess and filtered. The first mixture yielded a two-phase sample: orange single crystals of $Rb_8U_9O_{31}$ plus twinned yellow crystals of $Rb_3U_2MoO_{10}$. The second mixture yielded a two-phase sample: orange single crystals of $Rb_2U_2O_7$ plus twinned yellow crystals of $Rb_3U_2MoO_{10}$. Single crystals of $Rb_2U_2O_7$ and $Rb_8U_9O_{31}$ were subsequently selected for the X-ray diffraction analysis.

[2005YAG/OBB] showed that $Rb_2U_2O_7$ and $Rb_8U_9O_{31}$ crystallise with monoclinic (space group $P2_1/c$, Z=2) and orthorhombic (space group *Pbna,* Z = 4) symmetries, respectively. The corresponding cell parameters are $a$ = 7.323(2) Å, $b$ = 8.004(3) Å, $c$ = 6.950(2) Å, β = 108.8(1) ° for the former; and $a$ = 6.9925(9) Å, $b$ = 14.2884(19) Å, $c$ = 34.062(5) Å for the latter. The authors moreover found a very good agreement between calculated and measured densities for both compounds: $\rho_{meas}$ = 6.56(3) $g \cdot cm^{-3}$ and $\rho_{calc}$ = 6.54(2) $g \cdot cm^{-3}$ for $Rb_2U_2O_7$; $\rho_{meas}$ = 6.47(3) $g \cdot cm^{-3}$ and $\rho_{calc}$ = 6.48(2) $g \cdot cm^{-3}$ for $Rb_8U_9O_{31}$. In addition, no phase transitions or melting points were observed by DTA, and the X-ray diffraction data collected after the experiment showed that both phases were stable until 1573 K. The infrared spectrum of $Rb_2U_2O_7$ showed two strong bands at about 807 and 745 $cm^{-1}$, which were attributed to asymmetrical and symmetrical $UO_2^{2+}$ uranyl stretching vibrations for the uranyl ion in octahedral coordination. The spectrum of $Rb_8U_9O_{31}$ showed two asymmetrical and symmetrical vibration couples (805.740) and (835.760) $cm^{-1}$, corresponding to vibration bands of uranyl ions in octahedral and pentagonal bipyramid environments, respectively.

**[2006KES/AGA]**

The authors investigated the Cs-Sr-U-O quaternary phase diagram at 1173 K in air and reported stable phase boundaries based on their XRD analyses. Using $UO_3$, $Cs_2CO_3$ and $SrCO_3$ starting materials, [2006KES/AGA] prepared twenty phases mixtures of various compositions to identify coexisting phases in the Cs-Sr-U-O system. $UO_3$, $Cs_2CO_3$ and $SrCO_3$ were first dissolved in 1-2M $HNO_3$ and the three solutions mixed in different molar ratios of $UO_3$, $Cs_2O$ and SrO. A few drops of glycerol were added to homogenise the amorphous powders, and the solutions were evaporated to dryness. The mixtures were subsequently heated in platinum boats in air at 1173 K with intermediate grinding steps and finally quenched in air.

Among the many phases reported in the literature for the Cs-U-O system, namely $Cs_2UO_4$, $Cs_2U_2O_7$, $Cs_2U_4O_{13}$, $Cs_4U_5O_{17}$, $Cs_2U_5O_{16}$, $Cs_2U_7O_{22}$, $Cs_2U_{15}O_{46}$, $Cs_2U_{16}O_{49}$, only the well-characterised phases $Cs_2U_2O_7$, $Cs_2U_4O_{13}$, $Cs_4U_5O_{17}$ were included in the drawing of the $Cs_2O$-$UO_3$ pseudo-binary sub-system at 1173 K. The authors mentioned the conflicting data in the literature for this system and pointed to the need for a comprehensive investigation. As for the SrO-$UO_3$ pseudo-binary sub-system at 1173 K, the phases considered are: $Sr_3UO_6$, $Sr_2UO_5$, $Sr_3U_2O_9$, $SrUO_4$, $SrU_4O_{13}$. $SrU_2O_7$ and $Sr_2U_3O_{11}$, $Sr_3U_{11}O_{36}$, $Sr_5U_3O_{11}$ were excluded. No phases were reported for the SrO-$Cs_2O$ sub-system. [2006KES/AGA] could finally identify a novel quaternary phase, namely $Cs_2Sr_2U_4O_{15}$, with monoclinic symmetry (Z = 2) and cell parameters as $a$ = 9.627(6) Å, $b$ = 13.742(8) Å, $c$ = 7.681(5) Å, and β = 107.72(5)°, isostructural with $Rb_2Sr_2U_4O_{15}$ [2002KES/AGA].

**[2007DAH/KES]**

The authors investigated the phase relationships in the Na-U-Mo-O quaternary system and reported the phase boundaries in the $Na_2O$-$UO_3$-$MoO_3$ pseudo-ternary diagram. [2007DAH/KES] found five stable quaternary phases $Na_2UMo_2O_{10}$, $Na_2U_2Mo_2O_{13}$, $Na_2U_2Mo_3O_{16}$, $Na_2UMo_4O_{16}$, $Na_2U_2Mo_4O_{19}$ with orthorhombic symmetry, which they characterised using XRD, infrared and thermal analysis. All phases showed thermal stability in air up to 873 K, but decomposed to $Na_2U_2O_7$ at 1223 K. The five quaternary phases as well as seventeen mixtures of various compositions were prepared by mixing $UO_3$, $Na_2MoO_4$, $Na_2Mo_2O_7$, $UO_2MoO_4$, and $Na_2Mo_4O_{13}$ in the appropriate ratios and heating in air at 823 K.

The $Na_2U_2Mo_2O_{13}$, $Na_2U_2Mo_4O_{19}$, $Na_2U_2Mo_3O_{16}$ phases were identified and indexed for the first time. The $Na_4U_3Mo_2O_{17}$, $Na_2U_3Mo_9O_{37}$, $Na_2U_3Mo_4O_{22}$ compounds reported by Dion and Noel [1977DIO/NOE], [1981DIO/NOE], [1982DIO/NOE] were found to correspond to phase mixtures instead of pure compounds. The structural parameters for the five pure quaternary phases reported by [2007DAH/KES] are reported in Table A-157, together with the temperatures of identified reversible phase

transitions and melting points as measured by TG/DTA on the heating ramp. The infrared spectra showed spectral bands in the region 700-950 $cm^{-1}$ due to the presence $MoO_4^{2-}$ tetrahedral groups and bands in the region 905-920 $cm^{-1}$ due to the presence $UO_2^{2+}$ groups.

Table A-157: Summary of the structural parameters of orthorhombic $Na_2UMo_2O_{10}$, $Na_2U_2Mo_2O_{13}$, $Na_2U_2Mo_3O_{16}$, $Na_2UMo_4O_{16}$, $Na_2U_2Mo_4O_{19}$ as determined by [2007DAH/KES], phase transition and melting temperatures determined by TG/DTA on the heating ramp.

| Compound | Cell parameter /Å | Z | Phase transition temperature /K | Melting temperature /K |
|---|---|---|---|---|
| $Na_2UMo_2O_{10}$ | *a* = 6.923(5) | 4 | 823 | 863 |
| | *b* = 17.785(10) | | | |
| | *c* = 12.998(7) | | | |
| $Na_2U_2Mo_2O_{13}$ | *a* = 7.761(4) | 4 | | 853 |
| | *b* = 16.747(1) | | | |
| | *c* = 12.159(7) | | | |
| $Na_2U_2Mo_3O_{16}$ | *a* = 17.368(2) | 4 | 788 | 843 |
| | *b* = 8.952(1) | | | |
| | *c* = 12.750(9) | | | |
| $Na_2UMo_4O_{16}$ | *a* = 6.119(4) | 2 | 743 | 783 |
| | *b* = 13.528(4) | | | |
| | *c* = 20.075(4) | | | |
| $Na_2U_2Mo_4O_{19}$ | *a* = 8.833(2) | 2 | 788 | 833 |
| | *b* = 14.128(5) | | | |
| | *c* = 9.709(2) | | | |

The phases considered for the $Na_2O$-$MoO_3$ system are: $Na_2MoO_4$, $Na_2Mo_4O_{13}$, and $Na_2Mo_2O_7$. In the $UO_3$-$MoO_3$ system, only one compound, namely $UO_2MoO_4$ was reported in the literature. The ternary phases in the $Na_2O$-$MoO_3$ system were not considered in this work because not relevant for the studied partial quaternary phase diagram. On the basis of the X-ray diffraction results, the coexisting phases and hence phase boundaries in the Na-U-Mo-O system were drawn.

**[2009RAK/JAT]**

[2009RAK/JAT] measured the heat capacities of $Li_4UO_5$, $Li_2UO_4$, $Li_{22}U_{18}O_{65}$, $Li_2U_{1.75}O_{6.25}$, $Li_2U_2O_7$, $Li_2U_3O_{10}$, and $Li_2U_6O_{19}$ over the temperature range 300-860 K

using Differential Scanning Calorimetry. The aforementioned hexavalent compounds were prepared from $LiCO_3$ and $U_3O_8$ mixed in stoichiometric amounts, and heated under oxygen atmosphere at 1073 K ($Li_2U_{1.75}O_{6.25}$, $Li_2U_2O_7$, $Li_2U_3O_{10}$, and $Li_2U_6O_{19}$), and 923 plus 1073 K ($Li_4UO_5$, $Li_2UO_4$, $Li_{22}U_{18}O_{65}$), respectively, with intermediate regrinding steps. The purity of the synthesis phases was checked using X-ray diffraction. The authors did not perform any further chemical analysis of their sample, however. The cell parameters of $Li_4UO_5$, $Li_2UO_4$, $Li_2U_3O_{10}$ and $Li_{22}U_{18}O_{65}$ were found in reasonable agreement with those reported in the literature. No reference data could be found for the crystal systems or lattice parameters of $Li_2U_2O_7$, $Li_2U_{1.75}O_{6.25}$, and $Li_2U_6O_{19}$. The indexations of the former two phases were based on the isomorphous $Na_2U_2O_7$ and $K_2U_2O_7$ monoclinic compounds. $Li_2U_6O_{19}$ could not be indexed, however, as no structural analogue could be found.

The Differential Scanning Calorimetry measurements were performed under argon flow, at 5 $K \cdot min^{-1}$ heating rate. The accuracy of the method in the temperature range 300-860 K was estimated to be ± 2 % based on the results of nuclear grade $ThO_2$ and NIST standard molybdenum [1995BAR]. The authors did not list their experimental points, but only reported their least-squares fitted heat capacity equations in $J \cdot g^{-1} \cdot K^{-1}$. The corresponding equations were converted in this review in standard units of $J \cdot K^{-1} \cdot mol^{-1}$ (Table A-158).

Table A-158: Derived heat capacity equations for the lithium uranates [2009RAK/JAT].

| Phase | $T$ range /K | Heat capacity coefficients $C^{\circ}_{p,m}$ (298.15 K) = a +bT+eT$^{-2}$ /J·K$^{-1}$·mol$^{-1}$ | | | $C^{\circ}_{p,m}$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|
| | | a | b | e | |
| **$Li_4UO_5$(cr)** | 300-860 | 189.769 | $8.9905 \times 10^{-2}$ | – 804998.9 | (207.520 ± 4.150) |
| **$Li_2UO_4$(cr)** | 300-860 | 206.825 | $-1.5795 \times 10^{-2}$ | – 4821395.5 | (147.880 ± 2.960) |
| **$Li_{22}U_{18}O_{65}$(cr)** | 300-860 | 2735.305 | $2.7386 \times 10^{-1}$ | – 53106768.3 | (2219.54 ± 44.390) |
| **$Li_2U_{1.75}O_{6.25}$(cr)** | 300-860 | 227.183 | $6.3651 \times 10^{-2}$ | – 2843098.5 | (214.180 ± 4.280) |
| **$Li_2U_2O_7$(cr)** | 300-860 | 298.921 | $-1.2039 \times 10^{-2}$ | – 6574942.6 | (221.370 ± 4.430) |
| **$Li_2U_3O_{10}$(cr)** | 300-860 | 332.453 | $1.7759 \times 10^{-2}$ | – 2717165.9 | (307.180 ± 6.140) |
| **$Li_2U_6O_{19}$(cr)** | 300-860 | 545.813 | $1.3968 \times 10^{-1}$ | – 1344453.9 | (572.340 ± 11.450) |

The extrapolation at 298.15 K is compared in Table A-159 below to Neumann Kopp's rule using the auxiliary data for $Li_2O$(cr) [1998CHA] and $UO_3$(cr) [2003GUI/FAN] retained in this review. The values found experimentally are systematically higher than predicted by this rule. The difference is rather significant (between 5.2 and 9.3 %), except for $Li_2U_2O_7$ (1.8 %) and $Li_2U_3O_{10}$ (2.7 %). This review

therefore points to the need to repeat the measurements to confirm those results, and does not select the reported equations at this time.

Only the entropy at 298.15 K of $Li_2UO_4$(cr) was estimated in the literature based on Latimer's method [1992GRE/FUG], [2003GUI/FAN], while the enthalpies of formation of $Li_2UO_4$(cr), $Li_4UO_5$(cr), $Li_2U_2O_7$(cr), $Li_2U_3O_{10}$(cr) were measured experimentally using solution calorimetry [2003GUI/FAN]. [1992GRE/FUG] and [2003GUI/FAN] selected $S^o_m$ ($Li_2UO_4$, cr, 298.15 K) = (133.0 ± 6.0) $J \cdot K^{-1} \cdot mol^{-1}$, which is listed in Table A-159 for scoping calculations in this review.

[2009RAK/JAT] estimated the entropies of the synthesised phases using the update of Mills [1974MIL2] to Latimer's method [1998SPE] as listed in Table A-159. The value found for $Li_2UO_4$, *i.e.*, $S^o_m$ ($Li_2UO_4$, cr, 298.15 K) = 136.0 $J \cdot K^{-1} \cdot mol^{-1}$ is in good agreement with that reported by [1992GRE/FUG], [2003GUI/FAN]. However, those entropy values cannot be retained in this review, which selects only experimentally determined functions.

Table A-159: Comparison between the experimentally determined heat capacities [2009RAK/JAT] and those predicted by Neumann-Kopp's rule.

| Compound | $C^o_{p,m}$ (298.15 K) /$J \cdot K^{-1} \cdot mol^{-1}$(a) | $C^o_{p,m}$ (298.15 K) /$J \cdot K^{-1} \cdot mol^{-1}$(b) | Deviation from (b) (%) | $S^o_m$ (298.15 K) /$J \cdot K^{-1} \cdot mol^{-1}$(c) |
|---|---|---|---|---|
| $Li_4UO_5$ | (207.52 ± 4.15) | 189.84 | 9.3 | 169 |
| $Li_2UO_4$ | (147.88 ± 2.96) | 135.76 | 8.9 | 136 |
| $Li_{22}U_{18}O_{65}$ | (2219.54 ± 44.39) | 2065.02 | 7.5 | 2208 |
| $Li_2U_{1.75}O_{6.25}$ | (214.18 ± 4.28) | 197.01 | 8.7 | 212 |
| $Li_2U_2O_7$ | (221.37 ± 4.43) | 217.43 | 1.8 | 238 |
| $Li_2U_3O_{10}$ | (307.18 ± 6.14) | 299.10 | 2.7 | 340 |
| $Li_2U_6O_{19}$ | (572.34 ± 11.45) | 544.11 | 5.2 | 646 |

(a) Data obtained by extrapolation of the experimental data of [2009RAK/JAT]
(b) Estimation made in this review based on Neumann Kopp's rule
(c) Estimation made by [2009RAK/JAT] based on Latimer's method and the update of Mills [1974MIL2].

**[2011KES/AGA]**

The authors investigated the K-Sr-U-O quaternary phase diagram at 1123 K in air and reported the stable phase boundaries based on their XRD analyses. Using $UO_3$, $K_2CO_3$ and $SrCO_3$ starting materials, [2011KES/AGA] prepared nineteen phases mixtures of various compositions to identify coexisting phases in the K-Sr-U-O system. $UO_3$,

$K_2CO_3$ and $SrCO_3$ were mixed in different molar ratios and heated in a alumina boat at 873 K for four hours plus 1123 K for 30 hours with intermediate regrinding steps.

Among the many phases reported in the literature for the Sr-U-O system, namely $Sr_5U_3O_{14}$, $Sr_3U_{11}O_{36}$, $Sr_3UO_6$, $SrUO_4$, $Sr_2UO_5$, $SrU_4O_{12.8}$, $Sr_3U_2O_9$, $Sr_2U_3O_{11}$, $SrU_2O_7$, only the first five well-characterised phases were included in the drawing of the $SrO$-$UO_3$ pseudo-binary sub-system at 1023 K. As for the $K_2O$-$UO_3$ pseudo-binary sub-system at 1123 K, the phases considered were: $K_2U_4O_{13}$, $K_2U_2O_7$, $K_2UO_4$. No phases were reported for the $K_2O$-$Rb_2O$ sub-system. [2011KES/AGA] could identify only one quaternary phase, namely $K_8Sr_2U_6O_{24}$, isostructural with $Na_8Sr_2U_6O_{24}$ [2008KES/KAN] and $Rb_8Sr_2U_6O_{24}$ [2002KES/AGA], with cubic symmetry and cell parameter $a$ = 8.650(3) Å. In addition, the authors estimated the enthalpies of formation and Gibbs energies of formation of $A_2Sr_2U_4O_{15}$ and $A_8Sr_2U_6O_{24}$ (A = Na, K, Rb, Cs) at 298.15 K using the method of Chen *et al.* [1999CHE/EWI]. However, we have not pursued this approach since the derived functions have appreciable uncertainties. $Cs_8Sr_2U_6O_{24}$ could not be synthesised as a stable phase, however, which was related to the large ionic radius of $Cs^+$ resulting in a high tolerance factor (1.06) in this $KUO_3$ perovskite type of lattice.

**[2013LEL/OGU]**

[2013LEL/OGU] report for the first time the measurement of the low temperature heat capacity and enthalpy of formation of $K_2[(UO_2)(W_2O_8)]$ at 298.15 K using adiabatic calorimetry in the temperature range $T$ = (9 to 329 K) and solution calorimetry in HF(aq) medium, respectively. $K_2[(UO_2)(W_2O_8)]$ was synthesised by solid state reaction from $KNO_3$, $WO_3$ and $UO_3$ mixed in stoichiometric amounts and heated in a platinum crucible in air for 96 hours at 923 K. The sample was characterised by X-ray diffraction and X-ray fluorescence spectrometry. $K_2[(UO_2)(W_2O_8)]$ has orthorhombic symmetry in space group *Pmcn*. No secondary phases were detected by XRD. The X-ray fluorescence results gave a K:U:W ratio of (2.05:1.00:2.00). The purity of the prepared sample was thereafter assumed to be better than 0.998.

The low temperature heat capacity measurements were collected on 1.3696 g of material using a "AK-9.02/BCT-21" calorimeter (TERMAX, Russia). The heat of solutions were measured using a differential heat-conducting Tian-Calvet calorimeter-type "Calvet 2.0" operating at room temperature. The uncertainty on the measurement was assessed to be ± 2 % in the range $T$ = (7 to 15 K), ± 0.5 % in the range $T$ = (15 to 40 K), and ± 0.2 % in the range $T$ = (40 to 340 K), based on the results obtained on synthetic sapphire and benzoic acid materials. Moreover, the $K_2[(UO_2)(W_2O_8)]$ sample (about 100 mg) was dissolved in 25 ml of 8.5 mol·dm$^{-3}$ HF(aq) solution. The dissolution was complete after five to ten minutes. The uncertainty on the measurement was determined to be below 3 % based on the results obtained for the enthalpy of dissolution of potassium chloride in double distilled and deionised water.

Based on the data collected with the adiabatic calorimeter, the authors derived the following thermodynamic functions at 298.15 K:

$$C^{o}_{p,m}\ (K_2[(UO_2)(W_2O_8)],\ cr,\ 298.15\ K) = (353.7 \pm 0.7)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$S^{o}_{m}\ (K_2[(UO_2)(W_2O_8)],\ cr,\ 298.15\ K) = (423.3 \pm 1.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

The present review agrees with these results.

Combining the derived standard entropy together with the NEA selected data, the standard entropy of formation was recalculated in this review at 298.15 K as $\Delta_f S^{o}_{m}\ (K_2[(UO_2)(W_2O_8)],\ cr,\ 298.15\ K) = -\ (847.34 \pm 1.28)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$.

The thermochemical cycle employed by the authors to derive the enthalpy of formation of $K_2[(UO_2)(W_2O_8)]$ is the following:

Table A-160: Thermochemical cycle used to assess the standard enthalpy of formation of $K_2[(UO_2)(W_2O_8)]$.

| | Reaction | $\Delta_r H^o(298.15K)$ /kJ·mol$^{-1}$ |
|---|---|---|
| 1 | $K_2UO_2W_2O_8 + (HF)sln \rightleftharpoons sln(A1)$ | – (133.37 ± 4.29) |
| 2 | $Na_2U_2O_7 + sln(A1) \rightleftharpoons sln(A2)$ | – (247.78 ± 7.04) |
| 3 | $2H_2O + sln(A2) \rightleftharpoons sln(A3)$ | 0 |
| 4 | $3UO_3 + (HF)sln \rightleftharpoons sln(B1)$ | – (388.58 ± 8.16) |
| 5 | $Na_2WO_4 \cdot 2H_2O + sln(B1) \rightleftharpoons sln(B2)$ | – (87.09 ± 2.55) |
| 6 | $K_2WO_4 + sln(B2) \rightleftharpoons sln(B3)$ | – (103.41 ± 1.94) |
| 7 | $K_2UO_2W_2O_8 + Na_2U_2O_7 + 2H_2O \rightleftharpoons 3UO_3 + Na_2WO_4 \cdot 2H_2O + K_2WO_4$ | **(197.93 ± 12.03)** |

Supposing that solutions (A3) and (B3) are identical, and applying Hess law, the enthalpy of Reaction (7) is calculated using the expression $\Delta_r H^o_7 = \Delta_r H^o_1 + \Delta_r H^o_2 + \Delta_r H^o_3 - \Delta_r H^o_4 - \Delta_r H^o_5 - \Delta_r H^o_6$. The enthalpy of formation of $K_2UO_2W_2O_8$ is thereafter derived from the relation:

$\Delta_f H^o_m\ (K_2UO_2W_2O_8,\ cr,\ 298.15\ K) = 3\ \Delta_f H^o_m\ (\gamma\text{-}UO_3,\ cr,\ 298.15\ K) +$
$\Delta_f H^o_m\ (Na_2WO_4{\cdot}2H_2O,\ cr,\ 298.15\ K) + \Delta_f H^o_m\ (K_2WO_4,\ cr,\ 298.15\ K) -$
$\Delta_f H^o_m\ (Na_2U_2O_7,\ cr,\ 298.15\ K) - 2\ \Delta_f H^o_m\ (H_2O,\ l,\ 298.15\ K) - \Delta_r H_7.$

Using this approach the authors derived $\Delta_f H^o_m\ (K_2UO_2W_2O_8,\ cr,\ 298.15\ K) = -\ (3897 \pm 10)\ kJ{\cdot}mol^{-1}$. The latter value was recalculated in this review to correct for the selected NEA auxiliary data, and especially for the enthalpy of formation of $Na_2U_2O_7$ which was taken as $-\ (3196.6 \pm 4.2)\ kJ{\cdot}mol^{-1}$ in the work of [2013LEL/OGU] instead of $-\ (3203.8 \pm 4.0)\ kJ{\cdot}mol^{-1}$, yielding:

$$\Delta_f H^o_m\ (K_2UO_2W_2O_8,\ cr,\ 298.15\ K) = -\ (3890.0 \pm 14.1)\ kJ{\cdot}mol^{-1}.$$

Combining the recommended standard enthalpy of formation and standard entropy of formation, the Gibbs energy of formation was recalculated in this review as:

$$\Delta_f G_m^o (K_2UO_2W_2O_8, cr, 298.15\ K) = -(3637.336 \pm 14.105)\ kJ \cdot mol^{-1}.$$

**[2015IJD/AKE]**

The crystal structure of $Na_2U_2O_7$ was an unresolved issue until very recently. Cordfunke *et al.* [1971COR/LOO] and Kovba [1972KOV] reported a monoclinic structure in the 1970s, while earlier studies by Kovba *et al.* [1958KOV/SIM] and Carnall *et al.* [1966CAR/WAL] suggested a rhombohedral and an orthorhombic symmetry, respectively. Gasparin, who synthesised single crystals of $Na_2U_2O_7$ by accident while trying to make single crystals of $UNb_3O_{10}$ in an excess of $Na_2CO_3$, reported a rhombohedral structure (in space group $R\bar{3}m$) [1986GAS]. Thermodynamic investigations by Cordfunke *et al.* moreover suggested the existence of two reversible phase transitions for this phase above about 600 K (α-β), and around 1348 K (β-γ), which they observed with a high temperature X-ray Guinier camera [1971COR/LOO], [1982COR/MUI]. But the corresponding X-ray diffraction patterns and crystal structures were not reported.

In 2015, IJdo *et al.* [2015IJD/AKE] solved the α and β structures from powder neutron diffraction data. They reported a monoclinic symmetry, in space groups *P21/a* and *C2/m*, for the α and β forms, respectively. They also suggested that the rhombohedral crystal structure, as determined by Gasparin [1986GAS], could correspond to a high temperature modification, with delocalised U and O atoms [2015IJD/AKE]. The refined cell parameters are the following: $a$ = 12.7617(14) Å, $b$ = 7.8384(10) Å, $c$ = 6.8962(9) Å, β = 111.285(9) ° for α-$Na_2U_2O_7$; $a$ = 12.933(1) Å, $b$ = 7.887(1) Å, $c$ = 6.9086(8) Å, β = 110.816(10) ° for β-$Na_2U_2O_7$.

**[2015SMI]**

To complement the structural results reported by [2015SMI/RAI2], Smith performed thermodynamic calculations on the trisodium uranate compound in her Ph.D. thesis [2015SMI]. Indeed, [2015SMI/RAI2] could not confirm the existence of stoichiometric α-$Na_3UO_4$, but obtained instead the mixed valence state composition α-$Na_{3.16(2)}U_{0.84(2)}O_4$.

O'Hare *et al.* reported the preparation of the α-$Na_3UO_4$ stoichiometric compound, which was used to determine its enthalpy of formation [1972OHA/SHI], heat capacity, entropy and Gibbs energy at 298.15 K [1972OSB/FLO], as well as heat capacity at high temperatures [1972FRE/CHA]. The synthesis method, chemical analysis, X-ray diffraction, and metallography results reported in the paper of O'Hare *et al.* [1972OHA/SHI] were therefore re-examined by [2015SMI] to verify if their sample

could not correspond to a mixed valence state $Na_{3+x}U_{1-x}O_4$ phase rather than stoichiometric $Na_3UO_4$. The chemical analysis showed (2 ± 1.8) wt % $UO_2$ impurity. From this impurity content, [2015SMI] deduced that the synthesised compound could have corresponded to the $Na_{3.014}U_{0.986}O_4$ chemical composition with the associated synthesis reaction:

$$UO_{2.14}(cr) + 1.77Na_2O_{1.05}(cr) \rightleftharpoons 0.986Na_{3.014}U_{0.986}O_4(cr) + 0.028UO_2(cr) + 0.568Na(g)$$

$Na_{3.014}U_{0.986}O_4$ is a mixed valence state composition with 5.7 % U(VI) and 93.4 % U(V). [2015SMI] subsequently re-examined the solution calorimetry results of O'Hare *et al.* [1972OHA/SHI], as well as low [1972OSB/FLO] and high temperature [1972FRE/CHA] calorimetry measurements on this compound, to account for this corrected formula (corresponding to a molar mass of M = 367.986 g·mol$^{-1}$ as opposed to 370.996 g·mol$^{-1}$ for stoichiometric $Na_3UO_4$), and to assess the influence of the uncertainty introduced by the $UO_2$ content on the exact chemical composition.

The thermodynamic functions corresponding to the corrected $Na_{3.014}U_{0.986}O_4$ stoichiometry were derived as: $\Delta_f H^o_m(Na_{3.014}U_{0.986}O_4, \alpha, 298.15\ K) = -(2010.4 \pm 6.6)$ kJ·mol$^{-1}$, $C^o_{p,m}(Na_{3.014}U_{0.986}O_4, \alpha, 298.15\ K) = (173.9 \pm 0.1)$ J·K$^{-1}$·mol$^{-1}$, $S^o_m(Na_{3.014}U_{0.986}O_4, \alpha, 298.15\ K) = (199.2 \pm 0.4)$ J·K$^{-1}$·mol$^{-1}$.

However, the thermodynamic functions derived by O'Hare and co-workers were corrected for (0.68 ± 0.06) wt % $UO_2$ impurity, based on the low temperature specific heat results of Osborne *et al.* [1972OSB/FLO], and not (2 ± 1.8) wt % $UO_2$ impurity. Indeed, the latter authors observed a λ-type anomaly around 30 K in their low temperature specific heat data, which they attributed to the $UO_2$ impurity, and subsequently estimated the corresponding content based on the magnitude of the anomaly. With such impurity content, the chemical composition of the sample should be very close to $Na_3UO_4$, and the associated thermodynamic functions selected by [2003GUI/FAN] should be retained:

$$\Delta_f H^o_m(Na_3UO_4, \alpha, 298.15\ K) = -(2024.0 \pm 8.0)\ kJ{\cdot}mol^{-1}$$

$$C^o_{p,m}(Na_3UO_4, \alpha, 298.15\ K) = (173.0 \pm 0.4)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$S^o_m(Na_3UO_4, \alpha, 298.15\ K) = (198.2 \pm 0.4)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

It is difficult to definitively conclude between the chemical analysis results and those suggested by the low temperature specific heat, and therefore to decide between the assignment of one or the other stoichiometry. The work of [2015SMI/RAI2] and [2015SMI] therefore point to the need for a re-assessment of the thermodynamic functions of the trisodium uranate with a careful characterisation of the sample's exact stoichiometry using X-ray Absorption Spectroscopy for instance.

In addition, [2015SMI] reported structural and thermodynamic investigations of the Na-Np-O and Na-Pu-O systems. Most of the data were published in separate articles [2015SMI/RAI], [2015SMI/HEN], [2015SMI/HEN2], [2016SMI/MAR], and

we will not repeat the findings here. [2015SMI] measured the low temperature heat capacity of $Na_5NpO_6$ and $Na_5PuO_6$, but those data were not published to this date elsewhere. The measurements were performed in the temperature range $T$ = (2.0 to 283.7) K and $T$ = (8.5 to 262.9) K for $Na_5NpO_6$ and $Na_5PuO_6$, respectively. The derived heat capacity and entropy values are:

$$C^{o}_{p,m}(Na_5NpO_6, cr, 298.15\ K) = (293.0 \pm 8.9)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}(Na_5NpO_6, cr, 298.15\ K) = (334.3 \pm 9.0)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$C^{o}_{p,m}(Na_5PuO_6, cr, 298.15\ K) = (302.2 \pm 9.6)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}(Na_5PuO_6, cr, 298.15\ K) = (355.7 \pm 8.8)\ J\cdot K^{-1}\cdot mol^{-1}.$$

$Na_5NpO_6$ and $Na_5PuO_6$ were synthesised by the reaction of neptunium dioxide and plutonium oxide with sodium carbonate mixed in (1:3) ratio, and heating under $O_2$ flow at 1093 K . The synthesis reaction can be written as follows with M = (Np, Pu):

$$MO_2 + 3Na_2CO_3 \rightleftharpoons Na_5MO_6 + Na(g) + 3CO_2(g)\,.$$

[2015SMI] did not report any chemical analysis of the final samples unfortunately. Give that the synthesis was performed with a slight excess of sodium carbonate, we cannot rule out the possible presence of remaining sodium or sodium oxide impurities. The derived data are therefore not retained in this review, but can only be used for scoping calculations.

**[2015SMI/COL]**

[2015SMI/COL] reported for the first time a measurement of the sodium partial pressure over the ternary phase field $NaUO_3$-$Na_2U_2O_7$-$UO_2$ using Knudsen effusion mass spectrometry, hence complementing similar vaporisation studies carried out in neighbouring phase fields of the Na-U-O phase diagram by Battles *et al.* [1972BAT/SHI], Jayanthi *et al.* [1994JAY/IYE], and Pankajavelli *et al.* [2012PAN/CHA]. The purities of the $NaUO_3$ and α-$Na_2U_2O_7$ materials were checked using X-ray diffraction and ICPMS-analysis. No secondary phases were detected with the X-rays. The chemical analyses revealed sodium to uranium ratios of (0.999 ± 0.011) and (1.029 ± 0.011), respectively, and the mass fraction purities were evaluated as > 0.995 and > 0.99 for $NaUO_3$ and $Na_2U_2O_7$, respectively.

Their measurement refer to the following equilibrium reaction:

$$3NaUO_3(cr) \rightleftharpoons Na_2U_2O_7(cr) + UO_2(cr) + Na(g)$$

The temperature dependence of the sodium pressure was determined as:

$$\log(P_{Na}/Pa) = 10.98\ (\pm 0.04) - 14999(\pm 50) / (T/K).$$

The enthalpy of formation of α-$Na_2U_2O_7$ was subsequently derived by second and third law treatment of the data as: $\Delta_f H^o_m$ ($Na_2U_2O_7$, α, 298.15 K) = – (3208.4 ± 5.5) kJ·mol$^{-1}$ and – (3235.4 ± 1.2) kJ·mol$^{-1}$, respectively. The second law result is in very good agreement with the value selected by [2003GUI/FAN], which is based on the solution calorimetry studies of [1985TSO/BRO] obtained on a high purity sample prepared by thermal decomposition in oxygen atmosphere of $NaUO_2(CH_3COO)_3$, *i.e.*, $\Delta_f H^o_m$ ($Na_2U_2O_7$, α, 298.15 K) = – (3203.8 ± 4.0) kJ·mol$^{-1}$.

[2015SMI/COL] assigned the discrepancy between second and third law results to a possible poor description of the entropy function of $NaUO_3$. When using $S^o_m$ ($NaUO_3$, cr, 298.15 K) = (126.4) J·K$^{-1}$·mol$^{-1}$ instead of the value recommended by [2003GUI/FAN] (132.8 J·K$^{-1}$·mol$^{-1}$), the authors obtained a better agreement between second and third law analyses of their data. They selected the enthalpy of formation of α-$Na_2U_2O_7$ derived from the second law analysis, estimated independently of the entropy value of $NaUO_3$. We agree with their calculations which used the NEA auxiliary data, yielding $\Delta_f H^o_m$ ($Na_2U_2O_7$, α, 298.15 K) = – (3208.4 ± 5.5) kJ·mol$^{-1}$.

[2015SMI/COL] also performed high temperature X-ray diffraction measurements on α-$Na_2U_2O_7$, which revealed a phase transition to β-$Na_2U_2O_7$ between 623 and 748 K. The corresponding transition showed very slow kinetics. A second transition to a high temperature γ phase was observed between 1223 and 1323 K. The kinetics were rapid this time. This γ compound was characterised with a rhombohedral structure, in space group $R\bar{3}m$, and corresponded to the phase synthesised by [1986GAS] and quenched to room temperature.

**[2015SMI/GRI]**

The low temperature heat capacities of $Na_4UO_5$ and $Na_4NpO_5$ were measured for the first time over the temperature range 1.9 to 292 K using thermal relaxation calorimetry with a Physical Property Measurement System instrument (PPMS, Quantum Design). $Na_4UO_5$ was provided by NRG (Petten, The Netherlands). $Na_4NpO_5$ was prepared from $Na_2CO_3$ and $NpO_2$ mixed in stoichiometric amounts. The X-ray diffraction analyses showed minor secondary phases of α-$Na_2UO_4$ (1.6 wt %) and α-$Na_2NpO_4$ (0.5 wt %), respectively. Moreover the ICPMS analyses revealed sodium to uranium and sodium to neptunium ratios of (3.963 ± 0.016) and (4.006 ± 0.048), respectively. The corresponding mass fraction purities were estimated as 0.984 for $Na_4UO_5$ and 0.995 for $Na_4NpO_5$. The data were subsequently corrected for the α-$Na_2UO_4$ [1974OSB/FLO3] and α-$Na_2NpO_4$ impurities [2015SMI/GRI2].

The authors derived the following thermodynamic functions at 298.15 K:

$$C^o_{p,m}\ (Na_4UO_5, cr, 298.15\ K) = (220.6 \pm 6.7)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$S^o_m\ (Na_4UO_5, cr, 298.15\ K) = (247.5 \pm 6.2)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$C^{o}_{p,m}(Na_4NpO_5, cr, 298.15\ K) = (219.0 \pm 6.6)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$S^{o}_{m}(Na_4NpO_5, cr, 298.15\ K) = (247.5 \pm 6.2)\ J\cdot K^{-1}\cdot mol^{-1}.$$

We agree with their determination and assigned uncertainties.

Interestingly, $Na_4NpO_5$ revealed a broad anomaly between 3 and 15 K, with a maximum value at 7 K. This feature was interpreted as a Schottky type anomaly associated with low lying electronic energy levels [2015SMI/HEN]. Its entropy contribution was determined as 4.57 $J\cdot K^{-1}\cdot mol^{-1}$ after subtraction of the lattice contribution approximated with that of $Na_4UO_5$.

**[2015SMI/RAI2]**

The crystal structure of trisodium uranate $Na_3UO_4$ was the subject of controversy up to now, despite its technological importance for the safety assessment of Sodium-cooled Fast Reactors. [2015SMI/RAI2] have solved the structure of the α form of the compound for the first time using powder X-ray and neutron diffraction combined with X-ray Absorption Spectroscopy and $^{23}Na$ Magic Angle Spinning Nuclear Magnetic Resonance measurements. They showed α-$Na_3UO_4$ to be isotructural with $Na_3BiO_4$, *i.e.*, monoclinic in space group *P2/c*. Moreover, they found that this structure could accommodate some cationic disorder, with up to 16(2) % sodium on the uranium site, corresponding to the composition α-$Na_3(U_{1-x},Na_x)O_4$ ($0 < x < 0.18$). The α phase adopts a mixed valence state composition, which was never considered in past studies. α-$Na_3(U_{1-x}, Na_x)O_4$ is found on the pseudo binary section between $Na_3UO_4$ and $Na_4UO_5$. The extent of the solubility domain needs to be investigated in future studies.

[2015SMI/RAI2] also investigated the two polymorphs of this compound, m and β, reported in the literature. They showed that m-$Na_3UO_4$, which shows a cubic disordered structure of the NaCl type, must correspond to a metastable phase. In fact, [2015SMI/RAI2] could synthesise m-$Na_4UO_5$, but not m-$Na_3UO_4$, which would require very reducing conditions. The existence of the latter phase still needs to be confirmed. Finally, the high temperature β-phase, obtained after thermal treatment at 1473 K of the α-phase, was confirmed to be cubic, in space group $Fd\bar{3}m$, in good agreement with the studies of Marcon *et al.* [1972MAR/PES]. The NMR results on this phase also suggested the possible formation of a mixed valence state composition, *i.e.*, β-$Na_3(U_{1-x},Na_x)O_4$ ($0< x <0.2$).

## A-1.13 Uranium compounds with elements from other groups

**[2005DON/STE]**

[2005DON/STE] report the measurement of the low temperature heat capacity of brannerite $UTi_2O_6$ and cerium brannerite $CeTi_2O_6$ using adiabatic calorimetry in the temperature range 10-400 K. $UTi_2O_6$ shows a monoclinic symmetry, in space group *C2/m,* with cell parameters $a$ = 9.8123(15), $b$ = 3.7697(6), $c$ = 6.9253(9) Å, β = 119.15 ° [1982SZY/SCO]. $UTi_2O_6$ was synthesised by mixing uranium dioxide $UO_2$ and 99.9 % anatase $TiO_2$ for 300 hours in a gas mixture of 5 % CO and 95 % $CO_2$ at 1623 K. The final composition determined by X-ray diffraction was $U_{0.952}Ti_{2.04806}O_6$ mixed with 0.31 wt % $UO_2$ impurity. The uncertainty on the heat capacity measurements was estimated to be within the stated uncertainties for synthetic sapphire (NIST SRM-720), measured on the same apparatus. The uncertainty on temperature was estimated for be ± 0.03 K below $T$ = 13.8 K, ± 0.016 K between 13.8 < $T$ /K < 40 K, and ± 0.005 K for 40 < $T$ /K = 523 K. The heat capacity data of $U_{0.952}Ti_{2.04806}O_6$ were corrected for the $UO_2$ impurity, and especially for the magnetic transition of uranium dioxide around 30 K, based on the heat capacity data of Huntzicker and Westrum [1971HUN/WES] that refer to a well characterised sample. The standard entropy selected by [1992GRE/FUG], [2003GUI/FAN] for uranium dioxide corresponds to the CODATA value, which is based on the same results by Huntzicker and Westrum [1971HUN/WES], *i.e.* $S^{o}_{m}$ ($UO_2$, cr, 298.15 K) = (77.03 ± 0.20) J·K$^{-1}$·mol$^{-1}$. The heat capacity and standard entropy at 298.15 K reported for $U_{0.952}Ti_{2.04806}O_6$ are accepted in the present review, with uncertainties estimated by this review:

$$C^{o}_{p,m}\ (U_{0.952}Ti_{2.04806}O_6, \text{cr}, 298.15\ \text{K}) = (179.\ 46 \pm 3.4)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$S^{o}_{m}\ (U_{0.952}Ti_{2.04806}O_6, \text{cr}, 298.15\text{K}) = (175.56 \pm 3.5)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

Using the auxiliary data recommended in this review, we have recalculated the standard entropy of formation:

as $\Delta_f S^{o}_{m}$ ($U_{0.952}Ti_{2.04806}O_6$, cr, 298.15 K) = – (550.6 ± 3.5) J·K$^{-1}$·mol$^{-1}$.

**[2005VOL/MAY]**

[2005VOL/MAY] reported the preparation and structural characterisation of the thallium uranates $Tl_4UO_5$, $Tl_2UO_4$, $Tl_2U_2O_7$, and $Tl_2U_3O_{10}$ by IR, Raman spectroscopy, electronic and X-ray absorption spectroscopy at the U-$L_{III}$ edge. In addition, the authors studied the thermal stability by thermogravimetry, heating the samples under nitrogen to 1223 K at 5 K·min$^{-1}$. $Tl_2U_3O_{10}$ was found the most stable compound, followed by $Tl_2U_2O_7$, $Tl_2UO_4$ and $Tl_4UO_5$. The weight loss observed was attributed to thallium, but neither the black product formed during the DTA measurements nor the final red powders were analysed. The mechanism of decomposition is therefore still unclear. The authors reported this black

product could correspond to $UO_2$ or $UO_{2+x}$, an oxygen deficient uranate, or $Tl_2O$. [2005VOL/MAY] also made estimates for the enthalpies of formation for the thallium compounds based on comparison with other alkali metal uranates, *i.e.*, $\Delta_f H_m^o$ ($Tl_4UO_5$, cr, 298.15 K) = – 2437.0 kJ·mol$^{-1}$, $\Delta_f H_m^o$ ($Tl_2UO_4$, cr, 298.15 K) = – 1900.0 kJ·mol$^{-1}$, $\Delta_f H_m^o$ ($Tl_2U_2O_7$, cr, 298.15 K) = – 3182.0 kJ·mol$^{-1}$, $\Delta_f H_m^o$ ($Tl_2U_3O_{10}$, cr, 298.15 K) = – 4437.0 kJ·mol$^{-1}$. However, those data which are not based on experimental measurements cannot be retained in the present review.

**[2015POP/BEN]**

[2015POP/BEN] measured for the first time the low temperature heat capacity of α-$Bi_2UO_6$ in the temperature range $T$ = 1.85 to 270 K using hybrid adiabatic relaxation calorimetry, and the enthalpy increments in the temperature range $T$ = 430.3 to 1088.8 K using drop calorimetry. α-$Bi_2UO_6$ was prepared by solid state reaction between α-$Bi_2O_3$ and $UO_3$ mixed in stoichiometric amounts and heated under air at successively 1073 K and 1273 K. The X-ray diffraction analysis revealed a monoclinic structure in space group *C2* with cell parameters $a$ = 6.889(3) Å, $b$ = 4.007(4) Å, $c$ = 9.691(5) Å, β = 90.13(3) ° in good agreement with the literature [1999VAN/THE]. Electronic microprobe analysis indicated a (Bi:U) ratio of (2.068:0.966) normalised for 6 oxygen atoms per formula unit. DTA/TG measurements showed the compound was stable up to 1345.5 K under air. Above this temperature, $Bi_2UO_6$ decomposes to the corresponding oxides. Under reducing atmosphere (Ar-5 % $H_2$) it reduces to $UO_2$ and bismuth metal at 1173 K. The low temperature heat capacity measurement showed no anomaly over the whole temperature range. We agree with the derivation of the heat capacity and entropy values at 298.15 K. The errors have been estimated in this review:

$$C_{p,m}^o (\alpha\text{-}Bi_2UO_6, \text{cr}, 298.15\ \text{K}) = (185.1 \pm 5.6)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^o (\alpha\text{-}Bi_2UO_6, \text{cr}, 298.15\ \text{K}) = (238.8 \pm 7.7)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The equation for the enthalpy increment, and thereafter heat capacity at high temperatures was not reported correctly. We suspect a typing error. The evolution of the heat capacity for the temperature range $T$ = 298.15 to 1088.8 K is given by the equation below, which satisfies the constraints $H_m^o(T) - H_m^o(298.15\,\text{K}) = 0$ at 298.15 K and $C_{p,m}^o$ (298.15 K) = 185.1 J K$^{-1}$ mol$^{-1}$:

$$C_{p,m}^o (\alpha\text{-}Bi_2UO_6, \text{cr}, T) = 230.912 + 1.812\times10^{-2}\,T - 4.5526\times10^{6}\,T^{-2}\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad \text{(A.408)}$$

It should be pointed out that a phase transition to a trigonal fluorite like structure β-$Bi_2UO_6$ in space group $P\bar{3}$ was reported by [1975KOS/REN] between 873 and 1073 K. The transition was reported to be reversible, and the α and β structures were found to be closely related. [2015POP/BEN] performed an X-ray diffraction analysis after their drop calorimetry measurements, and found no change in the X-ray diffraction pattern. Moreover, the enthalpy increment data did not show any sign of a transition. We conclude that the measurements must refer to the α form over the full temperature range covered.

# Discussion of selected references for Neptunium

**[1977ERM/PER]**

Ermakov *et al.* investigated the formal redox potential of the Np(VII)/Np(VI) couple in 0.3-1.0 M LiOH solutions at constant ionic strength ($I$ = 1 M Li($NO_3$, OH)) by potentiometry at $T$ = (25.0 ± 0.2) °C under Ar atmosphere (with 15 minutes of equilibration time). The initial concentrations of both Np(VII) and Np(VI) were $3 \times 10^{-3}$ M. The authors reported $E$(Np(VI)/Np(V)) = 0.604 V in 1.0 M LiOH. Ermakov and co-workers recorded also polarographic curves for the reduction of Np(VII) to Np(VI) and Np(V), and for the reduction of Np(VI) to Np(V).

**[1998KAT/KIM]**

The work by Kato and co-workers was neither reviewed in [2001LEM/FUG] nor in [2003GUI/FAN], but represents a very relevant contribution for the assessment of Np(VI) solubility and aqueous speciation in carbonate systems. The authors conducted long-term solubility experiments ($t \geq 1$ year) with $NpO_2CO_3$(cr) in a controlled atmosphere with 80 % $CO_2$ / 20 % $O_2$. The stabilisation of Np(VI) was ensured with the systematic generation of ozone, which resulted in $E_h$ = 1.5-0.055 pH (in V, *vs.* SHE). Experiments were performed at $T$ = (25.0 ± 0.1) °C in 0.1 M $NaClO_4$ solutions with 2.79 ≤ pH ≤ 6.82. Solid phases equilibrated at different pH values (and thus carbonate concentrations) were characterised by XRD, UV-vis/NIR PAS and FT-IR PAS, confirming in all cases the only presence of a rather crystalline $NpO_2CO_3$(cr) phase. Experimental solubility data reported by the authors are in good agreement with results obtained in [1998VIT/CAP] for the solubility of $NpO_2CO_3$(s)[1] at $P_{CO_2}$ = 1 atm in 0.17 M $NaClO_4$ solutions (only three experimental data points). Kato and co-workers proposed the equilibrium Reactions (A.409) to (A.411) to explain their experimental solubility data. The incorporation of the species $NpO_2(CO_3)_2^{2-}$ in the chemical model was not necessary to satisfactorily reproduce the experimental results, and thus only an upper limit of the corresponding formation constant was reported by the authors. The possible formation of the trimeric species $(NpO_2)_3(CO_3)_6^{6-}$ was disregarded by the authors, on the basis of the slope analysis of their solubility data ($\log_{10}$[Np(VI)] *vs.* $\log_{10}[CO_3^{2-}]$) and the lesser stabilisation of this highly-charged species at low ionic strength. This hypothesis is consistent with the current knowledge available for An(VI) and it is supported by the

[1] The solid phase was not characterized in [1998VIT/CAP] but assumed to be $NpO_2CO_3$(s).

present review. Conditional equilibrium constants determined in 0.1 M $NaClO_4$ were extrapolated to $I = 0$ by SIT using the ion interaction coefficients previously reported for U(VI)-$CO_3$ species in [1992GRE/FUG].

$$NpO_2CO_3(cr) \rightleftharpoons NpO_2^{2+} + CO_3^{2-} \quad \text{(A.409)}$$

$$NpO_2^{2+} + CO_3^{2-} \rightleftharpoons NpO_2CO_3(aq) \quad \text{(A.410)}$$

$$NpO_2^{2+} + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{4-} \quad \text{(A.411)}$$

Chemical and thermodynamic models derived in [1998KAT/KIM] are accepted in the present review. The very minor differences in $\log_{10}[CO_3^{2-}]$ calculated by the authors and in the present review arise from the slightly different Henry constants of $CO_2$(g) ($K_H^o$) and dissociation constants of $H_2CO_3$ ($K_1^o$ and $K_2^o$) and lay well below the experimental uncertainty of the results. The authors argued that ionic strength was maintained constant with 0.1 M $NaClO_4$ as background electrolyte. Indeed, above $-\log_{10}[H^+] \approx 5.7$ the ionic strength in the experiments by Kato and co-workers increased steadily due to the contribution of $HCO_3^-$. Consequently, experimental solubility data reported above $-\log_{10}[H^+] \approx 6.2$ ($\log_{10}[HCO_3^-] \approx -1.6$; $I_m \approx 0.13$ mol·kg$^{-1}$) have been disregarded in this review. The extrapolation of the resulting conditional equilibrium constants to $I = 0$ using ion interaction coefficients summarised in Appendix B for $NpO_2^{2+}$, $CO_3^{2-}$ and $NpO_2(CO_3)_3^{4-}$ results in $\log_{10}K°$(A.409) = $-(14.88 \pm 0.07)$, $\log_{10}K°$(A.410) = $(9.86 \pm 0.10)$ and $\log_{10}K°$(A.411) = $(20.35 \pm 0.09)$.

**[1998MAY/TAY]**

May *et al.* [1998MAY/TAY] investigated the distribution of Np(IV) between nitric acid and 30 % tributylphosphate in odourless kerosene. Modelling of experimental data reported in this study is provided in [2009SAR/SIM] and [2011SAR/SIM].

**[2001GEL/VAN]**

Gelis *et al.* [2001GEL/VAN] investigated the redox behaviour of Np(VII/VI/V) in concentrated LiOH, NaOH and NaOH-$Na_2CO_3$ solutions using a combination of electrochemical and spectrophotometric methods. Experiments were performed at $T = 25$ °C under Ar atmosphere. MOH solutions were prepared from concentrated stocks (50 % NaOH and 5.1 M LiOH). The authors assumed carbonate-free conditions because of the low solubility of $M_2CO_3$ in these conditions. This is true for NaOH, but the method has been reported to be insufficient in the case of Li because the solubility of LiOH is too low as to salt out the carbonate [2000SIP/MAY]. Spectrophotometric experiments were performed with $[Np(V)]_0 = 1.12 \times 10^{-3}$ M in $1.0 \text{ M} \leq [\text{LiOH}] \leq 4.9$ M. The authors observed several spectroscopic features at 1027, 1029, 1036 and 1045 nm. Note that in this wavelength region, Neck *et al.* [1997NEC/FAN] reported the formation of

$NpO_2(OH)_2CO_3^{3-}$ and colloidal Np(V) hydroxide. Initial Np concentration was found to significantly decrease after three days in all cases, clearly indicating that the original solutions were oversaturated with respect to Li-Np(V)-OH(s) phases.

Although not clearly stated for all systems, cyclic voltammetry experiments in the absence of carbonate were apparently performed with $[Np]_0 = 2.0 \times 10^{-3}$ M. The precipitation of M-Np(V)-OH(s) and M-Np(VI)-OH is expected in these conditions, also in view of the observations collected by the same authors in the spectroscopic measurements with Np(V). In 3.1 M LiOH solutions, Gelis and co-workers observed a quasi-reversible and reversible behaviour of the Np(VII)/Np(VI) and Np(VI)/Np(V) couples, respectively. The irreversible reduction of Np(V) to Np(IV) was related with the precipitation of Np(IV) hydroxide. The reversibility observed for the Np(VI)/Np(V) couple above $[MOH] \approx 1.0$ M was used as criteria to define the existence of $NpO_2(OH)_4^{3-}$. A non-reversible behaviour of this couple was claimed at lower MOH concentrations, although these data are not shown in the publication. Formal potentials of the Np(VI)/Np(V) couple in 1.35 M ≤ [LiOH] ≤ 4.00 M and 1.00 M ≤ [NaOH] ≤10.50 M were quantified with emf measurements of the cells Pt, Hg ⎪ HgO, NaOH ‖ MOH, Np(VI), Np(V) ⎪ Pt or Pt, Hg ⎪ $HgCl_2$, $KCl_{sat}$ ‖ MOH, Np(VI), Np(V) ⎪ Pt. Significantly different values and trends of $E$(Np(VI)/Np(V)) with increasing [MOH] were obtained in NaOH and LiOH systems. The reported increase of the formal potential with increasing [LiOH] is in disagreement with other observations reported in the literature [1977ERM/PER], [2006SHI/YUS], and was explained with the formation of a previously unreported complex, $LiNp^{V}O_2(OH)_4^{2-}$. The unexpected behaviour in LiOH solutions could be related with the precipitation of Li-Np(V)-OH(s) and/or Li-Np(VI)-OH(s), but possibly also with the formation of Np(V)-OH-$CO_3$ aqueous species as a result of carbonate impurities present in LiOH. Indeed, scoping calculations conducted in this review assuming the presence of 0.5-1 % carbonate impurities predict the predominance of ternary Np(V)-OH-$CO_3$ complexes within the boundary conditions investigated in [2001GEL/VAN].

Cyclic voltammetry in mixed NaOH-$Na_2CO_3$ systems confirmed the irreversibility of the Np(VII)/Np(VI) couple in carbonate media, and showed a quasi-reversible behaviour for Np(VI)/Np(V). In the second case and provided the expected predominance of ternary Np-OH-$CO_3$ aqueous complexes of Np(V), the authors hypothesised on the possible formation of analogous ternary complexes for Np(VI). Besides the dimer $(AnO_2)_2CO_3(OH)_3^-$ (An = U, Np) reported to form under near neutral to weakly alkaline conditions, no such complexes have been previously defined for any An(VI). The hypothesis of ternary Np(VI)-OH-$CO_3$ complex formation is plausible from the perspective of chemical reasoning, but this review finds no compeling evidence in the voltammetry results reported by Gelis and co-workers. Hence, a quasi-reversible behaviour of the Np(VI)-OH/Np(V)-OH-$CO_3$ couple can also be expected in the case of a fast $OH^-/CO_3^{2-}$ ligand exchange.

Because of the relevant uncertainties and experimental shortcomings identified, no selection of thermodynamic data can be recommended from the experimental results reported in [2001GEL/VAN].

**[2001KIT/KOH]**

See comments under Kitamura and Kohara [2004KIT/KOH].

**[2001SER/ARA]**

[2001SER/ARA] have estimated the heat capacity of $NpO_2$(cr) between 300 and 1400 K from the sum of the phonon vibration $C_{ph,m}$, dilatation $C_{d,m}$ and Schottky $C_{s,m}$ contributions. The phonon contribution to the heat capacity was calculated based on the Debye temperature $\Theta_D$ = 435 K for $NpO_2$(cr), determined using X-rays [1999SER/ARA].

In addition, the authors measured the thermal expansion of neptunium dioxide up to $T$ = 1573 K using high-temperature X-ray diffraction under argon flow. Their results were found in good agreement with those of Yamashita *et al.* [1997YAM/NIT] reported up to 1273 K. The dilatation heat capacity $C_{d,m}$ was subsequently estimated from the compounds linear thermal expansion and Grüneisen constant γ using the relation $C_{d,m} = \alpha \cdot \gamma \cdot T \cdot C_{ph,m}$. By contrast with the work of [1997YAM/NIT] based on the Grüneisen constant of $UO_2$(cr), [2001SER/ARA] used γ = 1.93 for the Grüneisen constant of $NpO_2$(cr) as determined by [1999SER/ARA]. The authors also checked that the temperature dependence of γ had a very limited effect on the derived heat capacity. The electronic contribution to the heat capacity was estimated from the crystal field energies determined by Krupa and Gajek [1991KRU/GAJ], *i.e.*, a ground state quartet $\Gamma_8$, a first excited quartet $\Gamma'_8$ at 465.3 $cm^{-1}$ and a second excited doublet $\Gamma_6$ at 2051 $cm^{-1}$. The sum of all three contributions $C_{ph,m}$, $C_{d,m}$ and $C_{s,m}$, yields heat capacity values $C_{p,m}(T)$ in very good agreement with Westrum *et al.* [1953WES/HAT] at 300 K, the corresponding value being 66.86 $J \cdot K^{-1} \cdot mol^{-1}$, but somewhat lower than selected in this review at higher temperatures. The heat capacity determined by [2001SER/ARA] is about 5 $J \cdot K^{-1} \cdot mol^{-1}$ lower than derived by [2011BEN/GOT] at 1000 K. [2001SER/ARA] report a maximum error in their estimation of about 8.6 % at 1400 K and below 5 % between room temperature and 900 K, which is consistent with respect to the experimental data collected later by [2011BEN/GOT].

**[2002FAN/NEC]**

Fanghänel and Neck provide a review of experimental and thermodynamic data available for the solubility behaviour of actinide solid phases in carbonate-free aqueous systems. The solubility of actinide oxides and hydroxides are evaluated as function of several

parameters, such as crystallinity, particle size, pH and calculated stabilities. Experimental solubility data are compared with the data predicted from available thermodynamic data. The authors discuss the solubility of fresh and aged $NpO_2OH(s)$, $UO_2(OH)_2(s)$ and $NaUO_2(OH)_3(s)$, amorphous and crystalline $Am(OH)_3(s)$, amorphous hydrated and crystalline $AnO_2(s)$ solid phases with An = Th, U and Pu. The thermodynamic data used in this review for calculations and discussions are taken from the NEA TDB. No new experimental or thermodynamic data are provided.

**[2002KIT/KOH]**

See comments under Kitamura and Kohara [2004KIT/KOH].

**[2002MOR/FUJ]**

The authors use the effective charge of actinide ions in a hard sphere model to estimate formation constants of actinide carbonate and fluoride complexes. The authors used formation constants selected by the NEA TDB and averaged literature data for which an evaluation has not been performed. The SIT with evaluated or estimated ion-interaction parameters was applied to correct for ionic strength effects. The hard sphere model was applied by introducing the effective charge of the actinide ions and with the assumption that all actinide complexes exhibit an octahedral structure. The ionic radii for the hexacoordinated actinide ions were taken from the literature [1994CHO/RIZ]. The electric charge for $F^-$ and $OH^-$ ligands was assumed to be – 1, while the effective charge for the $CO_3^{2-}$ was calculated to be $-(1.219 \pm 0.23)$ with a ligand radius of $(1.735 \pm 0.017)$ Å. The effective charge of water used was – 0.57 with a dielectric constant of 7.60. The authors used a least-square fitting routine of formation constants according to the Equation (A.412):

$$\beta_n^o = \exp(-\Delta E/RT) \qquad \text{(A.412)}$$

where $R$ is the gas constant, $T$ is the absolute temperature and $\Delta E$ is the potential energy difference between the actinide complex and the actinide ion. The electrostatic potential energy (E) of each species is calculated from the electric charge of the hard spheres according to $E = \Sigma(Z_i Z_j/\varepsilon d_{ij})$ where Z is the effective charge of the species, ε is the dielectric constant and $d_{ij}$ is the distance between the hard spheres. The effective charges of the non-complexed actinide ions are calculated to be larger than their nominal values suggesting that additional non-electrostatic interactions are involved. The calculated $\log_{10}\beta_n^o$ values generally increase with the number of ligands and are within the uncertainty ranges of the reference data. However, some data show significant discrepancies between analogous U, Np, Pu and Am complexes of same oxidation states.

**[2002NAK/ARA]**

[2002NAK/ARA] report for the first time the measurement of the heat capacity of NpN(cr), in the temperature range 323-1023 K by Differential Scanning Calorimetry using the scanning method. The accuracy of the data was checked by measuring the heat capacities of UN(cr), PuN(cr) and $UO_2$(cr) using the same method. The NpN(cr) sample was obtained by carbothermic reduction of $NpO_2$(cr), pressed into a pellet with about 400 MPa, and sintered at 2003 K under Ar-8 % $H_2$. Oxygen and carbon impurities were estimated to be below 0.1 wt %. X-ray diffraction characterisations were performed before and after the DSC measurement. The DSC measurements were performed under high purity argon flow, and used sapphire as standard material. The derived heat capacity for NpN(cr), *i.e.*, $C^{\circ}_{p,\mathrm{m}}(\mathrm{NpN, cr}, T) = 43.4 + 2.31 \times 10^{-2}\,T - 7.62 \times 10^{-6}\,T^2 - 9.08 \times 10^{4}\,T^{-2}$ J·K$^{-1}$·mol$^{-1}$, was found about 3 % lower at 1000 K than the estimate by [2001LEM/FUG]. The derived function is also lower than that of UN(cr) and PuN(cr), which is unexpected. The authors stress that the accuracy of their measurement is about 3 % and is worse at higher temperatures. We therefore prefer in this review to retain the estimate by [2001LEM/FUG] for the temperature range 298.15-2000 K:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{NpN, cr}, T) = 47.67 + 1.3174\times10^{-2}T - 2.5762\times10^{5}T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

**[2002YUS/FED]**

Yusov and coworkers studied spectroscopically the interaction of Np(IV, V and VI) and Pu(IV and VI) with Al(III) hydroxo species at (20 ± 1) °C. Sodium nitrate (0.3 M) was used to maintain the ionic strength in the absence of Al(III), while 0.1 M $Al(NO_3)_3$ was used for experiments with Al(III). The hydrogen ion concentration was measured with a glass electrode. Electronic absorbance spectra for 400-1300 nm were recorded at pH between 2.0 and 4.2 to monitor the complexation reactions.

An isosbestic point in the pH-dependent absorbance spectra of Np(IV) indicates the presence of two solution complexes. The authors propose two species of general formula $Np(OH)_4Al^{3+}$ and $Np(OH)_5Al^{2+}$ and (without detailed explanation) report their formation constants $\beta_4 = (7.28 \pm 1.51) \times 10^{50}$ and $\beta_5 = (1.12 \pm 0.21) \times 10^{63}$, respectively, according to the equilibrium Reaction (A.413):

$$\mathrm{Np^{4+} + Al^{3+} + \mathit{x}OH^{-} \rightleftharpoons Np(OH)_{\mathit{x}}Al^{(7-\mathit{x})}} \qquad \text{(A.413)}$$

The authors suggest a formula for the tetrahydroxo complex, $(H_2O)_n(OH)Np(\mu\text{-}OH)_2Al(OH)(H_2O)_3^{3+}$, which is based on the assumption that $Np(OH)_2^{2+}$ and some fraction of $Np(OH)_3^{+}$ are the Np(IV) hydrolysis species present at pH 1-2. Based on the absence of spectral changes, Np(V) does not interact with Al(III) hydrolysis species below pH 5.

In the absence of Al(III), hydrolysis of Pu(VI) ($3.44 \times 10^{-4}$ M) is observed at pH 4.8-6.0 with the appearance of a broad absorption band at 844 nm and the concurrent

decrease of the absorbance at 830 nm, which is characteristic of $PuO_2^{2+}$. The appearance of a new absorption band at 838 nm in the presence of $Al(NO_3)_3$ at pH < 4 suggests the formation of a mixed Pu(VI)-Al-OH solution complex in equilibrium with $PuO_2^{2+}(aq)$. At pH 3-4, an isosbestic point suggests the presence of two Pu(VI) solution species, $PuO_2^{2+}$ and presumably a new Pu(VI)-OH-Al complex. The authors propose $(H_2O)_3PuO_2(\mu\text{-}OH)_2Al(H_2O)_4^{3+}$ or $(H_2O)_3PuO_2(\mu\text{-}OH)_2Al(OH)(H_2O)_3^{2+}$ with the 7-coordinate Pu(VI) as the hydrolysis products, however, complexes with bridging O atoms, such as $(H_2O)_4PuO_2OAl(OH)(H_2O)_4^{2+}$, could not be excluded. The potential formation reactions of these complexes are:

$$PuO_2^{2+} + Al^{3+} + 2OH^- \rightleftharpoons PuO_2(OH)_2Al^{3+} \quad \text{(A.414)}$$

$$PuO_2^{2+} + Al^{3+} + 3OH^- \rightleftharpoons PuO_2(OH)_2AlOH^{2+} \quad \text{(A.415)}$$

$$PuO_2^{2+} + Al^{3+} + 3OH^- \rightleftharpoons PuO_2OAlOH^{2+} + H_2O(l) \quad \text{(A.416)}$$

Under the experimental conditions investigated, the Al(III) undergoes hydrolysis and polymerisation reactions. The equilibrium constants for (A.414), (A.415), and (A.416) rely on the Al(III) hydrolysis constants to determine the fraction of $Al^{3+}$. The authors compared the impact of two sets of hydrolysis constants for monomeric Al(III) species on the formation constants of (A.415), and (A.416). As expected, the calculated equilibrium constants for the Pu(VI)-OH-Al complexes are different by about the amount the Al(III) hydrolysis constants differ. The authors ultimately preferred data derived from the Al(III) hydrolysis constants resulting in the small fraction of $Al^{3+}$, $\beta_1 = 2 \times 10^{12}$, $\beta_2 \sim 0$, $\beta_3 = 9.5 \times 10^{31}$, and $\beta_4 = 3.8 \times 10^{36}$ at $I = 0.1$ M. These data represent a small concentration of $Al^{3+}$ at pH ~ 4 where precipitation of $Al(OH)_3$ commences. Yusov *et al.* accepted the preferred stoichiometry $(H_2O)_3PuO_2(\mu\text{-}OH)_2Al(OH)(H_2O)_3^{2+}$ or $(H_2O)_4PuO_2OAl(OH)(H_2O)_4^{2+}$ as the mixed Pu(VI)-OH-Al complex with three hydroxo group coordinated. The equilibrium constant for Reaction (A.416) $\log_{10}\beta$(A.416) = (33.82 ± 0.06) in the presence of 0.02 M $Al(NO_3)_3$ is reported. Yusov and coworkers suggest that a further increase of the pH will most likely initiate the oligomerisation of the complexes to become larger and finally precipitate.

**[2003DAV/VOK]**

See review in Chapter 17 (Appendix A, Pu).

**[2003DEN/GRE]**

Den Auwer *et al.* attempted to assess the structure of Np(V) cation-cation complexes by means of EXAFS spectroscopy [2003DEN/GRE]. Due to the low signal-to-noise ratio and the poor fit quality, the authors were not able to provide conclusive evidence on the structure of such complexes. However, based on the better agreement with the Np-Np

distance previously reported by large angle X-ray scattering [1983GUI/HAH], Den Auwer and co-workers favoured the model involving one bridging oxygen between the axial bond of one $NpO_2^+$ oxocation and the equatorial plane of the other oxocation.

**[2003GRE/MOI]**

This is a very comprehensive study investigating cation-cation interactions of Np(V) with a combination of vis/NIR and Raman spectroscopy. The paper is further complemented with water activity, osmolality and density measurements [2003KAP/MOI], and EXAFS [2003DEN/GRE] conducted under analogous experimental conditions by the same research team. Experiments were performed under acidic conditions ($2 < pH < 4$ for vis/NIR; $0.13\ M \leq [HNO_3] \leq 0.35\ M$ for Raman) with $0.02\ M \leq [NpO_2NO_3] \leq 3.56\ M$. vis/NIR spectra were recorded within 350 and 1350 nm and confirmed the absence of Np(IV) and Np(VI). Two bands at $\lambda = 618$ and 980 nm were investigated for Np(V). Because of the strong absorbance in the region 900-1100 nm, samples with [Np] > 0.2 M could only be measured by depositing a solution film between two quartz slides. Thickness of the thin film was normalised using the less intense band at $\lambda = 618$ nm. Changes in wavelength and half-width of the peak at $\lambda \approx 980$ nm were interpreted using chemometric techniques (principal component analysis and evolving factor analysis). This analysis confirmed the predominance of only two Np species at $[Np] \leq 2\ M$, supposedly $NpO_2^+$ and the dimeric form of Np(V). Two additional species were identified above this concentration, probably hinting to higher polynuclear species. Raman was used to further investigate those systems with $[Np] \leq 2\ M$. Four bands were identified in the region 650-850 $cm^{-1}$: 768 and 810 $cm^{-1}$ corresponding to $NpO_2^+$, 719 $cm^{-1}$ corresponding to $NO_3^-$ and a band at 732 $cm^{-1}$ which was attributed to $NpO_2^+$ stretching vibrations in the Np(V) dimer. The assignment of the latter band was based on the previous work by Guillaume and co-workers [1982GUI/BEG], who reported a Raman band at 738 $cm^{-1}$ corresponding to the Np(V) dimer in concentrated $NpO_2ClO_4$ solutions. Peak deconvolution of Raman spectra collected for $0.03\ M \leq [Np] \leq 1.86\ M$ allowed the quantification of $[NpO_2^+]$ and $[NpO_2^+ \cdot NpO_2^+]$, and accordingly the calculation $\log_{10}K'$((A.417), $I = x\ M\ NpO_2NO_3 - y\ M\ HNO_3$). The very low values of the stability constants reported in [2003GRE/MOI] ($-0.6 \leq \log_{10}K'(A.417) \leq -0.1$) highlight the weak character of the Np(V) cation-cation complexes. Note further that the Raman interpretation by Gregoire-Kappenstein and co-authors is based on the assumption that no Np(V)-$NO_3$ complexes form within the boundary conditions of the experiment. This review considers underestimated the uncertainties assigned by the authors to $[NpO_2^+]$ (± 7%), $[NpO_2^+ \cdot NpO_2^+]$ (± 10%) and $\log_{10}K$(A.417) (± 15 %).

$$2NpO_2^+ \rightleftharpoons NpO_2^+ \cdot NpO_2^+ \qquad \text{(A.417)}$$

No extrapolation to $I = 0$ was attempted by the authors. Instead, Gregoire-Kappenstein and co-authors successfully managed to correlate $\log_{10}K$(A.417) with $a_{H_2O}$ and $\sigma$ (sum of concentrations of all the species in solution). This correlation allowed also

the authors to link their data with stability constants reported in the literature for Reaction (A.417) determined in $HClO_4$-$NaClO_4$ solutions [1982GUI/BEG], [1993STO/CHO]. No thermodynamic data can be selected from [2003GRE/MOI], but the empirical correlation derived by the authors is recommended to estimate $\log_{10}K$(A.417), provided that $a_{H_2O}$ and σ values of the investigated system are known.

**[2003KAP/MOI]**

Kappenstein *et al.* measured water activity, osmolality and density of a series of binary $NpO_2NO_3$-$H_2O$(l) and ternary $NpO_2NO_3$-$HNO_3$-$H_2O$(l) solutions with $0.22\ m \leq [NpO_2NO_3] \leq 4.5\ m$ [2003KAP/MOI]. The authors used their experimental measurements of water activity and osmolality to calculate the osmotic coefficients ($\phi$) of the investigated solutions. The SIT ion interaction coefficient $\varepsilon(NpO_2^+, NO_3^-)$ was derived by fitting $(\phi - 1)$ *vs.* $[NpO_2NO_3]$ for $I < 3.5\ m$. The fit was only successful including a term with the ionic strength dependency as proposed by Ciavatta [1980CIA]:

$$\varepsilon(NpO_2^+, NO_3^-) = \varepsilon_1 - \varepsilon_2 \ln I$$

with $\varepsilon_1 = 0.236$ kg·mol$^{-1}$ and $\varepsilon_2 = -0.246$ kg·mol$^{-1}$. The authors highlight the similarities between $\varepsilon(NpO_2^+, NO_3^-)$ calculated at $I \approx 1\ m$ and the reported value for $\varepsilon(NpO_2^+, ClO_4^-)$, arguing that the decrease of $\varepsilon(NpO_2^+, NO_3^-)$ at high ionic strengths is not caused by the tendency of nitrate to form complexes with $NpO_2^+$, but rather because of the formation of dimeric and further oligomeric forms of Np(V). Indeed, this review disregards the selection any $\varepsilon(NpO_2^+, NO_3^-)$ values from the results in [2003KAP/MOI] because of the confirmed co-existence of other Np(V) species within the complete range of $[NpO_2NO_3]$ investigated (see reviews of [2003DEN/GRE] and [2003GRE/MOI]). Although reported values of water activity, osmolality and density can be very useful for other purposes, no thermodynamic data can be selected from [2003KAP/MOI].

**[2003KIN/SET]**

[2003KIN/SET] reported the thermodynamic modelling assessments of the Th-O and Np-O systems using the CALPHAD method. The fluorite phases $ThO_{2-x}$ and $NpO_{2-x}$ were modelled using the general multi-sublattice [1981SUN/AGR] models $(Th)_1(O,VA)_2$ and $(Np)_1(O,VA)_2$, respectively, while the liquid phase was described using a ionic liquid model [1985HIL/JAN], *i.e.*, $(Th^{4+})_P(O^{2-},VA,O)_Q$ and $(Np^{4+})_P(O^{2-},VA,O)_Q$, respectively. The thermodynamic data for α-Th, β-Th, $ThO_2$(cr), Th(l), $ThO_2$(l), α-Np, β-Np, $NpO_2$(cr), Np(l), O(l), and $O_2$(g) were taken from the SGTE database [1991DIN], [1998SGT]. The enthalpy and entropy of $Np_2O_5$(cr) were optimised starting with the Gibbs energy parameters reported by [1987PHI/HAL]. The heat capacity function is that selected in this review based on the data of [1979BEL/DOB]. The calculated enthalpy of formation $\Delta_f H_m^\circ$ ($Np_2O_5$, cr, 298.15 K) = – (2147.246) kJ·mol$^{-1}$ and entropy value at

298.15 K $S^{o}_{m}$ ($Np_2O_5$, cr, 298.15 K) = 163.1 J·K$^{-1}$·mol$^{-1}$ are based on Belyaev *et al.* [1979BEL/SMI] (– 2148 kJ·mol$^{-1}$) and Lemire [1984LEM]. They are in poor agreement with the values selected in this review, namely $\Delta_f H^{o}_{m}$ ($Np_2O_5$, cr, 298.15 K) = – (2162.7 ± 9.3) kJ·mol$^{-1}$ and $S^{o}_{m}$ ($Np_2O_5$, cr, 298.15 K)= (186 ± 15) J·K$^{-1}$·mol$^{-1}$, respectively.

The enthalpy of fusion of $NpO_2$(cr) and heat capacity values for $NpO_2$(l) were estimated from the average values for $UO_2$ and $PuO_2$ [1998SGT], *i.e.*, $\Delta_{fus} H^{o}_{m}$ ($NpO_2$, cr, $T_{fus}$) ~ 70.6 kJ·mol$^{-1}$ and $C^{o}_{p,m}$ ($NpO_2$, l, $T$) ~ 131 J·K$^{-1}$·mol$^{-1}$. While the fusion enthalpy is in good agreement with this review, the heat capacity value is twice as high. The calculated Th-O phase diagram and oxygen potential data for $ThO_{2-x}$ are in good agreement with the experimental data of Benz [1969BEN] and Ackermann and Tetenbaum [1980ACK/TET]. The oxygen potential data for $NpO_{2-x}$ are in excellent agreement with Bartscher and Sari [1986BAR/SAR]. The $NpO_{2-x}$ phase region is much wider than predicted by the phase diagram data of Richter and Sari [1987RIC/SAR] in the lower temperature range, however. In particular, the beginning of the hypostoichiometric homogeneity range is calculated at about 300 K, whereas Richter and Sari reported it at about 1300 K [1987RIC/SAR]. Moreover, the optimised congruent melting temperature of neptunium dioxide is based on the data of Richter and Sari [1987RIC/SAR] and Chikalla *et al.* [1971CHI], which is about 240 K lower than recommended in this review.

[2003KIN/SET] furthermore compared the phase stabilities of $ThO_{2-x}$, $UO_{2-x}$, $NpO_{2-x}$ and $PuO_{2-x}$ based on the present models and those reported by [1998CHE/FIS] and [2003KIN/UNO]. The excess Gibbs free energies of $ThO_{2-x}$ and $UO_{2-x}$ showed positive deviation from the ideal behaviour, while $NpO_{2-x}$ and $PuO_{2-x}$ showed negative deviation. The partial molar enthalpies and oxygen potentials showed the same trend, *i.e.*, with an increase along the actinide series. The trend of the partial molar entropy appeared different, however, *i.e.*, in the order $PuO_{2-x}$, $ThO_{2-x}$, $NpO_{2-x}$ and $UO_{2-x}$, suggesting the plutonium oxide could accommodate a wider oxygen composition change.

**[2004KIM/ASA]**

See comments under Kim *et al.* [2005KIM/ASA].

**[2004KIT/KOH]**

Kitamura and Kohara investigated the solubility of Np(IV) in $NaHCO_3$-$Na_2CO_3$-NaOH-$NaClO_4$ solutions with 0.5 M ≤ $I$ ≤ 2.9 M. The description and discussion of the experimental results are distributed within three different publications:

- [2001KIT/KOH]. Oversaturation solubility experiments with $7.8 \leq -\log_{10}[H^+] \leq 12.1$ and $6.2 \times 10^{-3}$ M ≤ $[CO_3^{2-}]_{tot} \leq 0.1$ M. Experiments were performed at

two different ionic strengths (0.5 and 1.0 M $NaHCO_3$-$Na_2CO_3$-NaOH-$NaClO_4$) with short equilibration times (< four weeks). This publication was already reviewed in [2003GUI/FAN].

- [2002KIT/KOH]. Oversaturation solubility experiments with $8.0 \leq -\log_{10}[H^+] \leq 13.0$, $5 \times 10^{-3}$ M $\leq [CO_3^{2-}]_{tot} \leq 0.1$ M and $I = 2.0$ M $NaHCO_3$-$Na_2CO_3$-NaOH-$NaClO_4$. Longer equilibration times (up to six months) were considered.
- [2004KIT/KOH]. Oversaturation solubility samples prepared in [2002KIT/KOH] were further monitored with time up to $t = 1.6$ years. Additional undersaturation experiments were conducted in 2.0 and 2.9 M $Na_2CO_3$-NaOH-$NaClO_4$ solutions with $12.0 \leq -\log_{10}[H^+] \leq 13.0$ and $5 \times 10^{-2}$ M $\leq [CO_3^{2-}]_{tot} \leq 0.7$ M. The later samples were equilibrated for up to five months.

In all cases, Np(IV) was stabilised by the very reducing conditions set with $Na_2S_2O_4$. No solid phase characterisation was performed by the authors, who assumed $Np(OH)_4(am)$ as solubility-controlling phase in all the systems. Appropriate analytical methods were used for the determination of $[H^+]$ and [Np]. The +IV redox state of Np was confirmed by solvent extraction with 0.5 M TTA in xylene. The chemical model derived in [2001KIT/KOH] and [2002KIT/KOH] was based on the predominance of the ternary complexes $Np(OH)_2(CO_3)_2^{2-}$ and $Np(OH)_4(CO_3)_2^{4-}$ above and below $-\log_{10}[H^+] \approx 11$, respectively, according with the equilibrium Reactions (A.418) and (A.419):

$$Np(OH)_4(am) + 2HCO_3^- \rightleftharpoons Np(OH)_2(CO_3)_2^{2-} + 2H_2O(l) \qquad \text{(A.418)}$$

$$Np(OH)_4(am) + 2CO_3^{2-} \rightleftharpoons Np(OH)_4(CO_3)_2^{4-} \qquad \text{(A.419)}$$

In line with the discussion in [2003GUI/FAN], this chemical model was updated in [2004KIT/KOH] with the substitution of $Np(OH)_4(CO_3)_2^{4-}$ by $Np(OH)_4CO_3^{2-}$ according with the equilibrium Reaction (A.420):

$$Np(OH)_4(am) + CO_3^{2-} \rightleftharpoons Np(OH)_4CO_3^{2-} \qquad \text{(A.420)}$$

The predominance of the species $Np(OH)_4CO_3^{2-}$ above $-\log_{10}[H^+] \approx 11$ is consistent with the chemical model described for Th(IV) under analogous experimental conditions [2008RAN/FUG]. Note also that the error identified in [2003GUI/FAN] with the calculations of $[HCO_3^-]$ and $[CO_3^{2-}]$ at $I \neq 0$ was properly corrected in [2004KIT/KOH]. The authors considered the SIT approach to extrapolate $\log_{10}K$(A.418), $I = x$ M $NaHCO_3$-$Na_2CO_3$-NaOH-$NaClO_4$ and $\log_{10}K$(A.420), $I = x$ M $NaHCO_3$-$Na_2CO_3$-NaOH-$NaClO_4$ to $I = 0$, and to calculate $\varepsilon(Np(OH)_2(CO_3)_2^{2-}, Na^+)$ and $\varepsilon(Np(OH)_4CO_3^{2-}, Na^+)$ from the slope of the SIT-plot. Water activity was omitted in the SIT-plot of Reaction (A.418), whereas $\varepsilon(CO_3^{2-}, Na^+)$ = 0.08 kg·mol$^{-1}$ was equivocally used instead of $\varepsilon(CO_3^{2-}, Na^+) = -(0.08 \pm 0.03)$ kg·mol$^{-1}$ in the case of Reaction (A.420) (Appendix B). The amendment of these inaccuracies results in:

$$\log_{10}K°(\text{A.418}) = -(2.9 \pm 0.2)$$

$$\log_{10}K°(\text{A.420}) = -(6.2 \pm 0.2)$$

with $\varepsilon(\text{Np(OH)}_2(\text{CO}_3)_2^{2-}, \text{Na}^+) = -(0.3 \pm 0.2)$ kg·mol$^{-1}$ and $\varepsilon(\text{Np(OH)}_4\text{CO}_3^{2-}, \text{Na}^+) = (0.0 \pm 0.3)$ kg·mol$^{-1}$. These values agree well with the re-calculations provided in [2003GUI/FAN] based on experimental data in [2001KIT/KOH]: $\log_{10}K°(\text{A.418}) = -(3.1 \pm 0.4)$ and $\log_{10}K°(\text{A.420}) = -(6.5 \pm 0.4)$, with $\varepsilon(\text{Np(OH)}_2(\text{CO}_3)_2^{2-}, \text{Na}^+) = \varepsilon(\text{Np(OH)}_4\text{CO}_3^{2-}, \text{Na}^+) = -0.1$ kg·mol$^{-1}$ estimated according with charge analogies.

The series of publications by Kitamura and Kohara [2001KIT/KOH], [2002KIT/KOH], [2004KIT/KOH] represents the most comprehensive experimental study on the Np(IV)-$CO_3$ system under alkaline to hyperalkaline pH conditions, and provide a sound evidence on the formation of ternary complexes Np(IV)-OH-$CO_3$. However, the work by these authors suffers from relevant shortcomings, which prevent the selection by this review of the reported thermodynamic data:

- As indicated in [2003GUI/FAN], a very large scattering is observed in the solubility of Np(IV) in the range of $-\log_{10}[\text{H}^+] = 10$-11. Because of the steep slope in the solubility (both as $\log_{10}[\text{Np(IV)}]$ *vs.* $-\log_{10}[\text{H}^+]$ and $\log_{10}[\text{Np(IV)}]$ *vs.* $\log_{10}[\text{CO}_3^{2-}]$), this pH-region is very sensitive towards slight variations in $[\text{H}^+]$ and $[\text{CO}_3^{2-}]_{\text{tot}}$.

- All solubility experiments were performed in the presence of carbonate and under boundary conditions where Np(IV)-OH-$CO_3$ aqueous complexes were claimed to prevail. Thus, no information can be extracted on the solubility product of the Np(OH)$_4$(am) phase used by the authors, neither as $\log_{10}K^{\text{o}}_{\text{s,o}}$ nor as $\log_{10}K^{\text{o}}_{\text{s,(1,4)}}$. Note that the previous NEA TDB review [2003GUI/FAN] considered $\log_{10}K^{\text{o}}_{\text{s,(1,4)}} = -8.3$ for the interpretation of experimental data in [2001KIT/KOH]. This value accounted for the expectedly smaller particles formed from oversaturation conditions, and is significantly larger (although within the reported uncertainties) than $\log_{10}K^{\text{o}}_{\text{s,(1,4)}} = -(9.0 \pm 1.0)$ selected in [2003GUI/FAN].

- The particle size of a given solid is very sensitive to the ageing/equilibration time, especially if approaching the equilibrium from oversaturation conditions. Consequently, the different equilibration times used in experiments at different ionic strengths (< four weeks for $I = 0.5$ and 1.0 M; < 1.6 years for $I = 2.0$; $I = 2.9$ M only investigated by undersaturation) may introduce a relevant bias in the calculated conditional equilibrium constants.

- The determination of the stoichiometry of the complex prevailing above $-\log_{10}[\text{H}^+] \approx 11$ is mostly based on solubility data in 2.0 and 2.9 M $Na_2CO_3$-NaOH-$NaClO_4$ and can be considered (at most) weak. If disregarding solubility data at short equilibration times (0.5 and 1 months), the slope analysis ($\log_{10}[\text{Np}]$ *vs.* $\log_{10}[\text{CO}_3^{2-}]_{\text{tot}}$) in Figure 3a and b (in [2004KIT/KOH]) could indicate the

predominance of complexes in solution with Np(IV): $CO_3^{2-}$ ratio of 1:2 and 1:0, respectively, instead of the 1:1 selected by the authors ($Np(OH)_4(CO_3)^{2-}$). Furthermore, a relevant fraction of the background electrolyte is substituted in the systems with the highest carbonate concentration: 0.6 M $Na_2CO_3$ + 0.2 M $NaClO_4$ ($I$ = 2.0 M) or 0.7 M $Na_2CO_3$ + 0.8 M $NaClO_4$ ($I$ = 2.9 M). These conditions deviate significantly (in terms of $[Na^+]$, water activity, *etc.*) from pure $NaClO_4$ electrolyte systems, and thus impact the accuracy of the calculated conditional equilibrium constant for these ionic strengths.

**[2004KRO/GRI]**

This is a very comprehensive review dedicated to cation-cation interactions in crystalline actinide compounds. Impact of cation-cation interactions on the properties of Np(V) compounds is discussed in the paper. A short section compares cation-cation interactions in solutions and crystals of actinide compounds.

**[2004RAI/HES]**

This paper deals with the formation of $U_xNp_{1-x}O_2$(am) solid solutions in dilute to concentrated carbonate solutions. The work is out of the scope of this review, but it is very relevant in the context of nuclear waste disposal and deserves a close attention. The reader is referred to the volume 10 of the Chemical Thermodynamics Series [2007BRU/BOS] for a detailed description of the chemical thermodynamics of solid solutions of interest in nuclear waste management.

All experiments were performed in a controlled Ar atmosphere with special precautions to avoid the oxidation of U(IV) or Np(IV). Aliquots of stock solutions of both actinides were mixed in acidic conditions, and co-precipitated in a $Na_2S_2O_4$ solution with slow addition of KOH. Five different $U_xNp_{1-x}O_2$(am) systems with $x$ = 0.95, 0.85, 0.50, 0.15 and 0.05 were prepared. Two sets of experiments were conducted for each system: (i) with 0.1 M ≤ $[KHCO_3]$ ≤ 0.8 M in 0.01 M $Na_2S_2O_4$ and (ii) 1.0 M ≤ $[K_2CO_3]$ ≤ 4.6 M in 0.01 M NaOH and 0.01 M $Na_2S_2O_4$. Solubility data obtained for these systems were compared with results obtained by the same authors with pure $UO_2$(am) [1998RAI/FEL] and $NpO_2$(am) [1999RAI/HES] phases. The solid phases resulting from the co-precipitation experiments were thoroughly characterised by quantitative chemical analysis, SEM–EDAX, XAS and XRD. SEM–EDAX and XAS showed that Np and U were homogeneously distributed throughout the solid phases, strongly hinting towards the formation of solid solutions and disregarding phase separation, clustering or U- or Np-rich domains. XANES further confirmed the prevalence of both actinides in their +IV redox state. The characterisation by XRD of the co-precipitated solids showed broad but well-defined patterns, hinting towards a more ordered structure than pure $UO_2$(am) and $NpO_2$(am). In spite of this, the concentration of U(IV) and Np(IV) in the systems with

high mole fractions ($U_{0.95}Np_{0.05}O_2$(am) and $U_{0.05}Np_{0.95}O_2$(am), respectively) were very close to the solubility of the pure $UO_2$(am) and $NpO_2$(am) phases, thus indicating that an amorphous fraction of the solid was indeed controlling the solubility. A relevant decrease in the solubility of U(IV) and Np(IV) was observed in the mixtures with low mole fractions. For these systems, the relatively good agreement between predicted and experimentally measured solubility are consistent with the formation of an ideal solid-solution (*i.e.* decrease of ≈ 1.3 $\log_{10}$ units for [U] in equilibrium with $U_{0.05}Np_{0.95}O_2$(am), compared to the solubility of the end-member $UO_2$(am). Similar results were obtained for Np). The accurate work by Rai and co-workers represents a very relevant input in the modelling of U(IV)-Np(IV) solid solutions under repository relevant conditions, but it is disregarded in the present review to derive any thermodynamic data for either U(IV) or Np(IV).

**[2004RAO/SRI]**

Rao *et al.* study the hydrolysis of $^{237}$Np(V) in tetramethylammonium chloride (TMA-Cl) by potentiometric, calorimetric and spectrophotometric titrations at temperatures ranging between 10 and 80 °C. TMA-Cl (1.12 mol/kg) is used to avoid the precipitation of less-soluble Na-containing Np(V) hydroxide. At the end of each experiment, sample solutions are examined by laser light-scattering for particulate matter or hydroxide precipitates that potentially formed during the titration. For the titrations, TMA-OH is used as the titrant with an experimentally determined carbonate content of less than 0.5 %. Fifteen potentiometric titrations of acidic Np(V) (0.29-0.46 mM) solutions are performed at 10 to 80 °C with the $p_cH$ up to about 12. The parameters E°, $\gamma_H$ and $\gamma_{OH}$ are determined before each potentiometric titration by acid/base titrations to enable calculation of $[H^+]$ from the EMF data. Fifteen calorimetric titrations between 25 and 80 °C are carried out with the final $p_cH$ varying between 8.5 at 85 °C and 10.3 at 25 °C. The sample solutions contain 0.25-0.57 mM Np(V) in 0-0.5 mM HCl. Spectrophotometric titrations are performed with $1.8 \times 10^{-3}$ M and $1.75 \times 10^{-5}$ M Np(V).

Potentiometric titration data are analysed by using the Hyperquad code to determine the hydrolysis formation constants $\log_{10}K_{1n}$ for the Reactions (A.421) and (A.422):

$$NpO_2^+ + H_2O(l) \rightleftharpoons NpO_2OH(aq) + H^+ \quad \text{(A.421)}$$

$$NpO_2^+ + 2H_2O(l) \rightleftharpoons NpO_2(OH)_2^- + 2H^+ \quad \text{(A.422)}$$

The formation of polynuclear hydrolysis products is deemed to be insignificant under the conditions investigated. From calorimetric data, the reaction enthalpies are determined. The endothermic character of the hydrolysis reactions is found to decrease with increasing temperature. The enthalpy of water formation in 1 M TMA-Cl is experimentally determined at variable temperatures. The experimentally determined

values for the ion product of water ($-\log_{10} K_{H_2O}$) are about 0.1-0.25 logarithmic units higher than those for NaCl.

Since the experiments are conducted in 1 M TMA-Cl solutions, the impact of chloride complexation of Np(V) on the hydrolysis constants is evaluated. Based on the literature value $\log_{10}\beta_{Cl} = -0.85$ for the formation of $NpO_2Cl(aq)$ determined in LiCl, a correction factor of 0.06 at 25 °C is calculated and determined to be insignificant compared to the experimental uncertainties. In order to estimate the impact of the chloride complexation effect at elevated temperatures, the authors assume that the dehydration energy for Np(V) is less than for U(VI) and that $\Delta_r H_m^o$ ($NpO_2Cl$) is smaller than the value of $\Delta_r H_m^o$ ($UO_2Cl^+$) = 8.0 kJ mol$^{-1}$ at 25 °C as reported in [2003GUI/FAN]. By applying the Van't Hoff equation with $\log_{10}\beta_{Cl} = -0.85$ and $\Delta_r H_m^o$ ($NpO_2Cl$) = 4 kJ·mol$^{-1}$ at 25 °C the authors estimate $\log_{10}\beta_{Cl} = -0.73$ at 85 °C. The resulting correction factor of 0.07 to account for chloride complexation of Np(V) at 85 °C is also smaller than the reported experimental uncertainties.

Spectroscopic features at 980 nm ($\varepsilon$ = 375 mol$^{-1}$·dm$^3$·cm$^{-1}$) and 991 nm ($\varepsilon$ = 272 mol$^{-1}$·dm$^3$·cm$^{-1}$) are interpreted with the presence of $NpO_2^+$ and $NpO_2OH(aq)$, respectively. The species $NpO_2(OH)_2^-$ does not exhibit any spectral absorbance due to its centro-symmetric geometry, similar to $NpO_2(OH)_4^{2-}$. It is to note that the 991 nm absorbance band becomes very intense in the solution containing $1.75 \times 10^{-5}$ M Np(V), but is far less pronounced in the titration at $1.8 \times 10^{-3}$ M Np(V). Using the changes in the absorbance intensities at 980 nm and 991 nm the authors calculate $\log_{10}K_{11} = -(9.08 \pm 0.08)$ for $NpO_2OH(aq)$ and $\log_{10}K_{12} = -(18.85 \pm 0.07)$ for $NpO_2(OH)_2^-$ at 25 °C.

The SIT is used to correct for ionic strength effect and to calculate thermodynamic data. Although the authors point out the difference between $Na^+$ and TMA, the ionic strength correction of the water activity is considered as insignificant. However, the authors calculate the ion product of water for the different temperatures of interest in this study and correct to $I = 0$. The estimated value of $\varepsilon(OH^-, (CH_3)_4N^+)$ = 0.20 kg·mol$^{-1}$ is used to calculate $\Delta\varepsilon = \varepsilon(Cl^-, H^+) + \varepsilon(OH^-, (CH_3)_4N^+)$ = 0.32 kg·mol$^{-1}$. In the absence of corresponding ion interaction parameters, the value $\varepsilon(NpO_2(OH)_2^-, (CH_3)_4N^+)$ is estimated to be equal to $\varepsilon(NpO_2(OH)_2^-, K^+) = \varepsilon(NpO_2(OH)_2^-, Na^+) = -(0.01 \pm 0.07)$ kg·mol$^{-1}$ as reported in [2003GUI/FAN]. For ionic strength correction at temperatures different from 25 °C, the ion-interaction parameters at 25 °C are used in conjunction with the SIT Debye-Huckel term *D* calculated for different temperatures. The errors of using constant ion interaction parameters over the temperature range 10-85 °C are estimated to be small and negligible.

The reaction hydrolysis enthalpy values averaged over the investigated temperature range are obtained from plotting the apparent hydrolysis constants against 1/*T*. The obtained temperature-independent values $\Delta_r H_{1,m} = (20 \pm 3)$ kJ·mol$^{-1}$ and $\Delta_r H_{2,m} = (77.5 \pm 0.2)$ kJ·mol$^{-1}$ are quite different by about 30-40 kJ·mol$^{-1}$ from the

selected data in [2001LEM/FUG]. Calorimetric measurements in this study resulted in closer values of $\Delta_r H_{1,m} = (29.5 \pm 7.3)$ kJ·mol$^{-1}$ and $\Delta H_{2,m} = (79.5 \pm 4.6)$ kJ·mol$^{-1}$.

The spectrophotometric titrations at different Np(V) concentrations illustrate the complexation of Np(V) but also raise concerns of carbonate contamination (see also [2006NEC] and [2006RAO/SRI]). In this work, the absorbance at 991 nm is assigned to the formation of $NpO_2OH(aq)$. However, several reports in the literature have been shown that this absorbance feature is dependent on carbonate concentration and has been associated with the formation of the solution complex $NpO_2CO_3^-$. The carbonate solution species has been confirmed in several spectroscopic studies and solubility experiments. The study by Rao *et al.* suffers from the lack of evidence that the spectral feature at 991 nm is indeed the $NpO_2OH(aq)$ species and not the well-established $NpO_2CO_3^-$ complex. Consequently, the data reported herein cannot be accepted.

Table A-161: Thermodynamic constants for the equilibrium: $m\mathrm{NpO}_2^+ + n\mathrm{H}_2\mathrm{O(l)} \rightleftharpoons (\mathrm{NpO}_2)_m(\mathrm{OH})_n^{m-n} + n\mathrm{H}^+$ reported in [2004RAO/SRI].

| *n*:*m* | *t* /°C | Method | *I* (medium) | $\Delta G_m^o$ /kJ·mol$^{-1}$ | $\Delta H_m^o$ /kJ·mol$^{-1}$ | $\Delta S_m^o$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 1:1 | 10 | pot | 1.12 M TMACl | (50.4 ± 0.5) | | |
| 1:1 | 25 | pot | 1.12 M TMACl | (51.3 ± 0.5) | (31.6 ± 0.6) | – (66 ± 3) |
| 1:1 | 40 | pot | 1.12 M TMACl | (52.8 ± 0.7) | (29.7 ± 1.5) | – (74 ± 5) |
| 1:1 | 55 | pot | 1.12 M TMACl | (13.06 ± 0.8) | (30.4 ± 0.7) | – (74 ± 3) |
| 1:1 | 70 | pot | 1.12 M TMACl | (13.52 ± 1.4) | (28.6 ± 1.2) | – (82 ± 5) |
| 1:1 | 85 | pot | 1.12 M TMACl | (14.00 ± 0.9) | (27 ± 7) | – (88 ± 20) |
| 2:1 | 10 | pot | 1.12 M TMACl | (110.7 ± 0.8) | | |
| 2:1 | 25 | pot | 1.12 M TMACl | (109.7 ± 0.6) | (84.1 ± 0.9) | – (86 ± 5) |
| 2:1 | 40 | pot | 1.12 M TMACl | (110.0 ± 0.6) | (81.3 ± 1.7) | – (91 ± 6) |
| 2:1 | 55 | pot | 1.12 M TMACl | (112.2 ± 0.6) | (78.6 ± 0.5) | – (102 ± 2) |
| 2:1 | 70 | pot | 1.12 M TMACl | (115.6 ± 1.0) | (77.4 ± 0.9) | – (111 ± 4) |
| 2:1 | 85 | pot | 1.12 M TMACl | (116.8 ± 0.7) | (76 ± 4) | – (114 ± 11) |

**[2004SHI/FED]**

Shilov *et al.* studied the interaction of silicate with Np(VII), Np(VI) and Np(V) from acidic to hyperalkaline pH conditions by means of spectrophotometric and potentiometric measurements. All experiments were apparently performed under air atmosphere. Many relevant details are omitted in the experimental description in [2004SHI/FED]. The very extensive set of data collected by the authors is only shown in four figures, which hinders the traceability and correct assessment of the model provided by the authors for the interpretation of their data.

*Np(VII)-silicate system*

This is a qualitative evaluation of the complexation between Np(VII) cationic species and carbonate / silicate ligands. Np(VII) was prepared by ozonisation of a Np(VI) stock solution in hyperalkaline LiOH or NaOH solutions. The complex formation was indirectly assessed by determining the transition pH between $NpO_3^+$ (or $NpO_2^{3+}$) and

$NpO_4(OH)_2^{3-}$ species. The latter species shows a strong absorption band at $\lambda$ = 619 nm ($\varepsilon$ = 390 l·mol$^{-1}$·m$^{-1}$). In the absence of complexing ligands, the transition between both species takes place at pH ≈ 5-6, whereas the transition pH increases to 9-10 and 10.5-12 in carbonate ([$KHCO_3$] + [$K_2CO_3$] = 0.5 M) and silicate ([$Na_2SiO_3$] = 0.1 M) media, respectively. The authors interpreted this observation with the formation of stable Np(VII)-carbonate and Np(VII)-silicate complexes. Note that experiments with silicate were highly oversaturated with respect to amorphous silica, and thus the presence of colloids/polymers and their resulting interaction with Np(VII) cations is to be expected. No thermodynamic data useful for this review is provided in this section of the paper.

*Np(VI)-silicate system*

The formation of Np(VI)-silicate complexes under alkaline conditions was evaluated following the competition with carbonate ions. Experiments were conducted with a Np(VI) solution containing $5 \times 10^{-3}$ M $NaHCO_3$-$Na_2CO_3$ at pH = 10.13 and constant ionic strength (0.1 M $NaClO_4$). The prevailing $NpO_2(CO_3)_3^{4-}$ species provided an intense absorption band at $\lambda$ = 350 nm, which significantly decreased in silicate solutions. The titration of the initial Np(VI)-carbonate solution with 0.1 M $Na_2SiO_3$ led to the linear decrease of $D_{350}$, which was interpreted by the authors according with Reaction (A.423). Note that no quantification of Si polymeric/colloidal species was attempted by the authors although several of the experimental points in the titration curve were above the solubility limit of $SiO_2$(am) (~ 0.01 M at pH = 10.13). Equilibration time allowed after each titration step was not specified in the experimental description.

$$NpO_2(CO_3)_3^{4-} + SiO_2(OH)_2^{2-} \rightleftharpoons NpO_2SiO_2(OH)_2(aq) + 3CO_3^{2-} \quad \text{(A.423)}^2$$

The titration point with $D_{350} = ½(D_0 - D_1)$ (where $D_0$ and $D_1$ are the optical densities of $NpO_2(CO_3)_3^{4-}$ and $NpO_2SiO_2(OH)_2$(aq) species) was used to calculate $\log_{10}K$((A.424), 0.1 M $NaClO_4$) = 16.5 considering $\log_{10}K$((A.425), 0.1 M $NaClO_4$) = 20.41 [1998KAT/KIM]. The titration of analogous Np(VI) carbonate solutions at p$H$ = 10.5-12 led to similar values of $\log_{10}K$(A.424), although these titration data are not shown in the publication.

$$NpO_2^{2+} + SiO_2(OH)_2^{2-} \rightleftharpoons NpO_2SiO_2(OH)_2(aq) \quad \text{(A.424)}$$

$$NpO_2^{2+} + 3CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{4-} \quad \text{(A.425)}$$

No additional titration experiments at different carbonate concentrations were conducted by the authors, and thus the definition of $NpO_2SiO_2(OH)_2$(aq) as prevailing species in silicate-carbonate media remains speculative. The formation of mixed species (*e.g.* $NpO_2CO_3SiO_2(OH)_2^{2-}$ or $NpO_2(CO_3)_2SiO_2(OH)_2^{4-}$) cannot be disregarded from the experimental evidences presented by the authors. No selection of thermodynamic data can be recommended from this study.

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[2] $NpO_2SiO_2(OH)_2$(aq) was formulated as $NpO_2SiO_3$ in [2004SHI/FED]. The formulation $NpO_2SiO_2(OH)_2$(aq) has been favoured in this review to retain the consistency with Si speciation scheme in [1992GRE/FUG].

*Np(V)–silicate system*

Shilov *et al.* qualitatively evaluated the complexation of Np(V) with silicate under alkaline conditions (pH = 10.16-10.3) by means of UV-vis spectrophotometry and potentiometric measurements. In a first experimental series, UV-vis spectra of a Np(V) solution with $[Np]_{tot} = 1 \times 10^{-4}$ M and pH = 10.16 were collected in the absence and presence of silicate ($[Na_2SiO_3] = 8.6 \times 10^{-4}$ M). In both cases, the authors observed the complete predominance of the complex $NpO_2CO_3^-$ ($\lambda$ = 991 nm) and the absence of $NpO_2^+$ ($\lambda$ = 981 nm), clearly indicating the presence of an undefined amount of carbonate in the system (as contamination). These results were interpreted with the absence of strong Np(V)-silicate complexes outcompeting the formation of Np(V)-carbonate species.

In a second experiment, the formal redox potential of an equimolar solution of Np(V) and Np(VI) ($1\text{-}2 \times 10^{-4}$ M) was evaluated in the absence and presence of 0.1 M $Na_2SiO_3$ (pH = 10.2). The differences in the electrode readings were interpreted by the authors with the formation of Np(VI)-silicate complexes. Solutions were largely oversaturated with respect to $Np^{V}O_2OH$(am, fresh), $Na_2Np^{VI}_2O_7$(cr) and $SiO_2$(am), although no solid phase formation was reported by the authors. No quantitative interpretation of the Np(V)-silicate system can be done based on the data reported in [2004SHI/FED].

**[2004YUS/FED]**

Paper reporting on the hydrolysis of Np(IV) under acidic conditions. See comments under Yusov *et al.* [2004YUS/FED2].

**[2004YUS/FED2]**

Yusov *et al.* studied the hydrolysis of Np(IV) and Pu(IV) at $T$ = 25 °C and their complexation with orthosilicic acid, $Si(OH)_4$(aq), using spectrophotometric titrations. Experiments were performed in 0.1-1.0 M $NaClO_4$ at Np(IV) and Pu(IV) concentrations of $\geq 10^{-4}$ M. The pH was measured with a glass electrode and converted to proton concentration using experimentally determined correction factors of 0.03 for 0.1 M $NaClO_4$ and 0.24 for 1.0 M $NaClO_4$.

Alkaline solutions of dissolved $Na_2SiO_3 \cdot 9H_2O$ were diluted and quickly acidified to obtain 0.005-0.016 M $Si(OH)_4$ solutions. In spite of the large oversaturation with respect to $SiO_2$(am), the authors reported nearly pure solutions of monomeric $Si(OH)_4$(aq) as determined by titration with molybdate. This is attributed to the quick surpassing of the neutral pH range, where polymerisation of $Si(OH)_4$(aq) is fast, and to the experimental study at very acidic conditions ($0.3 \leq -\log_{10}[H^+] \leq 2.2$) where polymerisation takes place very slowly. No precautions were taken to prevent $CO_2$

adsorption, which is expected to be negligible in the very acidic pH conditions of this study. The 0.01 M-0.03 M Np(IV) and Pu(IV) stock solutions (1-2 M $HClO_4$) were spectroscopically verified to be free of other oxidation states. Changes in the electronic absorption spectra were recorded as function of pH and treated by non-linear least square methods to calculate the molar absorptivity and complex stability constants. The total actinide concentration in solution was determined by titration with standard Na-EDTA solutions.

*Np(IV) hydrolysis and silicate complexation*

Yusov and co-workers provide an extensive discussion of previous literature data on Np(IV) hydrolysis, including spectroscopy, solvent extraction and solubility studies. Focus is given to the discussion of the main drawbacks and problems of each technique. For spectroscopic studies, the main limitations arise from the high Np(IV) concentrations needed for an accurate detection and quantification in solution, which often requires work in oversaturation conditions with respect to the amorphous $NpO_2$(am, hyd) phase. This causes difficulties related with the formation of polymeric or colloidal species. The efforts undertaken by the authors to avoid the formation of polymers or colloids in this experimental study are commended but not convincing. In preliminary tests with $-\log_{10}[H^+] = 1.91$ and $[Np(IV)] = 1.07 \times 10^{-4}$ M, the authors observed the decrease in the Np(IV) absorbance after two days, clearly hinting to the formation of Np(IV) polymers or colloids and thus to non-equilibrium conditions. On the other hand, most of the quantitative studies with Np(IV) in [2004YUS/FED2] were performed with higher [Np(IV)] ($1.6\text{-}1.8 \times 10^{-4}$ M, four out of six series in Table 1 of the paper). No detailed report of the equilibration time in the quantitative studies is given in the experimental description of the paper, but it appears evident that several of the experimental points were oversaturated with respect to $NpO_2$(am, hyd).

In the absence of silicate and based on the observed isosbestic points at $\lambda$ = 728.2, 736.5 and 747.5 nm, the authors concluded that only two species were present within the investigated pH-range. Besides $Np^{4+}$ and consistently with the linear dependency observed with respect to $1/[H^+]$, Yusov *et al.* concluded that the second species was $NpOH^{3+}$ and that Reaction (A.426) was controlling the Np(IV) solution chemistry under these conditions:

$$Np^{4+} + H_2O(l) \rightleftharpoons NpOH^{3+} + H^+ \qquad \text{(A.426)}$$

Only a fraction of the experimental data generated by the authors is provided in the paper. In fact, only the two experimental series with $[Np(IV)] < 10^{-4}$ M are included in the plot of $[NpOH^{3+}]/[Np^{4+}]$ *vs.* $1/[H^+]$ from which the authors concluded the existence of only two Np(IV) solution species. Those data (partially) obtained under oversaturation conditions (see discussion above) are not shown in the publication. Because not clearly articulated in the description of the data treatment, this review is unclear if the authors performed their non-linear least square fitting considering the absorbance of a single wavelength at 723.2 nm or two wavelengths at 723.2 nm and 960.4 nm. Modeling data

obtained at only one wavelength is prone to errors due the large correlation between the equilibrium constants and the molar absorptivity. The fit resulted in $\varepsilon(Np^{4+}, 723.2\ nm) = 153\ L\cdot mol^{-1}\cdot cm^{-1}$, $\varepsilon(Np^{4+}, 960.4\ nm) = 215\ L\cdot mol^{-1}\cdot cm^{-1}$ and $\varepsilon(NpOH^{3+}, 723.2\ nm) = (41 \pm 5)\ L\cdot mol^{-1}\cdot cm^{-1}$. Values of $\varepsilon(Np^{4+}, 723.2\ nm)$ reported in the literature vary considerably, although are generally lower ($\leq 121$-$144\ L\cdot mol^{-1}\cdot cm^{-1}$) than the value determined in this study. According to Figure 3 in the paper, all experimental data but one have $[NpOH^{3+}]/[Np^{4+}] < 1$. Considering the molar absorptivity of $Np^{4+}$ and $NpOH^{3+}$ determined by the authors, the contribution of $NpOH^{3+}$ to the total absorption at 723.3 nm ranged between 0.5 and 12 %, this in combination with the uncertainties of the spectroscopic technique appear insufficient for an accurate quantification of thermodynamic data in this system.

The authors determined values for $\log_{10}K$((A.426), $I = 0.1, 0.3, 1.0$ M $NaClO_4$), which the authors extrapolated to $I = 0$ using SIT interaction parameters for $Np^{4+}$, $NpOH^{3+}$ and $H^+$ and water activities reported in [2001LEM/FUG]. The weighted average, including spectroscopy data previously reported in [1959SUL/HIN] and [1978FED/PER], resulted in $\log_{10}K°(A.426) = -(1.23 \pm 0.06)$. This value is significantly smaller than the NEA TDB value selected in [2003GUI/FAN] based on a combination of solvent extraction and solubility data, $\log_{10}K°(A.426) = (0.55 \pm 0.20)$. The reported $\log_{10}K°(A.426) = -(1.23 \pm 0.06)$ is also smaller than the analogous value for U(IV), $\log_{10}K°(UOH^{3+}) = -(0.54 \pm 0.06)$, selected in [1992GRE/FUG] and derived from a very large dataset, mostly relying on spectroscopic and potentiometric data. Considering the smaller size of $Np^{4+}$ compared to $U^{4+}$, a $\log_{10}K°(NpOH^{3+}) << \log_{10}K°(UOH^{3+})$ as reported in [2004YUS/FED2] appears unjustified and is opposite to the expected trend of $\log_{10}K°(NpOH^{3+}) > \log_{10}K°(UOH^{3+})$.

Yusov *et al.* also explored the variation of the absorption at 723.2 nm with increasing $[Si(OH)_4(aq)]$ to investigate the complexation Reaction (A.427):

$$Np^{4+} + Si(OH)_4(aq) \rightleftharpoons NpSiO(OH)_3^{3+} + H^+ \qquad \text{(A.427)}$$

The non-linear least square fitting performed by the authors considering $A = 5 \times (\varepsilon_1[Np^{4+}] + \varepsilon_2[NpOH^{3+}] + \varepsilon_3[NpSiO(OH)_3^{3+}])$ (where 5 cm is the optical pathlength) resulted in $\varepsilon_3 = \varepsilon(NpSiO(OH)_3^{3+}, 723.2\ nm) = (47 \pm 7)\ L\cdot mol^{-1}\cdot cm^{-1}$ and $\log_{10}K°(A.427) = 1.4$. As discussed above, this review considers the use of a single wavelength inadequate for the fit of four parameters ($\varepsilon(NpOH^{3+})$, $\varepsilon(NpSiO(OH)_3^{3+})$, $\log_{10}K°(A.426)$ and $\log_{10}K°(A.427)$), even if a very large dataset under varying experimental conditions is available. Although it is certainly possible to make a least-squares fit with such dataset, the uniqueness of the obtained values remains open as a result of the strong correlation between $\varepsilon$ and $K$.

No selection of thermodynamic data for the system Np(IV)-silicate can be recommended from this study.

*Pu(IV) hydrolysis and silicate complexation*

Yusov *et al.* also studied the hydrolysis behaviour of Pu(IV) spectroscopically. Far less information is provided regarding the approach used by the authors to quantify the hydrolysis reaction for Pu(IV). The authors infer from literature data that about 35 % of Pu(IV) is hydrolysed in 1 M $HClO_4$ according to the reaction:

$$Pu^{4+} + H_2O(l) \rightleftharpoons PuOH^{3+} + H^+ \quad \text{(A.428)}$$

The authors studied the Pu(IV) hydrolysis in solutions with $p_cH < 1.4$ and determined the molar extinction coefficient of 56 $L \cdot mol^{-1} \cdot cm^{-1}$ for the characteristic absorbance of $Pu^{4+}$ at 469.5 nm. However, the molar extinction coefficient was measured in 2 M $HClO_4$, while the hydrolysis constants are reported for $I = 0.1$ and 0.5 $mol \cdot L^{-1}$. The differences in ionic strength introduce additional uncertainties related to the known ionic-strength dependence of the molar extinction coefficient of Pu(IV). As in the case with Np(IV), it is unclear if the authors used the entire spectra recorded at 330-860 nm to derive the hydrolysis constants or only the characteristic absorbance for $Pu^{4+}$ at 469.5 nm with the reported molar extinction coefficient. The authors observed polymerisation to start at about $p_cH \geq 1.4$ for Pu(IV) which is lower compared to $p_cH \sim 2.2$ for Np(IV) at about $10^{-4}$ M actinide concentration. Thus, the Pu(IV) titrations were performed at $p_cH \leq 1.4$, however only three absorption spectra at $p_cH$ 1.00, 1.20 and 1.34 are shown in Figure 4 of the paper.

The conditional Pu(IV) hydrolysis constants $K_{1,1}$(A.428) = (0.027 ± 0.005) at $I = 0.5$ and $K_{1,1}$(A.428) = (0.063 ± 0.004) at $I = 0.1$ $mol \cdot L^{-1}$ were converted to a mean $\log_{10} K^{\circ}_{1,1} = -(0.59 \pm 0.02)$ using the SIT parameters provided in the literature. Similar to the Np(IV) hydrolysis constant, the value for $\log_{10} K^{\circ}_{1,1}$ ((A.428), Pu(IV)) = – (0.59 ± 0.02) reported by Yusov *et al.* differs by about one order of magnitude from the NEA TDB value of $\log_{10} K^{\circ}_{1,1}$ ((A.428), Pu(IV)) = (0.600 ± 0.200) selected in [2003GUI/FAN]. The authors discuss the discrepancy of hydrolysis constants referring to the difficulties of excluding polymerisation and formation of colloidal species, confirming the uncertainties associated with hydrolysis data from extraction and solubility data as pointed out by the NEA TDB. Even more inadequate is the use of one wavelength to iterate two parameters ($\varepsilon(PuOH^{3+})$, $K_{1,1}$(A.428)), using a molar extinction coefficient determined at a different ionic strength, and only utilise three absorbance spectra at $p_cH \leq 1.4$.

The hydrolysis constants for $PuOH^{3+}$ determined in this work were used to fit the spectroscopic data to calculate the complexation with $Si(OH)_4$(aq) according to the equilibrium (A.429):

$$Pu^{4+} + Si(OH_4)(aq) \rightleftharpoons PuSiO(OH)_3^{3+} + H^+ \quad \text{(A.429)}$$

The authors determined the apparent formation constants $\log_{10} K$(A.429) = (0.99 ± 0.06) at $I = 0.5$ $mol \cdot L^{-1}$ and $\log_{10} K$(A.429) = (1.04 ± 0.04) at $I = 1.0$ $mol \cdot L^{-1}$. A value of $\log_{10} K$(A.429) = (1.40 ± 0.04) at $I = 0.14$ $mol \cdot L^{-1}$ is provided, although the

accurate value of the ionic strength is uncertain. However, in contrast to Np(IV), where the authors discussed the fitting routine and reported molar extinction coefficients at 723 nm, no data are reported on the Pu(IV) silicate complex. By using the dissociation constant for $Si(OH)_4(aq)$, $\log_{10}K° = -9.81$, the conditional stability constants of $PuSiO(OH)_3^{3+}$ are corrected to zero ionic strength to be $\log_{10}K°(A.429) = 2.0$.

This formation constant cannot be accepted due to the fact that it relies on incompatible hydrolysis constant and inconsistent molar extinction coefficients for all solution species involved. Due to the lack of details on experimental data and analytical approach no selection of thermodynamic data for the system Pu(IV)-OH-silicate can be recommended from this study.

**[2005KIM/ASA]**

Kim *et al.* investigated the redox behaviour of Np(VI) in nitric acid solutions at $T = 25$ °C using a combination of electrochemical and spectroelectrochemical techniques [2004KIM/ASA], [2005KIM/ASA]. In a first step, experiments were only performed in 3.0 M $HNO_3$ [2004KIM/ASA], but these were later extended to 1.0 M ≤ [$HNO_3$] ≤ 8.0 M in [2005KIM/ASA]. Cyclic voltammetry (CV) experiments were conducted under $N_2$ atmosphere using a three-electrode system: both Pt and glassy carbon were tested as working electrodes, whereas Pt and Ag/AgCl were used as counter and reference electrodes, respectively. No mention is made to the filling solution of the reference electrode, which this review assumes as 3.0 M NaCl based on the type of electrode reported (BAS 002020). Cyclic voltammograms collected within + 1.20 V and + 0.60 V (*vs.* SSE) indicate the quasi-reversible reduction of Np(VI) to Np(V). Redox potentials (*vs.* SSE) determined according with $E = (E_{pc} + E_{pa})/2$ were reported as + 0.906 V (1.0 M $HNO_3$), + 0.908 V (2.0 M $HNO_3$), + 0.909 V (3.0 M $HNO_3$), + 0.902 V (4.0 M $HNO_3$), + 0.896 V (5.0 M $HNO_3$), + 0.895 V (6.0 M $HNO_3$), + 0.888 V (7.0 M $HNO_3$), + 0.884 V (8.0 M $HNO_3$). Liquid junction potential of the reference electrode was not accounted for by the authors, in spite of the relevant changes in $E_j$ expected with increasing $HNO_3$ concentration.

UV-vis/NIR and CV were combined in a series of spectroelectrochemical experiments to assess the *in-situ* reduction of Np(VI) to Np(V) in 1.0 M ≤ [$HNO_3$] ≤ 8.0 M. UV-vis/NIR spectra were collected within $300 \leq \lambda$ [nm] ≤ 1300. The scan of the redox potential from + 1.10 V to + 0.60 V (*vs.* SSE) led to the decrease of the peak at 1224 nm and the increase of the peaks at 980 and 1094 nm, corresponding to Np(VI) and Np(V), respectively. Spectroscopic data obtained at [$HNO_3$] > 1.0 M are neither shown nor discussed in the manuscript, and thus no quantitative evaluation of the equilibrium $Np(VI)\text{-}NO_3(aq) \rightleftharpoons Np(V)\text{-}NO_3(aq)$ can be performed from the spectroelectrochemical measurements conducted in [2005KIM/ASA]. Note that vis/NIR measurements reported in [2013LIN/APO] clearly hinted the predominance of $NpO_2NO_3^+$ ($\lambda$ = 1228 nm) and $NpO_2(NO_3)_2(aq)$ ($\lambda$ = 1120

nm) species above [ $NO_3^-$ ] ≈ 4 M and ≈ 7 M, respectively. The formation of inner-sphere Np(V)-$NO_3$ complexes at [ $NO_3^-$ ] = 5.0 M was also confirmed in [2008IKE/HEN] by means of EXAFS.

Data reported by Kim and co-workers have not been used in the thermodynamic evaluation of the Np(VI)-$NO_3$ and Np(V)-$NO_3$ systems due to the relevant experimental shortcomings and uncertainties discussed above.

**[2005KUR/ADA]**

Kurosaki *et al.* [2005KUR/ADA] reported a molecular dynamics (MD) study of the thermophysical properties of the actinide nitrides ThN, UN, NpN and PuN in the temperature range 25 300-2500 K and pressure range 0.1 MPa – 1.5 GPa. The complete review of this article is reported in the Appendix A for uranium.

**[2005MAG/SAN]**

This paper reports the measurement of the heat capacity of $NpO_2$(cr) in the temperature range 0.7-300 K using the relaxation method with a PPMS-9T Quantum Design calorimeter. The measurements were made on a 2.441 mg single crystal grown using the chemical-transport reaction method with $TeCl_4$ as transport agent. The sample was characterised by chemical analysis, scanning electron microscopy and X-ray diffraction. The numerical heat capacity values (reproduced in this review, private communication) obtained in this work have not been reported by [2005MAG/SAN]. They are compared in Figure A-15 and Figure A-16 to the experimental data of Westrum *et al.* obtained on 1.9250 g of polycrystalline material [1953WES/HAT]. The agreement between $T$ = 10 and 40 K is excellent. The data of [2005MAG/SAN] are slightly lower than those of [1953WES/HAT] above the latter temperature, but within the uncertainty limits considering the small mass of $NpO_2$(cr) used [2005MAG/SAN]. Combining the heat capacity data of [2005MAG/SAN] below 12.4 K with that of [1953WES/HAT] above the latter temperature, the entropy at 298.15 K is derived as $S_m^o$ ($NpO_2$, cr, 298.15 K) = (80.2 ± 0.4) J·K$^{-1}$·mol$^{-1}$ in excellent agreement with the data selected by [2003GUI/FAN] and [2014KON/BEN].

Figure A-15: Experimental heat capacity of $NpO_2$(cr) after Westrum *et al.* [1953WES/HAT] and Magnani *et al.* [2005MAG/SAN].

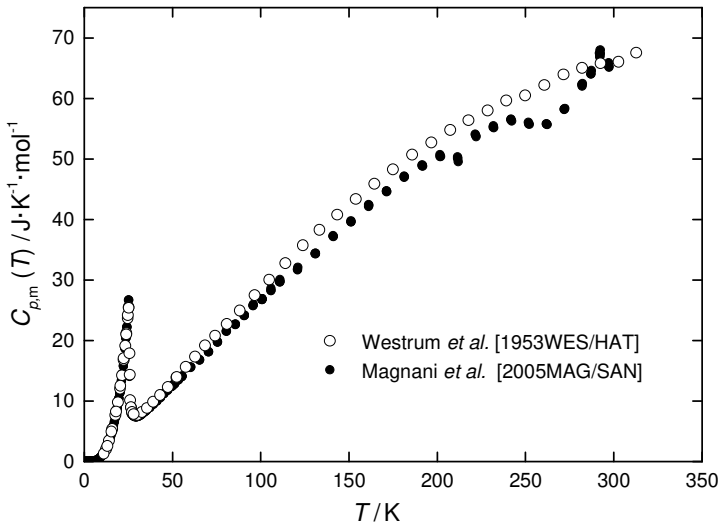
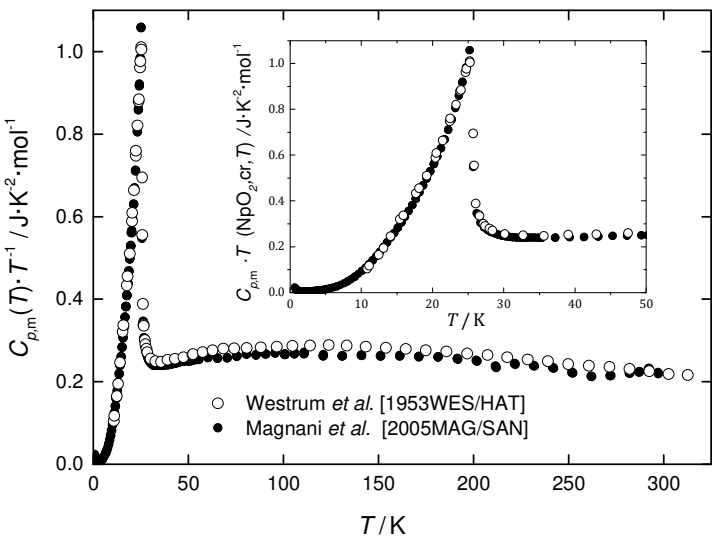



Figure A-16: Experimental heat capacity of $NpO_2$(cr) over temperature after Westrum *et al.* [1953WES/HAT] and Magnani *et al.* [2005MAG/SAN].



The discussion of [2005MAG/SAN] is focused on the λ-type anomaly observed at $T_0$ = 25.7 K and its significance for an octupolar order in $NpO_2$(cr) [2002PAI/DET]. [2005MAG/SAN] estimated the magnetic contribution to the heat capacity in $NpO_2$(cr) by subtracting its lattice contribution approximated with that of the isostructural compound $ThO_2$(cr). The corresponding magnetic entropy at $T_0$ was derived as $S_m = 6.99\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, which is much smaller than the expected spin-only value ($R$ ln4) of the $\Gamma_8$ crystal field ground state, but the crystal-field entropy is completely recovered at high temperatures. The occurrence of a second transition (phase transition or Schottky anomaly) between 1 and 11 K was excluded as no humps were observed in the magnetic contribution to the heat capacity. [2005MAG/SAN] therefore inferred that the ground state in the ordered phase was a singlet, and that the symmetry of the primary magnetic octupolar order parameter was $\Gamma_5$ (and not $\Gamma_2$ which would split the ground state into two doublets). More recent studies by Santini *et al.* [2006SAN/CAR] have concluded that the λ-anomaly at $T$ = 25.7 K was due to rank-5 triakontadipolar order.

**[2005MCK/SWA]**

McKee and Swart [2005MCK/SWA] studied $Hg_2^{2+}$ and cation-cation complexes of $NpO_2^+$ and $UO_2^{2+}$ using density functional theory (BPW91/TZ2P). Solvation effects were taken into consideration with a continuum method (COSMO). Although less stable than the individual ions, the authors identified a minimum in the gas phase for the T-shaped structures $NpO_2^+{\cdot}NpO_2^+$ and $NpO_2^+{\cdot}UO_2^{2+}$. No (even local) minimum was found for the complex $UO_2^{2+}{\cdot}UO_2^{2+}$ due to the great electrostatic repulsion. In the aqueous phase, the complexes $NpO_2^+{\cdot}NpO_2^+$ and $UO_2^{2+}{\cdot}NpO_2^+$ become more stable than the individual ions due to their significantly greater solvation energy. Np-Np distances calculated by the authors in $NpO_2^+{\cdot}NpO_2^+$ (4.222 Å) are in excellent agreement with the distance determined in [2008SKA/ANT] by high-energy X-ray scattering (4.20 ± 0.03) Å. McKee and Swart reported clearly overestimated binding free energies for $NpO_2^+{\cdot}NpO_2^+$ ($\Delta G_m$(aq) = – 176.1 $kJ{\cdot}mol^{-1}$) and $NpO_2^+{\cdot}UO_2^{2+}$ ($\Delta G_m$(aq) = – 122.2 $kJ{\cdot}mol^{-1}$). The authors argued the possible underestimation of solvation energies by COSMO in the case of strong solvent-solute interactions and differences in the number of waters in the first coordination sphere of reactants (9) and products (10) as main reasons for such deviations.

**[2005SED/KON]**

[2005SED/KON] reported *ab initio* calculations of the enthalpies of formation of the actinide mononitrides AnN(cr) (An = Ac, Th, Pa, U, Np, Pu, Am). The review is given in the Uranium, App. A section.

**[2005SOB]**

The authors estimated the isochoric specific heat, isobaric specific heat and isobaric coefficient of thermal expansion of $ThO_2$, $UO_2$, $NpO_2$, and $AmO_2$ from a simplified model of the equation of state (EOS). A quasi-harmonic approximation was applied to the lattice vibrations, and the discrete spectrum for the electronic excitations was taken from [1991KRU/GAJ], [2004KON]. The calculated isobaric heat capacity for $NpO_2$ from $T = 25$ to 1800 K was in good agreement with [2001SER/ARA] and [1953WES/HAT]. No new experimental data are reported.

**[2005YAM/WAT]**

Yamamura *et al.* [2005YAM/WAT] investigated electron transfer kinetics of the $Np^{3+}/Np^{4+}$ and $NpO_2^+/NpO_2^{2+}$ couples using cyclic voltammetry, and compared the results with the $V^{2+}/V^{3+}$ and $VO^{2+}/VO_2^+$ systems. Although the main focus of the paper is on kinetic processes, the authors reported also the formal potential of the investigated Np couples in 1.0 M $HNO_3$ and 1.0 M HCl. Four different carbon electrodes were used in the voltammetry measurements: glassy carbon (GC), plastic formed carbon (PFC) and two types of pyrolytic graphite (PG, *c* and *a* planes). For all these electrodes, the $Np^{3+}/Np^{4+}$ and $NpO_2^+/NpO_2^{2+}$ couples showed a reversible to pseudo-reversible behaviour. Ag/AgCl was chosen as reference electrode, although no information is provided in the paper on the filling solution (3.0 M KCl or NaCl ?). No information is provided either on the temperature at which measurements were performed. Yamamura and co-workers reported consistent values for the formal potentials of the $Np^{3+}/Np^{4+}$ and $NpO_2^+/NpO_2^{2+}$ couples measured with different working electrodes (Table A-162, *vs.* Ag/AgCl). Assuming $T =$ 25 °C and 3.0 M KCl as filling solution of the reference electrode, this review recalculates *vs.* SHE $E$(Np(IV)/Np(III), 1.0 M $HNO_3$) = 0.07 V, $E$(Np(IV)/Np(III), 1.0 M HCl) = 0.09 V, $E$(Np(VI)/Np(V), 1.0 M $HNO_3$) = 1.09 V and $E$(Np(VI)/Np(V), 1.0 M HCl) = 1.11 V. These values are clearly lower than the formal potentials selected in [2001LEM/FUG] for 1.0 M $HClO_4$ ($E$(Np(IV)/Np(III)) = (0.155 ± 0.001) V and $E$(Np(VI)/Np(V)) = (1.137 ± 0.001) V). Indeed, formal potentials in HCl and $HNO_3$ solutions are expectedly lower than in $HClO_4$ media due to the formation of stronger chloride and nitrate complexes with Np(IV)/Np(VI) than with Np(III)/Np(V). Note however that previous investigations in 1.0 M HCl [1949HIN/MAG] reported higher $E$(Np(IV)/Np(III)) and $E$(Np(VI)/Np(V)) than those obtained in [2005YAM/WAT]. No thermodynamic data can be selected from [2005YAM/WAT] due to the lack of relevant details in the experimental description.

Table A-162: Formal potentials *vs.* Ag/AgCl (with unknown filling solution and temperature) for the Np(IV)/Np(III) and Np(VI)/Np(V) couples in 1.0 M $HNO_3$ and 1.0 M HCl as reported in [2005YAM/WAT] using four different carbon working electrodes.

| Electrode | Medium | *E*(Np(IV)/Np(III)) (V) | *E*(Np(VI)/Np(V)) (V) |
|---|---|---|---|
| PG (*c* plane) | 1.0 M $HNO_3$ | – 0.14 | 0.88 |
| | 1.0 M HCl | – 0.12 | 0.90 |
| PG (*a* plane) | 1.0 M $HNO_3$ | – 0.14 | 0.88 |
| GC | 1.0 M $HNO_3$ | – 0.15 | 0.88 |
| PFC | 1.0 M $HNO_3$ | – 0.15 | 0.88 |

**[2005YUS/FED2]**

Yusov *et al.* investigated the hydrolysis of Np(V) and its complexation with silicate under weakly alkaline conditions ($8 \leq -\log_{10}[H^+] \leq 10$) using a spectrophotometric approach. Ionic strength was kept constant at $I = 0.1$ M $NaClO_4$. Experiments were performed in air, but all solutions were bubbled with Ar and titrations with NaOH were conducted under an Ar flow. The concentration of Np(V) ranged between $5 \times 10^{-5}$ M and $1 \times 10^{-4}$ M.

Np(V) hydrolysis was assessed by following the decrease in the absorption of the $NpO_2^+$ band at $\lambda = 981$ nm with increasing pH. The authors reported the contamination with $CO_2$ during the titration process and the consequent formation of $NpO_2CO_3^-$ (NIR band at $\lambda = 991$ nm). Both species were considered in the calculation of the concentration of the hydrolysis species ($[NpO_2OH(aq)] = [Np]_{tot} - [NpO_2^+] - [NpO_2CO_3^-]$) and corresponding stability constant, $\log_{10}{}^*K$ ((A.430), 0.1 M $NaClO_4$).

$$NpO_2^+ + H_2O(l) \rightleftharpoons NpO_2OH(aq) + H^+ \qquad \text{(A.430)}$$

The authors also acknowledged the precipitation of Np(V) hydroxide at $-\log_{10}[H^+] \geq 9.5$, and used only the spectroscopic data below this pH to provide an upper limit value for $\log_{10}{}^*K$((A.430), 0.1 M $NaClO_4$) $\leq -11$. The presence of a significant concentration of $NpO_2(CO_3)_2^{3-}$ in this pH-range should be also expected if assuming thermodynamic equilibrium with atmospheric $CO_2$(g). The upper limit reported in [2005YUS/FED2] at $I = 0.1$ M $NaClO_4$ for the first hydrolysis constant of Np(V) is consistent with the value selected in [2003GUI/FAN] ($\log_{10}{}^*K°$(A.430) = – (11.3 ± 0.7)).

The same approach was used to evaluate the complexation of Np(V) with silicate. The total concentration of silicate ranged between 0.004 and 0.02 M. Most of the samples evaluated were supersaturated with respect to amorphous silica, resulting in the formation of significant amounts of polymeric Si species (up to 80 % of $[Si]_{tot}$, as quantified by the molybdate method). The formation of the complex $NpO_2SiO(OH)_3(aq)$ according with Reaction (A.431) was proposed to explain the decrease in the absorption of the $NpO_2^+$ band at $\lambda = 981$ nm with increasing $[Si]_{tot}$,

$$NpO_2^+ + SiO(OH)_3^- \rightleftharpoons NpO_2SiO(OH)_3(aq) \qquad \text{(A.431)}$$

where the concentration of the Np(V)-silicate complex was calculated as $[NpO_2SiO(OH)_3(aq)] = [Np]_{tot} - [NpO_2^+] - [NpO_2CO_3^-] - [NpO_2OH(aq)]$. Conversely, $[NpO_2OH(aq)]$ was calculated using $\log_{10}{}^*\beta°(A.430) = -11.3$. The formation of $NpO_2(CO_3)_2^{3-}$ was not considered by the authors in the calculations, although it can be expected in significant proportions in some of the samples if assuming equilibrium with air ($\geq 50$ % $[Np]_{tot}$ at $-\log_{10}[H^+] \geq 9.6$ and $pCO_2 \approx -3.5$). This could partly explain the stronger absorption observed at higher wavelengths ($NpO_2(CO_3)_2^{3-}$: $\lambda_{max} = 999$ nm, $\varepsilon_{999} = (150 \pm 25)$ L·mol$^{-1}$·cm$^{-1}$ [1994NEC/RUN]). The concentration of $SiO(OH)_3^-$ was calculated from the mass balance $[SiO(OH)_3^-] = K_{dis}[Si]_{tot}([H^+] + K_{dis})^{-1}$, with $\log_{10}K^o_{dis} = -9.81$ (stability constant for the dissociation of orthosilicic acid, $Si(OH)_4(aq) \rightleftharpoons SiO(OH)_3^- + H^+$) as reported in [2002HUM/BER]. Based on these data, the authors calculated $\log_{10}K((A.431), 0.1\ M\ NaClO_4) = (2.1 \pm 0.3)$ as average of 16 independent measurements at different concentrations $[Np]_{tot}$, $[Si]_{tot}$ and $-\log_{10}[H^+]$. Note that the presence of polymeric Si species was not accounted for in the calculations, resulting in a likely overestimation of $[SiO(OH)_3^-]$ and consequent underestimation of $\log_{10}K((A.431), 0.1\ M\ NaClO_4)$.

**[2005YUS/SHI]**

Yusov *et al.* studied the complexation of Np(VI) with orthosilicic acid and polymeric silicic acids using spectrophotometry. Most of the experiments were performed within the ranges $1.7 \leq pH \leq 4.7$ and $0.022\ M \leq [Si]_{tot} \leq 0.088\ M$, however, a number of experiments were also performed at higher pH values to evaluate the complexation with polymeric silicate species. Spectrophotometric data collection focused on the VIS region of Np ($\lambda = 400$ and 600 nm). Relevant details (especially concerning equilibration time and kinetics of silicate polymerisation) are omitted in the experimental description of this study. Note also that only a small fraction of all the experimental data generated in this study are shown in the paper, which is an important limitation for an independent evaluation of the results.

In a first step, the authors evaluated the molar extinction coefficients of $NpO_2^{2+}$, $NpO_2OH^+$ and $(NpO_2)_2(OH)_2^{2+}$ species considering the stability constants reported for these species in [1972CAS/MAG][3]. Experimental conditions were chosen to minimise the contribution of $(NpO_2)_3(OH)_5^+$. Experiments in the presence of silicate were largely oversaturated with respect to $SiO_2$(am) (10-40 times above the solubility limit). In spite of this, the authors did not observe the formation of colloidal/polymeric Si species, but assumed the predominance of monomeric, dimeric and tetrameric species at $[Si]_{tot} = 0.022$, 0.044 and 0.088 M, respectively, and determined their concentrations based on the molybdate method and kinetic considerations reported elsewhere [1979ILE]. Although acknowledging the transient state of the considered system, the authors claimed

[3] Values originally reported at $I = 1.0$ M $NaClO_4$. Data were selected in [2001LEM/FUG] and extrapolated to $I = 0$ considering the same ion interaction coefficients as for U(VI) species.

the feasibility of a thermodynamic evaluation of the Np(VI)-silicate complexation because of the slow kinetics of the Si polymerisation reaction. The fraction/concentration of polymeric species in the experiments by [2005YUS/SHI] is a major concern of this review. In a parallel study on the U(VI)-silicate system, the same research team reported the predominance of dimeric species at $[Si]_{tot}$ = 0.018 M and 1.93 ≤ pH ≤ 3.58 (see Table 2 in [2005YUS/FED]), and indicated (page 347 in [2005YUS/FED]) "*We were able to avoid noticeable dimerization and further polymerization of Si(OH)$_4$ at its concentrations of up to 0.015 M; at higher concentrations, the dimeric and tetrameric silicate species became prevalent*". None of the two studies [2005YUS/SHI], [2005YUS/FED] provided a comprehensive information of the equilibration time and rate constants of the reaction between Si and molybdate, which are necessary to calculate the concentration of monomeric and polynuclear Si species in the experiments. The accurate knowledge of monomeric $Si(OH)_4(aq)$ concentration is mandatory for the determination of the complexation constant with Np(VI).

From the experimental VIS data, the authors quantified the absorptivity coefficients and concentrations of the main Np(VI)-silicate species forming in the system according with Reaction (A.432).

$$NpO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons NpO_2SiO(OH)_3^+ + H^+ \qquad (A.432)$$

The calculation of the $\log_{10}K$((A.432), 0.1-0.2 M $NaClO_4$) was performed based on these experimental data and assuming $[Si(OH)_4(aq)] = [Si]_{tot}$. This interpretation is erroneous in most of the samples, because the experimental evidences indicating the predominance of dimeric and tetrameric species in solution at $[Si]_{tot} \geq 0.044$ M (or ≥ 0.015 M if considering [2005YUS/FED]). The extrapolation to $I$ = 0 conducted by the authors assuming the same ion interaction coefficient estimated in [2003GUI/FAN] for $UO_2SiO(OH)_3^+$ resulted in $\log_{10}K°$((A.432), 298.15 K) = – (2.61 ± 0.12). This review does not accept this value as it has been obtained under non-equilibrium conditions, although $\log_{10}K$((A.432), 0.1 M $NaClO_4$) = – 2.8 calculated from the experiments with the lowest silicate concentration ($[Si]_{tot}$ = 0.022 M) can be considered in scoping calculations. Note also that $\log_{10}K°$((A.432), 298.15 K) reported by Yusov *et al.* is significantly lower than the stability constant selected in this review for the analogous U(VI) reaction, $\log_{10}K°$ ($UO_2SiO(OH)_3^+$, 298.15 K) = – (1.88 ± 0.19).

The authors also evaluated the formation of Np(VI) complexes with colloidal/polymeric Si species. The stability constants provided by the authors were found to vary with pH, which was attributed to the different Si:OH ratio in the polymeric Si species forming at different pH values. These remain as conditional stability constants for which neither the stoichiometry of the Np(VI) complex nor of the reacting polymeric species are known, and thus cannot be recommended in this review.

**[2006MOR/SAS]**

See review in Chapter 17 (Appendix A, Pu).

**[2006NEC]**

In this publication Neck is commenting on the hydrolysis study of Np(V) reported in [2004RAO/SRI]. Neck disagrees with the data presented in [2004RAO/SRI] suggesting the experiments and data were compromised by carbonate contamination. Neck is questioning the large differences between hydrolysis constants reported by Rao *et al.* compared to those obtained from solubility studies. Applying the hydrolysis constants reported in [2004RAO/SRI] to calculate the solubility of $NpO_2OH(am)$, the predicted Np(V) solubility at pH > 10 is orders of magnitude higher than the solubility calculated with the data selected in the NEA TDB ([2003GUI/FAN]. The major impact on solution speciation is that the thermodynamic data reported in [2004RAO/SRI] infer complexation of Np(V) in solution to occur at about pH > 9. However, no complexation has been observed spectroscopically in Np(V) solubility studies up to about pH 10.5-11, where only the $NpO_2^+$ ion is present in solution in the absence of carbonate. Neck refers to the electronic absorption band at 991 nm as indicator of the carbonate contamination in the form of the well-known Np(V) complex, $NpO_2CO_3^-$. A response to Neck's comments is provided in [2006RAO/SRI].

**[2006PER/KUL]**

The solubility of mixed-valent U(IV/VI) and Np(IV/V) hydroxides in simulated groundwater is compared to their solubility in 0.1 M $NaClO_4$ at pH 6.9. The solubility of the Np mixed-valent solid phase is found to be very similar with $(6.5 \pm 1.5) \times 10^{-6}$ M in the simulated groundwater and $(6.1 \pm 2.4) \times 10^{-6}$ M in 0.1 M $NaClO_4$. The measured neptunium solubility is orders of magnitude higher than the calculated solubility of pure $Np(OH)_4(s)$ caused by the oxidation of Np(IV) to Np(V) and the formation of a mixed $Np(OH)_4$-$NpO_2OH$ surface layer. No thermodynamic data are reported in this study.

**[2006RAO/SRI]**

This paper is a response of Rao *et al.* to the comments made by Neck [2006NEC] in reference to hydrolysis data reported in [2004RAO/SRI]. The authors disagree with the majority of concerns raised in [2006NEC] and acknowledge the need for further verification experiments. The authors reviewed the experimental procedures used for the potentiometric and spectrophotometric titration experiments in [2004RAO/SRI], which did not reveal a reasonable cause for contamination with carbonate. The authors explain the large differences in hydrolysis constants from solubility studies to those reported in

[2004RAO/SRI] by the lack of solid equilibrium phase characterisation. Most solubility data at low ionic strength are interpreted with $NpO_2OH(am)$ as the solid equilibrium phase with $NpO_2^+$ and $NpO_2OH(aq)$ as solution species at pH between 10.5 and 12, and $NpO_2(OH)_2^-$ as the dominant solution species at pH > 12 causing the increase in Np(V) solubility at high pH. The authors argue that the assumption of the solid equilibrium phase as $NpO_2OH(am)$ could be erroneous and the solubility data may also be interpreted with $NaNpO_2(OH)_2(s)$ as a potential solid equilibrium phase. Under this circumstance, the solubility data between pH 8 and 10 are interpreted with the presence of $NpO_2OH(aq)$ in order to match the slope of – 1 in the plot of $\log_{10}$[Np(V)] *vs.* pH. It is to note that the interpretation of Np(V) solubility data in carbonate-free solutions with a different solid phase requires changes in $\log_{10}\beta_{1n}$ to match the solubility data. However, other spectrophotometric studies have not shown complexation of Np(V) in this pH region and the formation constants are not consistent with the approach proposed by Rao *et al.* in this paper. The authors could not definitely exclude carbonate contamination during their spectrophotometric titrations. The authors agree that until further experimental verification is available, the hydrolysis constants reported in [2004RAO/SRI] obtained from spectrophotometric titrations should not be used further.

**[2006RAO/TIA]**

The complex formation of Np(V) with fluoride and sulfate was studied in the temperature range 25-70 °C by using isothermal microcalorimetry. The complexation reaction of Np(V) with fluoride or sulfate was explored by titrating about 0.90 $cm^3$ (at 25 °C) Np(V) solution with solutions containing the ligand. However, the authors did not provide critical experimental information, such as ligand concentrations in the stock solution or added during the titrations. At each temperature multiple titrations were performed with each titration consisting of 40-50 additions. The ionic strength was maintained at 1 M with $NaClO_4$ as the background electrolyte. Titration experiments were carried out at 25, 40, 55 and 70 °C.

The authors determined the protonation constant and enthalpy for fluoride and sulfate at each temperature. The protonation constants and enthalpy of fluoride and sulfate were determined by titrating about 0.90 $cm^3$ (at 25 °C) of solution containing each ligand with $HClO_4$. The protonation constants were found to increase with temperature. The heat capacities of the protonation reactions of fluoride and sulfate were obtained from the linear temperature-dependence of the enthalpy and calculated to be (96 ± 13) $J \cdot K^{-1} \cdot mol^{-1}$ and (599 ± 16) $J \cdot K^{-1} \cdot mol^{-1}$, respectively. To calculate the reaction enthalpies of the Np(V) complexation, the authors used these heat capacity data of the protonation reactions and complex formation constants that were interpolated to the temperatures in this study from the stability constants reported in [2006XIA/FRI] at 25, 35, 50 and 60 °C.

The SIT approach was used to correct the conditional equilibrium constants by using ion interaction parameters at 25 °C and the temperature-dependent values of the

parameter A in the Debye-Huckel equation. The error introduced by using only the ion interaction parameters for 25 °C was estimated to be small and may cancel each other out.

*Np(V)-sulfate system*

The complexation of Np(V) with sulfate was studied by adding a sulfate solution to the Np(V) perchlorate solution in increments of 5 µL. However, in this paper the authors did not provide any further experimental details (*i.e.*, sulfate concentration in titrant) and thus the total amount of sulfate added throughout the titration is unknown. The heat reaction data were interpreted with the formation of $NpO_2SO_4^-$ according to the Reaction (A.433):

$$NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^- \quad \text{(A.433)}$$

With increasing temperature the complexation of Np(V) with sulfate increases and the equilibrium constants increase significantly. The endothermic reaction enthalpy is found to increase with temperature. The heat capacity of Reaction (A.433) was calculated to be (244 ± 51) $J \cdot K^{-1} \cdot mol^{-1}$.

To correct to zero ionic strength, the authors adopted $\varepsilon(NpO_2SO_4^-, Na^+) = \varepsilon(NpO_2CO_3^-, Na^+) = -(0.18 \pm 0.15)$ $kg \cdot mol^{-1}$ and used $\varepsilon(NpO_2^+, ClO_4^-) = (0.25 \pm 0.05)$ $kg \cdot mol^{-1}$.

Table A-163: Thermodynamic data and reaction enthalpies for the reaction of $NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^-$ reported in [2006RAO/TIA]. Equilibrium constants for 55 and 70 °C extrapolated from the equilibrium constants at 25, 40 and 50 °C reported in [2006XIA/FRI].

| $t$ /°C | Method | Medium | $\log_{10}\beta_{11}$ | $\log_{10}\beta_{11}^{\circ}$ | $\Delta_r H_m$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| 55 | cal | 1 M $NaClO_4$ | (0.78 ± 0.20) | 1.29 | (25.1 ± 0.3) |
| 70 | cal | 1 M $NaClO_4$ | (0.93 ± 0.20) | 1.47 | (30.4 ± 1.3) |

These are the same calorimetric data reported in [2009RAO/TIA] for the system Np(V)-sulfate. Stability constants reported in [2006XIA/FRI] were used to calculate the aqueous speciation at each temperature and thus derive the reaction enthalpy. Because of the experimental shortcomings identified in [2006XIA/FRI], the interpretation of the calorimetric data in [2006RAO/TIA] have not been accepted by this review and the selected values are based on the study in [2009RAO/TIA].

*Np(V)-fluoride system*

Similar to the sulfate system, the authors did not provide sufficient experimental details in this paper, such as the fluoride concentrations added to the Np(V) solutions. The authors provided additional information in a follow-up report on their spectrophotometric and calorimetric studies of the fluoride complexation of Np(V) in [2009TIA/RAO3]. The

experimental heat reaction data were interpreted with the formation of $NpO_2F(aq)$ according to the Reaction (A.434):

$$NpO_2^+ + F^- \rightleftharpoons NpO_2F(aq) \qquad (A.434)$$

With increasing temperature the complexation of Np(V) with fluoride increases and the stability constants increase significantly. In contrast to the Np(V) sulfate complexation, the enthalpy of the endothermic reaction is found to decrease with temperature. The heat capacity of Reaction (A.434) was calculated to be (96 ± 13) $J \cdot K^{-1} \cdot mol^{-1}$.

Table A-164: Thermodynamic data and reaction enthalpies for the reaction of $NpO_2^+ + F^- \rightleftharpoons NpO_2F(aq)$ reported in [2006RAO/TIA]. The formation constants for 25, 40, 55 and 70 °C were inter/extrapolated from formation constants determined at 35, 50 and 60 °C reported in [2006XIA/FRI].

| $t$ /°C | Method | Medium | $\log_{10}\beta_{11}$ | $\log_{10}\beta_{11}^{\circ}$ | $\Delta_r H_m$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|
| 25 | cal | 1 M $NaClO_4$ | (1.47 ± 0.10) | 1.58 | (18.0 ± 0.3) |
| 40 | cal | 1 M $NaClO_4$ | (1.63 ± 0.10) | 1.75 | (12.2 ± 0.6) |
| 55 | cal | 1 M $NaClO_4$ | (1.78 ± 0.10) | 1.91 | (9.4 ± 0.8) |
| 70 | cal | 1 M $NaClO_4$ | (1.94 ± 0.10) | 2.08 | (8.2 ± 1.2) |

**[2006SHI/YUS]**

Shilov and Yusov [2006SHI/YUS] measured the formal potentials of the Np(VI)/Np(V) couple in MOH solutions with M = $Li^+$, $Na^+$, $K^+$, $Cs^+$ and $N(CH_3)_4^+$ using potentiometry. The authors performed emf measurements of the cells Pt ⎪ Np(VI) / Np(V), MOH ‖ NaOH ⎪ HgO/Hg, Pt or Pt ⎪ Np(VI)/Np(V), MOH ‖ $KOH_{sat}$, AgCl ⎪ Ag, Pt with $2 \times 10^{-5}$ M ≤ [Np] ≤ $1 \times 10^{-3}$ M and 0.2 M ≤ [MOH] ≤ 11.3 M. Several of the investigated systems were oversaturated with respect to M-Np(V)-OH(s) or M-Np(VI)-OH(s) phases.

The authors observed a close to Nernstian behaviour for the Np(VI)/Np(V) couple in 1.0 M NaOH and 1.0 M LiOH, with a slope for $E$(Np(VI)/Np(V)) *vs.* $\log_{10}$([Np(VI)]/[Np(V)]) ≈ 0.061 V. Significant deviations appeared in the case of KOH (slope ≈ 0.077 V), CsOH (slope ≈ 0.080 V) and $N(CH_3)_4^+$ (slope ≈ 0.069 V) solutions, although no discussion or explanation of these deviations were provided by the authors. The slope of the plot $E$(Np(VI)/Np(V)) *vs.* $\log_{10}[OH^-]$ in systems with [MCl] + [MOH] = 1 was found very close to – 0.120, thus indicating that 2 $OH^-$ are involved in the equilibrium reaction between Np(VI) and Np(V) at 0.2 M ≤ $[OH^-]$ ≤ 1.0 M. Considering that $NpO_2(OH)_4^{2-}$ prevails for Np(VI) within this pH range, the authors proposed the chemical Reaction (A.435) to control the redox equilibrium Np(VI)/Np(V), thus making the strong case that $NpO_2(OH)_3^{2-}$ does not form below 1.0 M MOH.

$$NpO_2(OH)_4^{2-} + e^- \rightleftharpoons NpO_2(OH)_2^- + 2OH^- \quad \text{(A.435)}$$

For systems with $[OH^-] \geq 1.0$ M, the slope of the plot $E$(Np(VI)/Np(V)) *vs.* $\log_{10} a_{OH^-}$ increases to – 0.048 (1.0 M < [LiOH] ≤ 4.0 M), – 0.023 (1.0 M < [NaOH] ≤ 11.3 M) and – 0.029 (1.0 M < [KOH] ≤ 10.85 M). Based on their observations in LiOH solutions, the authors concluded that Reaction (A.436) prevails above $[OH^-] \approx 1.0$ M.

$$NpO_2(OH)_4^{2-} + e^- \rightleftharpoons NpO_2(OH)_3^{2-} + OH^- \quad \text{(A.436)}$$

Although the hypothesis proposed in [2006SHI/YUS] appears plausible, this review does not consider the experimental evidences reported by the authors as sufficient proof on the formation of $NpO_2(OH)_3^{2-}$. Very large changes in ionic strength occur along the considered range of [MOH], and activity coefficients of Np(VI) and Np(V) species prevailing in solution are not accounted for in the slope analysis conducted by Shilov and Yusov. The authors also disregard the possible changes in Np(VI) speciation at very high MOH concentrations. No convincing explanations are provided either on the significant changes in slope (speciation?) observed between LiOH, NaOH and KOH systems.

According with the discussion above, no selection of thermodynamic data can be recommended from this study. Nevertheless, the work by Shilov and Yusov provides relevant qualitative insights on the chemistry of the Np(VI)/Np(V) couple in strongly alkaline systems, which are accordingly discussed in the main text of this review.

**[2006TSU/WAH]**

See review in Chapter 17 (Appendix A, Pu).

**[2006XIA/FRI]**

Xia *et al.* studied the complex formation of Np(V) with sulfate and fluoride by using solvent extraction at $T$ = 25, 35, 50, 60 °C ($F^-$) and $T$ = 25, 40, 50 °C ($SO_4^{2-}$). 0.01 M HDEHP dissolved in heptane and pre-equilibrated with 1.0 M $NaClO_4$ was used as extractant. Experiments were performed at $I$ = 1.0 M $NaClO_4$-NaF or 1.0 M $NaClO_4$-$Na_2SO_4$. Concentrations of $H^+$ were calculated from the experimentally measured pH ($pH_m$) values according to $-\log_{10}[H^+] = pH_m + b$, where $b$ is an empirical correction factor that includes the activity coefficient of $H^+$ and the liquid junction potential of the combined electrode for a given ionic strength and temperature. Based on a previous study by the main author [1996CHO/ERT], the value $b$ = 0.27 was used for the correction of the measured $pH_m$ in all the experiments. This value was determined at $I$ = 1.0 M $NaClO_4$ and $T$ = 25 °C, and thus may result in significant errors in the corrected $-\log_{10}[H^+]$ when using it for other background electrolyte compositions or temperatures. The extraction system used by Xia and co-workers was found to be very sensitive to pH, and the

experimentally measured distribution ratios ($D_{exp} = [Np]_{org}/[Np]_{aq}$) determined at different $-\log_{10}[H^+]$ were corrected using the empirical equation:

$$\log_{10} D = \log_{10} D_{exp} + n(-\log_{10}[H^+]_{avg} + \log_{10}[H^+]) \quad \text{(A.437)}$$

where $D_{exp}$ is the distribution ratio measured experimentally, $[H^+]_{avg}$ the average proton concentration of all extraction experiments at the same $T$ but increasing $[F^-]$ or $[SO_4^{2-}]$, and $n$ is the experimental slope of $\log_{10} D_{exp}$ *vs.* $-\log_{10}[H^+]$ in the absence of ligand at a given temperature and $NaClO_4$ concentration. No hydrolysis of Np(V) or protonation of $F^-$ or $SO_4^{2-}$ are expected in the pH-range investigated by the authors ($4.78 \leq -\log_{10}[H^+] \leq 5.74$).

*Np(V)-sulfate system*

Sulfate concentrations up to 0.21 M were used to follow the complex formation with Np(V). This involved the substitution of up to 63 % of the original $NaClO_4$ concentration to maintain $I = 1.0$ M. Because of the sensitivity of $D$ to variations in $-\log_{10}[H^+]$, the impact of the background electrolyte substitution on the $b$-factor for the correction of $pH_m$ is expected to introduce a systematic and increasing error in $D$ with increasing $[Na_2SO_4]$.

The increase of $D_0/D$ with increasing $[Na_2SO_4]$ confirmed the formation of Np(V)-sulfate complex/es. The slope of the plot $D_0/D$ *vs.* $[Na_2SO_4]$ also increased with increasing $[Na_2SO_4]$, which was interpreted with the formation of two different species according with Reactions (A.438) and (A.439).

$$NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^- \quad \text{(A.438)}$$

$$NpO_2^+ + 2SO_4^{2-} \rightleftharpoons NpO_2(SO_4)_2^{3-} \quad \text{(A.439)}$$

Note that a very important contribution to the increase in the slope of $D_0/D$ *vs.* $[Na_2SO_4]$ comes from the correction of $D_{exp}$ resulting from the variation in $-\log_{10}[H^+]$. Because of the systematic bias introduced in this correction, the chemical model derived by the authors is not accepted in the present review, and the corresponding equilibrium constants are disregarded in the final data selection for the Np(V)-sulfate system.

*Np(V) fluoride system*

The total fluoride concentration in the aqueous phase in the experiments ranged between $5 \times 10^{-3}$ M and $3.25 \times 10^{-2}$ M and thus only a minor fraction of the 1.0 M $NaClO_4$ background electrolyte was replaced. The values $n = 1.25$, 1.25, 1.41 and 1.41 in (A.437) were determined by the authors in 1.0 M $NaClO_4$ at $T = 25$, 35, 50 and 60 °C, respectively. With the addition of fluoride, the extraction of the $NpO_2^+$ cation into the HDEHP/heptane phase decreases and the distribution ratio $D$ of Np(V) in the organic and aqueous phase decreases. The slope of the plot $D_0/D$ *vs.* [fluoride] increased linearly, which was interpreted with the formation of one Np(V) fluoride complex according to Reaction (A.440):

$$NpO_2^+ + F^- \rightleftharpoons NpO_2F(aq) \quad \text{(A.440)}$$

No higher fluoride complexes of Np(V) were considered in the data analysis. The conditional formation constants are determined by linear regression of the $D_0/D$ values versus the concentration of fluoride in the aqueous phase. The stability of the Np(V) fluoride complex is found to increase with temperature.

The conditional formation constant of (1.42 ± 0.10) in 1 M $NaClO_4$ at 25 °C is slightly higher compared to those reported in [1984CHO/RAO] (1.26 ± 0.30) and in [2009TIA/RAO3] (1.25 ± 0.05). In part, this difference may be caused by the different number of complexes chosen to interpret each experimental data set. From the conditional formation constant in 1.0 M $NaClO_4$ at 25 °C, $\log_{10}\beta_1 = (1.42 \pm 0.10)$, the authors calculate an effective value of $\Delta_r G^\circ_m = -8.11$ kJ·mol$^{-1}$ at 25 °C. The enthalpy and entropy values at 25 °C, $\Delta_r H^\circ_m = 20.8$ kJ·mol$^{-1}$ and $\Delta_r S^\circ_m = 96.9$ J·K$^{-1}$·mol$^{-1}$, were calculated using the Van't Hoff equation.

**[2006XIA/FRI2]**

Xia *et al.* investigated the complexation of Np(V) with $H_2PO_4^-$ at $T = 25$, 40 and 55 °C using a solvent extraction method. Ionic strength was kept constant at $I = 1.0$ M $NaClO_4$, whereas pH was buffered to $4.6 \leq -\log_{10}[H^+] \leq 5.5$ using morpholine-4-etanesulfonic acid buffer. In this pH-range, the aqueous speciation of phosphate is dominated by $H_2PO_4^-$, although $HPO_4^{2-}$ represents up to 9 % of the total phosphate concentration in the less acidic conditions. The experimentally measured pH was converted to $-\log_{10}[H^+]$ using a correction factor ($b = 0.27$), determined previously by the same authors for aqueous solutions with 1.0 M $NaClO_4$ at $T = 25$ °C. Note that the use of $b = 0.27$ at temperatures other than 25 °C is expected to introduce a systematic bias in the calculated $-\log_{10}[H^+]$. The observed decrease in the extraction coefficient with increasing $[NaH_2PO_4]$ was explained with the formation of the aqueous species $NpO_2H_2PO_4(aq)$ according to the Reaction (A.441).

$$NpO_2^+ + H_2PO_4^- \rightleftharpoons NpO_2H_2PO_4(aq) \qquad \text{(A.441)}$$

As indicated in [1985INO/TOC2] and already discussed in [2001LEM/FUG], the formation of the complex $NpO_2HPO_4^-$ cannot be disregarded above pH ≈ 4.5. Consequently, extraction data reported in [2006XIA/FRI2] have been reinterpreted in this review considering the formation of both $NpO_2H_2PO_4(aq)$ and $NpO_2HPO_4^-$, and using the stability constant selected for the latter in [2003GUI/FAN]. $pK^\circ_{a1}$ and $pK^\circ_{a2}$ of phosphoric acid have been also extrapolated to $I = 1.0$ M $NaClO_4$ and $T = 40$ and 55 °C using ion interaction coefficients reported in Appendix B and the NEA TDB guidelines for the extrapolation of $\Delta_r H^\circ_m$ to $I > 0$, in order to calculate $[H_2PO_4^-]_{free}$ and $[HPO_4^{2-}]_{free}$ under the conditions of the experiment. The resulting equilibrium constants are $\log_{10}K$((A.441), $I = 1.0$ M $NaClO_4$, $T = 25$ °C) = (1.27 ± 0.10), $\log_{10}K$((A.441), $I = 1.0$ M $NaClO_4$, $T = 40$ °C) = (1.26 ± 0.10) and $\log_{10}K$((A.441), $I = 1.0$ M $NaClO_4$, $T = 55$ °C) = (1.72 ± 0.10). Because of the

uncertainties affecting the pH measurement at elevated temperatures in [2006XIA/FRI2], and due to the direct impact of these uncertainties in the calculation of [ $H_2PO_4^-$ ], [ $HPO_4^{2-}$ ], [$NpO_2H_2PO_4$(aq)] and [ $NpO_2HPO_4^-$ ], $\log_{10}K$((A.441), $I$ = 1.0 M $NaClO_4$) at $T$ = 40 and 55 °C have been disregarded in the final data selection of this review. Note further that greater pH values are reached at these temperatures ($-\log_{10}[H^+] \leq 5.40$), in contrast with data at $T$ = 25 °C ($-\log_{10}[H^+] \leq 4.86$), and thus a larger fraction of $NpO_2HPO_4^-$ is expected in the former experiments.

[2001LEM/FUG] considered the experimental evidences reported in [1964MOS/PER], [1985INO/TOC2] insufficient and disregarded the selection of the complex $NpO_2H_2PO_4$(aq). Although the formation of the complex $NpO_2HPO_4^-$ must be acknowledged in the experimental conditions of [2006XIA/FRI2], the presence of this species alone cannot explain the reported extraction data (Figure A-17a). The model including both $NpO_2H_2PO_4$(aq) and $NpO_2HPO_4^-$ complexes is consistent with the reported experimental observations, and confirms the predominance of $NpO_2H_2PO_4$(aq) at $T$ = 25 °C within the pH- and [$NaH_2PO_4$]-range investigated. (Figure A-17b). In combination with the previous studies by [1964MOS/PER] and [1985INO/TOC2], this review considers this as sufficient evidence for the selection of the species $NpO_2H_2PO_4$(aq).

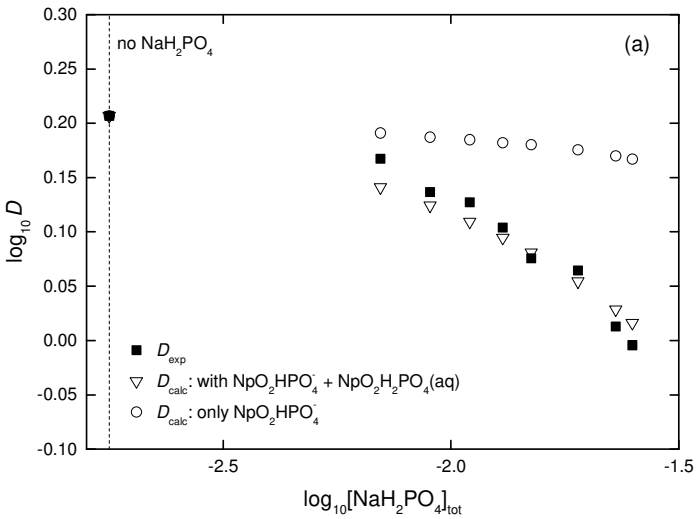
**[2007ALM/SKA]**

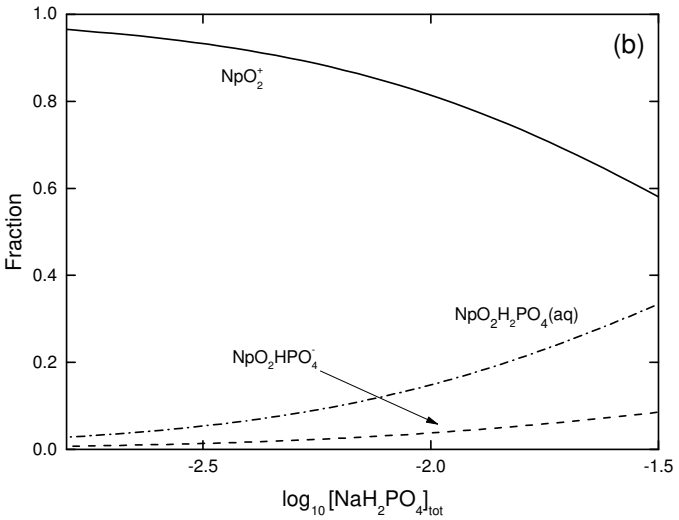
[2007ALM/SKA] reported the synthesis of single crystals of Na[$NpO_2(OH)_2$](cr) by hydrothermal reaction of Np(V) and NaOH in aqueous solution. The structure of Na[$NpO_2(OH)_2$](cr) was solved from the single-crystal data by direct methods and determined to be orthorhombic in space group $P2_12_12_1$ with cell parameters: $a$ = 5.8904(3) Å, $b$ = 7.6297(4) Å, $c$ = 8.1540(4) Å. In addition, the magnetic response of this compound was investigated on polycrystalline samples with magnetic susceptibility measurements in the temperature range 5-320 K under an applied field of 500 and 2000 G, and temperature-dependent measurements at several fields down to 20 G over the range 5-20 K. The results of those measurements indicated antiferromagnetic ordering of Np moments below 19.5(5) K, and an effective moment of 2.80(15) $\mu_B$ per formula unit in the range 35-300 K.

**[2007BAL/CAO]**

The authors report DFT and MP2 calculations on the structure, vibrational frequencies and energetics of Np(V) carbonate complexes. The complex geometries were optimised in the gas phase without symmetry restrictions. After the geometries were optimised, hydration effects were introduced by using the IEFPCM continuum model. From their calculations, the authors conclude that $NpO_2(CO_3)(H_2O)_3^-$, $NpO_2(CO_3)_2(H_2O)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ are the energetically favoured complexes in an aqueous system. It is to

Figure A-17: a. Experimental distribution ratios ($D_{exp}$) reported in [2006XIA/FRI2] at $T$ = 25 °C, and calculated values ($D_{calc}$) using a model including only $NpO_2HPO_4^-$ or both $NpO_2HPO_4^-$ and $NpO_2H_2PO_4(aq)$ complexes. $D_{calc}$ calculated using the pH values reported for each individual extraction sample ($4.72 \leq -\log_{10}[H^+] \leq 4.86$); b. Fraction diagram of Np(V) calculated for $[Np]_{tot} = 1.0 \times 10^{-5}$ M, $I$ = 1.0 M $NaClO_4$, $-\log_{10}[H^+]$ = 4.80 and $-2.8 \leq -\log_{10}[NaH_2PO_4]_{tot} \leq -1.5$.



note that the optimised structures for the biscarbonato complex differed significantly in the gas phase and aqueous solution. In contrast to the gas phase structure where water molecules coordinate with the carbonate ligands, in the aqueous phase water molecules are calculated to directly coordinate with the Np(V) atom. Hydration Gibbs energies were calculated by using the continuum model at the MP2 level according to:

$$\Delta G^{*}_{\text{solv}} = n\Delta G_{\text{vap}} + \Delta G^{*}_{\text{clust}} + \Delta G^{*}_{\text{solv}}(\text{NpO}_2(\text{CO}_3)_x(\text{H}_2\text{O})_n^{1-2x}) \qquad \text{(A.442)}$$

where $n\Delta G_{\text{vap}}$ is the Gibbs energy for the transfer of $n$ water molecules from the liquid to the gas phase, $\Delta G^{*}_{\text{clust}}$ is the Gibbs energy of formation of the cluster $NpO_2(CO_3)_2(H_2O)_n$ in the standard state, and $\Delta G^{*}_{\text{solv}}(\text{NpO}_2(\text{CO}_3)_x(\text{H}_2\text{O})_n^{1-2x})$ is the solvation Gibbs energy of the $\text{NpO}_2(\text{CO}_3)_x(\text{H}_2\text{O})_n^{1-2x}$ cluster corresponding to long-range interactions of the hydrated cluster. A value of 8.577 kJ·mol$^{-1}$ was used for the Gibbs energy of water vaporisation, $\Delta G_{\text{vap}}$. The calculated $\Delta G^{*}_{\text{solv}}$ values at the MP2 level were – 1650.520 kJ·mol$^{-1}$ for $\text{NpO}_2(\text{CO}_3)_2^{3-}$, – 1661.532 kJ·mol$^{-1}$ for $\text{NpO}_2(\text{CO}_3)_2(\text{H}_2\text{O})^{3-}$, and – 1405.886 kJ·mol$^{-1}$ for the bishydrate $\text{NpO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2^{3-}$; the corresponding values calculated at the DFT/B3LYP level were – 1609.992 kJ·mol$^{-1}$, – 1615.561 kJ·mol$^{-1}$, and – 1565.989 kJ·mol$^{-1}$, respectively. The pure continuum model was found to be inaccurate in calculating the hydration energy for the non-hydrated charged species. The authors provide structural properties, such as bond lengths and angles, and vibrational harmonic frequencies calculated for the optimised Np(V) carbonate complexes.

**[2007FOR/BUR]**

[2007FOR/BUR] reported a new method of synthesis of single crystals of $Np_2O_5$(cr) based on a low temperature, aqueous synthesis route. The single crystals were obtained using 0.05 g of natural calcite crystals mixed with 0.5 mL of 54 mmol·dm$^{-3}$ $NpO_2^+$ solution for seven days at 473 K. The use of the calcite crystals provided a substrate for heterogeneous crystallisation and allowed to progressively increase the pH of the solution from 1 to 7.5, hence allowing the formation of the $Np_2O_5$(cr) crystals which are less soluble with increasing pH. The structure of $Np_2O_5$(cr) was shown to be monoclinic in space group *P2/c* (Z = 4) with cell parameters as $a$ = 8.168(2) Å, $b$ = 6.584(1) Å, $c$ = 9.313(1) Å, $\beta$ = 116.09(1) °. $Np_2O_5$(cr) has three crystallographically independent $NpO_2^+$ units forming two-dimensional sheets of square and pentagonal bipyramids that are linked into a three dimensional network. The $Np(3)O_2^+$ moieties forming the square bipyramid are found approximatively parallel with the sheets, while their O atoms are shared with the equatorial vertices of the $Np(1)O_2^+$ and $Np(2)O_2^+$ moieties in the pentagonal bipyramids. Such connectivity, already reported for uranyl compounds [2006KUB/BUR], is said to be new for neptunyl compounds. In addition, the magnetic susceptibility of $Np_2O_5$(cr) measured using a SQUID magnetometer revealed a broad transition at 22(3) K that resembles antiferromagnetic ordering. The broadness of the

transition is reported consistent with the three Np sites having different magnetic moments, and is suggesting of a complex magnetic structure.

**[2007PAT/CHO]**

Pathak and Choppin determined the stability constants of Np(V)-silicate complexes forming under acidic conditions ($-\log_{10}[H^+] = (3.68 \pm 0.08)$) using a solvent extraction method. The ionic strength of the experiments was varied between 0.1 M and 1.0 M $NaClO_4$. The concentration of silicic acid ranged between $10^{-3}$ and $10^{-2}$ M. Several of the samples were consequently above the solubility limit of amorphous silica (~ $2 \times 10^{-3}$ M), although the authors reported no measurable concentrations of polymeric Si species (using the molybdate method) within the time scale of the experiment (~ 30 minutes).

Different solvents, extraction ligands and ligand concentrations were evaluated for the analysis of the extraction data. In most cases, both the uncomplexed metal ion and the Np(V)-silicate complex were extracted into the organic phase, preventing the use of these data for the evaluation of the equilibrium constants. The conditions finally chosen relied on a dilute solution ($10^{-3}$ M) of HDEHP in *n*-heptane, which was the only system showing a decrease of the extraction coefficient of neptunium ($D_{Np}$) in the presence of silicic acid.

The authors observed only minor changes in $D_{Np}$ with increasing $[Si]_{tot}$, which were interpreted as a result of the formation of the complex $NpO_2SiO(OH)_3(aq)$ according with Reaction (A.443). The largest variation in $D_{Np}$ observed in the presence of silicate accounted for ~ 4.5 % ($[(D_0/D) - 1] \leq 0.045$, Figure 3 in the paper), which casts severe doubts on the accuracy of the measurements, especially considering that the uncertainty reported by the authors in the mass-balance of the extraction process is 5 %.

$$NpO_2^+ + SiO(OH)_3^- \rightleftharpoons NpO_2SiO(OH)_3(aq) \qquad \text{(A.443)}$$

The conditional stability constant at each ionic strength (0.1 M $\leq I \leq$ 1.0 M $NaClO_4$) for Reaction (A.443) was determined from a plot of $[(D_0/D - 1]$ *vs.* $[SiO(OH)_3^-]$. The extrapolation to $I = 0$ using the SIT approach led to $\log_{10}\beta°$(A.443) = (7.04 ± 0.02). This value is significantly larger than the value reported in [2005YUS/FED2] ($\log_{10}\beta$(A.443), $I = 0.1$ M $NaClO_4$) = (2.1 ± 0.3), but also larger than the values for the corresponding Np(V) hydroxide ($\log_{10}\beta°(NpO_2OH(aq)) = (2.7 \pm 0.7)$) and carbonate ($\log_{10}\beta°(NpO_2CO_3^-) = (4.962 \pm 0.061)$) complexes. The value given by Pathak and Choppin has not been used in the evaluation of the Np(V)-silicate system due to the experimental shortcomings and uncertainties discussed above.

**[2008FUJ/KOH]**

Fujiwara and Kohara investigated the hydrolysis of Np(IV) using a solvent extraction method with TTA dissolved in xylene. Experiments were performed with $^{239}$Np obtained from the milking of $^{243}$Am. The concentration of Np used by the authors was not reported in the experimental description, but it is assumed low enough to avoid the formation of Np oligomeric species. Np(V) in the original stock solution was reduced to Np(IV) with a Zn amalgam. Experiments were conducted in a 0.5 % $H_2$-$N_2$ atmosphere to avoid re-oxidation of Np(IV) to Np(V). Fujiwara and Kohara extracted the original Np(IV) stock solution to the organic phase to prevent possible problems with traces of Np(V) in the original aqueous phase. The organic phase was then equilibrated with aqueous solutions of given pH ($0 \le -\log_{10}[H^+] \le 5.5$) and ionic strength ($I$ = 0.1, 0.5 and 1.0 M $HClO_4$-$NaClO_4$). Different TTA concentrations ($10^{-4}$ M $\le$ [TTA] $\le$ 0.1 M) were used to adjust the distribution ratio ($D$ = [Np(org)]/[Np(aq)]) within $-2 \le \log_{10}D \le 2$ throughout the complete pH-range evaluated. The time for agitation and phase separation of the extraction process was optimised to one minute. Fujiwara and Kohara derived a stoichiometry of 1:4 for the Np(IV)-TTA(org) complex forming in the organic phase from the slope of the plot $\log_{10}D$ *vs.* $\log_{10}$[TTA]. This information is important because it is directly linked with the number of $H^+$ released in the equilibrium reaction between the aqueous and organic phases (A.444), which is the basis for the assessment of the $Np(OH)_x^{4-x}$ species prevailing in the aqueous phase and thus the determination of the corresponding hydrolysis constants.

$$Np(OH)_x^{4-x} + 4HTTA(org) \rightleftharpoons Np(TTA)_4(org) + (4-x)H^+ + xH_2O(l) \qquad (A.444)$$

Note that the determination of the stoichiometry of the Np(IV)-TTA(org) complex was only conducted within $1.0 \le -\log_{10}[H^+] \le 3.0$, and thus the assumption of a 1:4 complex forming above $-\log_{10}[H^+] = 3.0$ remains speculative. The lack of this experimental evidence mostly affects the quantification of the hydrolysis constants for $Np(OH)_3^+$ and $Np(OH)_4$(aq).

The slope analysis of $\log_{10}D$ *vs.* $\log_{10}[H^+]$ resulted in a slope close to 4 at low $\log_{10}[H^+]$ (predominance of $Np^{4+}$), which decreased with increasing $\log_{10}[H^+]$ due to the stepwise formation of $Np(OH)_x^{4-x}$. Considering the stoichiometry of Reaction (A.444) and with the least-square fitting of the solvent extraction data, the authors determined the conditional equilibrium constants for Reactions (A.445) to (A.448) at $I$ = 0.1, 0.5 and 1.0 M $HClO_4$-$NaClO_4$ (Table A-165). Based on these conditional equilibrium constants, Fujiwara and Kohara derived $\log_{10}K°$(A.445), $\log_{10}K°$(A.446), $\log_{10}K°$(A.447) and $\log_{10}K°$(A.448) using the SIT approach. In combination with $\varepsilon(Np^{4+}, ClO_4^-)$ and $\varepsilon(OH^-, Na^+)$ reported in [2003GUI/FAN], the authors determined $\varepsilon(NpOH^{3+}, ClO_4^-)$ = (0.49 ± 0.15) kg·mol$^{-1}$, $\varepsilon(Np(OH)_2^{2+}, ClO_4^-)$ = (0.35 ± 0.11) kg·mol$^{-1}$ and $\varepsilon(Np(OH)_3^+, ClO_4^-)$ = (0.29 ± 0.15) kg·mol$^{-1}$.

$$Np^{4+} + OH^- \rightleftharpoons NpOH^{3+} \qquad (A.445)$$

$$Np^{4+} + 2OH^- \rightleftharpoons Np(OH)_2^{2+} \quad \text{(A.446)}$$

$$Np^{4+} + 3OH^- \rightleftharpoons Np(OH)_3^{+} \quad \text{(A.447)}$$

$$Np^{4+} + 4OH^- \rightleftharpoons Np(OH)_4(aq) \quad \text{(A.448)}$$

Table A-165: Equilibrium constants for Reactions (A.445) to (A.448) determined in [2008FUJ/KOH] in molar scale for $I$ = 0.1, 0.5 and 1.0 M $HClO_4$-$NaClO_4$ systems, and extrapolation to $I$ = 0 conducted by the authors using the SIT approach.

| | $I$ = 0.1 M | $I$ = 0.5 M | $I$ = 1.0 M | $I$ = 0 |
|---|---|---|---|---|
| $\log_{10}K$(A.445) | | | (12.62 ± 0.25) | (13.91 ± 0.23) |
| $\log_{10}K$(A.446) | | (24.76 ± 0.31) | (25.06 ± 0.14) | (27.13 ± 0.15) |
| $\log_{10}K$(A.447) | (35.85 ± 0.46) | (34.67 ± 0.45) | (34.58 ± 0.44) | (37.30 ± 0.30) |
| $\log_{10}K$(A.448) | (44.27 ± 0.48) | (43.20 ± 0.52) | (43.02 ± 0.28) | (46.16 ± 0.30) |

From data in Table A-165, it is unclear how the authors extrapolated $\log_{10}K$(A.445) (only available at $I$ = 1.0 M $HClO_4$-$NaClO_4$) to $I$ = 0, and how they determined $\varepsilon(NpOH^{3+}, ClO_4^-)$. Furthermore, the conversion of $\log_{10}K$ reported in [2008FUJ/KOH] to the molal scale and the plot of $\log_{10}K - \Delta z^2 D$ *vs.* $I_m$ for Reactions (A.446) to (A.448) (Figure A-18) gives different values of $\log_{10}K°$ (Table A-166) compared to those values reported in [2008FUJ/KOH]. Note that uncertainties calculated in this review following the NEA Guidelines [1999WAN/OST] are significantly larger than those reported in [2008FUJ/KOH].

Ion interaction coefficients calculated in this review from $-\Delta\varepsilon$ values in Figure A-18 ($\varepsilon(Np(OH)_2^{2+}, ClO_4^-) = -(0.38 \pm 0.63)$ kg·mol$^{-1}$; $\varepsilon(Np(OH)_3^{+}, ClO_4^-) = (0.51 \pm 0.67)$ kg·mol$^{-1}$) are very uncertain and deviate significantly from the values reported in [2008FUJ/KOH], which is critical. The SIT coefficient calculated in this review for $Np(OH)_2^{2+}$ from experimental data reported in [2008FUJ/KOH] is totally unexpected for a divalent cation, and it is very different from the value reported by the authors ($\varepsilon(Np(OH)_2^{2+}, ClO_4^-) = (0.35 \pm 0.11)$ kg·mol$^{-1}$) or in [2001NEC/KIM] ($\varepsilon(Np(OH)_2^{2+}, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol$^{-1}$). Dashed line in Figure A-18a has been calculated using the values of $\log_{10}\beta_2^o = 27.13$ and SIT coefficients ($\Delta\varepsilon = \varepsilon(Np(OH)_2^{2+}, ClO_4^-) - \varepsilon(Np^{4+}, ClO_4^-) - 2\varepsilon(Na^+, OH^-) = 0.35 - 0.82 - 2 \times 0.04 = -0.57$ kg·mol$^{-1}$) reported by the authors. From the comparison of solid and dashed lines in Figure A-18a, it appears evident that $\log_{10}\beta_2^o$ and SIT coefficients reported in [2008FUJ/KOH] have not been determined considering (only) their own experimental data. The calculation of $\varepsilon(Np(OH)_4, aq)$ results in an unexpectedly positive value ($\varepsilon(Np(OH)_4(aq), Na^+/ClO_4^-) = (0.36 \pm 0.56)$ kg·mol$^{-1}$), although again with a very large associated uncertainty.

Figure A-18: Extrapolation to $I = 0$ using the SIT approach of experimental (a) $\log_{10}K$ (A.446), (b) $\log_{10}K$ (A.447) and (c) $\log_{10}K$ (A.448) reported in [2008FUJ/KOH] and converted in this review to the molal scale. Dashed line in Figure (a) has been calculated using $\log_{10}K°$(A.446) and SIT coefficients reported in [2008FUJ/KOH].

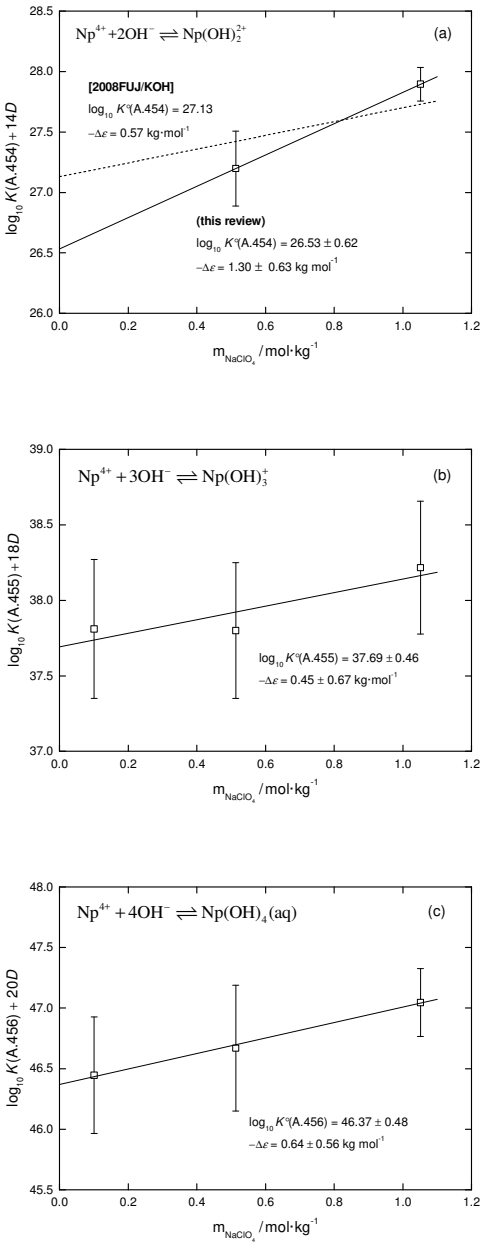


Table A-166: Equilibrium constants for Reactions (A.445) to (A.448) determined in [2008FUJ/KOH] for $I$ = 0.1, 0.5 and 1.0 M $HClO_4$-$NaClO_4$ systems and converted in this review to the molal scale. Extrapolation to $I$ = 0 conducted in this review using the SIT-plots in Figure A-18.

| | $I$ = 0.1 M | $I$ = 0.5 M | $I$ = 1.0 M | $I$ = 0 |
|---|---|---|---|---|
| $\log_{10}K$(A.445) | | | (12.60 ± 0.25) | |
| $\log_{10}K$(A.446) | | (24.74 ± 0.31) | (25.02 ± 0.14) | (26.53 ± 0.62) |
| $\log_{10}K$(A.447) | (35.84 ± 0.46) | (34.64 ± 0.45) | (34.51 ± 0.44) | (37.69 ± 0.45) |
| $\log_{10}K$(A.448) | (44.26 ± 0.48) | (43.15 ± 0.52) | (42.93 ± 0.28) | (46.37 ± 0.48) |

Due to insufficient experimental data and the shortcomings summarised above, this review disregards any thermodynamic data selection for Np(IV) hydrolysis species based on the experimental data reported in [2008FUJ/KOH].

**[2008IKE/HEN]**

Ikeda-Ohno *et al.* investigated the electrochemical and structural properties of Np(IV/V/VI) in 1.0 M $HClO_4$ and concentrated mixtures of $HNO_3$-$NH_4NO_3$ using a combination of cyclic voltammetry (CV), UV-vis/NIR and EXAFS [2008IKE/HEN]. CV was mostly considered as input in the bulk electrolysis carried out to adjust the oxidation state of Np in the sample solution, although for the Np(VI)/Np(V) couple CV was used to determine the formal potential in 1.0 M $NaClO_4$ ($E$ = 0.90 V), 1.0 M $HNO_3$ + 4.0 M $NH_4NO_3$ ($E$ = 0.91 V) and 4.4 M $HNO_3$ + 6.0 M $NH_4NO_3$ ($E$ = 0.89 V) systems. EXAFS data collected in 1.0 M $HClO_4$ indicated that Np(IV) is found as $Np(H_2O)_{10}^{4+}$, whereas both Np(V) and Np(VI) predominantly form $NpO_2(H_2O)_5^{n+}$ ($n$ = 1, 2) aqua ions. EXAFS evaluation confirmed that Np(IV), Np(V) and Np(VI) form inner-sphere complexes in concentrated nitrate solutions ($[NO_3^-] \geq 5.0$ M). In all cases, nitrate coordinates Np in a bidentate mode. An average of three and two nitrate ions were found in the primary coordination sphere of Np(IV) and Np(VI), respectively, in $[NO_3^-]$ = 10.4 and 14.5 M. Np(V) was found to oxidise to Np(VI) in $[HNO_3] > 5.0$ M. At this nitrate concentration, Np was predominantly found as mononitrato complex.

**[2008NIS/AKI]**

[2008NIS/AKI] measured the thermal diffusivity of neptunium dioxide in the temperature range 473 to 1473 K using the laser flash method and its enthalpy increment in the temperature range 334 to 1071 K using drop calorimetry. The authors subsequently derived the thermal conductivity of $NpO_2$(cr) from 873 to 1473 K from the thermal diffusivity, heat capacity and bulk density data. The sample used for the drop calorimetry measurements (53.89 mg) probably corresponds to hypostoichiometric $NpO_{2-x}$(cr) as it was heated under vacuum from 473 to 1473 K for the thermal diffusivity measurements

prior to the heat capacity determination. It was loaded in a platinum container (419.12 mg) sealed under argon atmosphere for the measurement. The measured enthalpy increments are in excellent agreement with those of [2011BEN/GOT]. The authors did not impose the necessary constraints on $H_m(T) - H_m^o(298.15\ K)$ and $C_{p,m}^o(NpO_2, cr, 298.15\ K)$ when deriving the heat capacity data. The extrapolation of their data to 298.15 K yields $C_{p,m}^o(NpO_2, cr, 298.15\ K) = 59.6\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, which is $6.6\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ lower than measured by [1953WES/HAT] and recommended in this review. The corresponding heat capacity function is, therefore, discarded.

**[2008NIS/ITO]**

The authors reported the measurement of the heat capacities of neptunium and americium mononitride in the temperature ranges 334-1067 K and 354-1071 K, respectively, using a twin-type drop calorimeter. The NpN(cr) and AmN(cr) samples were prepared by carbothermic reduction of neptunium and americium dioxides. The oxygen, nitrogen and carbon content were determined using an inert gas fusion technique and combustion technique. Oxygen was found at a level below 1.2 wt % and carbon below 0.2 wt %. The purity of the samples was also checked using X-ray diffraction. The samples in the form of sintered disks (102.06 mg NpN(cr) and 42.09 mg AmN(cr)) were sealed in platinum crucibles under argon atmosphere for the measurements, and sapphire was used as standard material. The numerical details of their measurements are not listed unfortunately. The heat capacity for NpN(cr), *i.e.*, $C_{p,m}^o(NpN, cr, T) = 1.872 \times 10^{-2}\,T + 42.75\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ is found below that of PuN(cr) [2001LEM/FUG] up to 680 K, and above after the latter temperature. In this review we prefer to retain the estimation by [2001LEM/FUG], where the heat capacity for NpN(cr) is between that for UN(cr) and PuN(cr).

The heat capacity for AmN(cr) is reported for the first time. It is found below that for PuN(cr) which is expected from the trend seen for UN(cr) and PuN(cr). The deviation is rather large, however, with 4 % difference between the heat capacity for PuN(cr) and AmN(cr) at 1000 K. We accept their equation in the present review, but recommend to repeat the measurement to confirm those results:

$$C_{p,m}^o(AmN, cr, T) = 42.44 + 1.563 \times 10^{-2}\,T\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

The heat capacity obtained at 298.15 K by extrapolation is $C_{p,m}^o(AmN, cr, 298.15\ K) = (47.1 \pm 3.3)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, which is lower than for UN(cr), NpN(cr) and PuN(cr).

**[2008SKA/ANT]**

Skanthakumar *et al.* studied cation-cation interactions of Np(V) and Np(VI) in 1.0 M $HClO_4$ using high-energy X-ray scattering (HEXS) [2008SKA/ANT]. A first series of

experiments with $[Np]_{tot}$ = 0.4 M indicated that 6-10 $H_2O$ molecules are present in the second coordination sphere of Np(VI) at a distance of (4.37 ± 0.03) Å, as compared to 4.2-4.6 Å, in second coordination sphere of Np(V). Based on the distance for the Np(V)-Np(V) interaction, the authors disregarded the presence of a dihydroxo bridged species $[O_2Np\text{-}(OH)_2\text{-}NpO_2]$ and concluded that cation-cation interactions result in the formation of the dimer $NpO_2^+ \cdot NpO_2^+$ according with Reaction (A.449):

$$2NpO_2^+ \rightleftharpoons NpO_2^+ \cdot NpO_2^+ \qquad \text{(A.449)}$$

The subtraction of the $H_2O$ contribution to the second coordination sphere of Np(V) was based on the analogy with Np(VI) and allowed the authors to calculate the fraction of $NpO_2^+ \cdot NpO_2^+$ and thus to determine $\log_{10}K$((A.449), $I$ = 1.0 M $HClO_4$ + 0.4 M $NpO_2ClO_4$) = – (0.13 ± 0.05). This review considers the uncertainty provided by the authors unrealistically low, especially in view of the assumptions made in the subtraction of the $H_2O$ contribution and the large uncertainty normally expected in the fitted coordination numbers. Additional HEXS measurements were conducted with $[Np(V)]_{tot}$ = 0.059, 0.118 and 0.236 M, which confirmed the formation of $NpO_2^+ \cdot NpO_2^+$ and the stability constant calculated for $\log_{10}K$(A.449). Note that important differences (ionic strength, water activity and activity coefficients of $NpO_2^+$ and $NpO_2^+ \cdot NpO_2^+$ arise among the matrix solution of the four investigated samples. The authors did not take into account these differences in the calculation of $\log_{10}K$((A.449), $I$ = 1.0 M $HClO_4$ + $x$ M $NpO_2ClO_4$).

The work by Skanthakumar and co-workers provides a sound spectroscopic proof on the existence of Np(V) cation-cation interactions. Conditional stability constants reported by the authors are not selected in this review but can be used in scoping calculations.

**[2008TAY/SIN]**

Taylor *et al.* investigated the distribution of Np(IV) between nitric acid and 30 % tributylphosphate in the presence of formohydroxamic and acetohydroxamic acids. Modelling of experimental data determined in this work is provided in [2011SAR/SIM].

**[2009IKE/TSU]**

The formation of Np(V), Np(VI) and Np(VII) carbonate complexes in concentrated carbonate solutions are investigated by a combination of experimental and theory methods. Cyclic voltammetry, X-ray absorption spectroscopy and DFT calculations were used to determine the electrochemical behaviour, composition and structural elements of Np(V) carbonate complexes. Four samples were prepared electrochemically and analysed by the different techniques: two samples of Np(V) and Np(VI) in 1.5 M $Na_2CO_3$ at pH 11.7, Np(VII) in 2 M $Na_2CO_3$ and 1 M NaOH and a reference Np(VII) solution in 2.5 M

NaOH. Electronic absorption features were used to identify and verify the oxidation states of Np in these sample solution. EXAFS data confirmed the known structures of the limiting carbonate complexes of Np(V) and Np(VI), $NpO_2(CO_3)_3^{5-}$ and $NpO_2(CO_3)_3^{4-}$, respectively. The structural parameters agree with the expected shortening of the Np(V) bonds compared to Np(VI) due to its lower effective charge and also disregard the potential presence of mixed hydroxy-carbonate complexes such as $NpO_2(CO_3)_2OH^{3-}$ in 1.5 M $Na_2CO_3$. Cyclic voltammetric measurements also confirmed the quasi-reversible nature of the $NpO_2(CO_3)_3^{5-}/NpO_2(CO_3)_3^{4-}$ redox couple. The comparison of EXAFS data of Np(VII) in 2 M $Na_2CO_3$/1 M NaOH and in 2.5 M NaOH revealed that Np(VII) is present as the square-planar $NpO_4(OH)_2^{3-}$ complex in hyperalkaline systems ([NaOH] ≥ 1 M), even in the presence of high carbonate concentrations.

No thermodynamic data are reported in this paper.

**[2009KIM/BAI2]**

Kim *et al.* conducted solubility experiments with $NpO_2$(s) in granitic groundwater. Experimental results were compared with Np(IV) solubility data in the presence of carbonate previously reported in the literature, as well as with thermodynamic calculations using different databases (NEA TDB, NAGRA-PSI, JNC). The granitic groundwater used by the authors was collected at the KAERI underground research tunnel (KURT), and contained $[C]_{tot} \approx 1.3 \times 10^{-3}$ M at pH = 8.44. The composition of the groundwater included also traces of Fe and $[SiO_2] \approx 7 \times 10^{-4}$ M, which may led to secondary redox processes and/or colloid formation. The granitic groundwater was contacted with a crystalline $NpO_2$(s) prepared by calcination of Np(IV) oxalate at $T$ = 500 °C. A total of five independent solubility experiments were conducted at room temperature within 9.5 ≤ pH ≤ 13. The redox potential was adjusted electrochemically within – 0.2 V (pH = 10.2) and – 0.44 V (pH = 13.0). The equilibration time was not indicated in the experimental description of the study. No solubility measurements were performed in the absence of carbonate, and the authors considered $NpO_2$ (am, hyd) as solubility-controlling phase in the investigated system arguing a radiolytic amorphisation and/or surface hydration of the initial crystalline Np(IV) material. Only three experimental points at $-\log_{10}[H^+] \leq 11$ were above the detection limit of the technique for the quantification of [Np] (LSC, DL = $5 \times 10^{-9}$ M), with the highest solubility (*ca.* one $\log_{10}$ unit above the detection limit) measured at $-\log_{10}[H^+] \approx 9.5$. Due to the very scarce solubility data reported and the limited knowledge of the solid phase controlling the solubility, the work by Kim and co-workers is disregarded in the present review for deriving thermodynamic data. However, this study can be considered as an additional hint supporting the formation of ternary Np(IV)-OH-$CO_3$ complexes in alkaline to hyperalkaline carbonated solutions.

**[2009MIN/TAK]**

The authors reported the measurement of the thermal expansion, heat capacities, thermal diffusivities, and oxygen potentials of neptunium, plutonium, and americium nitrides and oxides using high temperature X-ray diffraction, drop calorimetry, and the laser-flash method, and electromotive force method, respectively (Table A-167). The thermal conductivities of selected systems were subsequently calculated using the heat capacities, thermal diffusivities and densities. The numerical details of their measurements are, unfortunately, not listed. In particular, the enthalpy increments of NpN(cr), AmN(cr) and $NpO_2$(cr) were measured using a twin-type drop calorimeter on a disk loaded in a platinum container and sealed under argon atmosphere. The heat capacity for NpN(cr) was found in reasonable agreement with [2002NAK/ARA], but the latter data are lower than recommended in [2001LEM/FUG]. The heat capacity for AmN(cr) was found slightly lower than UN(cr), NpN(cr) and PuN(cr), which agrees with the general trend suggested by [2001LEM/FUG]. The derived heat capacity data for $NpO_2$(cr) were in reasonable agreement with Barin and Knacke [1973BAR/KNA] between 500 and 1071 K, and lower than reported by [1997YAM/NIT]. The quality of the latter results cannot be assessed from the reported information, however.

Table A-167: Thermophysical properties measured by [2009MIN/TAK].

| Property | Systems investigated |
|---|---|
| Thermal expansion | NpN, PuN, AmN, (Np,Am)N, (Pu,Am)N, (Np,Pu,Am,Cm)N, (Pu,Am,Zr)N |
| | $NpO_2$, $AmO_2$, $Am_2O_3$ |
| Heat capacity | NpN, AmN |
| | $NpO_2$ |
| Thermal conductivity | AmN |
| | $NpO_2$, $AmO_2$ |
| Oxygen potential | $AmO_{2-x}$, $(Np,Am)O_2$, $(Pu,Am)O_2$ |

**[2009MUL/FOE]**

Müller *et al.* [2009MUL/FOE] investigated the hydrolysis of Np(VI) and U(VI) under acidic conditions ($2 \leq pH \leq 5.3$) using a combination of attenuated total reflection Fourier transform infrared (ATR FT-IR) and NIR absorption spectroscopies. Experiments were performed under air atmosphere and thus in the presence of $CO_2$(g). No holding oxidising chemicals were used in the Np(VI) experiments, and a reduction to Np(V) was observed within a few hours (30 % reduction after six hours). For this reason, spectroscopic data for Np(VI) were collected within one hour after the sample preparation. Concentration of An(VI) was $5 \times 10^{-4}$ M in all cases except for samples at pH = 1.5, for which [An(VI)] = $5 \times 10^{-2}$ M was used. The authors observed the precipitation of U(VI) above

pH = 4.5. The formation of Np(VI) solid phases within the timeframe of the experiment was excluded based on photon correlation spectroscopy (PCS) and ATR FT-IR measurements before and after ultracentrifugation. Note however that the formation of $UO_3{\cdot}2H_2O$(cr) and $NpO_2(OH)_2{\cdot}H_2O$(cr) is predicted in some of the less acidic samples according with the current NEA TDB thermodynamic selection, and thus that some of the investigated system represent only metastable conditions.

No thermodynamic data is provided in the paper, but spectroscopic observations are compared with speciation calculations using the thermodynamic selection in [2003GUI/FAN]. The ATR FT-IR band observed at 931 $cm^{-1}$ suggests a relevant contribution of Np(VI) hydrolysis species at pH ≥ 4, which are not predicted in the speciation calculations using the NEA TDB selection. Müller and co-workers assigned this band to a monomeric hydrolysis species, although this review finds no definitive proof for this and speculates that polyatomic species may also be responsible for this observation. Qualitatively, these observations hint towards the possible underestimation of equilibrium constants currently selected for hydrolysis species of Np(VI). This possibility is discussed in the main text of the Np section in connection with the thermodynamic selection in [2001LEM/FUG] and [2003GUI/FAN].

**[2009RAO/TIA]**

Rao *et al.* conducted spectrophotometric and microcalorimetric experiments to assess the complex formation of Np(V) with sulfate at $T$ = 10, 25, 40, 55 and 70 °C. Experiments were performed in 1.0 M $NaClO_4$ as background electrolyte with $0 \le [SO_4^{2-}] \le 0.19$ M. The experiments were conducted using 0.5 M $Na_2SO_4$ as titrant, consequently retaining constant $[Na^+]$ throughout the experiment but leading to a slight increase of ionic strength in the test solutions with increasing sulfate concentration ($I_{max} \approx 1.19$ M). $H^+$ concentration varied between $1 \times 10^{-6}$ and $3 \times 10^{-7}$ M, where neither protonation of $SO_4^{2-}$ nor hydrolysis of $NpO_2^+$ play a role in the interpretation of the data. Both spectroscopic and calorimetric data were best explained by defining the formation of $NpO_2SO_4^-$ according with Reaction (A.450). The $\log_{10}K$((A.450), 1.0 M $Na(ClO_4/SO_4)$) values determined by spectroscopy at $T$ = 25-70 °C were considered in the corresponding calorimetric titrations to calculate the enthalpy of the complexation reaction at different temperatures.

$$NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^- \qquad \text{(A.450)}$$

Extrapolation of $\log_{10}K$((A.450), 1.0 M $Na(ClO_4/SO_4)$) was made using the SIT approach with $\varepsilon(Na^+, NpO_2SO_4^-) = \varepsilon(Na^+, NpO_2CO_3^-) = -(0.18 \pm 0.15)$ kg·$mol^{-1}$. The resulting $\Delta\varepsilon$(A.450) = – (0.31 ± 0.18) kg·$mol^{-1}$ is within the experimental uncertainty consistent with $\Delta\varepsilon$(A.450) = – (0.37 ± 0.18) kg·$mol^{-1}$ derived in [2001LEM/FUG] from experimental data reported in [1979RAO/GUD] and [1983HAL/OLI] for 0.5-2.0 M $NaClO_4$. The original $\log_{10}K$(A.450) values reported in 1.0 M $Na(ClO_4/SO_4)$ have been

used in this review for the extrapolation to $I = 0$ using the SIT-plot as discussed in Section 10.4.1.2.

Calorimetric data obtained in [2009RAO/TIA] confirmed that Reaction (A.450) is endothermic, and becomes increasingly endothermic with increasing temperature. Assuming a constant $\partial \Delta_r H_m^o / \partial T$, the authors calculated $\Delta_r C_{p,m}^o = (720 \pm 170)$ $J \cdot K^{-1} \cdot mol^{-1}$. This value is very high and may indicate that a parallel reaction is taking place at higher temperature. In spite of the observed $T$ dependence of the reaction enthalpy, Rao *et al.* also calculated an average value $\Delta_r H_m^o$ (A.450) from $\log_{10} K$((A.450), 1.0 M $Na(ClO_4/SO_4)$) data obtained between $T$ = 10-70 °C using the Van't Hoff equation. The resulting enthalpy value is in disagreement with $\Delta_r H_m^o$ experimentally determined at $T$ = 25 °C by calorimetry. The values of $\Delta_r H_m^o$ and $\Delta_r C_{p,m}^o$ reported in [2009RAO/TIA] are not selected in this review.

**[2009SAR/SIM]**

This is a comprehensive study on the extraction of Np(IV) into 30 % TBP in odourless kerosene (OK) from 0.08 M ≤ $[HNO_3]$ ≤ 4.5 M. The paper focusses on the modelling of experimental extraction data previously reported in [1998MAY/TAY] and [2008TAY/SIN]. Distribution ratios of Np(IV) ($D = [Np(IV)]_{org}/[Np(IV)]_{aq}$) reported as a function of $[HNO_3]$ are modelled using Reaction (A.451):

$$Np^{4+} + 4NO_3^- + 2TBP \rightleftharpoons Np(NO_3)_4(TBP)_2 \qquad \text{(A.451)}$$

Several chemical models are evaluated in Sarsfield *et al.*, including the formation of $NpNO_3^{3+}$, $Np(NO_3)_2^{2+}$, $NpOH^{3+}$ and $Np(OH)_2^{2+}$ in the aqueous phase, as well as the possible formation of $NpOH(NO_3)_3(TBP)_2$ or $Np(NO_3)_4(TBP)_2 \cdot HNO_3$ in the organic phase. According with the authors, the modelling exercise strongly hints to the presence of both $NpNO_3^{3+}$ and $Np(NO_3)_2^{2+}$ in aqueous solutions with $[HNO_3]$ ≤ 4.5 M. The consideration of higher Np(IV)-$NO_3$ complexes (up to $Np(NO_3)_4$(aq)) resulted in a further improvement of the fit.

Note that the modelling of the extraction data reported in [2009SAR/SIM] was made by using $HNO_3$ activities, but the concentration of Np species was due to the lack of an activity model for Np(IV) in nitrate media. As acknowledged by the authors, this approach does not allow deriving a thermodynamic model but rather provides a tool for the quantitative description of Np(IV) extraction by TBP in low to moderate $HNO_3$ concentrations. Data reported by Sarsfield and co-workers have not been used in the thermodynamic evaluation of the Np(IV)-$NO_3$ system.

**[2009SEI/GOU]**

[2009SEI/GOU] studied the oxidation of the surface of thin films of Np metal by molecular $O_2$ and atomic O using X-ray spectroscopy (using Mg-Kα excitation radiation) and Ultra-Violet Photoelectron Spectroscopy (using HeI and HeII UV light). Exposed to molecular $O_2$, metallic neptunium reacts to form the sesquioxide $Np_2O_3$ as transient species which appears only stable in the presence of the metal, followed by neptunium dioxide $NpO_2$. Based on the XPS Np-4f core level data, [2009SEI/GOU] estimated the $Np_2O_3$ layer thickness at about nine monolayers. The existence of this thin "bulk" $Np_2O_3$ species, was moreover attributed to the increasing 5f localisation along the series of the actinide elements (from U towards Pu). The sesquioxide involving only the ds valence electrons and non-bonding 5f states, is formed as a bulk species for plutonium, but does not exist in the case of uranium. Exposed to atomic oxygen produced by an electron cyclotron resonance plasma source, the $NpO_2$ surface further oxidises to form $Np_2O_5$. Moreover, the O-1s and Np-4f intensities combined with the presence of an additional O-2p line at 5-6 eV BE in the UPS spectra, suggests that further oxygen can be chemisorbed on the surface of $Np_2O_5$. $Np_2O_5$ was found to decompose under ultra-high vacuum at about 473 K.

**[2009SHI/YUS]**

Shilov *et al.* [2009SHI/YUS] investigated the potential of the couple Np(VII)/Np(VI) in acidic conditions using the reaction of Np(VII) with Ag(I) and Co(II). The decrease of [Np(VII)] was quantified following the peak of the Np(VII) cation at $\lambda$ = 430 nm. The pH was set within 1.5 and 3.05 using $HClO_4$. No quantification of the forming Np(VI) was attempted by the authors, in spite of the well-known spectroscopic features of $NpO_2^{2+}$. Limited experimental description and details of data interpretation are provided in the paper, thus hindering the traceability of the reported results. At pH = 2.2, the rate of Np(VII) consumption was reported unaffected by the presence of $1 \times 10^{-4}$ M Ag(I). This observation casts doubts on the role of Ag(I) in the reduction process followed by the authors. Shilov and co-workers obtained $E$(Np(VII)/Np(VI)) = 1.93 and 1.85 V at pH = 2.2 and 3.05, respectively. The uptake of two protons in the Reaction (A.452) results in a theoretical increase in the potential by 0.118 V per pH unity, based on this, the authors estimated $E°'$((A.452), 1 M $HClO_4$, 298.15 K) = (2.20 ± 0.01) V.

$$Np(OH)_6^+ + 2H^+ + e^- \rightleftharpoons NpO_2^{2+} + 4H_2O(l) \qquad \text{(A.452)}$$

This value significantly differs from the Np(VII)/Np(VI) potential previously reported in [1974MUS/COU], $E°'$((A.452), 1 M $HClO_4$, 298.15 K) = (2.04 ± 0.03) V). Shilov and co-workers argued that, because of the structural rearrangement involved in the reduction of $Np(OH)_6^+$ to $NpO_2^{2+}$, the Np(VII)/Np(VI) couple cannot be considered reversible in acidic conditions and thus potentiometric measurements of this system with a Pt electrode (as used in [1974MUS/COU]) may prove inaccurate. Note however that

the predominance of $Np(OH)_6^+$ under acidic conditions proposed by Shilov and co-workers in a previous publication [1991SHI/TAN] remains to be confirmed experimentally.

Although [2009SHI/YUS] used a theoretical slope of – 0.118 V (*E vs.* pH) to extrapolate $E°'$((A.452), 1 M $HClO_4$, 298.15 K) from their experimental values of *E*(Np(VII)/Np(VI)) at higher pH, the plot of *E*(Np(VII)/Np(VI)) *vs.* pH (only two experimental points at pH = 2.2 and 3.05 available) leads to *E*((A.452), 1 M $HClO_4$, 298.15 K) = 2.14 V and a slope of – 0.094 V significantly different from a Nernstian behaviour. In contrast to [1974MUS/COU] where ionic strength was kept constant throughout the experiments with $x\ HClO_4 + (1 - x)\ NaClO_4$, $HClO_4$ was the only electrolyte used by Shilov and co-workers [2009SHI/YUS] in the investigated systems at pH = 2.2 and 3.05. Consequently, a linear extrapolation of experimental *E*(Np(VII)/Np(VI)) at $I \leq 0.03$ M to *E*((A.452), 1 M $HClO_4$, 298.15 K) is not valid without accounting for $\varepsilon(NpO_2^{2+}, ClO_4^-)$ and $\varepsilon(Np(OH)_6^+, ClO_4^-)$. No thermodynamic data was selected in [2001LEM/FUG] for the redox couple Np(VII)/Np(VI) under acidic conditions, and this review considers that [2009SHI/YUS] does not provide any significant improvement in this respect.

**[2009SOB]**

A set of analytical models based on a simple model for the actinide dioxides phonon spectrum [2005SOB] and localised 5f-electron excitations using the spectra recommended by [2004KON], the quasi-harmonic approximation for the ideal solid lattice vibrations [1956KIT], and the Klemens approach for the thermal conductivity, are implemented for the determination of the thermophysical properties (isobaric heat capacity, isobaric volumetric thermal expansion, isothermal bulk elastic modulus, thermal conductivity) of $NpO_2$, $AmO_2$ and $CmO_2$, and compared to available literature data. The derived isobaric heat capacity functions for $NpO_2$ and $AmO_2$ are in good agreement with [1953WES/HAT], [2008NIS/AKI], [2001SER/ARA], [2011BEN/GOT] and those of the model in [2003THI/KON], respectively. No new experimental data are reported.

**[2009TIA/RAO3]**

Tian *et al.* report on the complexation of Np(V) with fluoride at temperatures between 10 and 70 °C studied by using spectrophotometric titrations and microcalorimetric measurements. This study is a follow-up to the data for Np(V) fluoride complexation obtained from calorimetric data reported in [2006RAO/TIA]. In contrast to the data reported in [2006RAO/TIA], in which the formation constants for $NpO_2F(aq)$ were interpolated from reported data in [2006XIA/FRI], complex formation constants are determined spectroscopically in this study. The electronic absorbance spectra were collected at various temperatures in the region 950-1050 nm, monitoring alterations of

the characteristic $NpO_2^+$ absorption band at 980 nm with a molar absorptivity of 395 $M^{-1}\cdot cm^{-1}$. For the spectrophotometric titrations, multiple aliquots of 0.9-1.1 mL of 1 M NaF solution are added to the initial 2.5 mL sample. The sample cells are sealed and immerged into a water bath of the desired temperature to avoid water evaporation and condensation. A set of 10-15 spectra is collected at each temperature with varying fluoride concentrations. The total fluoride concentrations in the spectrophotometric titrations range between 0 and 0.30 M. The calorimetric data are obtained at 25 °C by titrating 5 µL increments of a 1 M NaF solution into 0.9 mL Np(V)-containing 1 M $NaClO_4$ solution, similar to the titrations performed in [2006RAO/TIA]. Multiple titrations are performed at each temperature with 40-50 additions during each titration, which added up to about 250 µL of titrant solution. Calculated from the volumes added, the fluoride concentrations in the calorimetric experiments range between $5.5 \times 10^{-3}$ M and 0.21 M.

In order to compare stability constants at various temperatures, the authors assessed the conversion of molarity to molality scale. The authors decided to assume $\log_{10}\beta_m \sim \log_{10}\beta_M$ because the conversion factors for 1.0 M $Na(ClO_4/NO_3)$ solutions range between 0.014 and 0.021, which is small compared to the uncertainties of the experimental measurements.

With the addition of fluoride, the absorption band of $NpO_2^+$ at 980 nm decreases and the absorbance maximum continuously shifts to higher wavelengths. The spectrophotometric data were analysed using the HyperQuad program and best fit with three Np(V) solution species and their spectral features at 980, 984 and 989 nm according to the equilibria (A.453) and (A.454):

$$NpO_2^+ + F^- \rightleftharpoons NpO_2F(aq) \quad \text{(A.453)}$$

$$NpO_2^+ + 2F^- \rightleftharpoons NpO_2F_2^- \quad \text{(A.454)}$$

The uncertainties of calculated stability constants reported by Tian *et al.* took into account the statistic deviations of repetitive titrations at each temperature. These uncertainties are larger than the standard deviations determined purely from the analysis of the spectrophotometric data by HyperQuad. The formation constants for the complexation reactions are calculated from the spectrophotometric data measured at 10, 25, 40, 55 and 70 °C. The SIT is used to calculate thermodynamic formation constants. To account for the variations in temperatures, the authors adjust the parameter A in the Debye-Huckel term according to data reported in [2003GUI/FAN]. Ion-interaction coefficients available for ambient temperatures are used for other temperatures since the error introduced is considered small, estimated to be $(\Delta\varepsilon/\Delta T) \leq 0.005$ kg·mol$^{-1}$·K$^{-1}$ at $T < 200$ °C. The authors also assume $\varepsilon(NpO_2F_2^-, Na^+) \approx \varepsilon(NpO_2(OH)_2^-, Na^+) = -(0.01 \pm 0.07)$ kg·mol$^{-1}$. With $\varepsilon(NpO_2^+, ClO_4^-) = (0.25 \pm 0.05)$ kg·mol$^{-1}$, the authors derive $\Delta\varepsilon(25\ °C) = -(0.27 \pm 0.10)$ kg·mol$^{-1}$ for equilibrium (A.453) and $-(0.28 \pm 0.10)$ kg·mol$^{-1}$ for equilibrium (A.454).

The conditional equilibrium constant of $NpO_2F(aq)$ at 25 °C, $\log_{10}\beta_{11}$= (1.25 ± 0.05), matches well the previously reported data of (1.26 ± 0.30) in [1984CHO/RAO], but is lower than the reported values of (1.39 ± 0.30) ([1985INO/TOC]) and the more recently reported data of (1.42 ± 0.10) ([2006XIA/FRI]). The main difference between the two sets of data is the interpretation of the experimental data with one or two $NpO_2F_n^{1-n}$ complexes and the different fluoride concentration ranges investigated.

The reaction heat data measured by using calorimetry were used to calculate the enthalpy of the Np(V) complexation with fluoride. The values of the fluoride protonation constants and protonation enthalpies reported in [2006RAO/TIA] were used for this calculation. The average complexation enthalpies of (7.9 ± 1.9) kJ·mol$^{-1}$ for $NpO_2F(aq)$ and (21.5 ± 3.6) kJ·mol$^{-1}$ for $NpO_2F_2^-$ were derived from the Van't Hoff plot ($\log_{10}\beta$ *vs.* 1/*T*) are within the enthalpies calculated for each temperature investigated. The heat capacities of Reactions (A.453) and (A.454) were calculated to be (76 ± 30) J·K$^{-1}$·mol$^{-1}$ and (860 ± 100) J·K$^{-1}$·mol$^{-1}$. The latter value is very high, and reflects relevant discrepancies between spectroscopic and calorimetric data. The values of $\Delta_r H_m^\circ$ and $\Delta_r C_{p,m}^\circ$ reported in [2009TIA/RAO3] are not selected in this review.

Table A-168: Thermodynamic data for the reaction of $NpO_2^+ + nF^- \rightleftharpoons NpO_2F_n^{1-n}$ reported in [2009TIA/RAO3].

| *n* | *t* /°C | Method | Medium | $\log_{10}\beta_{n,1}^\circ$ | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_r S_m$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | 10 | spectr | 1 M $NaClO_4$ | (1.32 ± 0.12) | | |
| 1 | 25 | spectr, cal | 1 M $NaClO_4$ | (1.39 ± 0.12) | (8.1 ± 1.0) | (51 ± 5) |
| 1 | 40 | spectr, cal | 1 M $NaClO_4$ | (1.51 ± 0.12) | (8.8 ± 0.6) | (54 ± 4) |
| 1 | 55 | spectr, cal | 1 M $NaClO_4$ | (1.55 ± 0.12) | (10.2 ± 0.5) | (58 ± 4) |
| 1 | 70 | spectr, cal | 1 M $NaClO_4$ | (1.62 ± 0.12) | (11.2 ± 2.6) | (60 ± 11) |
| 2 | 10 | spectr | 1 M $NaClO_4$ | (1.50 ± 0.15) | | |
| 2 | 25 | spectr, cal | 1 M $NaClO_4$ | (1.92 ± 0.14) | (14.2 ± 3.1) | (82 ± 12) |
| 2 | 40 | spectr, cal | 1 M $NaClO_4$ | (2.15 ± 0.15) | (18.6 ± 1.6) | (98 ± 1.7) |
| 2 | 55 | spectr, cal | 1 M $NaClO_4$ | (2.21 ± 0.13) | (36.0 ± 1.4) | (149 ± 7) |
| 2 | 70 | spectr, cal | 1 M $NaClO_4$ | (2.30 ± 0.14) | (40.8 ± 8.8) | (159 ± 32) |

**[2009TOP/AUP]**

The authors report on the complexation of Np(V) and Pu(V) with sulfate and chloride by using capillary electrophoresis (CE) coupled to ICP-MS at $T$ = (25 ± 1) °C. Variation of $T$ during the chromatographic separation is discussed in the experimental section and falls within the reported uncertainty. Experiments were carried out with $NaClO_4$ as background electrolyte, which due to the weak ion interactions is replaced in significant fractions by $Na_2SO_4$ or NaCl in the course of the experiment. The pH was maintained close to 6 for all experiments, however, no details were provided regarding the methods to determine pH and to account for junction potential effects caused by the different ionic strengths. At this pH, no correction for An(V) hydrolysis or $SO_4^{2-}$ protonation is needed

in the interpretation of the data. The variation of the electrophoretic mobility ($\mu_{ov}$) with increasing ligand concentration was used to determine the equilibrium constants for the formation of An(V)-sulfate and An(V)-chloride complexes. Both Np(V) and Pu(V) were present in the sample solutions, which enables synergistic effects of competing complexation with the ligands. The analysis of the data and determination of $\log_{10}K$ requires also the determination of the electrophoretic mobility of the metal ($\mu_M$) and the complex ($\mu_{ML}$) at each ionic strength. The former was experimentally determined at [L] = 0, whereas the latter was estimated using a previously reported empirical model. The apparent stability constants obtained from the measured ionic mobilities in different electrolyte media were extrapolated to zero ionic strength by using the SIT approach.

*An(V)-sulfate system*

Experiments were conducted at four different ionic strengths, namely 0.35, 0.70, 1.0 and 1.5 M. Due to the weak An(V)-sulfate complexation, significant proportions of the background electrolyte ($NaClO_4$) were replaced by $Na_2SO_4$ in the course of the experiment (max. 43 % in 0.35 and 0.70 M systems; max. 30 % in 1.0 and 1.5 M systems[4]). The experimental data were explained with the formation of the complex $AnO_2SO_4^-$ according with Reactions (A.455) and (A.456):

$$NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^- \quad \text{(A.455)}$$

$$PuO_2^+ + SO_4^{2-} \rightleftharpoons PuO_2SO_4^- \quad \text{(A.456)}$$

In contrast to the high stability of Np(V), the stability of Pu(V) is of concern. The authors quickly disregard the potential contributions of Pu(IV) or Pu(VI) due to the stronger interactions with sulfate and expected different electrophoretic mobility of those species. However, redox reactions can cause partial oxidation state changes that could alter the electrophoretic mobility without developing a second mobility peak. The oxidation state stability in pure $NaClO_4$ and $NaClO_4/Na_2SO_4$ mixtures may be different and impact the accurate interpretation of the mobilities measured. In the absence of any oxidation state verification during and after the experiment and the obvious differences to the electrophoretic mobilities of the analogous Np(V) species, the potential presence of other oxidation states than Pu(V) cannot be excluded.

A simplified SIT approach[5] was used to extrapolate the conditional equilibrium constants to $I = 0$. With this approach, the impact of $Na_2SO_4$ in the activity coefficients of the ionic species was neglected and a standard SIT-plot with $\log_{10}K$((A.455)/(A.456)) + $4D$ *vs.* $I_m$ was used to derive $\log_{10}K°$(A.455) = (1.34 ± 0.12) and $\log_{10}K°$(A.456) = (1.30 ± 0.06), with $\varepsilon(NpO_2SO_4^-, Na^+) = \varepsilon(PuO_2SO_4^-, Na^+) = (0.14 \pm 0.17)$ kg·mol$^{-1}$. The

[4] The ionic medium changes were calculated with respect to [$NaClO_4$] in the system without sulfate.
[5] with $\Delta(\varepsilon_{ij}m_j) = \varepsilon(AnO_2SO_4^-, Na^+)\, I_m - \varepsilon(SO_4^{2-}, Na^+)\, I_m - \varepsilon(AnO_2^+, ClO_4^-)\, I_m$

authors obtained similar results when considering an extended SIT approach[6] with estimated $\varepsilon(AnO_2^+, SO_4^{2-})$ and $\varepsilon(AnO_2SO_4^-, Na^+)$ values.

In the case of weak complexes, the NEA TDB guidelines for the extrapolation to zero ionic strength [2013GRE/MOM] recommend a first estimate of the changes of activity coefficients during the experimental conditions at each ionic strength. For practical reasons, it is advantageous to carry out this part of the calculation in the molar scale. By using the pure background electrolyte ($NaClO_4$) as a reference at a given ionic strength $I$, it is possible to obtain an expression that takes the changes in activity coefficient in ($NaClO_4$-$Na_2SO_4$) mixtures of the same ionic strength into account:

$$\log_{10} K^{mix}((A.455)/(A.456)) = \log_{10} K^{NaClO_4}((A.455)/(A.456)) + \Sigma(\log_{10}\gamma^{mix} - \log_{10}\gamma^{NaClO_4}) \quad (A.457)$$

Hence:

$$\log_{10} K^{mix}((A.455)/(A.456)) = \log_{10} K^{NaClO_4}((A.455)/(A.456)) + \Delta\varepsilon'[SO_4^{2-}] \quad (A.458)$$

with:

$$\Delta\varepsilon' = -\varepsilon(Na^+, AnO_2SO_4^-) - (-\varepsilon(Na^+, SO_4^-)) - (\varepsilon(AnO_2^+, SO_4^{2-}) - 3\varepsilon(AnO_2^+, ClO_4^-)) \quad (A.459)$$

The use of Equation (A.458) allows the extrapolation of $\log_{10}K((A.455)/(A.456), I)$ values determined in $NaClO_4$-$Na_2SO_4$ mixtures to pure $NaClO_4$ conditions. Only the experimental points with $[AnO_2SO_4^-] \geq 10$ % $[An]_{tot}$ have been considered in this review for the recalculation of $\log_{10}K(A.455)/(A.456)$. The linear fit of $\log_{10} K^{mix}((A.455)/(A.456))$ *vs.* $[SO_4^{2-}]$ was accomplished by simultaneously using data from the four series at different ionic strengths ($I_M$ = 0.35, 0.70, 1.0 and 1.5 M) and a constant $\Delta\varepsilon'$. The resulting $\log_{10}K((A.455)/(A.456), I)$ for pure $NaClO_4$ systems are summarised in Table A-169 together with $\log_{10} K^{mix}((A.455)/(A.456), I)$ reported in [2009TOP/AUP]. Uncertainties resulting from the extrapolation of $\log_{10} K^{mix}((A.455)/(A.456), I)$ to $\log_{10} K^{NaClO_4}((A.455)/(A.456), I)$ have been increased to account for the error introduced by $\mu_M$ and $\mu_{ML}$, which are used in the calculation of $\log_{10} K^{mix}((A.455)/(A.456), I)$ but were only reported in pure $NaClO_4$ systems. The excellent agreement between $\log_{10} K^{NaClO_4}((A.455)/(A.456), I)$ and $\log_{10} K^{mix}((A.455)/(A.456), I)$ illustrates the small effect of $NaClO_4$ substitution by $Na_2SO_4$ on the equilibrium constant, at least up to substitution values of ≈ 40 %. $\text{Log}_{10} K^{NaClO_4}((A.455)/(A.456), I)$ values reported in Table A-169 have been used in the main text for the extrapolation of these equilibrium constants to $I = 0$.

[6] with $\Delta(\varepsilon_{ij}m_j) = \varepsilon(AnO_2SO_4^-, Na^+)\, m_{Na+} - \varepsilon(SO_4^{2-}, Na^+)\, m_{Na+} - \varepsilon(AnO_2^+, ClO_4^-)\, m_{ClO4-} - \varepsilon(AnO_2^+, SO_4^{2-})\, m_{SO42-}$

Table A-169: Equilibrium constants for Reactions (A.455) and (A.456) determined in [2009TOP/AUP] for $NaClO_4$-$Na_2SO_4$ mixtures and extrapolated in this review to pure $NaClO_4$ conditions. $\Delta\varepsilon' = 0.00$ for both Np and Pu.

| $I_M$ | $\log_{10}K^{mix}$ (A.455) /[2009TOP/AUP] | $\log_{10}K^{NaClO4}$(A.455) /this review | $\log_{10}K^{mix}$(A.456) /[2009TOP/AUP] | $\log_{10}K^{NaClO4}$(A.456) /this review |
|---|---|---|---|---|
| 0.35 M | (0.66 ± 0.11) | (0.65 ± 0.20) | (0.63 ± 0.11) | (0.63 ± 0.20) |
| 0.70 M | (0.54 ± 0.12) | (0.52 ± 0.20) | (0.49 ± 0.12) | (0.49 ± 0.20) |
| 1.0 M | (0.40 ± 0.11) | (0.41 ± 0.20) | (0.37 ± 0.11) | (0.37 ± 0.20) |
| 1.5 M | (0.31 ± 0.11) | (0.29 ± 0.20) | (0.26 ± 0.11) | (0.25 ± 0.20) |

*An(V)-chloride system*

Experiments were performed with chloride concentrations ranging from 0 to 1.0 M at a constant ionic strength $I = 1.0$ M $NaClO_4$-NaCl. Similar to the sulfate system, single peaks of overall positive ion mobilities were explained with the formation of the neutral $AnO_2Cl(aq)$ complex:

$$NpO_2^+ + Cl^- \rightleftharpoons NpO_2Cl(aq) \quad \text{(A.460)}$$

$$PuO_2^+ + Cl^- \rightleftharpoons PuO_2Cl(aq) \quad \text{(A.461)}$$

At the high chloride concentrations of 0.5, 0.85 and 1 M the background electrolyte ($NaClO_4$) is largely replaced. The authors applied the SIT approach to evaluate the impact of the electrolyte variations by using $\Delta(\varepsilon_{ij}m_j) = -\varepsilon(Cl^-, Na^+)\, m_{Na+} - \varepsilon(AnO_2^+, ClO_4^-)\, m_{ClO4-} - \varepsilon(AnO_2^+, Cl^-)\, m_{Cl-}$ and adopting $\varepsilon(AnO_2^+, Cl^-) = (0.09 \pm 0.05)$ kg·mol$^{-1}$ reported in [2001LEM/FUG]. The changes in $\Delta(\varepsilon_{ij}m_j)$ values from – 0.29 in 1 M $NaClO_4$ to – 0.12 in 1 M NaCl clearly reflect the changes in the electrolyte composition. An iterative fitting process of the standard SIT equation was used to derive $\log_{10}K°(AnO_2Cl, aq) = -(0.12 \pm 0.13)$ for both Equations (A.460) and (A.461).

Table A- 170: SIT parameters and experimental formation constants for the reaction $AnO_2^+ + Cl^- \rightleftharpoons AnO_2Cl(aq)$ at $I = 1$ M reported in [2009TOP/AUP].

| $[Cl^-]$ (M) | $\Delta(\varepsilon_{ij}m_j)$ (Np) | $\log_{10}\beta_1$ (A.458) | $\Delta(\varepsilon_{ij}m_j)$ (Pu) | $\log_{10}\beta_1$ (A.459) |
|---|---|---|---|---|
| 0.00 | – (0.29 ± 0.06) | – (0.22 ± 0.07) | – (0.28 ± 0.06) | – (0.23 ± 0.07) |
| 0.01 | – (0.29 ± 0.06) | – (0.22 ± 0.07) | – (0.28 ± 0.06) | – (0.23 ± 0.07) |
| 0.05 | – (0.29 ± 0.06) | – (0.23 ± 0.07) | – (0.28 ± 0.06) | – (0.24 ± 0.07) |
| 0.15 | – (0.27 ± 0.06) | – (0.25 ± 0.07) | – (0.26 ± 0.06) | – (0.26 ± 0.07) |
| 0.30 | – (0.24 ± 0.06) | – (0.27 ± 0.07) | – (0.24 ± 0.06) | – (0.28 ± 0.07) |
| 0.50 | – (0.21 ± 0.06) | – (0.31 ± 0.07) | – (0.20 ± 0.06) | – (0.32 ± 0.07) |
| 0.85 | – (0.15 ± 0.06) | – (0.37 ± 0.07) | – (0.15 ± 0.06) | – (0.38 ± 0.07) |
| 1.00 | – (0.12 ± 0.06) | – (0.40 ± 0.07) | – (0.12 ± 0.06) | – (0.40 ± 0.07) |

**[2009TOP/AUP2]**

The formation constants of the carbonate complexes of Np(V) and Pu(V) were determined at (25 ± 1) °C by using capillary electrophoresis coupled with ICP-SFMS.

The measurements are based on the changing charge of the actinyl species with complexation and the resulting different electrophoretic mobility ($\mu$) of the formed complexes in an applied electric field. The electrolyte solution was prepared by dissolving $Na_2CO_3$ in deionised water, and adding a buffer solution, which was adjusted by addition of $HCl/HClO_4$ or NaOH, and $2 \times 10^{-3}$ mol·L$^{-1}$ of the surfactant tetradecyltrimethylammonium bromide. Different buffer solutions were used to adjust the pH between 5 and 11 and minimising pH variations. Although the authors expected no complexation for these buffers, some inconsistencies up to 9 % were observed leading to discard data points at pH 9. The authors recognise that the concentration of carbonate is controlled by the pH, however no details regarding the measurement of the pH was provided. $NaClO_4$ (pH between 5.3 and 7.05) or NaCl (pH between 7.05 and 11.5) was added to adjust the ionic strength to 0.37 M. The carbonate concentrations were calculated by applying the dissociation constants of carbonic acid ($\log_{10}\beta_1^o = (10.329 \pm 0.020)$ and $\log_{10}\beta_2^o = (16.683 \pm 0.234)$) and SIT parameters selected by the NEA TDB in [2001LEM/FUG]. With the recommended SIT parameters $\Delta\varepsilon_{ij}$ for NaCl and $NaClO_4$, the carbonic acid dissociation constant in 0.37 M $NaClO_4$ ($\log_{10}\beta_1 = 9.711$ and $\log_{10}\beta_2 = 15.801$) and 0.37 M NaCl ($\log_{10}\beta_1 = 9.698$ and $\log_{10}\beta_2 = 15.777$) were calculated. Temperature variations during the experiment were discussed and the experimental temperature was calculated to be 25.8 °C.

Only one electrophoretic mobility peak was observed throughout the experiment due to the fast exchange rate between the species present. At low pH where no complex formation occurs, this mobility peak is associated with that of $AnO_2^+$. The electrophoretic mobilities of the $NpO_2^+$ and $PuO_2^+$ ions were determined in the absence of carbonate at about pH 5.3 to $(1.89 \pm 0.12) \times 10^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$ and $(1.93 \pm 0.12) \times 10^{-4}$ cm$^2$·V$^{-1}$·s$^{-1}$, respectively. Upon increase in pH and carbonate, this peak varied from a positive mobility at pH 5.3 to negative values above pH 7 indicating the formation of anionic An(V) solution complexes. Based on the very similar electrophoretic mobilities of Np(V) and Pu(V) species at the pH range investigated, the authors interpret the data with identical complexation reactions:

$$NpO_2^+ + nCO_3^{2-} \rightleftharpoons NpO_2(CO_3)_n^{1-2n} \quad \text{(A.462)}$$

$$PuO_2^+ + nCO_3^{2-} \rightleftharpoons PuO_2(CO_3)_n^{1-2n} \quad \text{(A.463)}$$

The stability constant for the first carbonate complex of Np(V) and Pu(V), $AnO_2CO_3^-$, was calculated from measurements in a $NaClO_4$ medium, while the stability constants of $AnO_2(CO_3)_2^{3-}$ and $AnO_2(CO_3)_3^{5-}$, were determined in NaCl solution. The NaCl medium was chosen for the experiments involving the negative ion mobilities of the anionic An(V) carbonate complexes to avoid the precipitation of the surfactant with $ClO_4^-$ anions. The stepwise formation constants were determined subsequently to minimise the number of fitting parameters. The first formation constant and the ion mobility of $AnO_2CO_3^-$ was calculated in the pH range 5 and 6.5; applying these data, the formation constant and the ion mobility of $AnO_2(CO_3)_2^{3-}$ was calculated in the pH range

6.5 to 8; the stability and ion mobility of $AnO_2(CO_3)_3^{5-}$ are calculated from data above pH 8.5. The data were then refined by using all experimental results and their uncertainties. The mobility ratios of Np(V) species were found to be 1.3 for $\mu(NpO_2CO_3^-)/\mu(NpO_2^+)$ and $\mu(NpO_2(CO_3)_3^{5-})/\mu(NpO_2(CO_3)_2^{3-})$, and 1.7 for $\mu(NpO_2(CO_3)_2^{3-})/\mu(NpO_2(CO_3)_3^-)$. These factors were used to constrain the fitting routine of the Pu(V) electrophoretic mobility data, assuming different species mobilities but identical ratios for Pu(V) to those observed for Np(V).

The calculated thermodynamic data for both Np(V) and Pu(V) are close to the NEA TDB selected values, however, the Pu(V) data exhibit significant discrepancies. This can be attributed to problems in calculating the carbonate concentrations, but also in the fitting procedure used to calculate formation constants. The pH ranges that are used to extract the formation constants are intended to contain two species only, but may include a third species. Up to pH 6.5, $AnO_2^+$ and $AnO_2CO_3^-$ are the prominent solution species and based on the ion mobility in the absence of carbonate the properties of the An(V) complex can be calculated. The second complex, $AnO_2(CO_3)_2^{3-}$, begins to form at about pH 6.5. However, the formation of $AnO_2(CO_3)_3^{5-}$ starts at about pH 7.3 and significantly overlaps with the stability area of $NpO_2(CO_3)_2^{3-}$. Thus, the $\log_{10}\beta_2$ value can be erroneous if $AnO_2(CO_3)_3^{5-}$ is not taken into account in the pH range above 7.5. The formation constant of $AnO_2(CO_3)_3^{5-}$ was determined above pH 8.5 with the majority of data at pH above 9.5. Under these conditions only the $AnO_2(CO_3)_3^{5-}$ exists in solution and the parameters $\beta_3$ and $\mu(AnO_2(CO_3)_3^{5-})$ can be fitted with unlimited mathematical solutions. The authors used the NEA TDB recommended value, $\log_{10}\beta_3^o = 5.500$ for Np(V) and arbitrarily limited the parameter fitting routine by its uncertainty of ± 0.150 to calculate $\mu(NpO_2(CO_3)_3^{5-}) = -(3.38 \times 10^{-4})$ $cm^2 \cdot V^{-1} \cdot s^{-1}$. This fitting procedure results in a very uncertain $\beta_3$ value, which is distributed in the final fitting routine involving all experimental data.

Using the SIT parameters in [2001LEM/FUG], the authors calculated thermodynamic stability constants for $NpO_2(CO_3)_n^{1-2n}$, $\log_{10}\beta_1^o = (4.878 \pm 0.118)$, $\log_{10}\beta_2^o = (6.559 \pm 0.108)$, and $\log_{10}\beta_3^o = (5.636 \pm 0.145)$; and $\log_{10}\beta_1^o = (4.947 \pm 0.099)$, $\log_{10}\beta_2^o = (6.341 \pm 0.100)$, and $\log_{10}\beta_3^o = (5.607 \pm 0.162)$ for the Pu(V) carbonate complexes $PuO_2(CO_3)_n^{1-2n}$ where $n$ = 1-3. It is to note that the authors do not specify the ion-interaction parameters used for the calculation of the thermodynamic constants of the Pu(V) carbonate complexes. Since only ion-interaction parameters in [2001LEM/FUG] are provided for $PuO_2^+$ ($\varepsilon(PuO_2^+, ClO_4^-) = (0.24 \pm 0.05)$ $kg \cdot mol^{-1}$) and $PuO_2CO_3^-$ ($\varepsilon(PuO_2CO_3^-, Na^+) = -(0.18 \pm 0.15)$ $kg \cdot mol^{-1}$), which is identical to the corresponding $NpO_2^+$ value), we assume that the authors used the values for the analogous Np(V) species ($\varepsilon(NpO_2^+, Cl^-) = (0.09 \pm 0.05)$ $kg \cdot mol^{-1}$), ($\varepsilon(NpO_2(CO_3)_3^{2-}, Na^+) = -(0.33 \pm 0.17)$ $kg \cdot mol^{-1}$, ($\varepsilon(NpO_2(CO_3)_3^{5-}, Na^+) = -(0.53 \pm 0.19)$ kg $mol^{-1}$). By using these parameters, the conversion from experimental to thermodynamic values can be reproduced fairly well. However, the thermodynamic constant $\log_{10}\beta_2^o$ (Np) = (6.559 ± 0.108) could not be reproduced and appears to be erroneous.

**[2009XIA/FRI]**

Xia *et al.* studied the complexation of Np(V) with phosphate at $T$ = 25, 40 and 55 °C using a solvent extraction method with TTA and TOPO dissolved in toluene. Experiments were performed at $I$ = 1.0 M $NaClO_4$ and $-\log_{10}[H^+] \sim 7.4$. Total phosphate concentration was varied between $1.0 \times 10^{-4}$ M and $3.1 \times 10^{-3}$ M. Based on the $-\log_{10}[H^+]$ values in the experiment, the authors considered $HPO_4^{2-}$ as main complexing ligand for Np(V) and calculated its free concentration using the p$K_{a2}$ at different $T$ reported in [2005PAR/COV] and the SIT ion interaction coefficients selected in [2003GUI/FAN] for the species $H^+$, $H_2PO_4^-$ and $HPO_4^{2-}$ in $NaClO_4$ systems. Note that $-\log_{10}[H^+]$ was calculated as $pH_m + b$, where $pH_m$ is the experimentally measured pH and $b$ is an empirical correction factor that includes the activity coefficient of $H^+$ and the liquid junction potential of the combined electrode for a given ionic strength and temperature. The value $b$ = 0.27 used by the authors was determined in a previous study at $I$ = 1.0 M $NaClO_4$ and $T$ = 25 °C, and thus leads to a bias in $-\log_{10}[H^+]$ if used at temperatures other than 25 °C. The uncertainties of the thermodynamic parameters derived from this work have been consequently enlarged to account for the impact of biased $-\log_{10}[H^+]$ values. The incorrect value of $\Delta\varepsilon = -0.21$ kg·mol$^{-1}$ calculated by the authors for the chemical reaction $HPO_3^{2-} + H^+ \rightleftharpoons H_2PO_3^-$ has been recalculated in this work as $\Delta\varepsilon = -(0.07 \pm 0.07)$ kg·mol$^{-1}$ using $\varepsilon(H_2PO_3^-, H^+) = -(0.08 \pm 0.04)$ kg·mol$^{-1}$, $\varepsilon(HPO_3^{2-}, H^+) = -(0.15 \pm 0.06)$ kg·mol$^{-1}$ and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol$^{-1}$ as selected in [2003GUI/FAN]. This value has been used in combination with $\Delta_r H_m^o = -(3.6 \pm 1.0)$ kJ·mol$^{-1}$ selected in [2003GUI/FAN] and extrapolated to $I$ = 1.0 M $NaClO_4$ ($\Delta_r H_m^{'} = -(7.6 \pm 1.0)$ kJ·mol$^{-1}$) according with the guidelines summarized in Appendix B to derive the p$K_{a2}$ of phosphoric acid at $I$ = 1.0 M $NaClO_4$ and $T$ = 40 and 55 °C. These values have been used in this review to determine $[HPO_4^{2-}]_{free}$ at each experimental condition in the study.

Complexation Reactions (A.464) and (A.465) were defined by the authors based on their solvent extraction data, and the corresponding equilibrium constants determined at $T$ = 25, 40 and 55 °C.

$$NpO_2^+ + HPO_4^{2-} \rightleftharpoons NpO_2HPO_4^- \quad \text{(A.464)}$$

$$NpO_2^+ + 2HPO_4^{2-} \rightleftharpoons NpO_2(HPO_4)_2^{3-} \quad \text{(A.465)}$$

The concentration of $NpO_2(HPO_4)_2^{3-}$ forming at the highest phosphate concentrations ranges, according with the thermodynamic model derived in [2009XIA/FRI], from 3 % ($T$ = 25 °C) to 9 % ($T$ = 55 °C). This review considers such fraction of $NpO_2(HPO_4)_2^{3-}$ insufficient to unequivocally confirm the formation of this species, and thus the extraction data has been reinterpreted considering $NpO_2HPO_4^-$ as only forming Np(V)-phosphate complex. The simplified model explains very well the reported experimental extraction data, resulting in $\log_{10}K$((A.464), 1 M $NaClO_4$, $T$ = 25 °C) = (2.34 ± 0.10), $\log_{10}K$((A.464), 1 M $NaClO_4$, $T$ = 40 °C) = (2.16 ± 0.10) and $\log_{10}K$((A.464), 1 M $NaClO_4$, $T$ = 55 °C) = (2.13 ± 0.15). Assuming that the heat capacity

change of reaction is zero at all temperatures (*i.e.*, the standard molar enthalpy of reaction does not vary with temperature), the value $\Delta_r H_m^{'}$ ((A.464), 1 M $NaClO_4$) = – (15 ± 11) kJ·mol$^{-1}$ is calculated. The extrapolation of this value to $I = 0$ using SIT (see Appendix B) and neglecting the contribution of the term $RT^2 m \Delta\varepsilon_L$ (expectedly lower than 1 kJ·mol$^{-1}$) results in $\Delta_r H_m^{o}$ (A.464) = – (11 ± 11) kJ·mol$^{-1}$.

**[2010FEL/NEC]**

The solubility of $^{237}$Np(IV) and $^{242}$Pu(IV) was studied in alkaline $CaCl_2$ solutions at $T = (22 \pm 2)$ °C under reducing conditions. Amorphous hydroxides were precipitated from colloidal Np(IV) suspension or Pu(III)/(IV) solutions at pH ≈ 10-12 or 5-6, respectively. The Pu precipitate was equilibrated in 0.1 M NaCl for one year. X-ray diffraction and EXAFS were used to characterise the solid phases and to verify the composition of $AnO_2$(am, hyd). Sample solutions were prepared under argon atmosphere and equilibrated for up to six months. Iron powder or $Na_2S_2O_4$ were used to maintain reducing conditions, which clearly supported the presence of Np(IV) and Pu(IV) as the predominant oxidation states in solution. After ultrafiltration (10 kD pore size) liquid scintillation was used to determine the soluble concentrations of Np(IV) and Pu(IV). The pH was measured with a combination glass electrode and converted to $H^+$ concentration with correction factors determined for chloride solutions. The redox potential was measured with a combined Pt electrode and Ag/AgCl reference electrode corrected for the standard potential of Ag/AgCl.

X-ray diffraction showed the most intense peaks of $NpO_2$(cr) and $PuO_2$(cr) as weak broad bands, confirming the amorphous character of the solid phases used in the experiments. The authors assumed the number of hydration waters in $AnO_2 \cdot xH_2O$(am) to be $x \approx 2$, as found in hydrous oxides of Th(IV) and Tc(IV). The solubility of Np(IV) and Pu(IV) at $-\log_{10}[H^+] \geq 11$ increases with a slope ($\log_{10}$[An] *vs.* $\log_{10}[H^+]$) of + 4, which indicates the release of 4 $H^+$ in the chemical reaction controlling the solubility. This observation is consistent with the formation of the aqueous complex $Ca_4[An(OH)_8]^{4+}$ previously described for Th(IV). Note that because of the greater solubility of Th(IV), the formation of the complex $Ca_4[Th(OH)_8]^{4+}$ could be spectroscopically validated by EXAFS [2007BRE/ALT]. The increase in Np(IV) and Pu(IV) solubility is dependent on the $CaCl_2$ concentration but, in contrast to the analogous Th(IV) system, is not observed at $CaCl_2$ concentrations below 2.0 M. The authors compared data in this study with published data on the solubility of Pu(IV) in $CaCl_2$ in the absence of reducing agents [2008ALT/NEC]. Under the latter conditions, Pu(IV) solubility is higher due to the likely contribution of Pu(V) solution species. Based on their solid phase characterisation, slope analysis and analogy with Th(IV), the authors proposed the chemical Reaction (A.466) as to control the solubility of Np(IV) and Pu(IV) under the investigated experimental conditions:

$$An(OH)_4(am) + 4Ca^{2+} + 4H_2O(l) \rightleftharpoons Ca_4[An(OH)_8]^{4+} + 4H^+ \qquad (A.466)$$

Fellhauer and co-workers determined $\log_{10}K$((A.466), $I$ = 2.0 and 4.5 M $CaCl_2$), and used the SIT and Pitzer formalisms to extrapolate the conditional equilibrium constants to $I$ = 0. The ion-interaction coefficients for both models were derived from the data for $Ca_4[Th(OH)_8]^{4+}$ and applied to $Ca_4[Np(OH)_8]^{4+}$ and $Ca_4[Pu(OH)_8]^{4+}$. The SIT regression for Th(IV) resulted in $\log_{10}K°$(A.466) = – (54.2 ± 0.5) and $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-)$ = – (0.01 ± 0.10) kg·mol$^{-1}$ using four data points at [$CaCl_2$] = 0.5 M (0.51 m), 1.0 M (1.02 m), 2.0 M (2.11 m) and 4.5 M (5.26 m). The values reported in [2010FEL/NEC] for Np(IV) and Pu(IV) extrapolated to $I$ = 0 using SIT are:

$$\text{Np: } \log_{10} K°(\text{A.466}) = -(56.8 \pm 0.6)$$

$$\text{Pu: } \log_{10} K°(\text{A.466}) = -(58.5 \pm 0.4)$$

$$\varepsilon(Ca_4[Np(OH)_8]^{4+}, Cl^-) = \varepsilon(Ca_4[Pu(OH)_8]^{4+}, Cl^-) = -(0.01 \pm 0.10)\ \text{kg·mol}^{-1}.$$

Limiting the data to [$CaCl_2$] ≤ 2.0 M resulted in lower $\log_{10} K°$(A.466) values, but the authors disregarded those because of the absence of ternary complexes of Np(IV) and Pu(IV) at [$CaCl_2$] < 2.0 M. The combination of $\log_{10}K$(A.466) with the solubility products of $Np(OH)_4$(am) and $Pu(OH)_4$(am) as reported in [2003GUI/FAN]

$$An(OH)_4(am) \rightleftharpoons An^{4+} + 4OH^- \qquad \text{(A.467)}$$

$$\text{Np: } \log_{10} K°(\text{A.467}) = -(56.7 \pm 0.5)$$

$$\text{Pu: } \log_{10} K°(\text{A.467}) = -(58.3 \pm 0.5)$$

resulted in:

$$4Ca^{2+} + An^{4+} + 8OH^- \rightleftharpoons Ca_4[An(OH)_8]^{4+} \qquad \text{(A.468)}$$

$$\text{Np: } \log_{10} K°(\text{A.468}) = (55.9 \pm 0.8)$$

$$\text{Pu: } \log_{10} K°(\text{A.468}) = (55.8 \pm 0.6)$$

This review accepts the data demonstrating the formation of the ternary species $Ca_4[Np(OH)_8]^{4+}$ and $Ca_4[Pu(OH)_8]^{4+}$, which result in a significant enhancement of the solubility of Np(IV) and Pu(IV) in alkaline concentrated $CaCl_2$ solutions. These species are only observed in [$CaCl_2$] ≥ 2.0 M ($I$ ≥ 6.0 M), and thus beyond the accepted applicability of SIT. Consequently, no selection is recommended by this review, although $\log_{10} K°$(A.468) values reported in [2010FEL/NEC] for Np and Pu can be used in scoping calculations with SIT. A better approach to correct for ionic strength at these high salt concentrations is provided by the Pitzer model reported by the authors, which is out of the scope of this review.

**[2010KIM/OH]**

This paper evaluates the solubility of neptunium in granitic groundwater and the impact of carbonate based on predicted solubility data using the PHREEQC 2.0 geochemical

code. The authors used the thermodynamic data selected in 2003 by the NEA TDB to calculate the solubility of $NpO_2$(am, hyd) (referred in [2010KIM/OH] as $Np(OH)_4$(am)) hyd and the distribution of Np(IV) and Np(V) solution species. At carbonate concentrations above $2.5 \times 10^{-3}$ M at $E_h$ = – 100 mV and $1.5 \times 10^{-2}$ M at $E_h$ = – 200 mV, the neptunium solubility increases due to the formation of carbonate complexes. Calculated solubilities and species distributions are compared with experimental solubility measurements at a total carbonate concentration of $1.3 \times 10^{-3}$ M and pH between 8 and 13. The experimental data reported exceed the calculated Np solubility by several orders of magnitude, which led the authors to consider ternary complexes such as $Np(OH)_x(CO_3)_y^{4-x-2y}$ or $NpO_2(OH)_x(CO_3)_y^{1-x-2y}$, even though they admit that spectroscopic evidence is needed for their characterisation. Formation constants for such ternary species were estimated by fitting solubility data taken from the literature. Upper limits for the formation constants were estimated according to the reactions:

$$Np(OH)_4(am) + 2HCO_3^- \rightleftharpoons Np(OH)_2(CO_3)_2^{2-} + 2H_2O(l) \qquad (A.469)$$

$$Np(OH)_4(am) + HCO_3^- \rightleftharpoons Np(OH)_3CO_3^- + H_2O(l) \qquad (A.470)$$

$$Np(OH)_4(am) + CO_3^{2-} \rightleftharpoons Np(OH)_4CO_3^{2-} \qquad (A.471)$$

to be $\log_{10}K^o_{122} = -(3.0 \pm 0.5)$ for the formation of $Np(OH)_2(CO_3)_2^{2-}$ in (A.469), $\log_{10}K^o_{131} = -(5.0 \pm 0.5)$ for $Np(OH)_3CO_3^-$ in (A.470), and $\log_{10}K^o_{141} = -(6.0 \pm 0.5)$ for $Np(OH)_4(CO_3)^{2-}$ in (A.471). The complex $Np(OH)_4CO_3^{2-}$ is expected to dominate solution speciation at pH > 10.5. No thermodynamic data reported in [2010KIM/OH] is selected in the present review.

**[2010SHI/BES]**

Shilov *et al.* [2010SHI/BES] investigated the oxidation of Np(VI) to Np(VII) with $Fe(CN)_6^{3-}$ in alkaline solutions (0.1-1.0 M MOH; M = $Li^+$, $Na^+$, $K^+$) with high salt concentrations: 9.7-10.9 M LiCl, 9.7 M LiBr, 3.8 M NaCl, 7.7 M $NaClO_4$, 6.2 M NaBr, 12.1-13.2 M $KNO_2$, 2-7.15 M KF, 2.05-4.8 M $K_2CO_3$ and 7.90-8.26 M $KCH_3COO$. Additional data on the the Np(VI)/Np(V) couple in LiOH-LiCl and KOH-$KCH_3COO$ systems are reported, but the lack of any experimental description prevents the critical review of this part of the work.

In a first step, the authors determined the formal potential of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple in the investigated systems with emf measurements of the cell Pt | $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, MX, MOH ‖ $KCl_{sat}$, AgCl | Ag, Pt with X = $F^-$, $Cl^-$, $Br^-$, $NO_2^-$, $CH_3COO^-$ and $CO_3^{2-}$ according with $E(Fe(CN)_6^{3-}/Fe(CN)_6^{4-}) = E_{exp} + E^\circ_{Ag/AgCl} - E_j$. The term $E_j$ for the diffusion potential (or liquid junction potential) was disregarded in the calculations because of the difficulties in extrapolating ion mobilities tabulated for infinite dilution to concentrated solutions of mixed composition. Note however that a significant contribution of $E_j$ is expected in strongly alkaline

conditions, and thus the reported $E(\mathrm{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}})$ values can be affected by systematic errors. In a second step, Np(VI) solutions in MX-MOH systems were spiked with $K_3Fe(CN)_6 + K_4Fe(CN)_6$. The formation of Np(VII) in these mixtures was determined following the absorption of $NpO_4(OH)_2^{3-}$ at $\lambda = 618$ nm, and $\log_{10}K$((A.472), $I = x$ M MX + $y$ M MOH) was calculated accordingly. The reported $E$(Np(VII)/Np(VI)) values were obtained by combining $\log_{10}K$(A.472) with $E(\mathrm{Fe(CN)_6^{3-}/Fe(CN)_6^{4-}})$ previously determined for the same MX-MOH systems.

$$\mathrm{Np(VI) + Fe(CN)_6^{3-} \rightleftharpoons Np(VII) + Fe(CN)_6^{4-}} \qquad \text{(A.472)}$$

Shilov and co-workers observed that a small excess of $\mathrm{Fe(CN)_6^{3-}}$ was sufficient to oxidise Np(VI) to Np(VII) in concentrated KF-KOH and $KCH_3COO$-KOH systems, whereas a larger excess of oxidant was needed in NaCl-NaOH and LiCl-LiOH systems. The authors attributed this observation to the formation of K-complexes with $\mathrm{Fe(CN)_6^{3-}}$, which reduce the electrostatic repulsion with $NpO_2(OH)_4^{2-}$ and thus facilitate its oxidation to Np(VII). Because of the very high ionic strengths used and the expected bias in the reported $E$(Np(VII)/Np(VI)) values, no thermodynamic data is selected for the Np(VII)/Np(VI) system from the experimental results reported in [2010SHI/BES].

**[2010TOP/AUP]**

Topin *et al.* investigated the complexation of nitrate with Np(V) and Pu(V) at (25 ± 1) °C by using capillary electrophoresis coupled with ICP-MS (CE-ICP-MS). Experiments were performed in perchlorate/nitrate solutions with a constant ionic strength $I = 1.0$ M $NaClO_4/NaNO_3$. The experimental solutions also contained 20 % N,N-dimethylformamide (DMF). The pH of each sample solution was stated to be close to 6 for all experiments, however no details were provided regarding the methods to accurately determine the pH. Because of the weak An(V)-nitrate interaction, a large fraction of $NaClO_4$ (up to 90 %) was substituted by $NaNO_3$ in the course of the experiment. This exchanged fraction goes far beyond the limit recommended in the NEA TDB guidelines (≤ 10%) for the determination of equilibrium constants in the case of weak complexes.

Single peaks for the electrophoretic mobility ($\mu_{ov}$) of Np(V) and Pu(V) complexes were observed that shifted with increasing nitrate concentrations up to 0.9 M at $I = 1$ M. The changes in $\mu_{ov}$ were interpreted with the formation of the Np(V) and Pu(V) mononitrate complexes according to (A.473) and (A.474), respectively:

$$\mathrm{NpO_2^+ + NO_3^- \rightleftharpoons NpO_2NO_3(aq)} \qquad \text{(A.473)}$$

$$\mathrm{PuO_2^+ + NO_3^- \rightleftharpoons PuO_2NO_3(aq)} \qquad \text{(A.474)}$$

No discussion is provided on the effect of the background electrolyte (and its variations) on the electrophoretic mobility of $AnO_2^+$ ($\mu_{AnO2+}$). This parameter is used in the calculation of $\log_{10}K$((A.473)/(A.474), 1.0 M $NaClO_4/NaNO_3$), as described in

equation 3 in [2010TOP/AUP]. The authors used the mobility of $AnO_2^+$ experimentally determined in pure 1.0 M $NaClO_4$ for the determination of $\log_{10}K$((A.473)/(A.474), 1.0 M $NaClO_4$-$NaNO_3$) in all $NaClO_4$-$NaNO_3$ mixtures. The effect of this assumption on $\log_{10}K$((A.473)/(A.474), 1.0 M $NaClO_4$-$NaNO_3$) is unclear because of the very large fraction of $NaClO_4$ replaced by $NaNO_3$, and represents one of the main shortcomings identified in the publication.

The authors used SIT to extrapolate $\log_{10}K$((A.473)/(A.474), 1.0 M $NaClO_4$-$NaNO_3$) to $I = 0$, taking into account the ion interaction of $AnO_2^+$ with both $ClO_4^-$ and $NO_3^-$. Besides $\varepsilon(NpO_2^+, ClO_4^-) = (0.25 \pm 0.05)$ kg·mol$^{-1}$, $\varepsilon(PuO_2^+, ClO_4^-) = (0.24 \pm 0.05)$ kg·mol$^{-1}$, and $\varepsilon(Na^+, NO_3^-) = -(0.04 \pm 0.03)$ kg·mol$^{-1}$ taken from [2001LEM/FUG], the authors estimated $\varepsilon(AnO_2^+, NO_3^-) = (0.08 \pm 0.10)$ kg·mol$^{-1}$ using the empirical equation $\varepsilon(AnO_2^+, NO_3^-) = \varepsilon(Na^+, NO_3^-) + 0.12$ kg·mol$^{-1}$ reported in [2007VIT/PHR] and accordingly calculated $\log_{10}K°$(A.473) = (0.13 ± 0.14) and $\log_{10}K°$(A.474) = (0.14 ± 0.14). A greater ion interaction coefficient of $\varepsilon(AnO_2^+, NO_3^-) = (0.16 \pm 0.05)$ kg·mol$^{-1}$ was proposed in [1998SPA/PUI] and [2001LEM/FUG] for Np(V). This proposed value allows an accurate description of the experimental evidences reported in [1979RAO/GUD] only with changes in activity coefficients and disregarding the formation of the complex $NpO_2NO_3$(aq). The use of the same $\varepsilon(NpO_2^+, NO_3^-)$ value does not accurately describe the experimental observations in [2010TOP/AUP], although an accurate recalculation of the primary data is not feasible due to the unknown impact of the background electrolyte substitution on $\mu_{AnO2+}$.

**[2011BEN/GOT]**

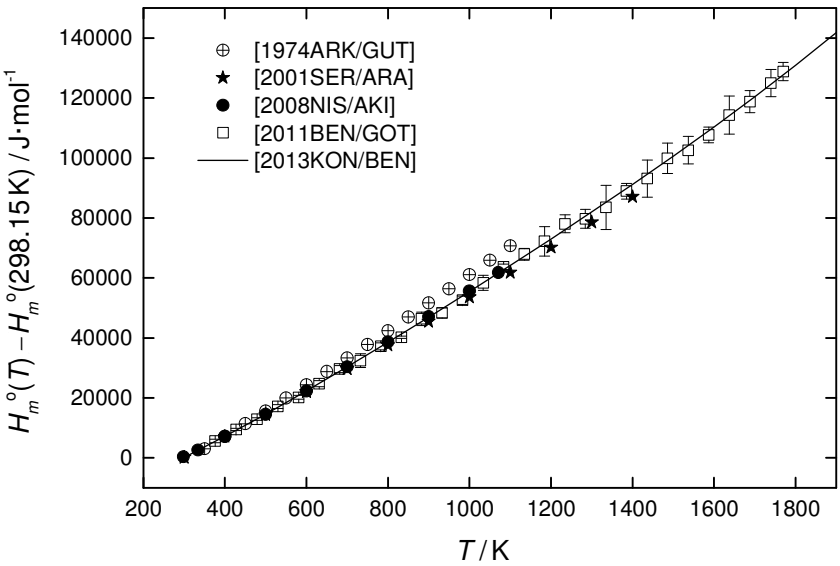
[2011BEN/GOT] reported the measurement of the enthalpy increment of $NpO_2$(cr) in the temperature range 376 to 1770 K using drop calorimetry. The purity of the neptunium dioxide sample was checked using ICP-MS analysis, which revealed no more than 0.0013 mass fraction impurities. The starting material was moreover annealed in air at 1800 K for 7.5 hours before measurement to ensure its stoichiometric composition. The drop calorimetry measurements were subsequently performed using four $NpO_2$ samples (with masses between 140 and 190 mg) at each temperature point and using high purity platinum ingots as standard material. The enthalpy increment data were fitted by imposing the necessary constraints $H_m(T) - H_m^o(298.15\ K) = 0$ at $T = 298.15$ K and $C_{p,m}^o(NpO_2, cr, 298.15\ K) = 66.2$ J·K$^{-1}$·mol$^{-1}$ as determined by Westrum Jr. *et al.* [1953WES/HAT] and recommended in this review. We agree with their calculation, which yielded:

$$C_{p,m}^o(NpO_2, cr, T) = (71.608 \pm 0.747) + (0.015845 \pm 0.001742)T - (900648 \pm 23152)T^{-2}\ \text{J·K}^{-1}\text{·mol}^{-1}$$

The enthalpy increment results of [2011BEN/GOT] are preferred in this review over those of Nishi *et al.* [2008NIS/ITO] collected from 334 to 1071 K and Arkhipov *et*

*al.* [1974ARK/GUT] from 350 to 1100 K (Figure A-19). The enthalpy increment data of [2008NIS/ITO] are in good agreement with [2011BEN/GOT], but the derived heat capacity function does not fit the low temperature heat capacity data of [1953WES/HAT]. The data of [1974ARK/GUT] are much higher than [2008NIS/ITO], [2011BEN/GOT] and inconsistent with [1953WES/HAT]. They are discarded in this review.

Figure A-19: Experimental enthalpy increment data for $NpO_2$(cr) *versus* temperature.




**[2011GOT/COL]**

[2011GOT/COL] reported vapour pressure measurements of neptunium dioxide using Knudsen effusion mass spectrometry. The neptunium dioxide material was sintered in air at 1723 K for five hours prior to the Knudsen measurements to ensure an oxygen-to-metal ratio O/Np = 2.0. The X-ray diffraction analysis of the starting material was in good agreement with stoichiometric $NpO_2$(cr). The ICP-MS analysis showed less than 0.0013 mass fraction impurities (mainly P, W, Pb), while alpha spectroscopy showed that the $^{237}Np$ to ($^{241}Am + {}^{238}Pu$) ratio was about 50 400. The Knudsen measurements were performed both under vacuum in a W cell and W cell with additional Ir liner at the bottom of the cell, and under $O_2$ flow in a $ThO_2$ cell. The authors firstly performed isothermal ionisation potential measurements under oxidative and vacuum conditions to derive the ionisation and dissociation energies of $NpO_2$(g), NpO(g) and Np(g). Their results were found in good agreement with the literature. The total pressure measurements under

vacuum in the W and W/Ir cell in the temperature range $T$ = 2000 to 2200 K revealed very similar results. The second and third law analyses in W/Ir yielded results in very poor agreement, however, namely $\Delta_{sub}H^{o}_{m}$ ($NpO_2$, cr, 298.15 K) = 546 kJ·mol$^{-1}$ (second law) and 623 kJ·mol$^{-1}$ (third law), respectively. The latter discrepancy is probably due to a slight but continuous reduction of the O/Np ratio during the ramp in temperature. For a more accurate determination of the sublimation enthalpy of neptunium dioxide (based on the equilibrium reaction $NpO_2$(cr) ⇌ $NpO_2$(g)), the measurements under oxidative conditions should be preferred. The sublimation enthalpy derived from the second law analysis for the measurements under $O_2$ flow in the $ThO_2$ cell is $\Delta_{sub}H^{o}_{m}(NpO_2, cr, 298.15\ K) = 637$ kJ·mol$^{-1}$. The latter value is in reasonable agreement with the results of Ackermann *et al.*, which are the selected data in the review of [2014KON/BEN], *i.e.*, $\Delta_{sub}H^{o}_{m}(NpO_2, cr, 298.15\ K) = (621 \pm 20)$ kJ·mol$^{-1}$. [2011GOT/COL] could not perform a third law analysis under oxidative conditions as their calibration failed (private communication). Finally, [2011GOT/COL] investigated the vapour composition above neptunia under vacuum at 2260 K based on their ionisation efficiency curves measurements. They found 93 % $NpO_2$(g), 6 % NpO(g) and 1 % Np(g), which corresponds to an overall composition $NpO_{1.939}$(g). The authors assigned the same composition to their condensed phase, supposing a congruent equilibrium was reached in their experiment, but the latter interpretation must be adjusted. The vapour composition was directly analysed after applying a 10 K·min$^{-1}$ heating ramp, with no stabilisation time at the investigated temperature (private communication), so as to stay as close as possible from a stoichiometric composition. This means their data refer to a slightly but continuously changing O/Np ratio.

**[2011KOC/ESE]**

The authors report a new analytical method for the determination of the heat capacity of $UO_2$(cr) and $NpO_2$(cr) in the temperature range $T$ = 300-1500 K based on the series expansion of integer and non-integer $n$-dimensional Debye functions. Their results are in reasonable agreement with the estimates of Yamashita *et al.* [1997YAM/NIT] and experimental data of Nishi *et al.* [2008NIS/AKI] and Benes *et al.* [2011BEN/GOT] between 500 and 900 K. Their data are higher than recommended in this review above the latter temperature, however. No new experimental data are reported in the work of [2011KOC/ESE].

**[2011SAR/SIM]**

Sarsfield *et al.* [2011SAR/SIM] modelled previously reported experimental data on Np(IV) solvent extraction between 30 % TBP and nitric acid in the absence [1998MAY/TAY] and presence [2008TAY/SIN] of simple hydroxamic acids. As an improvement of a previous work by the same authors [2009SAR/SIM], the fit of the

extraction data in the absence of hydroxamic acids included the activity model for the binary system Np(IV)-$NO_3$ in the aqueous phase. Hence, $\varepsilon(NpNO_3^{3+}, NO_3^-)$ and $\varepsilon(Np(NO_3)_2^{2+}, NO_3^-)$ were taken from [1998BER/VEI] in analogy to Pu(IV), whereas $\varepsilon(Np^{4+}, NO_3^-)$ was a fitting parameter besides $\log_{10}K$(A.475), $\log_{10}K$(A.476) and $\log_{10}K$(A.477). The authors assumed ideality of the TBP phase ($\gamma = 1$), and considered the density and molecular weight of kerosene to be the same as *n*-dodecane. The ionic strength and $[NO_3^-]_{free}$ were calculated by taking account of the dissociation of $HNO_3$ as described by Redlich *et al.* [1968RED/GAR] and Clegg and Brimblecombe [1990CLE/BRI]. The variation of $[TBP]_{free}$ with increasing $HNO_3$ concentration was calculated considering the formation of 1:2, 1:1 and 2:1 $HNO_3$:TBP solvates in the organic phase.

$$Np^{4+} + 4NO_3^- + 2TBP(org) \rightleftharpoons Np(NO_3)_4(TBP)_2(org) \quad \text{(A.475)}$$

$$Np^{4+} + 5NO_3^- + H^+ + 2TBP(org) \rightleftharpoons Np(NO_3)_4(TBP)_2 \cdot HNO_3(org) \quad \text{(A.476)}$$

$$Np(OH)_n^{4-n} + (4-n)NO_3^- + 2TBP(org) \rightleftharpoons Np(OH)_n(NO_3)_{4-n}(TBP)_2(org) \quad \text{(A.477)}$$

with $n = 1$ and 2. SIT ion interaction coefficient determined in [2011SAR/SIM] for $Np^{4+}$ ($\varepsilon(Np^{4+}, NO_3^-) = (0.473 \pm 0.004)$ kg·mol$^{-1}$) is in moderate agreement with the value selected in [2008RAN/FUG] for $Th^{4+}$ $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)$ kg·mol$^{-1}$), and agrees well with the estimate reported in [2006NEC/ALT] based on the correlation $\varepsilon(M^{n+}, ClO_4^-)$ *vs.* $\varepsilon(M^{n+}, NO_3^-)$. Although the paper represents a relevant step forward in the understanding of An(IV) behaviour in the PUREX and UREX processes, it is not considered valid for deriving thermodynamic data because of the large number of fitting parameters and assumptions required.

**[2011SMI/RAI]**

[2011SMI/RAI] reported structural studies in the Na-Np-O systems with the synthesis and structural characterisation of the sodium neptunates α-$Na_2NpO_4$, β-$Na_2NpO_4$, β-$Na_4NpO_5$, $Na_5NpO_6$, $Na_2Np_2O_7$ using X-ray diffraction. α-$Na_2NpO_4$ is orthorhombic in space group *Pbam*, β-$Na_2NpO_4$ is orthorhombic in space group *Pbca*, β-$Na_4NpO_5$ is tetragonal in space group *I4/m,* $Na_5NpO_6$(cr) is monoclinic in space group *C2/m*, $Na_2Np_2O_7$(cr) is monoclinic in space group $P2_1$. In addition, the thermal expansion and thermal stability of α-$Na_2NpO_4$ was investigated by high temperature X-ray diffraction under helium up to 1273 K. Those measurements showed that a phase transition occurs between 1073 K and 1273 K with the formation of a tetragonal γ-$Na_2NpO_4$ phase. The β-form of the $Na_2NpO_4$(cr) compound is obtained upon cooling to room temperature, suggesting that the high temperature phase of the compound is tetragonal and that the α-β transition is irreversible. No thermodynamic data are reported in the work of [2011SMI/RAI] for these phases.

**[2011WAN/ALE]**

The three-dimensional structure of a new Np(V) solid state compound, $K(NpO_2)_3(H_2O)Cl_4$(cr), contains bridging and terminal chloride coordinated to Np atoms. Three unique Np atoms are connected by three bridging $\mu^2$-Cl atoms and one $\mu^3$-bridging O atom to form $(NpO_2)_3(H_2O)Cl_4^-$ polyhedra. The compound is synthesised hydrothermally at 220 °C and is not soluble in water.

**[2012BEN/ZAO]**

The authors investigated the electronic structure, magnetic, dynamical and thermodynamic properties of NpN, PuN and AmN using *ab initio* pseudopotential and DFT methods. The calculations were performed using the LDA (local density approximation) in a plane wave basis. The norm-conserving pseudopotentials of Troullier and Martin [1991TRO/MAR] were used for the actinide atoms, while the Vanderbilt pseudopotentials [1985VAN2] were used for nitrogen. The obtained lattice parameters for the ground state NaCl phases were found slightly lower than reported in the literature (~ 0.09-0.14 Å), as usually observed in DFT calculations. The calculation of the partial density of states revealed a metallic behaviour for AmN and NpN, and half-metallic ferromagnetic behaviour for PuN. From the calculation of the phonon density of states, the entropy and heat capacity variations were also calculated in the temperature range 0-1000 K. The results of the calculations were neither listed nor compared to experimental data. The authors reported that the entropy and heat capacity at high temperatures mainly originate from X-acoustic and N-optical modes, and to a lesser extent from the N-acoustic modes. The heat capacity increases strongly below 200 K, and more slowly above 600 K, approaching the Dulong-Petit limit (50 $J \cdot K^{-1} \cdot mol^{-1}$) around 1000 K for all three compounds. This is about 10 $J \cdot K^{-1} \cdot mol^{-1}$ lower at 1000 K than recommended in this review for NpN(cr) and PuN(cr).

**[2012BOH/WEL]**

[2012BOH/WEL] reassessed the melting temperature of $NpO_2$(cr) using a quasi-containerless fast laser heating technique and multi-wavelength pyrometry. The experimental melting temperature, *i.e.*, $T_{fus}$ = (3070 ± 62) K, was found much higher than in previous studies by Chikalla *et al.* [1971CHI], (2830 ± 50) K, and Richter and Sari [1987RIC/SAR], (2820 ± 60) K. The latter measurements were probably affected by the interaction with the tungsten containment material, as also observed in the case of plutonium dioxide [2011BRU/BOB]. The new measurement of [2012BOH/WEL] is, therefore, retained in this review. It is also in better agreement with the trend followed by $UO_2$(cr) [2014KON/BEN] and $PuO_2$(cr) [2011BRU/BOB].

Two neptunium dioxide samples were used for the investigation in the form of disks of 6 mm diameter and 1.2-1.5 mm thickness. Sintering in $Ar/H_2$ atmosphere was applied to obtain dense materials, followed by heat treatment under air flow at 1123 K and 2000 K to adjust to the exact O/Np = 2 stoichiometry. The stoichiometry, microstructure, homogeneity and purity of the unmolten and molten materials were checked using X-ray diffraction and Scanning Electron Microscopy. The quasi-containerless conditions were achieved by heating with short heating pulses (70-720 ms) on a limited area (about 3 mm in diameter) on the sample surface. The pyrometer was operated at 652 nm and calibrated against a standard tungsten-ribbon lamp in the range 1800-2500 K in accordance with the International Temperature Scale of 1990.

The melting temperature, identified on the cooling stage of the thermograms, was found reproducible over 31 experiments, independent of the laser pulse power or atmosphere (air, air/argon mixture, Ar/2 % $H_2$). The XRD and SEM analyses moreover did not show any significant change in stoichiometry before and after the experiment, with a composition estimated as $1.98 \leq O/Np \leq 2$ for the congruent melting point. Given the high oxygen potential of neptunium dioxide at temperatures close to the melting point, the congruent melting composition is probably slightly hypostoichiometric [2014KON/BEN].

**[2012GAO/TIT]**

The redox behaviour of $^{237}Np(V)$ and $^{237}Np(VI)$ in alkaline TMA-OH/Cl solutions is investigated spectroscopically under argon atmosphere at (25 ± 1) °C. A range of redox conditions ($-0.8\ V \leq E_h \leq 1\ V$) were studied both in the absence and presence of hypochlorite. The redox potentials are measured with a combined Pt and Ag/AgCl reference electrode with an equilibration time of 5 min. The sample solutions contain a total Np concentration of about $2 \times 10^{-3}$ M and are adjusted to $-\log_{10}[H^+]$ values ranging between 9 and 13.5. All solutions contain about $(2\text{-}2.7) \times 10^{-3}$ M carbonate as impurity of TMA-OH. A combination glass electrode is used to measure the pH, and calibrated against standard buffer solutions. The pH correction factors for ionic strength effects are determined in 0.5-0.7 M TMA-Cl solutions with known HCl concentrations and are found to be small (ranging between 0.05 and 0.10) compared to other chloride solutions, such as NaCl or $CaCl_2$. After four days of equilibration, sample aliquots are centrifuged before measuring the soluble neptunium concentration by using liquid scintillation counting and obtaining UV-vis/NIR absorption spectra (800 and 1200 nm) for oxidation state analysis. After washing with ethanol, the solid phase is analysed by ICP-OES and SEM-EDX. The Na:Np ratio in the solid phase is determined by chemical analysis and SEM-EDS. EXAFS and XANES measurements, including *in situ* spectro-electrochemical measurements, are used to examine oxidation states and composition of the solution complexes. Reference EXAFS Np $L_{III}$-edge spectra are obtained by oxidising electrochemically Np(III) in 1 M $HClO_4$ at 200 mV and at 1000 mV to prepare Np(V) and Np(VI). From the EXAFS

measurements the authors derived hydration numbers for neptunium cations and report the formulas of the hydrated cations as $Np(H_2O)_9^{3+}$, $Np(H_2O)_{10}^{4+}$, and $NpO_2(H_2O)_5^{2+}$. These numbers are in agreement with other experimental and theoretical data reported in the literature. The authors also provide a number of SIT ion interaction parameters for the Np(V) and Np(VI) species with $TMA^+$ and $Cl^-$. Many of these parameters are estimated based on the charge correlation at $I = 0.64$ m according to $\varepsilon(TMA^+, X^{Z-}) = -0.40\ Z - 0.48$ and $\varepsilon(M^{Z+}, Cl^-) = 0.10\ Z - 0.05$.

In the absence of hypochlorite, the authors report measured redox potentials between – 0.010 V and + 0.059 V. The spectral analysis revealed the presence of the Np(V) solution species $NpO_2^+$, $NpO_2CO_3^-$ and a ternary complex of general formula $(NpO_2)_m(OH)_x(CO_3)_y^{m-x-2y}$. However, the latter species is not clearly identified and defined, but proposed based on similar spectral features observed in [1997NEC/FAN]. The low redox potentials suggests that Np(V) in the observed greenish solid phase is $NpO_2OH(s)$. In the presence of hypochlorite, the measured redox potentials range between 226 mV and 835 mV as a function of pH and [NaClO]. Since no absorbance features are observed for these samples, the authors postulate the presence of symmetric Np(VI) species such as $NpO_2(OH)_4^{2-}$ or $NpO_2(CO_3)_3^{4-}$ over a Np(VI)-containing brownish-purple precipitate, suggested to be $NpO_3{\cdot}xH_2O(s)$ or a Na-containing Np(VI) solid phase. The larger amounts of $Na^+$ introduced with the high concentration of $5 \times 10^{-2}$ M $ClO^-$ initiate the formation of the Na-containing Np(VI) solid phase at $-\log_{10}[H^+]$ of about 12.

Gaona *et al.* evaluate and estimate thermodynamic formation constants and SIT ion interaction parameters to describe the Np(V) and Np(VI) complexation behaviour in TMA-OH solutions. Since no ion interaction parameters are available for TMA solutions, a number of SIT ion interaction parameters are estimated for $I = 0.64$ m by correlating the species' effective charge. A linear relationship between $\varepsilon$ values and the charge of the aqueous species has also been observed for other $TMA^+/X^-$ systems. The formation constants of $NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$ are extrapolated from the linear correlation between the effective charge $Z_{eff}$ (2.3 for the $AnO_2^+$ ion and 3.2 for the $AnO_2^{2+}$ ion) and hydrolysis constants $\log_{10}\beta_{1n}^o$ with $n$ = 1-4 reported in the literature for U, Np, Pu and Am. From plotting $\log_{10}\beta_{1n}^o$ *vs.* $Z_{eff}$ the authors interpolated the values $\log_{10}\beta_{13}^o = -(19.6 \pm 1.0)$ for $NpO_2(OH)_3^-$ and $\log_{10}\beta_{14}^o = -(31.6 \pm 1.0)$ for $NpO_2(OH)_4^{2-}$ according to the chemical Reactions (A.478) and (A.479). This review does not select any thermodynamic quantity derived from estimation methods, although these equilibrium constants are in line with those selected for the U(VI) analogous species.

$$NpO_2^{2+} + 3H_2O(l) \rightleftharpoons NpO_2(OH)_3^- + 3H^+ \quad \text{(A.478)}$$

$$NpO_2^{2+} + 4H_2O(l) \rightleftharpoons NpO_2(OH)_4^{2-} + 4H^+ \quad \text{(A.479)}$$

Gaona *et al.* performed also ionic strength corrections of $\log_{10}K$((A.480), 3.0 M $NaClO_4$) and $\log_{10}K$((A.481), 3.0 M $NaClO_4$) previously reported in [1997NEC/FAN] for the mixed Np(V) hydroxy-carbonate complexes $NpO_2OHCO_3^{2-}$

and $NpO_2(OH)_2CO_3^{3-}$. The associated SIT ion interaction parameters are taken from [2009HUM] and used to calculate $\log_{10}K°$((A.480), 298 K) = (7.0 ± 0.3) and $\log_{10}K°$((A.481), 298 K) = (7.66 ± 0.15). Lemire and co-workers [2001LEM/FUG] disregarded any thermodynamic data selection for the species $NpO_2OHCO_3^{2-}$ and $NpO_2(OH)_2CO_3^{3-}$ reported in [1997NEC/FAN], but suggested these data for scoping calculations. The same criteria is adopted in the present review.

$$NpO_2^+ + OH^- + CO_3^{2-} \rightleftharpoons NpO_2OHCO_3^{2-} \quad \text{(A.480)}$$

$$NpO_2^+ + 2OH^- + CO_3^{2-} \rightleftharpoons NpO_2(OH)_2CO_3^{3-} \quad \text{(A.481)}$$

**[2012RIO/MIC]**

See review in Chapter 17 (Appendix A, Pu).

**[2012SHI/GOG]**

This is a comprehensive review work on Np(III), Np(IV), Np(V), Np(VI) and Np(VII) solution chemistry, including both aqueous species and solid compounds. The review covers hydrolysis, complexation with carbonate, silicate, heteropolycompounds (in particular $SiW_{11}O_{39}^{8-}$, $PW_{11}O_{39}^{7-}$ and $P_2W_{17}O_{61}^{10-}$), but also redox, disproportionation and reproportionation processes. All publications discussed in [2012SHI/GOG] and providing thermodynamic data for systems included in the present update book have been also reviewed.

**[2012SHI/TSU]**

The authors reported first-principles calculations of the equilibrium lattice constants, thermal expansion coefficients, bulk moduli, and specific heat at constant volume and pressure in the temperature range 0-1500 K of neptunium mononitride NpN(cr). The simulations were done using the Vienna Ab initio Simulation Package (VASP) code, using the projector augmented wave (PAW) method within the Perdew-Burke-Ernzerhof generalised gradient approximation for the exchange-correlation functional. The obtained lattice constants (4.8931 Å at 298 K) were in good agreement with the experiment within a 1 % difference. The linear thermal expansion coefficients ($8.9 \times 10^{-5}$ $K^{-1}$ at 293 K) were found slightly larger than in [1996PER/BUR], [2008TAK/AKA] ($7.6\text{-}7.9 \times 10^{-5}$ $K^{-1}$). The specific heat was calculated from the phonon DOS. The influence of the spin-orbit coupling on the specific heat was found to be negligible. The calculated electronic contribution (10.4 $mJ \cdot mol^{-1} \cdot K^{-1}$) was slightly higher than in [2007ATT/RAY] (8.69 $mJ \cdot mol^{-1} \cdot K^{-1}$). The heat capacity for NpN(cr) comprising lattice and electronic contributions, is very close to that measured experimentally by [2008NIS/ITO], *i.e.*, $C_{p,m}^{o}$(NpN, cr, $T$) = $1.8549 \times 10^{-2}\,T + 42.936 - 4794\,T$ $J \cdot K^{-1} \cdot mol^{-1}$. The latter equation

was derived from the experimental enthalpy data of [2008NIS/ITO], when applying the necessary constraints $H - H(298.15\ \text{K}) = 0$ at 298.15 K. It is found below that of PuN(cr) [2001LEM/FUG] up to 660 K, and above after the latter temperature. In this review we prefer to retain the estimation by [2001LEM/FUG], where the heat capacity for NpN(cr) is between that for UN(cr) and PuN(cr). Finally, the calculated entropy at 298.15 K is 5.8 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ lower than the value recommended in [2001LEM/FUG] and [2003GUI/FAN]. We prefer to retain in this review the data selected by [2001LEM/FUG] and [2003GUI/FAN], which was estimated from the data on UN(cr) and PuN(cr).

**[2012XIA/TIA]**

Xian and co-workers [2012XIA/TIA] performed a very comprehensive study on the cation-cation interactions between $NpO_2^+$ and $UO_2^{2+}$ at different temperatures (283.15 K ≤ $T$ ≤ 358.15 K) and ionic strengths (3.0 M ≤ $I$ ≤ 4.5 M; Mg-$UO_2(NO_3)_2$). All experiments were performed under acidic conditions with 0.02 M ≤ $[HNO_3]$ ≤ 0.1 M. The authors used a combination of spectrophotometry at different temperatures and microcalorimetry measurements conducted at $T$ = 298.15 K. The titration of a Np(V) solution with U(VI) resulted in the decrease of the $NpO_2^+$ peak at 980.5 nm and the systematic increase of a new peak at ~ 992 nm, which was assigned to the formation of the complex $NpO_2^+ \cdot UO_2^{2+}$ according with Reaction (A.482). The existence of a single isosbestic point confirmed the presence of only two Np species in the investigated system.

$$NpO_2^+ + UO_2^{2+} \rightleftharpoons NpO_2^+ \cdot UO_2^{2+} \qquad \text{(A.482)}$$

Based on their spectroscopic data, Xian and co-workers calculated a series of $\log_{10}K((\text{A.482}), T, I_m)$ in the ionic strength and temperature conditions of their experiments. The authors took also into account the formation of the complex $UO_2NO_3^+$ for the calculation of $[UO_2^{2+}]_{\text{free}}$. The Van't Hoff equation was used to calculate $\Delta_r H_m^{'}((\text{A.482}), 298.15\ \text{K}, I_m)$ = (4.85 ± 0.31), (4.86 ± 0.42), (4.34 ± 0.42), (5.03 ± 0.73) and (4.84 ± 0.75) for $I_m$ = 4.91, 4.42, 3.98, 3.58 and 3.22 *m*, respectively, hinting to an almost negligible impact of $I_m$ on $\Delta_r H_m^{'}$. These results are in excellent agreement with $\Delta_r H_m^{'}((\text{A.482}), 298.15\ \text{K}, 1.5\ \text{M Mg-}UO_2(NO_3)_2)$ = (4.2 ± 1.6) $\text{kJ}\cdot\text{mol}^{-1}$ determined in the same work by microcalorimetry. The endothermic enthalpy determined in [2012XIA/TIA] supports the inner-sphere character of the complex formed. This is consistent with recent spectroscopic evidences collected for the complex $NpO_2^+ \cdot NpO_2^+$, and is in line with the strong perturbations induced in the UV-vis/NIR, Raman, IR and NMR spectra. Note however that the reported value is in disagreement with enthalpy data determined by spectroscopy in [1993STO/CHO], $\Delta_r H_m^{'}((\text{A.482}), 298.15\ \text{K}, 6.0\ \text{M}\ NaClO_4)$ = – (12.0 ± 1.7) $\text{kJ}\cdot\text{mol}^{-1}$.

Xian and co-workers extrapolated $\log_{10}K((\text{A.482}), T, I_m)$ to $I$ = 0 using SIT, and obtained – (1.24 ± 0.04), – (1.18 ± 0.05), – (1.18 ± 0.05), – (1.22 ± 0.04), – (1.15 ± 0.06) and – (1.24 ± 0.07) at $T$ = 283.15, 298.15, 313.15, 328.15, 343.15 and 358.15 K,

respectively. In spite of the quality of the data reported in [2012XIA/TIA] for Mg-$UO_2(NO_3)_2$ solutions with $3.22\ m \leq I_m \leq 4.91\ m$, this review disregards the selection of $\log_{10}K°$(A.482) because of the uncertainties associated to the extrapolation of such high ionic strengths to $I = 0$. Reported values of $\log_{10}K$((A.482), $T$, $I_m$) can be confidently used to quantify the extent of Np(V)-U(VI) cation-cation interactions in concentrated nitrate solutions with $283.15\ K \leq T \leq 358.15\ K$.

**[2013CLA/CON]**

Clark *et al.* [2013CLA/CON] investigated the aqueous speciation of Np(VI) in strongly alkaline conditions using a combination of EXAFS, Raman and $^{17}O$ NMR. TMA-OH was used in EXAFS (2.5 and 3.5 M) and $^{17}O$ NMR (3.5 M) studies, whereas 2.2 M LiOH-$LiNO_3$ solutions with $0.6\ M \leq [LiOH] \leq 2.2\ M$ were considered for the Raman investigations due to the presence of a Raman-active band of $TMA^+$. For comparative purposes, the authors characterised the structure of $[Co(NH_3)_6]_2[NpO_2(OH)_4]\cdot H_2O$(cr) using single crystal XRD, EXAFS and Raman spectroscopy.

Structural parameters determined by EXAFS for Np(VI) in 2.5 M TMA-OH are consistent with those obtained for $[Co(NH_3)_6]_2[NpO_2(OH)_4]\cdot H_2O$(cr), thus supporting the predominance of the aqueous species $NpO_2(OH)_4^{2-}$ in these conditions. Controversial results were obtained in 3.5 M TMA-OH. Virtually the same Np-$O_{ax}$ and Np-$O_{eq}$ distances as in 2.5 M TMA-OH were determined for this system, in contrast to the clear increase in the equatorial coordination number of Np (+ 20-25 % with respect to 2.5 M TMA-OH). The latter finding may suggest an important contribution of the species $NpO_2(OH)_5^{3-}$, although such increase in the coordination number is not consistent with the nearly identical bond lengths determined in both TMA-OH systems. Raman spectra of all investigated aqueous samples showed a single Np feature, which was assigned by the authors to $NpO_2(OH)_4^{2-}$. The relevant shift observed between the main Np feature in aqueous samples ($\nu_1 = 769\ cm^{-1}$) and in $[Co(NH_3)_6]_2[NpO_2(OH)_4]\cdot H_2O$(cr) ($\nu_1 = 741\ cm^{-1}$) was attributed to matrix effects rather than to changes in the equatorial coordination number. Based on their EXAFS and Raman results, and in combination with the knowledge on the U(VI) chemistry under strongly alkaline conditions [2000MOL/REI], [2010SZA/GRE], the authors proposed the predominance of the species $NpO_2(OH)_4^{2-}$ in the investigated aqueous systems, with a minor contribution of $NpO_2(OH)_5^{3-}$ in 3.5 M TMA-OH. This review agrees with the main conclusions by Clark and co-workers, but acknowledges the need of further experimental efforts to clarify the role of the species $NpO_2(OH)_5^{3-}$ in the aqueous chemistry of Np(VI) under strongly alkaline conditions.

**[2013GAO/FEL]**

The solubility of $^{237}Np(VI)$ from undersaturation is studied in NaCl solutions under argon atmosphere at (22 ± 2) °C. A total of 35 batch samples are prepared by distributing a solid phase in 0.1 M, 0.5 M, 1.0 M, 2.5 M and 5.0 M NaCl solutions containing NaClO as oxidising agent to maintain the hexavalent oxidation state of Np. The solid phase was prepared by precipitating Np(VI) in 2.5 M NaCl at around pH ~ 12 solution and aged for two months. X-ray diffraction, SEM-EDS and quantitative chemical analysis (Np by LSC, Na by ICP-OES) are used for the characterisation of the solid phase before and after the solubility experiments. The XRD pattern matched those reported in the literature for $Na_2Np_2O_7$(cr). The absence of hydration water or hydroxo groups is reported based on TGA-DTA data. However, this review notes that a minor weight-loss and thus a minor contribution of water cannot be disregarded ($Na_2Np_2O_7 \cdot xH_2O$(cr), with $x \leq 0.1$), after a personal communication with the authors. The solid-solution samples are equilibrated for about 450 days. The pH was measured using a combination glass electrode and calibrated against standard pH buffers. The measured pH value is corrected for ionic strength effects by an operational correction factor determined as function of NaCl concentration. The $E_h$ was measured with a combined Pt electrode with Ag/AgCl reference electrode and corrected for the reference electrode potential in 3 M KCl at 22 °C. Changes of up to 20 mV in the liquid junction potentials at the experimental conditions investigated are calculated to be negligible and within the uncertainty of the $E_h$ measurement. All thermodynamic quantities derived in [2013GAO/FEL] correspond to equilibria between Np(VI) species/compounds, and thus the large uncertainty reported for $E_h$ values has no impact on the data reported by the authors. The soluble Np concentration is determined by liquid scintillation counting after filtration through 10 kD filters. UV-vis/NIR spectra are collected after sample centrifugation where the Np concentration was above $10^{-5}$ M to identify solution species and oxidation state distribution. The authors developed thermodynamic data by using the SIT and the Pitzer formalism and applying solution complexes in analogy to the U(VI) hydrolysis system.

The authors separate the solubility curves in four regions according to the different slopes of the $\log_{10}s$ as a function of pH: region I at $-\log_{10}[H^+] \leq 9$ is characterised by a decrease in Np concentration; region II at $-\log_{10}[H^+]$ between about 9 and 10.5 is defined as the minimum solubilities with nearly pH-independent Np concentrations; region III at $-\log_{10}[H^+]$ between 10.5 and 13.5 exhibits increasing Np concentrations with slope $\approx +1$; and region IV at $-\log_{10}[H^+] > 13.5$ with a steeper increase in the solubility curve. Data in regions I and IV are not considered for thermodynamic data analysis. Region I is characterised by a large data scattering and the existence of Np(V) in solution. The authors obtained by UV-vis/NIR strong indications that the increased slope in region IV is caused by the oxidation of Np(VI) to Np(VII) with the consequent formation of the species $NpO_4(OH)_2^{3-}$. This hypothesis was later confirmed by the same authors using EXAFS spectroscopy [2014GAO/FEL]. Data in regions II and III are well defined and are accurately modeled with the model developed

in this study. However, data in region II are restricted to a relatively narrow pH-range because of the reduction of Np(VI) to Np(V) in region I, and thus this review assigns a larger uncertainty to the derived thermodynamic data.

The original solid phase, $Na_2Np_2O_7{\cdot}xH_2O$(cr), is maintained as solubility-controlling phase in regions II and III of all investigated NaCl systems with a measured Na:Np ratio between 0.9 and 1.2. On the contrary, a solid phase transformation takes place in region I. While $Na_2Np_2O_7{\cdot}xH_2O$(cr) is predominant in 5 M NaCl, the authors report a second phase to be present in 0.5 M and 2.5 M NaCl at pH = 8.0 and 8.3. The composition of this second phase is not identified despite its intensive Bragg reflections at 13.45 and 20.18 2Θ degrees. Accordingly, the determined ratio in the solid phase, Na:Np = 0.7 differs significantly from the nominal ratio in $Na_2Np_2O_7{\cdot}xH_2O$(cr), indicating a lower Na content in the unidentified second phase. The formation/presence of this solid phase is not discussed in detail by the authors, but shows certain analogies with non-stoichiometric Na-U(VI) solid phases in [$NaClO_4$] > 0.5 M reported in [1998DIA/GRA]. At low NaCl concentration, $NpO_2(OH)_2{\cdot}H_2O$(cr) is identified as the solubility-controlling solid phase based on the perfect match with XRD pattern reported for this solid phase by Saito *et al.* [1999SAI/WAN]. XRD patterns in [2013GAO/FEL] and [1999SAI/WAN] show also a good agreement with XRD data reported in the solubility study by Kato and co-workers [1996KAT/KIM], which was considered in [2001LEM/FUG] for the selection of $\log_{10}K^{\circ}_{s,o}$ ($NpO_3{\cdot}H_2O$, cr). The assignment of the solid phase controlling the solubility in [1996KAT/KIM] (either $NpO_2(OH)_2{\cdot}H_2O$(cr) or $NpO_3{\cdot}H_2O$(cr)) is discussed in Section 10.2.2.3.1 of this book.

Based on the XRD pattern of the solid phases in 0.1 M NaCl, the authors reported a solid phase transformation of $NpO_2(OH)_2{\cdot}H_2O$(cr) into $Na_2Np_2O_7$(cr) within $7.6 \le pH_m \le 8.6$. The transition point between both solid phases can be described with the chemical Reaction (A.483):

$$0.5Na_2Np_2O_7{\cdot}xH_2O(cr) + (1.5-0.5x)\,H_2O(l) + H^+ \rightleftharpoons NpO_2(OH)_2{\cdot}H_2O(cr) + Na^+ \quad \text{(A.483)}$$

and

$$\log_{10}{}^{*}K^{\circ}_{s,o}(0.5Na_2Np_2O_7{\cdot}xH_2O, cr) + (1.5-0.5x)\log_{10}a_{H_2O} + \log[H^+] + \log_{10}\gamma_{H^+} = \log_{10}{}^{*}K^{\circ}_{s,o}(NpO_2(OH)_2{\cdot}H_2O, cr) + \log_{10}[Na^+] + \log_{10}\gamma_{Na^+} \quad \text{(A.484)}$$

Equation (A.484) allows the calculation of $\log_{10}{}^{*}K^{\circ}_{s,o}(0.5Na_2Np_2O_7{\cdot}xH_2O, cr)$ provided that $[Na^+]$, $-\log_{10}[H^+]$ and $\log_{10}{}^{*}K^{\circ}_{s,o}(NpO_2(OH)_2{\cdot}H_2O, cr)$ are known. This indirect approach for the determination of $\log_{10}{}^{*}K^{\circ}_{s,o}(0.5Na_2Np_2O_7{\cdot}xH_2O, cr)$ has relevant limitations, which are acknowledged by the authors with a very large associated uncertainty of ± 1.1.

One should note that the model calculations represent well the experimental data at $-\log_{10}[H^+]$ above 9.5, where $NpO_2(OH)_3^-$ and $NpO_2(OH)_4^{2-}$ are proposed to be the dominant solution species based on the known solid phase controlling the solubility

($Na_2Np_2O_7{\cdot}xH_2O$, cr), slope analysis (≈ 0 and ≈ + 1 for regions II and III, respectively) and analogy with U(VI). The authors calculated the conditional equilibrium constants according to the chemical Reactions (A.485) and (A.486) (see Table A-171):

$$0.5Na_2Np_2O_7{\cdot}xH_2O(cr) + (1.5 - 0.5x)H_2O(l) \rightleftharpoons NpO_2(OH)_3^- + Na^+ \qquad (A.485)$$

$$0.5Na_2Np_2O_7{\cdot}xH_2O(cr) + (2.5 - 0.5x)H_2O(l) \rightleftharpoons NpO_2(OH)_4^{2-} + H^+ + Na^+ \qquad (A.486)$$

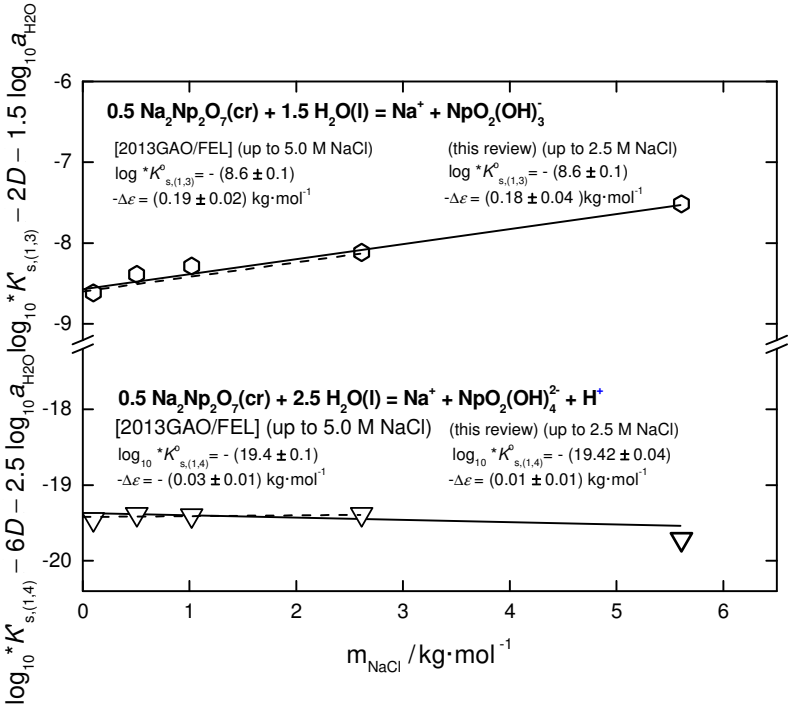
and obtained from linear regression analysis the values of $\log_{10}K°$((A.485), 298.15 K) and $\log_{10}K°$((A.486), 298.15 K), as well as the SIT parameters for the Np(VI) hydroxo complexes (Figure A-20). By using $\varepsilon(H^+, Cl^-)$ = (0.12 ± 0.01) kg·mol$^{-1}$ and $\varepsilon(Na^+, Cl^-)$ = (0.03 ± 0.01) kg·mol$^{-1}$ the authors calculate $\varepsilon(NpO_2(OH)_3^-, Na^+)$ = – (0.20 ± 0.02) kg·mol$^{-1}$ and $\varepsilon(NpO_2(OH)_4^{2-}, Na^+)$ = – (0.12 ± 0.01) kg·mol$^{-1}$. Note that the linear trend observed in Figure A-20 further supports the chemical model proposed by the authors. Gaona and co-workers included solubility data up to 5.0 M NaCl in their SIT linear regression (Figure A-20). SIT is usually considered valid up to $I_m \approx 3.5$ m, and thus the last experimental point reported by the authors in 5.0 M NaCl is outside the range of applicability of SIT. Figure A-20 shows the SIT plot for Reactions (A.485) and (A.486) recalculated in this review excluding the data in 5.0 M NaCl; the resulting solubility constants are summarised in Table A-171. The values of $\log_{10}K°$((A.485), 298.15 K) and $\log_{10}K°$((A.486), 298.15 K) recalculated in this review are in excellent agreement with those reported in [2013GAO/FEL] including solubility data in 5.0 M NaCl. Slight deviations arise the slope of the SIT plots – $\Delta\varepsilon$, which result in $\varepsilon(NpO_2(OH)_3^-, Na^+)$ = – (0.21 ± 0.04) kg·mol$^{-1}$ and $\varepsilon(NpO_2(OH)_4^{2-}, Na^+)$ = – (0.16 ± 0.02) kg·mol$^{-1}$ (recalculated in this review) compared to $\varepsilon(NpO_2(OH)_3^-, Na^+)$ = – (0.20 ± 0.02) kg·mol$^{-1}$ and $\varepsilon(NpO_2(OH)_4^{2-}, Na^+)$ = – (0.12 ± 0.01) kg·mol$^{-1}$ (reported in [2013GAO/FEL]).

Table A-171: Conditional equilibrium constants determined in [2013GAO/FEL] for the chemical Reactions (A.485) and (A.486) in 0.1, 0.5, 1.0, 2.5 and 5.0 M NaCl, and corresponding extrapolation to $I$ = 0 with the SIT-plot in Figure A-20.

| $t$ /°C | Method | $I$ (medium) | $\log_{10}K$(A.485) | $\log_{10}K$(A.486) |
|---|---|---|---|---|
| (22 ± 2) | sol | 0.1 M NaCl | – (8.40 ± 0.08) | – (18.80 ± 0.03) |
| (22 ± 2) | sol | 0.5 M NaCl | – (8.05 ± 0.09) | – (18.35 ± 0.03) |
| (22 ± 2) | sol | 1.0 M NaCl | – (7.90 ± 0.18) | – (18.21 ± 0.02) |
| (22 ± 2) | sol | 2.5 M NaCl | – (7.70 ± 0.08) | – (18.05 ± 0.02) |
| (22 ± 2) | sol | 5.0 M NaCl | – (7.15 ± 0.12) | – (18.40 ± 0.05) |
| | | $I$ = 0 | – (8.6 ± 0.1) | – (19.4 ± 0.1) |
| | | | – (8.6 ± 0.1) [(a)] | – (19.42 ± 0.04) [(a)] |

(a) Recalculated in this review excluding solubility data in 5.0 M NaCl.

Figure A-20: SIT extrapolation to $I = 0$ of experimental $\log_{10}K$(A.485) and $\log_{10}K$(A.486) reported in [2013GAO/FEL] (solid lines) and recalculated in this review excluding solubility data in 5.0 M NaCl (dashed lines).




The combination of $\log_{10}K°$((A.485), 295.15 K) and $\log_{10}K°$((A.486), 295.15 K) with $\log_{10}K^{o}_{s,o}$ ($Na_2Np_2O_7$, cr) also determined in [2013GAO/FEL] results in:

$$NpO_2^{2+} + 3H_2O(l) \rightleftharpoons NpO_2(OH)_3^- + 3H^+ \qquad \text{(A.487)}$$

$$\log_{10}K°((A.487), 298.15\ K) = -(21.2 \pm 1.1)$$

$$NpO_2^{2+} + 4H_2O(l) \rightleftharpoons NpO_2(OH)_4^{2-} + 4H^+ \qquad \text{(A.488)}$$

$$\log_{10}K°((A.488), 298.15\ K) = -(32.0 \pm 1.1)$$

The large errors reported in [2013GAO/FEL] for $\log_{10}K°$((A.487), 298.15 K) and $\log_{10}K°$((A.488), 298.15 K) are due to the large uncertainty associated to $\log_{10}K^{o}_{s,o}$ ($Na_2Np_2O_7{\cdot}xH_2O$, cr). This review selects $\log_{10}K°$((A.487), 298.15 K) and $\log_{10}K°$((A.488), 298.15 K), but acknowledges the need of additional experimental studies to decrease the very large uncertainty associated to these equilibrium constants.

**[2013KON/BEN]**

[2013KON/BEN] estimated the contribution of oxygen Frenkel pair formation to the high temperature heat capacity of $NpO_2$(cr) by interpolation of the values for $ThO_2$(cr), $UO_2$(cr) and $PuO_2$(cr). The experimental enthalpy increment and heat capacity data for neptunium dioxide cover the temperature range up to 1770 K only [2013KON/BEN], so that there is no experimental evidence of a sudden increase in the heat capacity around 2000 K. However, such behaviour is expected by analogy with the $ThO_2$(cr), $UO_2$(cr) and $PuO_2$(cr) oxides [2014KON/BEN], which show an anomalous behaviour and significant increase in their heat capacity around the latter temperature due to the formation of oxygen Frenkel pair and its thermally induced disorder.

The excess contribution to the heat capacity due to Frenkel pair formation on the oxygen lattice can be expressed using the following expression (A.489):

$$C_{p,\mathrm{exc}} = (\Delta H_{OFP}^2/\sqrt{2RT^2})\exp(-\Delta H_{\mathrm{OFP}}/2RT)\exp(\Delta S_{\mathrm{OFP}}/2R) \quad \text{(A.489)}$$

where $\Delta H_{\mathrm{OFP}}$ and $\Delta S_{\mathrm{OFP}}$ are the enthalpy and entropy of oxygen Frenkel pair formation assumed to be independent of temperature, $R$ the universal gas constant and $T$ the temperature.

Based on the heat capacity data reported by [2014KON/BEN] for $ThO_2$(cr), $UO_2$(cr) and $PuO_2$(cr), and estimating the baseline contribution (sum as phonon, dilatation and electronic (Schottky) contributions) below 1800 K with a Maier-Kelly type polynomial $C_p = A + BT + CT^{-2}$ fitted to the enthalpy increment and heat capacity data, [2013KON/BEN] derived the excess heat capacity contributions for the series $ThO_2$(cr), $UO_2$(cr) and $PuO_2$(cr). The latter excess contributions were subsequently fitted to Equation (A.489) to derive the enthalpies and entropies of oxygen Frenkel pair formation for the series. The corresponding enthalpy values were found in good agreement with experimental neutron diffraction and oxygen diffusion experiments and *ab initio* calculations reported in the literature [2013KON/BEN].

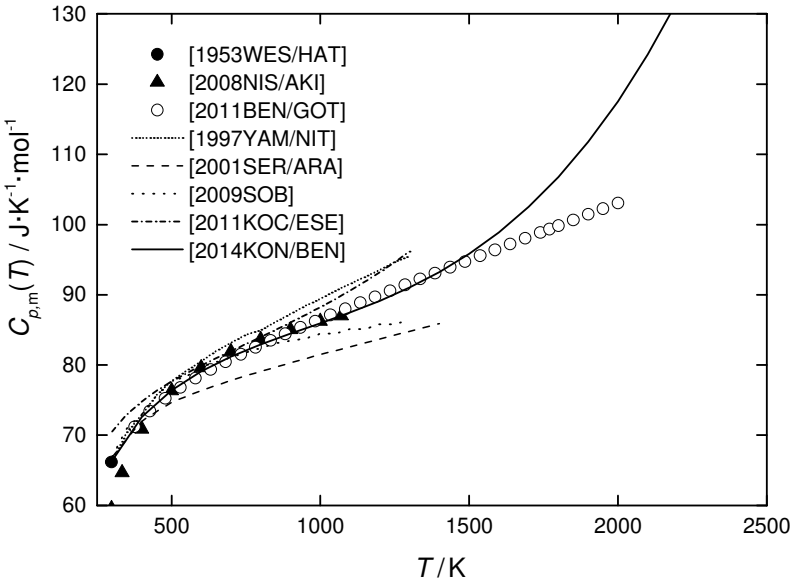
The values for $NpO_2$(cr) were thereafter estimated by interpolation of the values for the series $ThO_2$(cr), $UO_2$(cr) and $PuO_2$(cr) plotted as a function of the An-O (An = Th, U, Pu) atomic distances, yielding $\Delta H_{\mathrm{OFP}}(NpO_2, \mathrm{cr}) = 300\ \mathrm{kJ\cdot mol^{-1}}$ and $\Delta S_{\mathrm{OFP}}(NpO_2, \mathrm{cr}) = 66.6\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. The latter enthalpy value (3.1 eV) was found much lower than predicted by the DFT (4.5 eV) and molecular dynamics (5.8 eV) calculations of Tiwary *et al.* [2011TIW/VAN]. We note that the corresponding values would yield a very small excess contribution to the heat capacity, which is rather unlikely by analogy with the $ThO_2$(cr), $UO_2$(cr) and $PuO_2$(cr) systems. Various possible reasons for this discrepancy are listed by [2013KON/BEN].

Summing up the excess contribution and the lattice contribution derived from the experimental data by Nishi *et al.* [2008NIS/AKI] and Beneš *et al.* [2011BEN/GOT], [2013KON/BEN] finally derived the following function for the heat capacity of $NpO_2$(cr) up to its melting temperature:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{NpO_2},\mathrm{cr},T) = 64.7712 + 43.8574\times10^{-3}T - 35.0695\times10^{-6}T^2 + 13.1917\times10^{-9}T^3 - 7.8932\times10^{5}T^{-2} \quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

The latter equation is selected in this review.

Figure A- 21: Heat capacity *versus* temperature for $NpO_2$(cr).




**[2013LIN/APO]**

Lindqvist-Reis *et al.* investigated the complex formation of Np(VI) with nitrate in dilute to concentrated $HNO_3$ solutions using a combination of spectroscopic techniques (vis-NIR, IR, Raman, EXAFS) [2013LIN/APO]. This information was compared with the crystal structure of $NpO_2(NO_3)_2{\cdot}H_2O$(cr), also determined by the authors. Although no thermodynamic data is reported, the work provides insights on the formation of inner-sphere Np(VI)-$NO_3$ complexes, where $NpO_2NO_3^+$ becomes predominant only at $[HNO_3] \geq 4$ M, whereas $NpO_2(NO_3)_2$(aq) prevails only above $[HNO_3] \approx 7$ M. In contrast to U(VI), the formation of $NpO_2(NO_3)_3^-$ is not observed in the very concentrated nitrate conditions reached in this study ($[HNO_3] \leq 14$ M).

**[2013POM/TIW]**

See review in Chapter 15 (Appendix A, U).

**[2013SMI/COL]**

[2013SMI/COL] report the mass spectrometric study of the vaporisation behaviour of α-$Na_2NpO_4$ using Knudsen effusion cell mass spectrometry, and the derivation of its enthalpy of formation at 298.15 K. α-$Na_2NpO_4$ (orthorhombic in space group *Pbam*) was prepared from neptunium dioxide and sodium oxide mixed in stoichiometric amounts. The X-ray diffraction data did not show any secondary phase, while the ICPMS analysis yielded a sodium to neptunium ratio of (2.01 ± 0.04). The sample was placed in Knudsen cells made of tungsten and alumina, and heated up to $T = 2700$ K and $T = 1900$ K, respectively.

The measurement refers to the equilibrium Reaction (A.490) in the temperature range 1030-1115 K, in agreement with the high temperature X-ray diffraction studies of [2011SMI/RAI]:

$$Na_2NpO_4(cr) \rightleftharpoons NpO_2(cr) + Na_2O(cr) + 1/2O_2(g) \quad (A.490)$$

The enthalpy of formation of α-$Na_2NpO_4$ was derived at 298.15 K by second law analysis of the data as $\Delta_f H^\circ_m$ (α-$Na_2NpO_4$, cr, 298.15 K) = – (1761.0 ± 7.7) kJ·mol$^{-1}$, in very good agreement with the value obtained by Goudiakas *et al.* [1991GOU/JEM] using solution calorimetry, *i.e.*, – (1763.9 ± 7.0) kJ·mol$^{-1}$, which is also the value recommended in [1992GRE/FUG], [2003GUI/FAN].

[2015SMI] re-evaluated the mass spectrometric data of [2013SMI/COL] using the total ionisation cross section of $O_2$(g) determined experimentally in the studies of Straub *et al.* [1996STR/REN] rather than that obtained with the simple additivity rule of Otvos and Stevenson [1956OTV/STE]. [2015SMI] obtained – (1768.0 ± 7.3) kJ·mol$^{-1}$, in very good agreement with [1991GOU/JEM] and [2013SMI/COL]. This review agrees with the calculations of [2013SMI/COL] and [2015SMI] and the assigned uncertainties.

In the temperature range 1115 to 1206 K, the vaporisation of sodium oxide was identified next to the decomposition Reaction (A.490). The sublimation mechanism of sodium oxide is a subject of controversy in the literature. [2013SMI/COL] therefore suggested two possible equilibrium reactions based on the sodium oxide vaporisation mechanisms of Hildenbrand and Lau [1993HIL/LAU] (A.491) and Steinberg and Schofield [1991STE/SCH] (A.492), respectively:

$$Na_2NpO_4(cr) \rightleftharpoons NpO_2(cr) + 2Na(g) + O_2(g) \quad (A.491)$$

$$Na_2NpO_4(cr) \rightleftharpoons NpO_2(cr) + 3/2Na(g) + ½\ NaO_2(g) + 1/2\ O_2(g) \quad (A.492)$$

The enthalpy of formation of $Na_2NpO_4(cr)$ was again derived in this temperature range with a second analysis of the data as $-(1761.9 \pm 20.4)$ kJ·mol$^{-1}$ and $-(1758.8 \pm 22.6)$ kJ·mol$^{-1}$ for the Reactions (A.491) and (A.492), respectively. The vaporisation of $Na_2O(cr)$ is a complex process, and the assignment of one or the other mechanism is intricate. The studies of [1988MAL/CHA] describe the congruent vaporisation mechanism of $Na_2O(cr)$ as follows:

$$2Na_2O(cr) \rightleftharpoons 2Na(g) + ½\ O_2(g) + Na_2O(g) \qquad (A.493)$$

The calculation of [2015SMI] for the equilibrium Reaction (A.491) in this temperature region yielded $-(1765.9 \pm 16.6)$ kJ·mol$^{-1}$ when using the experimentally determined cross section of $O_2(g)$ [1996STR/REN] instead of the additivity rule of Otvos and Steveson [2013SMI/COL]. The present review agrees with the determinations of [2013SMI/COL] and [2015SMI], and assigned uncertainties.

The calculations of [2013SMI/COL] and [2015SMI] finally confirm the solution calorimetry results of Goudiakas *et al.* [1991GOU/JEM], [1992GRE/FUG], [2003GUI/FAN]. This review therefore retains the latter value:

$$\Delta_f H_m^o\ (\alpha\text{-}Na_2NpO_4, cr, 298.15\ K) = -(1763.8 \pm 5.7)\ kJ{\cdot}mol^{-1}.$$

**[2013VER/PAT]**

Verma *et al.* [2013VER/PAT] investigated cation-cation interactions between $NpO_2^+$ and $UO_2^{2+}$ by means of vis/NIR measurements at 283 K ≤ $T$ ≤ 343 K. Most of the experiments were performed in 4.0 M $HNO_3$ with $1 \times 10^{-4}$ M ≤ [U(VI)] ≤ 1.2 M. A relevant shortcoming in the experimental approach by Verma and co-workers arises from the significant variation of ionic strength (4.0 M to 7.6 M) and nitrate concentration (4.0 M to 6.4 M) in the course of their titrations with U(VI). The authors observed the decrease of the $NpO_2^+$ absorption peak at 980 nm and corresponding increase of the peak at 992 nm, attributed to the $NpO_2^+ \cdot UO_2^{2+}$ complex. At elevated temperatures, a further peak at ~ 964 nm indicated a very significant contribution of Np(IV). Disproportionation of Np(V) to Np(IV) and Np(VI) can occur in concentrated $HNO_3$ solutions, especially at elevated temperatures. Unfortunately, vis/NIR measurements by the authors were limited to < 1100 nm, and thus the possible presence of Np(VI) could neither be confirmed nor disregarded. Based on their spectroscopic data, the authors derived conditional equilibrium constants for the formation of the $NpO_2^+ \cdot UO_2^{2+}$ complex at 283 K ≤ $T$ ≤ 343 K with $I$ = 5.5 and 6.55 M. The Van't Hoff equation was used to accordingly calculate $\Delta_r H_m^{'}$. In contrast to [2012XIA/TIA], Verma *et al.* reported an endothermic enthalpy for the formation of $NpO_2^+ \cdot UO_2^{2+}$ and a strong dependency of $\Delta_r H_m^{'}$ with ionic strength. This review finds a flaw in the data interpretation by the authors, where the Van't Hoff plots shown in Figure 4 of the paper are attributed to [U(VI)] = 0.5 and 0.85 M systems in 4.0 M $HNO_3$ (corresponding to $I$ = 5.5 and 6.55 M, respectively). It seems clear that for the determination of $\log_{10}K'$ at different $T$, the authors

must have performed titrations with increasing [U(VI)] as shown in Figure 2 of the paper. Due to the relevant shortcomings in the experimental approach and data interpretation, this review disregards any selection of thermodynamic data from [2013VER/PAT].

**[2014CHA/FED]**

A mixed-valent Np(IV)/(V) solid state compound, $[Np(NpO_2)_6(H_2O)_8(OH)Cl_9]\cdot H_2O$(cr), is reported that contains chloride ligands bound to Np(V) in the equatorial coordination sphere of pentagonal bipyramidal polyhedra.

**[2015SMI]**

In her PhD thesis, Smith [2015SMI] reported the structural and thermodynamic investigations of the Na-Np-O and Na-Pu-O systems. Most of the data were published in separate articles [2015SMI/RAI], [2015SMI/HEN], [2015SMI/HEN2]. In addition, [2015SMI] measured the low temperature heat capacity of $Na_5NpO_6$(cr) and $Na_5PuO_6$(cr). The review of those measurements is reported in the Appendix A for uranium.

**[2015SMI/GRI]**

The low temperature heat capacity of $Na_4UO_5$(cr) and $Na_4NpO_5$(cr) were measured for the first time over the temperature range 1.9 to 292 K using thermal relaxation calorimetry. The complete review of this article is reported in the Appendix A for uranium.

**[2015SMI/GRI2]**

The low temperature heat capacity of α-$Na_2NpO_4$ was measured for the first time over the temperature range 2.1 to 301 K using thermal relaxation calorimetry. α-$Na_2NpO_4$ was prepared from neptunium dioxide and sodium oxide mixed in stoichiometric amounts. The X-ray diffraction data did not show any secondary phase, while the ICPMS analysis revealed a sodium to neptunium ratio of (2.01 ± 0.04). The corresponding mass fraction purity was estimated as > 0.99.

The authors derived the following thermodynamic functions at 298.15 K by fitting their data with an harmonic model in the range $T$ = (3.7 to 6.0) K, a series of cubic spline polynomials in the range $T$ = (6.0 to 14.6) K, and polynomial functions above the latter temperature:

$$C^{o}_{p,m}\,(\alpha\text{-}Na_2NpO_4, \text{cr}, 298.15\ \text{K}) = (151.9 \pm 4.6)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S^{o}_{m}\,(\alpha\text{-}Na_2NpO_4, \text{cr}, 298.15\ \text{K}) = (178.3 \pm 4.3)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

We agree with their determination and assigned uncertainties. The standard entropy value of α-$Na_2NpO_4$ was moreover found to be in good agreement with the trend shown by the isostructural compound α-$Na_2UO_4$ and the alkaline-earth uranates $MgUO_4$(cr), $SrUO_4$(cr), $BaUO_4$(cr), and $Cs_2UO_4$(cr).

Using the auxiliary data recommended in [2003GUI/FAN], [2015SMI/GRI2] derived the Gibbs energy of formation at 298.15 K as:

$$\Delta_f G^o_m (\alpha\text{-}Na_2NpO_4, \text{cr}, 298.15\ \text{K}) = -(1648.993 \pm 5.848)\ \text{kJ}\cdot\text{mol}^{-1}.$$

The present review agrees with this number. Comparing the latter value with that reported for the isostructural uranium compound, the sodium neptunate was found to be slightly more stable than the sodium uranate.

Interestingly, α-$Na_2NpO_4$ revealed a lambda type anomaly at 12.5 K, which was moreover found to be shifted to slightly lower temperatures when a magnetic field was applied. The interpretation of this feature and derivation of its associated entropy contribution is described in [2015SMI/HEN2].

**[2015SMI/HEN]**

[2015SMI/RAI] reported the synthesis and structural refinement of the sodium neptunates $Na_4NpO_5$(cr) and $Na_5NpO_6$(cr) phases based on X-ray diffraction data. $Na_4NpO_5$(cr) crystallises with tetragonal symmetry in space group *I4/m*, while $Na_5NpO_6$(cr) adopts a monoclinic symmetry in space group *C2/m*. The valence states of neptunium in those compounds, *i.e.*, Np(VI) and Np(VII) were moreover confirmed from the isomer shift values of their Mössbauer spectra. Magnetic susceptibility measurements performed on $Na_4NpO_5$(cr) from $T$ = (3 to 301 K) in a field of B = 1 T confirmed the absence of magnetic ordering. Low temperature heat capacity measurements performed on this phase using the thermal relaxation technique revealed a broad anomaly between 3 and 15 K, which was shifted to lower temperatures when a field was applied. This feature was interpreted as a Schottky-type anomaly associated with two low lying electronic states with the same degeneracy and separated by 14 $cm^{-1}$. The electronic excess entropy was derived as 4.57 $J\cdot K^{-1}\cdot mol^{-1}$ after substraction of the lattice contribution approximated with that of isostructural $Na_4UO_5$(cr). No thermodynamic data for $Na_4NpO_5$(cr) and $Na_5NpO_6$(cr) are reported in this work.

**[2015SMI/HEN2]**

[2015SMI/HEN2] investigated the physical and chemical properties at low temperatures of α-$Na_2NpO_4$ using Mössbauer spectroscopy, magnetisation, magnetic susceptibility, and low temperature heat capacity measurements. The hexavalent state of neptunium, and therefore chemical composition, was confirmed from the isomer shift values of the

Mössbauer spectra. The low temperature heat capacity measurements revealed the existence of a sharp λ-peak at 12.5 K, which was found to shift to lower temperatures with the application of a magnetic field, suggesting antiferromagnetic ordering. However, the magnetisation and magnetic susceptibility measurements did not reveal any anomaly, which shows that the interpretation is more intricate. The heat capacity measurements moreover revealed the existence of a Schottky type anomaly above 15 K associated with a low-lying electronic doublet about 60 $cm^{-1}$ above the ground state doublet. The electronic excess entropy was estimated at 1.1 $J \cdot K^{-1} \cdot mol^{-1}$ for the λ-peak and 5.5 $J \cdot K^{-1} \cdot mol^{-1}$ for the Schottky anomaly after subtraction of the lattice contribution approximated with that of $Na_2UO_4$(cr). No thermodynamic data are reported for α-$Na_2NpO_4$ in this work.

**[2015SMI/RAI]**

Smith *et al.* [2015SMI/RAI] reported for the first time the synthesis and structural characterization of α-$Na_3NpO_4$ and α-$Na_3PuO_4$ using X-ray diffraction and $^{237}Np$ Mössbauer spectroscopy. α-$Na_3NpO_4$ and α-$Na_3PuO_4$ were synthesized by the solid state route using sodium carbonate or sodium oxide, and neptunium oxide or plutonium oxide starting materials. The structures were solved *ab initio* as no structural analogues could be found in the literature. The compounds adopt an orthorhombic structure in space group Fmmm with cell parameters $a$ = 13.352(2) Å, $b$ = 9.629(2) Å, and $c$ = 6.673(2) Å for the neptunium compound, and $a$ = 13.302(2) Å, $b$ = 9.634(2) Å, and $c$ = 6.651(2) Å for the plutonium compound. In addition, the pentavalent state of neptunium, and therefore chemical composition, was confirmed from the isomer shift values of the $^{237}Np$ Mössbauer spectroscopy measurements. The existence of a low temperature ($T$ < 873 K) metastable phase, of the NaCl type and completely disordered, was also suggested for these compounds, which transforms to the equilibrium α-phases upon heating above 1093 K. No thermodynamic data were reported for those phases.

**[2016FEL/ALT]**

This paper is the follow-up to the experimental description in [2016FEL/ROT] discussing the experimental data used to obtain thermodynamic data that describe the Np(V) solubility behaviour. The authors applied the SIT and the Pitzer approach to derive thermodynamic constants from the experimental data. Ion-interaction coefficients ($\varepsilon(NpO_2^+, Cl^-)$ = (0.09 ± 0.05) $kg \cdot mol^{-1}$, $\varepsilon(Ca^{2+}, Cl^-)$ and $\varepsilon(H^+, Cl^-)$) and stability constants for the established Np(V) hydroxo species $NpO_2OH(aq)$ and $NpO_2(OH)_2^-$, $\log_{10}\beta^o_{1,1}$ = – (11.3 ± 0.7) and $\log_{10}\beta^o_{1,2}$ = – (23.6 ± 0.5), were taken from the NEA TDB.

In the solubility studies reported in [2016FEL/ROT] new solid phases and solution species of Np(V) in $CaCl_2$ solutions were identified and characterised. At $pH_m \leq$ 10.5, $NpO_2^+$ and at $CaCl_2$ > 2 M inner-sphere Np(V) chloro complexes $NpO_2Cl(aq)$ and

$Ca[NpO_2Cl]^{2+}$, are the governing solution species. For the description of the solubility behaviour only the $NpO_2Cl(aq)$ complex was included in the chemical reactions. With increasing pH the solubility data at $pH_m > 10.5$ are best modelled with two Np(V) hydrolysis products, $Ca_xNpO_2(OH)_2^{2x-1}$ and $Ca_xNpO_2(OH)_5^{2x-4}$. The use of Ca-free solution species, such as $NpO_2(OH)_2^-$, and associated formation constants accepted by the NEA TDB could not describe the experimental data. In fact, the fraction of $NpO_2(OH)_2^-$ is less than 5 % for $[CaCl_2] > 0.1$ M. The fraction of $Ca^{2+}$ in the ternary hydrolysis species is estimated from SIT calculations based on a set of criteria. The authors derived the best fit considering estimated of chloride interaction parameters solely based on the cation charge as described in [2009HUM], no inflection point in the relation between $\log_{10}\beta'$ and $\log_{10}\beta°$, minimisation of experimental and modelled data, and agreement of the calculated formula of $Ca_xNpO_2(OH)_5^{2x-4}$ with data from EXAFS experiments that bracketed the value of $x = (2.4 \pm 1.5)$. Stability constants and SIT ion interaction parameters were calculated for $Ca_xNpO_2(OH)_2^{2x-1}$ complexes with x = 0-4 and $Ca_xNpO_2(OH)_5^{2x-4}$ complexes with $x = 0$-5. The formula with the lowest difference between SIT calculated and experimental stability constants are $Ca[NpO_2(OH)_2]^+$ and $Ca_3[NpO_2(OH)_5]^{2+}$. The experimental formation constants were reported at 0.25 M, 1.0 M and 2.0 M $CaCl_2$ according to the reactions:

$$NpO_2^+ + Ca^{2+} + 2H_2O(l) \rightleftharpoons Ca[NpO_2(OH)_2]^+ + 2H^+ \quad \text{(A.494)}$$

$$NpO_2^+ + 3Ca^{2+} + 5H_2O(l) \rightleftharpoons Ca_3[NpO_2(OH)_5]^{2+} + 5H^+ \quad \text{(A.495)}$$

The associated ion-interaction parameters for these new ternary Np(V) complexes are $\varepsilon(Ca[NpO_2(OH)_2]^+, Cl^-) = -(0.07 \pm 0.08)$ kg·mol$^{-1}$ and $\varepsilon(Ca_3[NpO_2(OH)_5]^{2+}, Cl^-) = -(0.20 \pm 0.11)$ kg·mol$^{-1}$.

While the authors are characterising the solid phases very well using different techniques, they do not provide experimental solubility products for each phase. However, they provide the thermodynamic solubility products for the three phases calculated by using the SIT and the Pitzer formalism according to the reactions:

$$CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O(cr) + 2.6H^+ \rightleftharpoons NpO_2^+ + Ca^{2+} + 4.6H_2O(l) + 0.4Cl^- \quad \text{(A.496)}$$

$$Ca_{0.5}NpO_2(OH)_2\cdot 1.3H_2O(cr) + 2H^+ \rightleftharpoons NpO_2^+ + 0.5Ca^{2+} + 4.6H_2O(l) \quad \text{(A.497)}$$

$$Ca_{0.5}NpO_2(OH)_2(cr) + 2H^+ \rightleftharpoons NpO_2^+ + 0.5Ca^{2+} + 2H_2O(l) \quad \text{(A.498)}$$

The results for $CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O(cr)$ ($\log_{10}K^o_{s,o} = (19.90 \pm 0.10)$ by SIT and $\log_{10}K^o_{s,o} = (19.89 \pm 0.15)$ by Pitzer) and for $Ca_{0.5}NpO_2(OH)_2\cdot 1.3H_2O(cr)$ ($\log_{10}K^o_{s,o} = (12.30 \pm 0.07)$ by SIT and $\log_{10}K^o_{s,o} = (12.26 \pm 0.10)$ by Pitzer) agree very well with each other. It is to note that the authors could calculate the apparent solubility product and hydrolysis constants only for $Ca_{0.5}NpO_2(OH)_2\cdot 1.3H_2O(cr)$. The solubility data of $CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O(cr)$ are limited to $pH_m > 10.8$ and thus cannot be used to calculate the solubility product independent of hydrolysis reactions in solution. For the calculation of the solubility product of $CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O(cr)$, the formation

constants of the Np(V) solution complexes obtained with $Ca_{0.5}NpO_2(OH)_2 \cdot 1.3H_2O$(cr) were used. The thermodynamic solubility product of $Ca_{0.5}NpO_2(OH)_2$(cr) formed in 4.5 M $CaCl_2$, $\log_{10} K^{\circ}_{s,o} = (12.26 \pm 0.10)$, is determined with the Pitzer formalism only since the electrolyte concentration of 4.5 M $CaCl_2$ is well outside the applicability range of the SIT.

**[2016FEL/ROT]**

Fellhauer *et al.* continued previous studies [2010FEL/NEC] on the solubility behaviour of actinides in $CaCl_2$ solutions. This paper is the first part of a solubility study of Np(V) in $CaCl_2$ solutions describing the experimental methods and results. The follow-on paper [2016FEL/ALT] describes the data analysis and development of thermodynamic data to describe the Np(V) solubility and complexation behaviour.

The authors investigate the solubility of Np(V) in $CaCl_2$ solutions from both under- and oversaturation at (23 ± 2) °C. For the batch experiments from undersaturation two Np solid phases, $CaNpO_2(OH)_{2.6}Cl_{0.4} \cdot 2H_2O$(cr) and $Ca_{0.5}NpO_2(OH)_2 \cdot 1.3H_2O$(cr), were equilibrated in 0.25 M, 1.0 M, 2.0 M, 3.5 M, 4.5 M and 5.5 M $CaCl_2$ solutions with the $pH_m$ pre-adjusted to between 8 and 12. Several measurements of $pH_m$ and [Np] were taken within several weeks to months. For the oversaturation experiments, Np(V) stock solution was added to $pH_m$-adjusted 0.25 M, 1.0 M and 4.5 M $CaCl_2$ solutions. After measuring the $pH_m$ and [Np] within 60 days of sample preparation, the samples were stored for 41-44 months. Sample preparation and storage was conducted under argon atmosphere. The $pH_m$ was measured with a conventional pH glass electrode and the empirical factor to convert measured $pH_{exp}$ values into $pH_m$ was determined for the different $CaCl_2$ concentrations. The Np concentration was measured after ultrafiltration with 10 kD filters by using liquid scintillation counting with α/β-discrimination. Electronic absorption spectra were collected in the range 250-1350 nm. The fraction of hydrolysed Np(V) in solution was determined spectroscopically after acidification of the alkaline sample solutions with HCl.

The authors characterised the solid equilibrium phases formed in the experiments from undersaturation, but did not characterise the solid phases formed from oversaturation. Three solid phases were observed to form in the $CaCl_2$ solutions. In 2 M $CaCl_2$ at $pH_m = 11.6$, the initial green $NpO_2OH$(am, hyd) solid phase converted to the greyish phase $CaNpO_2(OH)_{2.6}Cl_{0.4} \cdot 2H_2O$(cr). The solid phase transformation occurred within a few weeks indicated by colour changes and decrease of the soluble Np(V) concentration. The transformation of $CaNpO_2(OH)_{2.6}Cl_{0.4} \cdot 2H_2O$(cr) into a reddish phase, $Ca_{0.5}NpO_2(OH)_2 \cdot 1.3H_2O$(cr), was observed during the solubility experiments at $CaCl_2 <$ 2.0 M and $pH_m = 8.5$-9.5. At lower $pH_m$ values, this solid is expected to convert into $NpO_2OH$(am, hyd) or completely dissolved. In the concentrated $CaCl_2$ (4.5 M) solution at $pH_m$ 11.6, the quantitative formation of a second reddish phase, $Ca_{0.5}NpO_2(OH)_2$(cr), was observed. The solids formed in the undersaturation experiments were characterised

by using X-ray diffraction, thermogravimetric analysis, SEM-EDX, EXAFS, and chemical analysis to determine the Ca:Np ratio. It is to note that the authors combined solid phases from several batches to determine the water content with TGA. The powders are washed with ethanol and stored in a desiccator under argon for some days. The combination of samples introduces uncertainties about the exact water content in each solid phase at different $pH_m$ values.

The solubility data exhibit the typical U-shaped behaviour as observed for other Np(V) solid phases. A decrease in soluble Np concentrations at $pH_m < 10.5$ indicate the presence of $NpO_2^+$ in solution; while increasing Np concentrations at $pH_m > 11.5$ suggest the formation of Np(V) hydroxo species. Slope analysis of the solubility data and some EXAFS studies were used to investigate the Np(V) solution speciation. However, slope analysis is limited the ability to derive the composition of the solution species since different combinations of solid phase and solution species could result in the same slope. At $pH_m > 11.5$, the ternary complex $Ca_xNpO_2(OH)_5^{2x-4}$ was proposed as the limiting Np(V) hydrolysis species in alkaline $CaCl_2$ solution. In less alkaline solutions with $pH_m < 10.5$ and $[CaCl_2] > 2M$, inner-sphere chloro complexes, $NpO_2Cl(aq)$ and $Ca[NpO_2Cl]^{2+}$, were identified by using EXAFS spectroscopy.

The authors provide a compilation of experimental data obtained in the solubility studies from undersaturation, including the $pH_m$ and Np concentrations at the different $CaCl_2$ concentrations investigated in this study. The data listed for $CaNpO_2(OH)_{2.6}Cl_{0.4}\cdot 2H_2O(cr)$ at the $CaCl_2$ concentrations applicable for the SIT (0.25 M, 1.0 M and 2.0 M) are all at $pH_m > 10.5$. At these experimental conditions, hydrolysis reactions of Np(V) occurs. Similarly, solubility data for $Ca_{0.5}NpO_2(OH)_2(cr)$ are at $pH_m > 11.3$. The solubility products of these two solid phases cannot be derived from these data and are correlated to the hydrolysis constants used for the Np(V) hydroxo species that are present in solution.

No thermodynamic data for the solid phases and solution species are reported in this study.

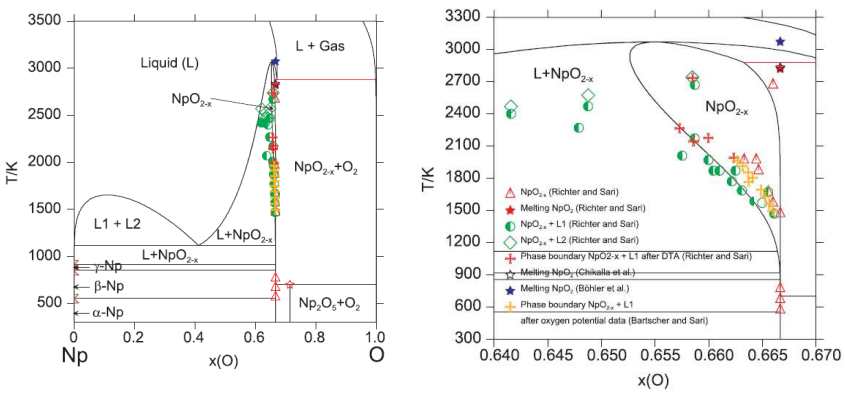
**[2016SMI/COL]**

[2016SMI/COL] reported Knudsen effusion mass spectrometric studies of the vaporisation behaviour of neptunium dioxide and a thermodynamic model of the Np-O system using the CALPHAD method. The authors performed Knudsen effusion studies both under vacuum and under oxygen flow to estimate the composition of neptunium dioxide at congruent vaporisation, and the sublimation enthalpy of $NpO_2(cr)$, respectively. The authors carefully controlled the applied oxygen pressure in the Knudsen cell to ensure that Knudsen conditions were satisfied while maintaining the composition of the sample as close as possible from the stoichiometric O/Np = 2 phase boundary. The results obtained for the sublimation reaction $NpO_2(cr) = NpO_2(g)$ by second law, *i.e.*

$\Delta_{sub}H^{o}_{m}$ ($NpO_2$, cr, 298.15 K) = (606.9 ± 1.9) kJ·mol$^{-1}$ and $\Delta_{sub}H^{o}_{m}$ ($NpO_2$, cr, 298.15 K) = (606.7 ± 0.2) kJ·mol$^{-1}$ were found in very good agreement. The average value, *i.e.*, $\Delta_{sub}H^{o}_{m}$ ($NpO_2$, cr, 298.15 K) = (606.8 ± 1.9) kJ·mol$^{-1}$ is accepted in this review. This is about 15 kJ·mol$^{-1}$ lower than the value selected in the review by [2014KON/BEN] based on the results of Ackerman *et al.* [1966ACK/FAI] obtained under vacuum on ~ 300 mg of sample. The latter data refer to a slightly hypostoichiometric composition and accordingly we prefer to retain the results of [2016SMI/COL] obtained under oxygen flow.

Smith *et al.* moreover reported a thermodynamic model for the Np-O system using the CALPHAD method [2016SMI/COL]. They used the compound energy formalism with ionic constituents to describe the non-stoichiometric $NpO_{2-x}$(cr) phase, and the ionic two-sublattice model for the liquid phase. Their model, shown in Figure A-22, reproduces the main features as suggested by Richter and Sari [1987RIC/SAR], in particular the boundary between the single phase region $NpO_{2-x}$(cr) and the two-phases region {$NpO_{2-x}$(cr) + Np(l)}, as well as the oxygen potential data of [1986BAR/SAR]. The melting temperature of neptunium dioxide is calculated at $T_{fus}$($NpO_2$, cr) = 3069.5 K, in good agreement with the value recommended in this review [2012BOH/WEL]. In this model, the temperature of the monotectic reaction is calculated at 1117 K, whereas Richter and Sari suggested it to be around 2450 K [1987RIC/SAR]. [2016SMI/COL] showed that the three data-sets, namely miscibility gap, oxygen potential data and limit of the hypostoichiometric $NpO_{2-x}$(cr) domain were conflicting, as also exemplified by the results of Kinoshita *et al.* [2003KIN/SET]. The authors argued that the oxygen potential and $NpO_{2-x}$(cr) phase boundary data were most probably reliable based on the comparison with the U-O and Pu-O systems [2016SMI/COL]. As there is no experimental evidence for the existence of a miscibility gap in the Np-O system up to date, the authors suggested that complementary investigations of the liquidus line and temperature of the monotectic reaction were highly desirable.

Figure A-22: Np-O phase diagram calculated by [2016SMI/COL] and comparison with experimental data. Figure reproduced from [2016SMI/COL]. (Reprinted with permission from *J. Chem. Thermodyn.*, **2016**, *103*, 257. Copyright (2016) Elsevier).



The thermodynamic data optimised in their work are shown in Table A-172. The agreement with our selected data is good, except for the standard entropy of $Np_2O_5$(cr).

Table A-172: Optimised thermodynamic data in the work of [2016SMI/COL] and comparison with the selected experimental data.

| Phase | $\Delta_f H_m^\circ$ (298.15 K) /kJ·mol$^{-1}$ | $S_m^\circ$ (298.15 K)/J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|
| $NpO_2$(cr) | – 1076.8 | 80.3 | [2016SMI/COL] |
| | – (1074.0 ± 2.5) | (80.3 ± 0.4) | [2003GUI/FAN] |
| $Np_2O_5$(cr) | – 2172 | 242.4 | [2016SMI/COL] |
| | – (2162.7 ± 9.5) | (174 ± 20) | [2003GUI/FAN] |

The adjustment to the high value $S_m^\circ$ ($Np_2O_5$, cr, 298.15 K) = 242.4 J·K$^{-1}$·mol$^{-1}$ appeared necessary to satisfy the decomposition temperature around 700 K for this compound. The recommended entropy value by Merli and Fuger [1994MER/FUG] (186 ± 15) J·K$^{-1}$·mol$^{-1}$gave a decomposition temperature around 236 K. This inconsistency shows that one of the values of the thermodynamic functions for $NpO_2$(cr), $Np_2O_5$(cr) or $O_2$(g) must be ill-defined since the latter define the equilibrium decomposition temperature for the reaction:

$$Np_2O_5(cr) \rightleftharpoons NpO_2(cr) + O_2(g)$$

The ill-defined functions are most probably the standard entropy for $Np_2O_5$(cr) (never measured experimentally) or the decomposition temperature, which both need to be re-assessed.

**[2017PET/FEL]**

Petrov *et al.* characterised the solid Np(V) hydroxide phases formed in NaCl solution at (22 ± 2) °C by using XRD, SEM-EDS and EXAFS. Green $^{237}NpO_2OH$(am) was precipitated from NaOH solutions at pH 11.5 and about 2 mg of the solid was contacted with 0.1, 1.0, 3.0 and 5.0 M NaCl solutions at different pH. The samples were equilibrated for up to two years, while a few samples in 5 M NaCl were equilibrated for about six years. The pH and soluble Np concentrations were measured after ultrafiltration through 10 kD using liquid scintillation counting. The pH was calibrated against standard pH buffers and corrected by an empirical factor to account for the liquid junction potential at the different NaCl concentrations. The solution speciation in some samples at $-\log_{10}[H^+] \leq 10.3$ was analysed by using UV-vis-NIR absorbance spectroscopy.

At low NaCl concentrations, the greenish $NpO_2OH$(am) phase matches the solubility data previously reported in the literature. The ageing of this green solid and lower Np solubility at higher NaCl concentrations as reported in previous solubility studies was not observed. A solid phase transformation occurs in the alkaline range of

≥ 1 M NaCl solutions. A lower Np solubility is associated with the formation of a white solid phase at pH ≥ 11.5 and two pink phases at pH ~ 13.2. While the green phase shows a low Na:Np ratio below 0.3, the Na:Np ratio of the white and pink phases range between 0.6 and 1.6. The average ratio in the pink phase is (0.9 ± 0.2) and most likely represents $NaNpO_2(OH)_2$(cr). The large variations in the Na:Np ratio (0.6-1.6) do not allow the assignment of a specific solid phase.

The solution speciation was investigated at pH ≤ 10.3 by absorption spectroscopy and compared to the spectra after acidification of the solution sample. All spectra investigated in this pH range exhibited the main absorbance peak at 980.2 nm, which is characteristic for the Np(V) aquo ion in non-complexing acidic solutions. With increasing $Cl^-$ concentrations, the peak maximum shifts to 981.0 nm and the molar extinction coefficients decreases from 384 $L \cdot mol^{-1} \cdot cm^{-1}$ to 358 $L \cdot mol^{-1} \cdot cm^{-1}$. These changes are explained with small fractions of Np(V) chloro and/or hydroxo complexes estimated to be below 5 %. These spectroscopic observations are of great importance due to the controversial debate on the Np(V) solution speciation at pH ≤ 10. The predominance of $NpO_2^+$ at the pH range investigated in this study is in stark contrast to the claim by Rao et al. [2004RAO/SRI] that hydrolysis of Np(V) already takes place as interpreted from calorimetric and potentiometric data. The observations reported by Petrov *et al.* are in agreement with the interpretation of previously reported Np(V) solubility studies and the Np(V) hydrolysis reactions selected in the NEA TDB.

# Discussion of selected references for Plutonium

**[1998BER/VEI]**

The complexation of Pu(IV) with nitrate is investigated spectroscopically in solutions with an ionic strength up to 19 m at (20 ± 3) °C. Spectrophotometric titrations were performed of solutions by varying $HNO_3/HClO_4$ concentration ratios at a constant ionic strength. It is to note that the Pu(IV) stock solution used to prepare the sample solutions was 2.3 M in $HNO_3$ and therefore even the solutions with nominal 0 m nitrate contained a small amount of $HNO_3$. Electronic absorbances of the solutions were recorded at 400-900 nm. To minimise the dilution of the Pu(IV) during each titration, the spectra were normalised to 1 M Pu(IV) prior to data analysis. The data fitting routine used by the authors modeled the single component spectra of $Pu^{4+}$, $PuNO_3^{3+}$, and $Pu(NO_3)_2^{2+}$ and calculated associated equilibrium constants according to the Reactions (A.499) and (A.500):

$$Pu^{4+} + NO_3^- \rightleftharpoons PuNO_3^{3+} \quad \text{(A.499)}$$

$$Pu^{4+} + 2NO_3^- \rightleftharpoons Pu(NO_3)_2^{2+} \quad \text{(A.500)}$$

The equilibrium constants for (A.499) and (A.500) are calculated based on the total nitrate concentrations as well as the available free nitrate ions calculated from the dissociation degree of $HNO_3$. The impact of the nitric acid dissociation was most visible at high ionic strengths. The SIT was applied to correct to zero ionic strength over the entire range of ionic strengths investigated, $I$ = 2-19 m.

The electronic absorbance spectrum of $Pu^{4+}$ is characterised by absorbances at about 407 nm and 424 nm and its most intense absorbance at 469 nm with a shoulder at 474 nm. The latter is generally used to assess the complexation of Pu(IV) in aqueous solutions. The titrations in this study clearly show the characteristic band for the $Pu^{4+}$(aq) ion at about 469 nm to become less intense while the shoulder at 474 nm becomes more prominent with increasing nitrate concentrations. The authors deconvoluted the absorbance spectra at 2 m $HNO_3$ to obtain the single component spectra of $Pu^{4+}$ ion, $PuNO_3^{3+}$ and $Pu(NO_3)_2^{2+}$. It is to note, that the fitting procedure did not use the established spectrum of $Pu^{4+}$(aq) as a baseline, but was also included in the fitting process. The SIT was applied to correct the empirical data for ionic strength. The common SIT plot of the experimental formation constants corrected for $HNO_3$ dissociation, $\log_{10}\beta_{1,n} - \Delta z^2 D$ *versus* $I_m$, shows a linear relationship up to 19 m.

The authors report the best fitting parameters as $\log_{10}\beta^{o}_{1,1} = (2.12 \pm 0.20)$ and $\Delta\varepsilon_{ij} = (0.17 \pm 0.02)$ for $PuNO_3^{3+}$ and $\log_{10}\beta^{o}_{1,2} = (3.66 \pm 0.40)$ and $\Delta\varepsilon_{ij} = (0.36 \pm 0.03)$ for $Pu(NO_3)_2^{2+}$.

The interpretation of the spectrophotometric data and the determination of thermodynamic constants in this work are associated with several problems. The spectra deconvolution would have been benefitted from a Pu(IV) standard spectrum in $HClO_4$ as a baseline spectrum at each ionic strength to reduce the large numbers of fitting parameters. In the absence of more detailed discussion on the fitting procedure and more absorbance spectra available, conclusions have to be drawn from the figures presented in this paper. In Figure 1, the authors provide a subset of the Pu(IV) absorbance spectra at $I = 2$ m for varying nitrate concentrations. Multiple isosbestic points are visible, which indicate the presence of only two solution species under these conditions. Interpreting these spectra with three solution species causes erroneous single component spectra and complex formation constants. Consequently, splitting the complexation of Pu(IV) into two steps at $I = 2$ m resulted in an underestimated formation constant for the $PuNO_3^{3+}$ complex. The deconvoluted single-component spectra for $PuNO_3^{3+}$ and $Pu(NO_3)_2^{2+}$, depicted in Figure 2 in this report, are suspiciously very similar in the region 460-500 nm, however, the authors do not address the results of the spectra deconvolution analysis. Since the concentration ratios for $HNO_3/HClO_4$ are not provided, it is unclear how much perchlorate is replaced by nitrate, which is important for the determination of the ion-interaction parameters. The vast majority of the thermodynamic data and ion-interaction parameters were obtained at $I \geq 5$ m, outside the validity range of the SIT. Therefore, the data for $\log_{10}\beta^{o}_{1,n}$ and $\Delta\varepsilon_{ij}$ reported in this study cannot be recommended by this review.

**[2002FUJ/YAM]**

The solubility of $PuO_2{\cdot}xH_2O$(s) was measured at (25 ± 1) °C in the presence of $NaS_2O_4$ to maintain reducing conditions. The solubility was determined from oversaturation at $I = 1.0$ M and from undersaturation at $I = 0.5$, 1.0 and 2.0 M with samples allowed to age up to about six months, with samples at $I = 1.0$ M aged for over 350 days. The pH was measured by using the electrochemical cell I M $NaClO_4$/0.9 M $NaClO_4$, 0.1 M NaCl/AgCl, Ag. The soluble Pu concentration was determined by using α-spectrometry and UV-vis-NIR absorption spectrophotometry. The solid phase was not characterised but assumed to be Pu(IV) hydrous oxide based on its "olive-green colour".

In the experiments from oversaturation, the Pu concentrations decreased with equilibration time. From undersaturation the Pu concentrations increase within the first month. Steady state concentrations are claimed to be established after two to three months. The authors consider the soluble Pu concentrations measured after two months contact time as the equilibrium concentrations and are used to calculate thermodynamic data. The absorption spectra of solutions below pH 6 exhibit features in the range

550-670 nm that are characteristic of Pu(III). At pH > 6, no spectral features were observed because of the low concentrations of soluble Pu.

The spectroscopic data showed Pu(III) to be dominant in solution over a assumed Pu(IV) solid equilibrium phase. The solubility data were interpreted with the dissolution equilibrium:

$$PuO_2 \cdot xH_2O(s) + e^- \rightleftharpoons Pu^{3+} + 4OH^- + (x-2)H_2O(l) \quad \text{(A.501)}$$

The authors considered the contribution of $Pu^{4+}$ according to Equation (A.502) to derive the dissolution equilibrium (A.503):

$$Pu^{3+} \rightleftharpoons Pu^{4+} + e^- \quad \text{(A.502)}$$

$$PuO_2 \cdot xH_2O(s) \rightleftharpoons Pu^{4+} + 4OH^- + (x-2)H_2O(l) \quad \text{(A.503)}$$

Fujiwara *et al.* used the standard potential for the Pu(IV)/(III) redox couple reported by Capdevila and Vitorge [1998CAP/VIT] to calculate $\log_{10}K_{III,IV}$(A.502). The apparent equilibrium constants of $\log_{10}K_{s,IV}$(A.503) were then calculated by combining the calculated data of $\log_{10}K_{s,IV,III}$(A.501) and $\log_{10}K_{III,IV}$(A.502). The thermodynamic equilibrium constant $\log_{10}K^{o}_{s,IV}$ (A.503) was determined from the SIT plot with the fitted values $\log_{10}K^{o}_{s,IV}$ (A.503) = – (57.97 ± 0.24) and $\varepsilon(Pu^{4+}, ClO_4^-)$ = (0.99 ± 0.20) kg·mol$^{-1}$. These data are in good agreement with published data and the thermodynamic data selected in the NEA TDB.

Table A-173: Experimental equilibrium constants used by Fujiwara *et al.* to calculate $\log_{10}K^{o}_{s,IV}$ (A.503).

| *t* /°C | Method | *I* (medium) | $\log_{10}K_w$ | $\log_{10}K_{III,IV}$(A.501) | $\log_{10}K_{III,IV}$(A.502) | $\log_{10}K^{o}_{s,IV}$ (A.503) | Reference |
|---|---|---|---|---|---|---|---|
| 25 | sol [(a)] | 1.0 M $NaClO_4$ | –13.76 | – (38.14 ± 0.23) | – (16.53 ± 0.08) | – (54.67 ± 0.24) | [2002FUJ/YAM] |
| 25 | sol [(b)] | 0.5 M $NaClO_4$ | –13.72 | – (38.83 ± 0.05) | – (16.63 ± 0.17) | – (55.46 ± 0.18) | [2002FUJ/YAM] |
| 25 | sol [(b)] | 1.0 M $NaClO_4$ | – 13.76 | – (37.73 ± 0.09) | – (16.53 ± 0.08) | – (54.26 ± 0.12) | [2002FUJ/YAM] |
| 25 | sol [(b)] | 2.0 M $NaClO_4$ | – 13.88 | – (39.30 ± 0.05) | – (16.72 ± 0.06) | – (56.01 ± 0.08) | [2002FUJ/YAM] |

[(a)] denotes experiments from oversaturation;
[(b)] denotes experiments from undersaturation.

**[2002HAS/BAS]**

The authors provide a qualitative review of dissolution data of $PuO_2$(s) and $Pu(OH)_4$(s) in aerobic aqueous solutions and compare experimental observations with assumptions of the thermodynamic model. The authors extract data from graphical illustrations in published manuscripts for their interpretations and perform solubility calculations by

using the geochemical code EQ3/6. The authors' major hypothesis is that the experimental observations are inconsistent with the thermodynamic and kinetic models and that the dissolution of $PuO_2(s)$ is not an equilibrium process. The experimentally observed Pu oxidation state fractions are suggested to not be consistent with a solubility system in equilibrium state. The observed fractions of Pu(V) and Pu(VI) concentrations in steady-state, aerobic solutions at pH 1-9 do not match the predicted dominance of Pu(III) and Pu(IV). The authors claim that based on the dissolution kinetics of $PuO_2(s)$ the steady-state concentrations of Pu are kinetically controlled by the rate Pu(V) is dissolved into the solution. Solubility data taken from the literature are evaluated based on two sections: acidic solutions with pH 1-2.5 and solutions at pH 2.5-8, which show two solubility branches with higher-soluble $Pu(OH)_4(s)$ and about two orders of magnitude lower Pu concentrations of $PuO_2(s)$. In contrast, calculations predict a difference of about eight orders of magnitude between $Pu(OH)_4(s)$ and $PuO_2(s)$. Plutonium concentrations are calculated to be independent of $E_h$ in the range 0.1-0.4 V, leading the authors to develop a linear relationship $E_h(V) = (0.74 \pm 0.02) - (0.0596 \pm 0.0035)$ pH. The authors conclude from reported solubility data that $Pu(OH)_4(s)$ is a metastable phase and does not represent conservative solubility assumptions. A transformation of both $PuO_2(s)$ and $Pu(OH)_4(s)$ into a less-crystalline $PuO_2(s)$ is proposed based on reported X-ray diffraction data. The transformation reaction $Pu(OH)_4(am) \rightarrow PuO_2(s) + 2H_2O(l)$ is associated with a free energy of $\Delta_r G_m^o(298\ K) = -41\ kJ \cdot mol^{-1}$ and the transformation should result in lower soluble Pu concentrations. The solid phase transformation reactions can be analysed via the lattice parameter $a_0$ and its deviation from $(0.5396 \pm 1)$ nm in the ideal cubic structure of $PuO_2(s)$. Radiation damage is assumed to account for only 67 % of the observed lattice expansion of $Pu(OH)_4(s)$.

Modeling the steady-state Pu concentrations is enhanced by using $Pu(OH)_4(s)$ as the solubility-controlling solid phase instead of $PuO_2(s)$; however the authors also claim that the use of $Pu(OH)_4(s)$ as solubility-controlling phase and $PuO_2(s)$ as the thermodynamically stable phase fails to correctly predict oxidation state distributions and Pu concentration differences. Besides the interpretation of experimental data taken from the open literature and comparison to model calculations, this study does not provide any new experimental data or thermodynamic data.

**[2002HAS/OVE]**

Haschke and Oversby review experimental dissolution data of $PuO_2(s)$ to develop a model that includes kinetic and thermodynamic data to predict Pu steady state concentrations. The model is based on the oxidation of the solid Pu(IV) oxide phase by water to form a mixed-valent Pu oxide and hydrogen according to Reaction (A.504):

$$PuO_2(s) + nH_2O(l,g) \rightleftharpoons PuO_{2+x}(s) + nH_2(g) \qquad (A.504)$$

According to the authors, the temperature-dependent reaction rate $\ln R(\text{mol } H_2O/m^2h) = -6.441 - (4706/T)$ indicates that this oxidation reaction is of chemical nature and is not caused by radiolytic effects. The reaction is catalysed by the presence of water or moisture, which is chemisorbed as $OH^-$ and transformed to $O^{2-}$. The formation of $PuO_{2+x}(s)$ is accompanied by an extension of the lattice parameter of the $PuO_2$ cubic structure, $a_0(\text{nm}) = 0.53643 + 0.001764(2 + x)$, although the expected maximum value of $x = 0.5$ still has to be experimentally verified. A reported change of $\Delta_f G_m^o$ from $-998$ to $-1146\ \text{kJ}\cdot\text{mol}^{-1}$ when $x$ increases from 0 to 0.5 supports the formation of $PuO_{2+x}(s)$. However, Neck *et al.* [2007NEC/ALT], [2007NEC/ALT2], [2007NEC/ALT3] challenged the validity of this reaction because the formation of hydrogen cannot be explained by thermodynamic calculations.

The dissolution behaviour of $PuO_2(s)$ is also discussed in [2002HAS/BAS] and the main aspects of the hybrid kinetic-thermodynamic model used to predict the solubility of Pu(IV) oxide are reiterated in this study:

• The solid phase is oxidised to a mixed-valent solubility-controlling solid, $PuO_{2+x}(s)$, which releases Pu(V) into the solution as correlated with the dissolution rate of $PuO_{2+x}(s)$.

• A complex interplay between solid phase oxidation, dissolution of Pu(V) and reduction and disproportionation reactions determine the steady-state concentration of Pu.

• The mechanism of the kinetically-controlled solubility behaviour begins with the dissolution of Pu(V) from $PuO_{2+x}(s)$ and its disproportionation to form Pu(VI) and Pu(IV) which precipitates as Pu(IV) hydroxide solid, which converts to the corresponding oxide:

$$2PuO_2^+ + H_2O \rightleftharpoons 2PuO_2^{2+} + Pu(OH)_4(am) \qquad \text{(A.505)}$$

• The concentration of Pu(VI) increases due to the disproportionation of Pu(V) until the rates of the reduction and disproportionation of Pu(VI) equals its rate of formation. The proposed reaction path via the formation of transient Pu(VII) seems unlikely given the extreme alkaline conditions required to produce Pu(VII). The authors acknowledge that the proposed mechanism for the disappearance of Pu(VI) from solution lacks experimental evidence.

• The primary path for the instability and disappearance of Pu(VI) is its disproportionation to form Pu(V) and Pu(VII), which reacts with water to form Pu(VI).

• The steady-state concentration of Pu(IV) is given by its equilibrium constant with $Pu(OH)_4(s)$.

• Kinetics and thermodynamics of chemical processes and not radiolytic processes (including reactions of Pu with radiolytic products such as peroxide) are the

dominant reaction pathways that govern the solubility and solution behaviour of $PuO_2$(s).

The proposed dissolution reaction of $PuO_2$(s) and the disproportionation mechanism of Pu(VI) raised concerns and criticism. The exclusion of radiolytic processes initiated a response of Newton and Hobart [2004NEW/HOB], and the inconsistency of Reaction (A.505) with experimental observations and $\Delta_f G_m^o$ values are discussed in [2007NEC/ALT], [2007NEC/ALT2].

**[2002KUL/FUJ]**

The authors report on the apparent solubility of U(VI) mixed with Np(V), Pu(IV) or Am(III) in carbonate-free simulated groundwater and seawater. The solubility of Pu(IV) hydroxide in simulated groundwater at pH 7-9 is reported to be $10^{-8}$ M compared to $(4.4\text{-}7.0) \times 10^{-7}$ M in a U(VI)-Pu(IV) mixture. The order of decreasing solubility of the corresponding hydroxides followed the trend Np(V) > U(VI) > Am(III) > Pu(IV) for both aquatic systems. No new thermodynamic data are reported.

**[2002MOR/FUJ]**

See review in Chapter 16 (Appendix A, Np).

**[2002YUS/FED]**

See review in Chapter 16 (Appendix A, Np).

**[2003CHI/SOD]**

Chiang and coworkers investigated the redox chemistry of Th(IV), U(IV), $^{237}$Np(IV), $^{242}$Pu(IV) and $^{243}$Am(III) in the presence of the complexing heteropolyoxoanion $\alpha$-2-$P_2W_{17}O_{61}^{20-}$ by using XANES and cyclic voltammetry. Electrochemical measurements were performed at 25 °C between – 1.0 and + 1.4 V *vs.* Ag/AgCl using a graphite working electrode and a Ag/AgCl reference electrode with 3 M NaCl. In-situ XANES spectra were collected for sample solutions of mixed 0.5 M $CH_3CO_2Li$ buffer and 1 M $HClO_4$ at pH 3.5 under reducing and stepwise oxidising conditions induced by controlled bulk electrolysis at different potentials. The XANES data for $[Np(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ and $[Pu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ were collected at rest potential under nitrogen atmosphere, while the reduced trivalent actinide clusters were prepared by electrolysis at – 1.00 V (for Np(III)) and – 0.30 V (for Pu(III)). These spectra were used to fit the XANES data at intermediate electrode potential with a mixture of An(III)/(IV) polyoxoanion complexes.

The formal electrode potential for the An(IV)/(III) redox couple and associated number of electrons transferring during the redox process is determined by plotting the applied potential (*vs.* Ag/AgCl) against $\log_{10}$([An(IV)]/[An(III]) as determined from the XANES data at different potentials. The slope of the Np(IV)/(III) Nernst Plot of $RT/nF$ = (0.061 ± 0.003) V at 25 °C relates to $n$ = (0.97 ± 0.05) representing a single-electron transfer. Less electrons are transferred during the reduction of Pu(IV). The slope of the Pu(IV)/(III) Nernst plot of $RT/nF$ = (0.082 ± 0.003) V and $n$ = (0.72 ± 0.03) indicate that electrons also participate in the reduction of the polyoxoanion framework. The Np(IV)/(III) redox potential is determined to be – (0.84 ± 0.01) V compared to – (0.17 ± 0.01) V for the analogous Pu(IV)/(III) reduction potential in $[An(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16/17-}$. This work illustrates the redox behaviour of An(IV)/(III) couples in the corresponding polyoxoanion complex $[An(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16/17-}$. However, due to the lack of analytical details, in particular the correction for ionic strength differences in sample and electrode solutions, the reported electrochemical potentials will not be used to determine thermodynamic standard parameters.

**[2003CON/BEG]**

[2003CON/BEG] performed XAFS measurements at the Pu-$L_3$ edge of ordered $PuO_2$ (prepared *via* decomposition of $KPu_2Se_6$), high and low fired $PuO_2$, $PuO_{2+x}$ with $x$ = 0.17 ($a$ = 5.4022 Å) and $x$ = 0.26 ($a$ = 5.4038 Å) (prepared by reacting high fired $PuO_2$ with water vapour at 300 °C, $x$ being determined by the $H_2$ generated by the reaction), high fired $PuO_2$ equilibrated for two weeks above 65, 51 and 15 wt % $H_2SO_4$ (15 %, 37 %, 80 % humidity), and finally a sample of δ PuGa chip oxidised with $H_2O$ vapour at room temperature. The XAFS measurements were collected at 80 K. Only the EXAFS spectrum of the ordered $PuO_2$ sample could be fitted in the work of [2003CON/BEG] using only the crystallographic radial distribution function. The fitting of the other spectra required to introduce additional O shells and/or large Pu Debye-Waller factors. In particular, the excess oxygen in the $PuO_{2+x}$ samples resulted in oxo Pu=O groups at 1.86-1.91 Å ($x$ = 0.17) and 1.83-1.87 Å ($x$ = 0.26), respectively. For the latter samples, the shift in the edge inflection point of the XANES spectra were found at $\Delta E$ = 0.8 and – 0.7 eV relative to the ordered $PuO_2$ sample, respectively. The shift is affected by the Pu valence, the type of ligands, and disorder. The energy shifts of the $PuO_{2+x}$ samples were found below those for Pu(IV) colloids ($\Delta E$ = 0.5-1.2 eV), and [2003CON/BEG] suggested these results to be consistent with a Pu(IV/V) rather than Pu(V/VI) mixture, meaning the excess O in $PuO_2$ occurs as Pu(V)-oxo moieties.

**[2003DAV/VOK]**

David and Vokhmin have used a semi-empirical model mainly based on structure data and bond distances as described in their previous publications (listed in

[2003DAV/VOK]), to propose Gibbs energies of hydration and molar entropies for $An^{3+}$ and $An^{4+}$ aquo-ions. The review is given in the Uranium section.

**[2003FUJ/YAM]**

The solubility of $^{239}Pu(VI)$ hydrous oxide was determined under argon in 0.1, 0.5 and 1.0 M $NaClO_4$ solution with the $pH_c$ ranging between 4 and 5.5 at (25 ± 1) °C. The hexavalent oxidation state was maintained by using ozone with the ozone concentration of $10^{-6}$ g/ml calculated from the measured redox potential of the solutions. The $E_h$ was measured with a redox combination electrode (Pt-electrode *vs.* Ag/AgCl). The hydrogen concentration was measured with an electrochemical cell ($x$ M $NaClO_4$/($x$ – 0.01) M $NaClO_4$, 0.01 M NaCl/AgCl, Ag), in which the reference compartment was adjusted to each ionic strength investigated. The cell followed the linear relationship $E = E_0 + \ln a_{H+} + E_j$, where $E_j$ is the liquid junction potential. The electrode was calibrated by the Gran plot for each ionic strength. After filtration through 30,000 molecular weight-limit filters, the concentration of soluble Pu(VI) was measured by using α-spectrometry and UV-vis spectrophotometry. The solubility experiments were performed from both over- and undersaturation. Solubility studies were conducted up to six weeks although steady-state equilibrium was achieved within one week.

The solubility-governing solid phase was not characterised and identified, but it was assumed to be the Pu(VI) hydroxide, $PuO_2(OH)_2(s)$. Accordingly, the solid phase present in the experiments is difficult to assign as amorphous or crystalline solid. The presence of Pu(VI) in solution was verified spectroscopically *via* its main electronic absorption band at 830 nm, which is characteristic of $PuO_2^{2+}$. Other species, such as Pu(VI) hydrolysis products or Pu(V), were not observed in the pH range investigated. This finding is supported by calculations with published thermodynamic data that show that the amount of Pu(VI) hydrolysis complexes in the investigated pH range is expected to be significantly lower than the total soluble Pu(VI) concentrations. Fujiwara and coworkers tested the potential presence of $PuO_2OH^+$ and $PuO_2^+(aq)$ in solution and calculated the concentrations of these solution species as far lower than the concentration of $PuO_2^{2+}$.

As Pu(VI) is present in the solution phase over presumably $PuO_2(OH)_2(s)$ as the solid equilibrium phase, Fujiwara and coworkers interpreted the measured solubility data with the equilibrium reaction:

$$PuO_2(OH)_2(s) \rightleftharpoons PuO_2^{2+} + 2OH^- \qquad \text{(A.506)}$$

For the calculation of [$OH^-$] from measured pH, ionic strength dependent $pK_{H_2O}$ values (– 13.77 at $I$ = 0.1 M; – 13.72 at $I$ = 0.5 M; – 13.76 at $I$ = 1.0 M; and – 13.997 at $I$ = 0) reported in [1976BAE/MES] were adopted.

The authors calculated the apparent solubility products for $PuO_2(OH)_2(s)$ and used the SIT plot to determine the thermodynamic solubility product, $\log_{10} K^{o}_{sp} = -(22.88 \pm 0.39)$. With $\varepsilon(OH^-, Na^+) = (0.04 \pm 0.01)$ kg·mol$^{-1}$ the ion-interaction parameter $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.30 \pm 0.09)$ kg·mol$^{-1}$ was calculated. This is slightly lower than the selected value in the NEA TDB, $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)$ kg·mol$^{-1}$. It is to note that this selected value does originate from experimental data, but is transferred from the analogue data, $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol$^{-1}$.

**[2003MAR/GRA]**

[2003MAR/GRA] reported X-ray Absorption spectroscopy (XANES and EXAFS) measurements on plutonium dioxide samples exposed to water vapour. According to Haschke *et al.* [2000HAS/ALL], plutonium dioxide should oxidise following the reaction: $PuO_{2.00} + xH_2O \rightleftharpoons PuO_{2+x} + xH_2$. [2003MAR/GRA] prepared (from Pu(IV) nitrate solution) a $PuO_{2.00 \pm 0.02}$ powder of specific surface ranging from 10 to 20 m$^2$·g$^{-1}$ to facilitate the expected reaction with water. The latter powder was exposed to a flow of moisturised argon (around 5 ml·min$^{-1}$) at $T = (613 \pm 10)$ K for 900 and 1800 hours, conditions under which the plutonium oxide powder is expected to reach the composition $PuO_{2.27}$ [2000HAS/ALL]. XAS measurements were subsequently performed at LURE (France) on beamline D44 at the plutonium $L_3$-edge. However, the intensity and position of the white lines of the XANES spectra of $PuO_2$ remained unchanged after contact with the water vapour, excluding any oxidation of plutonium during the annealing treatment. In addition, the EXAFS spectra before and after treatment also appeared quasi identical, suggesting no change in stoichiometry. The results of [2003MAR/GRA] could therefore not substantiate the oxidation of plutonium dioxide by water vapour under those specific conditions.

**[2003NIL/ALB]**

Nilsson and coworkers investigate the solubility of Pu(III) and Pu(IV) under highly reducing conditions in 0.1 M NaCl. Pu(III) and Pu(IV) hydroxide solids were precipitated with deoxygenated NaOH from the corresponding stock solutions. Pu(III) was prepared by reduction in a lead column and subsequent filtration to remove any particulates. Absorbance spectroscopy was used to verify the presence of 95 % Pu(III). A green Pu(IV) hydroxide was obtained from a Pu(IV) stock solution. The authors note that the initially blue Pu(III) hydroxide turned khaki after drying indicating a transition of the solid phase. X-ray diffraction analysis verified the amorphous character of the blue and green hydroxide phases.

The precipitates were equilibrated for up to 665 days in 0.1 M NaCl solution at pH 5.6, 6.7 and 7.0 for $Pu(OH)_3$(s) and pH 5.5 for $PuO_2$(am,hyd). The soluble Pu concentrations were measured by using liquid scintillation counting after centrifugation at 41000 rpm. All experiments were carried out under nitrogen atmosphere. The pH and $E_h$ were measured but no details are given in this paper. This paper is related to a similar publication [2004NIL/ALB].

**[2003PET/SVA]**

[2003PET/SVA] reported first-principles calculations of the electronic structure of $PuO_{2\pm x}$ using the self-interaction corrected (SIC) local spin density (LSD) approximation, which allows to describe some of the 5f electrons of Pu as localised and others as delocalised. In this method, the ground state configuration corresponds to the minimum of the different total energies of the various localised Pu $f^n$ configurations. In the ground state configuration of insulating $PuO_2$, *i.e.*, $5f^4$, the four f electrons are localised on the Pu site, which corresponds to a calculated lattice parameter of 5.34 Å, in reasonable agreement with the experiment. [2003PET/SVA] calculated the electronic configuration of $PuO_{2+x}$ by a supercell of the conventional fluorite cubic cell of $Pu_4O_8$ and introducing an additional O on the octahedral interstitial site at the centre of the cell, which corresponds to the hypothetical $Pu_4O_9$ compound. The calculation of the total energies of the various electronic configurations for the hypothetical $Pu_4O_9$ compound showed that a large gain in energy ($\Delta E$ = – 54 mRy with respect to $Pu_4O_8 + 1/2O_2$) was obtained when a single f electron became delocalised ( $Pu^{5+}Pu_3^{4+}O_9$ ) with respect to the original tetravalent configuration $Pu_4^{4+}O_9$. The gain in energy when delocalising a second electron ( $Pu_2^{5+}Pu_2^{4+}O_9$ ) was also significant, *i.e.*, $\Delta E$= – 21 mRy. The delocalisation energies for the third ( $Pu_3^{5+}Pu^{4+}O_9$ ) and fourth ( $Pu_4^{5+}O_9$ ) f electrons were rather small (1.6 and 1.2 mRy, respectively), however. These results hence showed that at least two $Pu^{5+}$ sites should be present among the O impurity neighbours. However, the results of [2003PET/SVA] are in disagreement with the work of [2000HAS/ALL] and [2004KOR/VIT] regarding the evolution of the lattice parameter. [2003PET/SVA] found the lattice parameter of $PuO_{2.25}$ to be slightly lower than $PuO_2$ [2003PET/SVA], whereas [2000HAS/ALL] and [2004KOR/VIT] found it slightly higher. [2003PET/SVA] suggested this difference could occur due to dynamical correlations in the narrow band formed by the delocalised f electrons and overestimation of their bonding contribution. From their calculations [2003PET/SVA] found $PuO_2$ to be stable with respect to the oxidation reaction $PuO_2 + 1/8O_2 \rightleftharpoons PuO_{2.25}$, in agreement with the experiment. The authors nevertheless suggested that higher oxidation states may be possible under specific conditions due to electrons absorption by the extra O impurities accompanied by f-electron delocalisation leading to formation of $Pu^{5+}$ ions.

**[2003SCH/PRI]**

The authors performed *ab initio* calculations in the gas phase to determine the reaction enthalpies for several reactions of U(VI), Np(VI) and Pu(VI) oxide and fluoride (see a detailed discussion on the uranium system in [2002PRI/SCH]). The CCSD(T) method was used to obtain reaction energies and enthalpies for uranium and neptunium, while calculations with plutonium were performed at the MP2 level. Optimised geometries with bond distances and vibrational frequencies were reported for a number of complexes, including $MO_2F_2$, $MO_2(OH)_2$, $MF_6$, and $MO_3$ where M = U, Np and Pu. The enthalpies for the following gas phase reactions were calculated:

$$2MO_3(g) + MF_6(g) \rightleftharpoons 3MO_2F_2(g) \quad \text{(A.507)}$$

$$MO_2F_2(g) + 2H_2O(g) \rightleftharpoons MO_2(OH)_2(g) + 2HF(g) \quad \text{(A.508)}$$

$$MF_6(g) + 2H_2O(g) \rightleftharpoons MO_2F_2(g) + 4HF(g) \quad \text{(A.509)}$$

$$MO_3(g) + H_2O(g) \rightleftharpoons MO_2(OH)_2(g) \quad \text{(A.510)}$$

$$MF_6(g) + 3H_2O(g) \rightleftharpoons MO_3(g) + 6HF(g) \quad \text{(A.511)}$$

The calculated reaction enthalpies for the U and Np reactions are reasonably similar with maximum differences of up to about 80 kJ·mol$^{-1}$. The reaction enthalpies calculated for the Pu reactions differ significantly from those calculated for U and Np when $PuF_6(g)$ is involved as the reactant. The authors explain the differences with the weaker bonding in $PuF_6$ compared to the analogous U and Np compounds.

Table A-174: Calculated reaction enthalpies $\Delta_r H_m^o$ at 298.15 K for selected gas phase reactions of U, Np and Pu reported in [2003SCH/PRI].

| Reaction | $\Delta_r H_m^o$(U) /kJ·mol$^{-1}$ | $\Delta_r H_m^o$(Np) /kJ·mol$^{-1}$ | $\Delta_r H_m^o$(Pu) /kJ·mol$^{-1}$ |
|---|---|---|---|
| $2MO_3(g) + MF_6(g) \rightleftharpoons 3MO_2F_2(g)$ | – 306 | – 222 | – 455 |
| $MO_2F_2(g) + 2H_2O(g) \rightleftharpoons MO_2(OH)_2(g) + 2HF(g)$ | 86 | 71 | 90 |
| $MF_6(g) + 2H_2O(g) \rightleftharpoons MO_2F_2(g) + 4HF(g)$ | 168 | 158 | – 4 |
| $MO_3(g) + H_2O(g) \rightleftharpoons MO_2(OH)_2(g)$ | – 151 | – 119 | – 136 |
| $MF_6(g) + 3H_2O(g) \rightleftharpoons MO_3(g) + 6HF(g)$ | 405 | 349 | 222 |

**[2003SHI/FED]**

The solubility of $^{238\text{-}242}$Pu(IV) is studied in $NaClO_4$ (0.1 and 0.2 M) and NaOH (0.09 and 0.90 M) solutions in the absence and presence of $10^{-3}$-0.09 M $Na_2SiO_3$. The pH of the experimental solutions ranged between 8.9 and 13.8. A freshly precipitated green

Pu(IV) solid phase was produced from Pu(VI) contacted with an alkaline solution (pH > 13) containing hydrazine and washed with 0.1 M $NaClO_4$. The solid phase was assumed to be $Pu(OH)_4(am)$ although the composition of the solid phase was not experimentally verified. The solid phase was contacted with silicate solutions to allow equilibration up to 89 days at (20 ± 1) °C. The pH was measured with a glass pH electrode, but no details were provided for correction of electrode and ionic strength effects. No information is provided regarding the atmospheric conditions under which the Pu samples were prepared and stored in order to avoid potential contamination with carbonate. The soluble Pu concentrations were measured *via* liquid scintillation counting after centrifugation and before and after filtration through 1.3 nm pore size filters.

The measured solubility data exhibit significant scattering, which complicates the determination of reliable equilibrium constants. The presence of $SiO_3^{2-}$ increases the solubility of Pu(IV) at pH > 11, but has no effect on the Pu(IV) solubility at pH 9. The authors explained the low impact at pH 9 with the low concentration of silicate anions available due to the silicic acid dissociation constants $pK_a = 9.66$ and 11.80. Without speciating the soluble Pu(IV) fraction, the authors determined the equilibrium constants for the reaction:

$$\mathrm{Pu(IV)} + n\mathrm{SiO_3^{2-}} \rightleftharpoons \mathrm{Pu(SiO_3^{2-})}_n \qquad \text{(A.512)}$$

by using the equation:

$$K = ([\mathrm{Pu}]_0 - [\mathrm{Pu}]_t)/([\mathrm{Pu}]_t[\mathrm{SiO_3^{2-}}]^n) \qquad \text{(A.513)}$$

where $[Pu]_0$ and $([Pu]_t$ are the soluble Pu(IV) concentrations in the absence and presence of $SiO_3^{2-}$ respectively. The value for $n$ was determined from slope analysis, $n = \Delta\log_{10}[Pu]/\Delta\log_{10}[Na_2SiO_3]$, to be 0.7 in 0.9 M NaOH and 1.2 in 0.09 M NaOH. This study lacks details on the speciation of Pu(IV) in alkaline systems and information of the silicate complex formed in solution. The stability constant for the proposed complexation Reaction (A.512) is only of qualitative nature and cannot be recommended for quantitative calculations.

**[2003VIT/CAP]**

The authors provide an operational thermodynamic database for actinide speciation modelling in aquatic systems. The operational database builds on the validated NEA thermodynamic database complemented by estimated formation constants, solubility products and redox potentials for additional species and redox couples. Additional formation constants of, sometimes hypothetical, Np(IV) and Pu(IV) solution species (*e.g.* $Pu(CO_3)_2(OH)_3^{6-}$) were added to the NEA TDB to improve the fitting of experimental data reported in the literature. The maximum values for some complex formation constants were estimated from reported solubility data. The authors

acknowledge that in some cases there is not sufficient experimental evidence available to support the authors' assumptions.

**[2003YUS/FED]**

Paper reporting on the hydrolysis of Np(IV) under acidic conditions. See comments under Yusev *et al.* [2004YUS/FED2].

The reaction of Pu(VI) with orthosilicic acid, $Si(OH)_4(aq)$, in 0.2 M $NaClO_4$ is studied spectroscopically at (21 ± 2) °C. Dilute alkaline solutions were prepared from amorphous $SiO_2 \cdot nH_2O$ (average value for n after calcination at 1000 °C was 0.9) or $Na_2SiO_3 \cdot 9H_2O$ and acidified to obtain polymer-free $Si(OH)_4(aq)$ solutions. The working solutions were quickly acidified with 2-5 M $HClO_4$ to pH 2-2.5 to avoid polymerisation of the silicic acid at neutral pH. Contamination at $p_cH > 5$ with $CO_2$ is minimised by purging the working solutions with high-purity argon. The pH was measured with a glass electrode and converted to hydrogen concentration using a correction factor of 0.06 for the ionic medium 0.2 M $NaClO_4$. The concentration of orthosilicic and polymeric silicic acid were determined from time-dependent optical density measurements by monitoring the reaction kinetics with acidic molybdate solution. The reaction between molybdic acid and monomeric $Si(OH)_4(aq)$ is fast and completed within about 100 seconds, while the reaction rates of polymeric silicic acid with molybdic acid decreases with the degree of polymerisation. The total concentration of $Si(OH)_4(aq)$ was calculated from the optical density of the molybdate complex after 5-10 minutes extrapolated to t = 0 min. The authors observed that in solutions with $[Si(OH)_4(aq)] > 0.005$ M dimeric or oligomeric silicate species were present.

The Pu(VI) complexation reaction is monitored via changes of the prominent electronic absorption bands of $PuO_2^{2+}$ at 830.4 nm and at 841 nm, which is assigned to $PuO_2OH^+$. Dimerisation and the formation of $(PuO_2)_2(OH)_2^{2+}$ is observed *via* an absorbance at about 844 nm at $p_cH = 4.5$-6 and Pu(VI) concentrations at (3-7) × $10^{-4}$ M. The peak at 844 nm shifts to about 842 nm in the presence of $Si(OH)_4(aq)$. The impact of silicate is only observed at $p_cH \geq 4.3$ and $[Si(OH)_4(aq)] \geq 0.005$ M. Due to its complete overlap with the broad absorbance for $PuO_2OH^+$ with its maximum at 844 nm, the broad absorbance associated with a Pu(VI) silicate complex with a maximum intensity at about 841 nm (estimated molar extinction coefficient $\varepsilon_{841} = (200 \pm 80)$ L·mol$^{-1}$·cm$^{-1}$) could not be used for spectra deconvolution and quantitative speciation calculations. The concentration of $PuO_2SiO(OH)_3^+$ formed was obtained from the spectral differences of Pu(VI) at $p_cH = 2$-6 with and without orthosilicic acid. The authors calculated the $OH^-$ concentration from the water dissociation constant of $10^{-13.78}$ and the measured $p_cH$. The authors determined the Pu(VI) hydrolysis constants from nine experiments and calculated the stability constants $\log_{10}\beta_{1,1} = (7.95 \pm 0.12)$ for $PuO_2OH^+$ using a molar extinction coefficient of $\varepsilon_{841} = (138 \pm 12)$ L·mol$^{-1}$·cm$^{-1}$, and calculated the apparent stability constants for

$PuO_2(OH)_2(aq)$ (14.54 ± 0.24) and $(PuO_2)_2(OH)_2^{2+}$ (19.60 ± 0.30) in 0.2 M $NaClO_4$.

The equilibrium constant for Reaction (A.514) was calculated as the residual Pu(VI) concentrations after subtracting the concentrations of the hydrolysis products from the total Pu concentration with and in the absence of orthosilicic acid. The first dissociation constant for $Si(OH)_4(aq)$ of – 9.81 was used to calculate $\log_{10}K_{1,1}$ = – (3.91 ± 0.17) for (A.514) and $\log_{10}\beta_{1,1}$ = (5.90 ± 0.17) for the formation of the cationic complex $PuO_2SiO(OH)_3^+$ according to (A.515):

$$PuO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons PuO_2SiO(OH)_3^+ + H^+ \quad \text{(A.514)}$$

$$PuO_2^{2+} + SiO(OH)_3^- \rightleftharpoons PuO_2SiO(OH)_3^+ \quad \text{(A.515)}$$

The complex $PuO_2SiO(OH)_3^+$ is the dominant species at $p_cH < 5.5$. At $p_cH > 5.5$ the equilibrium constant increases with $p_cH$, indicating the formation of a new Pu(VI) species or the increasing oligomerisation of the silicic acid. The complex $PuO_2(OH)_2(aq)$ is found at $p_cH > 7$ and its absorbance at about 851 nm. At low $Si(OH)_4(aq)$ concentrations and $p_cH$ between 6 and 6.5, the formation of a new Pu(VI) complex with a broad absorbance with the intensity maximum at 847 nm is postulated. Without evidence of the composition and charge of this second Pu(VI) silicate complex, the authors suggested three reactions to occur:

$$PuO_2^{2+} + Si(OH)_4(aq) \rightleftharpoons PuO_2SiO_2(OH)_2(aq) + 2H^+ \quad \text{(A.516)}$$

$$PuO_2^{2+} + Si(OH)_4(aq) + H_2O(l) \rightleftharpoons PuO_2(OH)SiO(OH)_3(aq) + 2H^+ \quad \text{(A.517)}$$

$$PuO_2^{2+} + 2Si(OH)_4(aq) \rightleftharpoons PuO_2[SiO(OH)_3]_2(aq) + 2H^+ \quad \text{(A.518)}$$

The postulated complex, $PuO_2SiO_2(OH)_2(aq)$, is a deprotonation product of $PuO_2SiO(OH)_3^+$ and its stability constant is calculated to be $\log_{10}K_{1,2}$((A.516), $PuO_2SiO_2(OH)_2$, aq) ~ – 10.5. With the silicic acid dissociation constants of 9.81 and 13.33, the authors calculated the formation constant $\log_{10}\beta_{1,2}$((A.519), $PuO_2SiO_2(OH)_2$, aq) ~ 12.6 for the equilibrium (A.519):

$$PuO_2^{2+} + SiO_2(OH)_2^{2-} \rightleftharpoons PuO_2SiO_2(OH)_2(aq) \quad \text{(A.519)}$$

Accordingly, the authors estimated the equilibrium constants $\log_{10}\beta$ ~ 13 for (A.520) and $\log_{10}\beta$ ~ 11.5 for (A.521):

$$PuO_2^{2+} + SiO_2(OH)_2^{2-} + H_2O(l) \rightleftharpoons PuO_2(OH)SiO(OH)_3(aq) \quad \text{(A.520)}$$

$$PuO_2^{2+} + 2SiO(OH)_3^- \rightleftharpoons PuO_2[SiO(OH)_3]_2(aq) \quad \text{(A.521)}$$

The authors preferred Reactions (A.516) and (A.517) over Reaction (A.518) and postulated the addition of three water molecules to be coordinated by Pu(VI) such as $PuO_2(H_2O)_3SiO_2(OH)_2(aq)$ or $PuO_2(H_2O)_3(OH)SiO(OH)_3(aq)$. Potentiometric measurements were used to support the spectroscopic determination of reaction mechanisms and nature of the Pu(VI) silicate species. This study is complicated by the

increasing polymerisation of $Si(OH)_4(aq)$ at higher $p_cH$ and competing hydrolysis reactions of Pu(VI). Polymerisation of the silicic acid is observed in experiments with $p_cH > 5.5$, which is the range of the second complex. The authors attempted to minimise polymerisation reactions by lowering the silicic acid concentration. However, this also resulted in lower fractions of Pu(VI) silicate complexes at pH > 5. Thus, the analysis of released protons and the reliability of the proposed formula and the stability constants of the second Pu(VI) complex cannot be considered reliable and need to be verified.

**[2004CON/BEG]**

[2004CON/BEG] studied 24 samples of $PuO_{2+x}$ prepared by various routes as well as two related Pu substituted oxides by X-ray Absorption spectroscopy at the Pu-$L_{III}$ edge. We shall not make a detailed analysis of this paper which is out of the scope of this review, but only list the main findings as reported in the abstract of this article. The authors found the nearest-neighbour O atoms to be in a multisite distribution, even when $x = 0$ and pointed out that the corresponding Pu-O distances were consistent with the incorporation of $OH^-$ (and possibly $H_2O$ and $H^+$) into the $PuO_2$ lattice. They found the excess O from oxidation at Pu-O distances < 1.9 Å. This distance is consistent with multiple bound "oxo"-type ligands found in molecular complexes of Pu(V) and Pu(VI). [2004CON/BEG] reported that the Pu associated with these oxo groups is most likely Pu(V), so that the excess O is probably incorporated as $PuO_2^+$ moieties aperiodically distributed through the lattice. Finally, the authors suggested that a more accurate description of $PuO_2$ is $PuO_{2+x-y}(OH)_{2y}\cdot zH_2O$, and that pure, ordered, homogeneous $PuO_2$ can only be attained if $H_2O$ is rigorously excluded and the O activity is relatively low.

**[2004DOU/SCH]**

[2004DOU/SCH] performed X-ray photoelectron spectroscopy (XPS) measurements on the surface of plutonium dioxide $PuO_2$, plutonium (IV) hydroxide $Pu(OH)_4$, colloidal Pu(IV) hydroxide, plutonium (VI) carbonate $PuO_2CO_3$, and hyperstoichiometric plutonium oxide $^{239}PuO_{2+x}$ samples prepared by the reaction of high-fired $^{239}PuO_2$ with $H_2O$ vapour at high temperatures. The composition of the latter $PuO_{2+x}$ oxide was calculated to be $PuO_{2.26}$ based on the $H_2$ pressure generated at 300 °C, corresponding to a lattice parameter $a = 5.4022$ Å, *i.e.,* slightly higher than pure $PuO_2$ (5.3975 Å).

The characteristic Pu $4f_{5/2}$ and Pu $4f_{7/2}$ photoemission peaks for $PuO_{2+x}$ were found at higher binding energy than for $PuO_2$ and Pu(IV) hydroxides, indicating that Pu was in a more electron-withdrawing environment. In addition, the shift of the main 4f peak to higher energy without any shift or increased intensity in the shake-up satellite peak suggested the presence of Pu oxidation states higher than + 4. When exposing a high fired $PuO_2$ sample to high humidity, [2004DOU/SCH] identified $Pu(OH)_4$ formation at the surface, which moreover disappeared by heat treatment up to 600 °C

under ultra-high vacuum. When performing a similar thermal dehydration treatment on the $^{239}PuO_{2+x}$ sample, the Pu 4f and O 1s binding energies were found to shift to lower energies, finally yielding the characteristic lines of $PuO_2$ at 600 °C, hence showing the effect of surface de-hydroxylation.

[2004DOU/SCH] moreover performed curve fitting in the O 1s region of the thermal dehydration experiments for hydrated $PuO_2$ and $PuO_{2+x}$ samples. Significant differences were found at low temperatures (100 °C), with a main peak at 532 eV for the hydrated $PuO_2$ sample but at 531 eV for the $PuO_{2+x}$ sample. This difference was attributed to reduced C presence on the surface (about two times lower), hence fewer C-O bonding for $PuO_{2+x}$, as well as more pronounced surface hydroxylation. When comparing the spectra of hydrated $PuO_2$, $PuO_{2+x}$ and $Pu(OH)_4$, it appeared that $PuO_{2+x}$ showed predominantly surface hydroxides $Pu(OH)_4$ and/or the presence of O in another withdrawing environment causing the same binding energy shift. [2004DOU/SCH] suggested this could correspond to O bound to Pu in a higher oxidation state, namely Pu(V) or Pu(VI). By curve-fitting the intensity ratios of the satellite to the main peak of $PuO_{2+x}$, [2004DOU/SCH] estimated a fraction of maximum 10 % for this higher oxidation state. [2004DOU/SCH] therefore showed that the XPS spectroscopic features of $PuO_{2+x}$ were consistent with surface hydroxylation and presence of plutonium as Pu(V). The results of [2004DOU/SCH] are consistent with those of Conradson *et al.* [2003CON/BEG], [2004CON/BEG] using X-ray Absorption Spectroscopy suggesting the formation of hydroxyls and Pu=O bonds at the surface by hydration.

**[2004KOR/VIT]**

Korzhavyi and co-workers reported a density functional theory (DFT) study of the oxidation of plutonium dioxide using the local density approximation (LDA), including gradient corrections with the local Airy gas (LAG) approximation and generalised gradient approximation (GGA). Spin-polarisation was moreover accounted for to model the localised character of the 5f states of plutonium, the spin-order being calculated as ferromagnetic. The electron density and the total energy were calculated self-consistently within the local density approximation. The calculations were performed for the $UO_2$, $U_4O_9$, $PuO_2$ and $Pu_4O_9$ compounds, and the LAG approximation was found to yield the best overall agreement with the experiment (with respect the enthalpies of formation in particular). [2004KOR/VIT] found an increase of the lattice parameter of $PuO_{2+x}$ with oxygen content, in good agreement with [2000HAS/ALL]. The enthalpy of formation of $Pu_4O_9$(cr) was estimated to be $\Delta_f H_m^\circ$ ($Pu_4O_9$, cr, 298.15 K) = – (4200 ± 15) kJ·mol$^{-1}$ based on the energy difference $\Delta E_1 - \Delta E_2$ for Reactions (A.522) and (A.523) obtained by first-principles total-energy calculations, and the well-known thermodynamic data for $UO_2$, $U_4O_9$ and $PuO_2$:

$$4\,PuO_2(cr) + 1/2\,O_2(g) \rightleftharpoons Pu_4O_9(cr) \qquad (A.522)$$

$$\Delta E_1 = + 1.1 \text{ eV}$$

$$4UO_2(cr) + 1/2\,O_2(g) \rightleftharpoons U_4O_9(cr) \qquad \text{(A.523)}$$

$$\Delta E_2 = - 0.9 \text{ eV}$$

Assuming that the excess entropy associated with oxygen interstitials in $Pu_4O_9$ was the same as in $U_4O_9$, *i.e.*, $S_m^o(U_4O_9, cr, 298.15\text{ K}) - S_m^o(UO_2, cr, 298.15\text{ K})$ the Gibbs energy of formation of $Pu_4O_9$ was estimated as $\Delta_f G_m^o(Pu_4O_9, cr, 298.15\text{K}) = - (3950 \pm 20)\ \text{kJ}\cdot\text{mol}^{-1}$. This estimate is based on the assumption that systematic errors to calculate reaction energy differences and reaction entropies are similar for $U_4O_9$ and $Pu_4O_9$ and thus cancel each other out. In agreement with experimental observations, the values of $\Delta E_1$ and $\Delta E_2$ show that $PuO_2$ cannot be oxidised in air in stark contrast to $UO_2$. $Pu_4O_9$ is thermodynamically unstable and decomposes to $PuO_2$ and $O_2(g)$: $\Delta_r H$ (A.522) = + 0.2 eV and $\Delta_r G$ (A.522) = + 0.5 eV as calculated by [2004KOR/VIT], compared to $\Delta_r H$ (A.523) = – 1.8 eV and $\Delta_r G$ (A.523) = – 1.5 eV).

Korzhavyi and coworkers found the reaction of $PuO_2$ with water to be strongly endothermic in their calculations, in accordance with the experimental observations of Martin *et al.* [2003MAR/GRA] who failed to observe $Pu^{5+}$ by X-ray Absorption Spectroscopy when treating $PuO_2$ under water vapour:

$$4PuO_2(cr) + H_2O(l) \rightleftharpoons Pu_4O_9(cr) + H_2(g) \qquad \text{(A.524)}$$

$$\Delta H(\text{A.524}) = + 3.2 \text{ eV}, \Delta G(\text{A.524}) = + 2.8 \text{ eV}$$

The authors also calculate the values for the analogous reaction with U, $\Delta_r H$ (A.524) = + 1.2 eV and $\Delta_r G$ (A.524) = + 0.8 eV. However, in order to explain the hydrogen production as observed by [2000HAS/ALL], [2001HAS/ALL] and [2002HAS/ALL], the authors suggested a new mechanism based on the radiolysis of water when absorbed on the $PuO_2$ surface, suggesting the oxidation mechanism:

$$PuO_2 + H_2O \rightleftharpoons PuO_{2+x} + H_2(g) \qquad \text{(A.525)}$$

However, the authors acknowledge the fact that $UO_2$ does react with oxidising agents by overcoming the energy barrier by a non-chemical mechanism. The authors assign the occurrence of such thermodynamically unfavorable reactions to the radiolysis reactions initiated by the radioactivity of the actinides. The authors propose a surface-catalysed decomposition of hydrogen peroxide (Reaction (A.528)) and a subsequent reaction of formed $Pu_4O_9$ according to Reaction (A.529). [2004KOR/VIT] calculated with molecular oxygen according to: [2004KOR/VIT] calculated the Gibbs energies associated with the oxidation of plutonium dioxide with the products of water radiolysis such as $O_2(g)$ and $H_2O_2(l)$ which are strong oxidants and found strongly exothermic values.

$$4PuO_2 + O(g) \rightleftharpoons Pu_4O_9 \qquad \text{(A.526)}$$

$$\Delta H(\text{A.526}) = - 2.3 \text{ eV} ; \Delta G(\text{A.526}) = - 1.9 \text{ eV}$$

$$Pu_4O_9 + O(g) \rightleftharpoons 4PuO_2 + O_2(g) \quad \text{(A.527)}$$

$$\Delta H(\text{A.527}) = -2.8 \text{ eV} \; ; \; \Delta G(\text{A.527}) = -2.9 \text{ eV}$$

$$4PuO_2 + H_2O_2(l) \rightleftharpoons Pu_4O_9 + H_2O(l) \quad \text{(A.528)}$$

$$\Delta H(\text{A.528}) = -0.8 \text{ eV} \; ; \; \Delta G(\text{A.528}) = -0.6 \text{ eV}$$

$$Pu_4O_9 + H_2O_2(l) \rightleftharpoons 4PuO_2 + H_2O(l) + O_2(g) \quad \text{(A.529)}$$

$$\Delta H(\text{A.529}) = -1.3 \text{ eV}; \; \Delta G(\text{A.529}) = -1.6 \text{ eV}$$

The calculated Gibbs energies suggest that hyperstoichiometric plutonium dioxide $PuO_{2+x}(s)$ could be formed under oxic conditions, but only as intermediate product of surface-catalysed generation of oxygen, and should ultimately form stable $PuO_2(s)$. This proposition is not supported by experimental data and the reported formation of $PuO_{2+x}(s)$ in aqueous solutions in the presence of trace oxygen or air. It is to note that the authors limit the systems in their calculations to compounds with the fluorite crystal structure, such as $PuO_2$ and other Pu oxyhydroxides.

**[2004NEW/HOB] and [2004HAS]**

The report of Haschke and Oversby [2002HAS/OVE] initiated a discussion regarding the validity of the authors' claim that the instability of Pu(VI) is due to the disproportionation of Pu(VI) into Pu(V) and transient Pu(VII) and is not caused by the self-induced alpha-reduction of Pu(VI). In their response to [2002HAS/OVE], Newton and Hobart argued that in acidic solutions below pH ~ 2.2 radiolytic effects are consistent with experimental observations and that the rate laws for the disproportionation of Pu(V) and Pu(VI) are indeed different. According to Newton and Hobart, the net reaction of Pu(VI) with water:

$$PuO_2^{2+} + 0.5H_2O \rightleftharpoons PuO_2^{+} + H^{+} + 0.25O_2 \quad \text{(A.530)}$$

cannot proceed to a significant extent without additional energy source. In his response [2004HAS], Haschke discards the claims made in [2004NEW/HOB] and insists that the time-dependent concentration of $^{239}Pu(VI)$ is accurately described by using a second-order rate law identical to that of Pu(V) disproportionation. According to Haschke, no additional energy source is needed when the kinetically-controlled process involves hydroxo-bridged dimeric species. However, the experimental evidence of the formation of proposed species such as the speculative trimeric complex $(PuOH)_3^{9+}$ as proposed in [2007HAS] to support the kinetically-controlled reaction mechanism are lacking.

Haschke provides additional details regarding the reduction and disproportionation mechanism of Pu(VI) in [2005HAS] and [2007HAS].

**[2004NIK/GOG]**

Nikonov and coworkers discuss the disproportionation reactions of Pu(VI) and Am(III) in alkaline solutions and investigate the stability of Am oxidation states under highly oxidising conditions. Based on similarities of its solution spectra with Np(VII) and Pu(VII), the authors postulate the formation of a green soluble Am(VII) species. After precipitating a solid from a Am(VI) solution in 1 M NaOH at 20 °C in the presence of perxenate, the Am hydroxide precipitate was treated with ozone to obtain a green solution. The green solution was assigned to a Am(VII) compound because its absorbance spectrum was considered to be "alike" the the spectra of Np(VII) and Pu(VII) in 4 M NaOH. Although there are spectral similarities to the spectrum of Pu(VII), the spectrum is very different from Np(VII) in NaOH.

Hexavalent Am is found to be readily reduced by water in alkaline, oxidised solutions. Using the redox potential of $RuO_4^-/RuO_4^{2-}$ of 0.6 V *vs*. NHE and the reversible reaction between Am(VI) and $RuO_4^{2-}$, the authors estimate the redox potential for the Am(VI)/Am(V) couple in 1 M NaOH to be about 0.7 V *vs.* NHE.

The treatment of a $PuO_3 \cdot H_2O$(s) precipitate with saturated NaOH and 5 M LiOH resulted in the changes in the absorption spectra with bands at 605 and 630 nm, which were previously assigned to Pu(VII). The authors estimated that about 20 % of the total Pu content was oxidised to Pu(VII). The redox potential for Pu(VII)/Pu(VI) in 2-12 M NaOH is expressed by Equation (A.531):

$$E(Pu(VII)/Pu(VI)) = 0.874 - 0.0355 \cdot [NaOH] \quad \text{(A.531)}$$

The data reported in this study are generally of qualitative nature and do not identify the solution species involved in the chemical reactions. No new thermodynamic data are reported.

**[2004NIK/GOG2]**

The authors report on the spectroscopic investigation of the oxidation reaction of Pu(VI) with ozone in alkaline solutions. The formation of Pu(VIII) and Pu(VII) is postulated to occur in 0.7-3.5 M NaOH solutions, which can be reduced by Fe(III) or Pu(VI). Nikonov and coworkers claim the co-production of about 12 % Pu(VIII) besides Pu(VII). Without providing any details on solution speciation the contribution of Pu(VIII) in the final solution is estimated based on changes in the electronic absorption spectra and associated estimated molar extinction coefficient for Pu(VIII) at 635 nm, $\varepsilon_{635} = (2600 \pm 400)\ L \cdot mol^{-1} \cdot cm^{-1}$. The molar extinction of blue-black Pu(VII) solutions have been reported to range between 530 and 600 $L \cdot mol^{-1} \cdot cm^{-1}$, which the authors associated with oscillating absorbances observed in this study. These variations results in large uncertainties of the molar extinction coefficients and associated amounts of

Pu(VIII) and Pu(VII) estimated in this study. No thermodynamic data are reported in this study.

**[2004NIL/ALB]**

This paper describes the dissolution studies of Pu(III) hydroxide under a 50 bar hydrogen atmosphere. Trivalent Pu was prepared in 1 M HCl by bubbling hydrogen through the stock solution. The oxidation state purity was verified spectroscopically, indicating that only trace amounts of other Pu oxidation states were present. After addition of NaOH, a blue precipitate formed, which was washed with water and dried. During the drying period the initially blue $Pu(OH)_3(s)$ precipitate turned brown. X-ray diffraction was used to characterise the solid phase, but no Bragg reflections were observed which is evident of a highly amorphous solid phase. A total of six pressure vessel were prepared by adding the precipitate to 30 mL 0.1 M NaCl and Pt wire, and adjusting the pressure to 50 bar $H_2$. After two weeks the vessels were opened and the analytic measurements suggested that all Pu was dissolved in solution. Additional NaOH was added to adjust pH and to form new precipitates.

Samples were taken after 150, 320 and 480 days and centrifuged at 41 000 rpm. After acidifying with 2 M $HNO_3$ the Pu concentration was measured by liquid scintilation counting. The pH of the samples was measured against pH 4 and 7 buffer standards; the $E_h$ of the uncentrifuged samples was measured with a Ag/AgCl reference and Pt-wire counter electrode, calibrated against quinhydrone at pH 7 buffer ($E_h$ = 286 mV).

The authors report dissolved Pu concentrations at pH between 3 and 10. The data are very scattered without uncertainties provided, but show increasing concentration with decreasing pH. The authors state that solubilities around pH 8 are consistent with both crystalline $PuO_2(cr)$ and $Pu(OH)_3(cr)$, which is contrary to the results from X-ray diffraction analysis that no crystalline solids could be observed. The authors conclude their study acknowledging Pu(III) as the dominant solution species over a $PuO_2$-type solubility limiting phase. No thermodynamic data are provided in this study.

**[2004ODE/ALB]**

The authors report apparent solubility data of Pu(III) in $NaClO_4$ solutions with the pH ranging between 7 and 8 in the absence of carbonate and at 0.03 % $CO_2$ atmosphere. The soluble Pu concentrations were measured after 10, 21 and 41 days ranging between $10^{-7}$ and $10^{-9}$ M. Hydrogen was used to maintain a reducing environment and to stabilise Pu(III). The solubility data do not appear stable after 41 days indicating that the solid-

liquid equilibrium has not been reached. No new thermodynamic data are derived from the measured solubilities.

**[2004ROT/WAL]**

This study reports on the formation and structure of $^{242}$Pu(IV) colloids using X-ray absorption fine structure spectroscopy (EXAFS) and laser-induced breakdown detection (LIBD). All samples were prepared under $N_2$ atmosphere to avoid contamination with oxygen. The Pu(IV) concentrations ranged between 0.23 mM and 16.1 mM at $H^+$ concentrations between 0.018 and 1 M. $H^+$ concentrations were measured with a glass electrode. The authors verified that no precipitate was present in the samples prepared for the LIBD measurements. The EXAFS data of colloid samples show a range of Pu-O distances due to the presence of different coordination modes of oxygen atoms, *e.g.* Pu-O, Pu-OH and Pu-$OH_2$. Although the EXAFS data did not allow the development of a structural model, the authors discuss colloid formation and colloid growth mechanisms. The LIBD data show two sets of mean particle diameters of about 12 and 24 nm and their solubility matches the predicted solubility calculated by using $\log_{10} K^{o}_{sp} = -(58.7 \pm 0.3)$. The points of colloid formation determined by LIBD were linear and dependent on $-\log_{10}[H^+]$ with a slope of $-2$ indicating the presence of $[Pu(OH)_2]^{2n+}_n$ species. Monomeric Pu(IV) hydroxo complexes such as $Pu(OH)_2(H_2O)^{2+}_6$ are postulated as reactants that hydrolyse and condensate to form larger charge-neutral, polymeric species according to the Reaction (A.532).

$$Pu(OH)^{2+}_2 + 2H_2O(l) \rightleftharpoons Pu(OH)_4(coll) + 2H^+ \qquad (A.532)$$

**[2004YUS/FED2]**

See review in Chapter 16 (Appendix A, Np).

**[2005CAP/COL] and [2006GIB/SAN]**

Capone and coworkers [2005CAP/COL] report a new experimental study to better define the ionisation potential of the $PuO_2$ molecule. The ionisation of a molecular vapor beam of $PuO_2$ was heated in a Knudsen cell and measured by mass spectrometry. The Knudsen cell was heated to 2500 K and near melting temperature of $PuO_2$ assuming a thermodynamic equilibrium at the given temperatures. However, the study at higher temperatures raises questions because of offset signals reported by the authors and the changing $[PuO^+]/[PuO^+_2]$ ratios in the vapor beam. The authors' study supported the $PuO_2$ ionisation potential to be at the upper boundary of a 6.2-6.6 eV range and derived the relation $I_0(PuO_2) = I_0(PuO) + (0.42 \pm 0.005)$ eV. This results in an ionisation

potential of 6.2 eV for PuO. The authors also report the reaction enthalpies $\Delta_r H^o_m$ (A.533) = 7.1 eV and $\Delta_r H^o_m$ (A.534) = 5.8 eV.

$$PuO(g) \rightarrow Pu(g) + O(g) \quad \text{(A.533)}$$

$$PuO(g) \rightarrow PuO^+(g) + e^- \quad \text{(A.534)}$$

Although the ionisation potential of 6.6 eV is close to the value of (7.03 ± 0.12) eV reported in [2002SAN/MAR], the paper by Capone *et al.* initiated a response by Gibson *et al.* [2006GIB/SAN] challenging the methodology in the experiment reported in [2005CAP/COL]. Gibson's claim is supported by calculated concentration ratios of Pu species that are quite different and incompatible with those reported in [2005CAP/COL]. The authors cite as the main reason for this discrepancy the erroneous assumption of a thermodynamic equilibrium achieved in the Knudsen cell.

**[2005GIB/HAI]**

The gas phase reactions of dipositive ions of Th, U, Np, Pu and Am with oxidising agents ($N_2O$, ethylene oxide, $H_2O$, $O_2$, $CO_2$, NO and $CH_2O$) are investigated by using ion cyclotron resonance mass spectrometry. The samples prepared for the measurements consisted of binary actinide alloys in a Pt matrix. The kinetics of the reactions of $An^{2+}$ with oxidants and/or water to form $AnO^{2+}$, $AnOH^{2+}$, and $AnO_2^{2+}$ are evaluated to determine bond energies, ionisation energies and formation enthalpies and hydration enthalpies for $AnO_2^+$ and $AnO_2^{2+}$ ions. The reactions of $An^{2+}$ with the oxidising agents or water lead to the formation of $AnO^{2+}$ and $AnOH^{2+}$, respectively.

The authors revised reported values for $AnO_2$ ionisation potentials [1985HIL/GUR] to re-evaluate the formation enthalpy of the $AnO_2^+$ ion and concluded $\Delta_f H^o_m(UO_2^+, g)$ = (115 ± 50) kJ·mol$^{-1}$ and $\Delta_f H^o_m(PuO_2^+, g)$ = (270 ± 54) kJ·mol$^{-1}$. The old values of IE[$UO_2$] = (5.5 ± 0.5) eV and IE[$PuO_2$] (9.4 ± 0.5) eV in [1985HIL/GUR] were replaced with IE[$UO_2$] = (6.128 ± 0.003) eV and IE[$PuO_2$] = (7.03 ± 0.12) eV. By combining the data for $\Delta_f H^o_m(UO_2^+, g)$ and $\Delta_f H^o_m(PuO_2^+, g)$ with the new ionisation energies reported in this study for $AnO_2^+$ (IE[$UO_2^+$] = (14.6 ± 0.4) eV and IE[$PuO_2^+$] = (15.1 ± 0.4) eV), the authors derive $\Delta_f H^o_m(UO_2^+, g)$ = (1524 ± 63) kJ·mol$^{-1}$ and $\Delta_f H^o_m(PuO_2^+, g)$ = (1727 ± 66) kJ·mol$^{-1}$. By combining $\Delta_f H^o_m(UO_2^{2+}, g)$ and $\Delta_f H^o_m(UO_2^{2+}, aq)$ = – (1019 ± 3) kJ·mol$^{-1}$ as selected in [2003GUI/FAN] the authors report the hydration enthalpy of the $UO_2^{2+}$ ion to be $\Delta_{hydr} H^o_m(UO_2^{2+})$ = – (1665 ± 64) kJ·mol$^{-1}$. Similarly, combining $\Delta_f H^o_m(PuO_2^{2+}, g)$ and $\Delta_f H^o_m(PuO_2^{2+}, aq)$ = – (822 ± 7) kJ·mol$^{-1}$ from [2003GUI/FAN] the authors calculate $\Delta_{hydr} H^o_m(PuO_2^{2+})$ = – (1671 ± 67) kJ·mol$^{-1}$. Assuming $\Delta_{hydr} H^o_m(AnO_2^{2+}) \sim -1670$ kJ·mol$^{-1}$ applies to $NpO_2^{2+}$ and $AmO_2^{2+}$ and using $\Delta_f H^o_m(NpO_2^{2+}, aq)$ = – (861 ± 5) kJ·mol$^{-1}$ and $\Delta_f H^o_m(AmO_2^{2+}, aq)$ = – (652 ± 2) kJ·mol$^{-1}$, the authors estimate the reaction enthalpies $\Delta_f H^o_m(NpO_2^{2+}, g) \sim 1687$ kJ·mol$^{-1}$ and $\Delta_f H^o_m(AmO_2^{2+}, g) \sim 1896$ kJ·mol$^{-1}$. The latter value is in close

agreement with the estimated value of $\Delta_f H^o_m(AmO_2^{2+}, g) = (1924 \pm 100)$ kJ·mol$^{-1}$ derived from $IE[AmO_2^+] = (15.7 \pm 0.9)$ eV and $\Delta_f H^o_m(AmO_2^+, g) = (410 \pm 50)$ kJ·mol$^{-1}$.

Gibson *et al.* used the relationship (A.535) to calculate the corresponding enthalpy of hydration:

$$\Delta_{hydr}H^o(UO_2^{2+}, g) = \Delta_{hydr}E^o(UO_2^{2+}, g) + \Delta^*(UO_2^{2+}, g) + T\Delta_{hydr}S \quad \text{(A.535)}$$

$\Delta^*(UO_2^{2+}, g) \approx 209$ kJ·mol$^{-1}$ is the estimated difference between the calculated electronic hydration energy and the Gibbs energy at 298 K. Using $\Delta_{hydr}S(UO_2^{2+}) = 400$ J·K$^{-1}$·mol$^{-1}$, they find an enthalpy of hydration, $\Delta_{hydr}H^o_m(UO_2^{2+}, g) = -1676$ kJ·mol$^{-1}$, in excellent agreement with the experimental value, but very different from $\Delta_{hydr}H^o_m(UO_2^{2+}, g) = -1345$ kJ·mol$^{-1}$ reported in [1986MAR/LOE] based on semi-empirical methods.

Hydration enthalpies were also calculated for the monopositive actinide ions, $AnO_2^+$. Using the values for $\Delta_f H^o_m(AnO_2^+, g)$ and $\Delta_f H^o_m(UO_2^+, aq) = -(1033 \pm 6)$ kJ·mol$^{-1}$ and $\Delta_f H^o_m(PuO_2^+, aq) = -(915 \pm 6)$ kJ·mol$^{-1}$ reported in [2003GUI/FAN], the authors calculate $\Delta_{hydr}H^o_m(UO_2^+) = -(709 \pm 51)$ kJ·mol$^{-1}$ and $\Delta_{hydr}H^o_m(PuO_2^+) = -(746 \pm 55)$ kJ·mol$^{-1}$. From estimated bond energies for $NpO_2^+$ and $AmO_2^+$ the authors estimate $\Delta_f H^o_m(NpO_2^+, g) = (215 \pm 82)$ kJ·mol$^{-1}$ and $\Delta_f H^o_m(AmO_2^+, g) = (410 \pm 50)$ kJ·mol$^{-1}$. With $\Delta_f H^o_m(NpO_2^+, aq) = -(978 \pm 5)$ kJ·mol$^{-1}$ and $\Delta_f H^o_m(AmO_2^+, aq) = -(805 \pm 5)$ kJ·mol$^{-1}$, the authors obtained the hydration enthalpies for $NpO_2^+$ and $AmO_2^+$, $\Delta_{hydr}H^o_m(NpO_2^+) = -(754 \pm 83)$ kJ·mol$^{-1}$ and $\Delta_{hydr}H^o_m(AmO_2^+) = -(776 \pm 51)$ kJ·mol$^{-1}$.

The ionisation energies of $AnO_2^+$ are calculated from the exothermic reactions of $AnO^{2+}$ with $N_2O$ and $O_2$. The bare actinyl ion, $AnO_2^{2+}$, was formed by reacting $AnO^{2+}$ with $N_2O$ (An = U, Np, Pu) or $O_2$ (An = U, Np). The second ionisation energies of the $AnO_2^+$ ions are estimated from these electron transfer reactions to (14.6 ± 0.4) eV for $UO_2^+$ and (15.1 ± 0.4) eV, for both $NpO_2^+$ and $PuO_2^+$.

Gibson *et al.* also discuss bond dissociation and ionisation energies but these fall outside the scope of the present review. The present review accepts the enthalpies of hydration of $AnO_2^{2+}(g)$ and $AnO_2^+(g)$ where An = U and Pu reported by Gibson *et al.*, but these data are not included among the selected values as the NEA reviews do not include thermodynamic data for ions in gas phase. Since thermodynamic data for gaseous ions are not included in the NEA reviews, the information from Gibson *et al.* is therefore not listed among selected thermodynamic data.

**[2005HAS]**

Haschke examines the reduction mechanism of Pu(VI) in aqueous systems and discusses the effect of disproportionation reactions and radiolysis. The reduction of Pu(VI) in aqueous solution is claimed to be consistent with the disproportionation of

Pu(VI) and the fast subsequent reaction of the transient Pu(VII) with water, as well as be impacted by the reduction induced by alpha-radiolysis. The author suggests that the reduction of Pu(VI) follows the fastest path given that radiolysis effects are independent but disproportionation is dependent on system parameters such as pH and [Pu(VI)]. The disproportionation rate of Pu(VI) is assumed to be similar to disproportionation rate of Pu(V), and the author proposes the disproportionation reaction to produce hydroxo-bridged dimeric species of Pu(V) and Pu(VI). For his analysis, the author used data that are extracted from graphical sources in the open literature. No new experimental or thermodynamic data are presented.

**[2005JAV/WAS]**

[2005JAV/WAS] report the measurement of the low temperature heat capacity of PuSb, $PuGa_3$, $PuCoGa_5$, $NpCoGa_5$, and NpTe in the temperature range 1.8-300 K and magnetic fields up to 9 T using thermal relaxation calorimetry. The authors described the use of Stycast 2850 FT for encapsulating transuranium materials for such measurements, and tested the reliability of this technique by comparing their experimental results with literature data. The heat capacity of Stycast 2850 FT was measured alone, and its contribution subsequently subtracted to the experimental results of the encapsulated materials. Testing on non-transuranium materials showed that the encapsulation in Stycast 2850 FT yielded the same results as the literature within instrumental accuracy of 2-3 %. The heat capacity of $^{242}$PuSb was recorded on 19 mg of material, yielding results in good agreement with the quasi-adiabatic data of [1986HAL/JEF] collected in the temperature range 10-300 K. The authors unfortunately did not report the numerical details of their measurements. The derived heat capacity and entropy at 298.15 K, *i.e.*, $C^{o}_{p,m}$(PuSb, cr, 298.15 K) = 51.5 J·K$^{-1}$·mol$^{-1}$ and $S^{o}_{m}$(PuSb, cr, 298.15 K) = 106.2 J·K$^{-1}$·mol$^{-1}$, are in very good agreement with the data recommened by [2001LEM/FUG] based on the results of [1986HAL/JEF] and [1990HAL/MOR], *i.e.*, $C^{o}_{p,m}$(PuSb, cr, 298.15 K) = (52.8 ± 3.5) J·K$^{-1}$·mol$^{-1}$ and $S^{o}_{m}$(PuSb, cr, 298.15 K) = (106.9 ± 7.5) J·K$^{-1}$·mol$^{-1}$. The electronic component to the specific heat and Debye temperatures was derived as $\gamma$ = (6 ± 2) mJ·K$^{-2}$·mol$^{-1}$, in good agreement with the value reported in [2001LEM/FUG], *i.e.*, $\gamma$ = (5 ± 5) mJ·K$^{-2}$·mol$^{-1}$. Finally, the measurements of [2005JAV/WAS] reproduced the two phase transitions reported at 75 K and 87 K. In this review, we retain the data recommended by [2001LEM/FUG] for the heat capacity and entropy of PuSb.

**[2005KUR/ADA]**

[2005KUR/ADA] reported a molecular dynamics (MD) study of the thermophysical properties of the actinide nitrides ThN, UN, NpN and PuN in the temperature range

300-2500 K and pressure range 0.1 MPa-1.5 GPa. The complete review of this article is reported in the Appendix A for uranium.

**[2005MOR/SAS]**

Moriyama and coworkers calculate hydrolysis constants for the tetravalent oxidation state of Th, U, Np and Pu using an electrostatic hard-sphere model and evaluate the trends across the series. The model is based on the effective charge, radii, dielectric constants and distances between the hard-spheres. A large number of An:OH combinations are calculated to consider monomeric and polymeric Pu(IV) hydrolysis products, although experimental evidence for the majority of those species is absent. For the analysis of the trends of the hydrolysis constants, thermodynamic formation constants of the monomeric complexes $An(OH)_n^{4-n}$ with $n$ = 1-6 were calculated as reference values. The effective charge of + 4.42 for Np(IV) and Pu(IV) was transferred from the analogous U(IV), compared to the effective charge of + 4 applied to Th(IV). The predicted higher hydrolysis constants deviate from selected data in the NEA TDB by orders of magnitude and experimental and calculated solubility data differ significantly, especially at $p_cH \geq 6$. No new experimental data are provided in this study and the calculated data are not considered by this review for data selection.

Table A-175: Comparison of thermodynamic Pu(IV) hydrolysis constants selected in the NEA TDB and calculated by Moriyama *et al.* using a hard-sphere model.

| Pu:OH ratio | $\log_{10}\beta^\circ$ /NEA TDB | $\log_{10}\beta^\circ$ /Calc. |
|---|---|---|
| 1:1 | (14.60 ± 0.20) | 14.51 |
| 1:2 | (28.60 ± 0.30) | 26.13 |
| 1:3 | (39.70 ± 0.40) | 37.10 |
| 1:4 | (47.50 ± 0.50) | 45.19 |
| 1:5 | – | 47.72 |
| 1:6 | – | 47.35 |

**[2005NIK/GOG]**

The reaction of Pu(VI) with ozone in NaOH solutions is measured spectroscopically. The authors interpret spectral changes caused by ozonolysis of the hydroxide solution with the formation of Pu(VII) and Pu(VIII). The reduction potential for the Pu(VII/VI) redox couple is estimated to be $E^{\circ\prime}$(Pu(VII)/Pu(VI)) = (0.685 ± 0.35) V based on the ability of ferrate ($E^{\circ\prime}$(Fe(VI)/Fe(III) = 0.72 V in 1 M NaOH) to oxidise Pu(VI) in 1.5 M NaOH and by comparison with the redox potential of Am(VI) $E^{\circ\prime}$(Am(VI)/Am(V)) = 0.65 V, which does not oxidise Pu(VI). No new thermodynamic data are provided in this study.

**[2005RAI/XIA]**

Rai *et al.* studied the solubility of $(AnO_2)_3(PO_4)_2 \cdot 4H_2O$(s) with An = U and Pu, and developed thermodynamic speciation models for U(VI) and $^{239}$Pu(VI) solubilities in phosphate-containing aqueous solutions. The experimental methods and data analysis used in this paper follow the same pattern as in [2005FEL/XIA]. The An(VI) solid phases used in the solubility studies were precipitated from a 0.1 M $HNO_3$/1 M $Na_2HPO_4$ solution and aged for several days before used for sample preparation. Characterisation of the solid phases was performed with EXAFS and X-ray diffraction. The solubility experiments were conducted under argon atmosphere, with varying phosphate concentrations (0.001 M-0.01 M) over a wide range of pH (2.5-10.5). The soluble concentrations of U(VI) and phosphate were analysed by ICP-MS, while liquid scintillation α-counting was used to determine the Pu concentrations after filtration with a pore size filter of 40 Å. The pH values were measured with a combination glass electrode, but no information is provided regarding the relationship between pH and $p_cH$. The pH of 3.5 in some of the experiments was adjusted with HCl and $Na_2HPO_4$ as calculated with the GMIN code. The solubility experiments were performed over a long duration (up to 870 days) and solubility studies at various phosphate concentrations allowed to examine the speciation in solution. The solubility data were analysed and interpreted by applying the Pitzer formalism.

*U(VI) solubility studies*

These solubility studies are discussed in the uranium section.

*Pu(VI) solubility studies*

In contrast to U(VI), the absence of any Bragg reflections in the X-ray diffraction data of the Pu(VI) precipitates indicated an amorphous nature, and disabled the clear identification of these solid phases. Further analysis of the Pu(VI) solid by Pu $L_{III}$-edge X-ray absorption spectroscopy suggested the presence of a microcrystalline Pu(VI) phosphate with short-range order. However, significant differences in the coordination of U(VI) and Pu(VI) was observed reflected in the different An-P (3.66 Å for U and 3.06, 3.45 and 3.78 Å for Pu) and An-An (4.10, 5.18 and 6.78 Å for U and 3.94 Å for Pu) distances. Despite these differences, the authors designated the solid as $(PuO_2)_3(PO_4)_2 \cdot 4H_2O$(am) in analogy to U(VI) and justified this designation with the similar thermodynamic analysis of U(VI) and Pu(VI) solubility data. However, it is to note that the authors adopted the U(VI) solubility speciation model to fit the Pu(VI) data.

The solubility behaviour of U(VI) and Pu(VI) in the aqueous phosphate systems investigated show very similar trends. Identical soluble concentrations are observed at pH ≤ 5 and 0.01 m phosphate, but higher Pu(VI) concentrations are found in the pH range 6-8.5 as well as in solutions of pH = 3.5 with phosphate concentrations above about 0.03 m. This difference suggests a slightly different solution speciation of

U(VI) and Pu(VI). At pH > 9 the U(VI) and Pu(VI) concentrations overlap each other again. The comparison of U(VI) and Pu(VI) solubility data must be undertaken with some caution because the authors used data with quite different equilibration periods (18 days for Pu(VI) *versus* 29 or 870 days for U(VI) in their Figure 8). The authors report that steady-state conditions for U(VI) are reached in less than three days, while Pu(VI) concentrations after 3 and 20 or 35 days can differ by up to 0.3 log concentration units. Ageing effects can be observed in the documented solubility data up to 35 days of equilibration.

As a noticeable feature in the solubility study in 0.01 m $NaH_2PO_4$, the Pu(VI) soluble concentration appears to follow the trend of decreasing solubility down to about $10^{-6.5}$ M at about pH 6.3 where a significant increase in [Pu(VI)] of up to about 0.7 logarithmic concentration units is observed. Similar steps and incoherences in solubility data are known to occur in solubility experiments where the solid equilibrium phase undergoes a transition or when polynuclear solution species are formed. The authors did not provide any explanation of this phenomenon occurring and it raises suspicion about the nature of the solid phase and proposed solution speciation.

Due to the similar solubility behaviour of Pu(VI) and U(VI), the authors adopted analogous solution species as proposed for the U(VI) system by using $PuO_2H_2PO_4^+$, $PuO_2(H_2PO_4)_2(aq)$, and $PuO_2HPO_4(aq)$. Although they did not play any significant role and lack any evidence of formation, Rai *et al.* also included $PuO_2H_3PO_4^{2+}$ and $PuO_2(H_2PO_4)(H_3PO_4)^+$ in the data analysis. The Pu(VI) hydrolysis species $PuO_2OH^+$, $PuO_2(OH)_2(aq)$, and $(PuO_2)_2(OH)_2^{2+}$ as proposed in [2003GUI/FAN] were also employed in the data analysis.

The solubility data at low pH were modeled according to the dissolution Reaction (A.536):

$$(PuO_2)_3(PO_4)_2\cdot 4H_2O(am) \rightleftharpoons PuO_2^{2+} + 2PO_4^{3-} + 4H_2O(l) \qquad (A.536)$$

Rai *et al.* use the Pitzer model to report the solubility product $\log_{10} K_s^o$ (A.536) = – (48.97 ± 0.69), which is close to the analogous U(VI) values discussed above. However, this model represents the Pu(VI) solubility data at low (0.001 m) $NaH_2PO_4$ very well, but slightly overpredicts data at increased (0.01 m) $NaH_2PO_4$ concentrations. The authors also determined the thermodynamic equilibrium constants for a number of Pu(VI) solution species:

$$PuO_2^{2+} + PO_4^{3-} \rightleftharpoons PuO_2PO_4^- \qquad (A.537)$$

$$PuO_2^{2+} + H_2PO_4^- \rightleftharpoons PuO_2H_2PO_4^+ \qquad (A.538)$$

$$PuO_2^{2+} + 2H_2PO_4^- \rightleftharpoons PuO_2(H_2PO_4)_2(aq) \qquad (A.539)$$

$$PuO_2^{2+} + HPO_4^{2-} \rightleftharpoons PuO_2HPO_4(aq) \qquad (A.540)$$

The quality and agreement of this speciation models with experimental data varies with pH and phosphate concentration. The associated equilibrium constants tend to model very well the solubility data in 0.001 m $NaH_2PO_4$ up to pH ~ 9. The model starts to overpredict the solubility at pH > 9 where $PuO_2PO_4^-$ and $PuO_2(OH)_2$(aq) are calculated to be the predominant solution species. The solution speciation at high pH is uncertain and may be affected by the formation of ternary solution species of general formula $PuO_2(OH)_x(PO_4)_y^{2-x-3y}$. In 0.01 m $NaH_2PO_4$ solution, the suggested speciation model fits the solubility data very well at pH > 6, while Pu(VI) solubilities in the acidic range are quite overpredicted. The equilibrium constant of $PuO_2HPO_4$(aq) appears to satisfy the upper Pu(VI) solubility curve, but significantly overpredicts the lower Pu(VI) solubility branch at pH < 6. The mismatch of the two solubility branches and the solubility overprediction at pH ≤ 6.3 are suggestive of a transformation in the solid phase.

Due to the uncertainties of the solution speciation at high pH, $(\Delta_f G_m^o/RT)(PuO_2PO_4^-) \geq -748.3$ is considered only an estimated value, despite the fact that the inclusion of $PuO_2PO_4^-$ improved the solubility predictions in the pH range 8-10. Using the Pitzer formalism, the authors calculated the following thermodynamic data: $(\Delta_f G_m^o/RT)((PuO_2)_3(PO_4)_2 \cdot 4H_2O, am) = -(2245.4 \pm 1.4)$; $(\Delta_f G_m^o/RT)(PuO_2PO_4^-) \geq -(748.3 \pm 1.6)$; $(\Delta_f G_m^o/RT)(PuO_2HPO_4, aq) = -766.332$; $(\Delta_f G_m^o/RT)(PuO_2H_2PO_4^+) = -773.774$; $(\Delta_f G_m^o/RT)(PuO_2(H_2PO_4)_2, aq) = -1236.327$; $(\Delta_f G_m^o/RT)(PuO_2H_3PO_4^{2+}) = -772.945$; $(\Delta_f G_m^o/RT)(PuO_2(H_2PO_4)(H_3PO_4)^+) = -1238.653$.

**[2005SED/KON]**

[2005SED/KON] reported *ab initio* calculations of the enthalpies of formation of the actinide mononitrides AnN(cr) (An = Ac, Th, Pa, U, Np, Pu, Am). The review is given in the Uranium, App. A section.

**[2005THI/KON]**

The heat capacity of $PuPO_4$(cr) was measured between 5 K and 300 K by adiabatic relaxation calorimetry. The sample was prepared successfully by coprecipitation from a Pu-nitrate solution by adding $Na_2HPO_4$ in stoichiometric amounts. The derived standard entropy of $PuPO_4$(cr) is $S_m^o(298.15\ K) = (137.0 \pm 2.7)\ J \cdot K^{-1} \cdot mol^{-1}$ and the heat capacity $C_{p,m}^o(298.15\ K) = 114.5\ J \cdot K^{-1} \cdot mol^{-1}$.

**[2005VER/AME]**

In this paper, Vercouter *et al.* report a spectroscopic study of the interactions of trivalent lanthanum and europium in aqueous sulfate solutions. Although this paper does not discuss the complexation of actinides with hydrogensulfate or sulfate, it provides ion-

interaction coefficients for the sulfate system that have not been elected in the NEA TDB: $\varepsilon(H^+, HSO_4^-)$ = (0.10 ± 0.06) kg·mol$^{-1}$ and $\varepsilon(H^+, SO_4^{2-})$ = – (0.03 ± 0.06) kg·mol$^{-1}$. These parameters were used to calculate thermodynamic equilibrium constants in Section 11.4.1.2 of Aqueous plutonium(IV) sulfates.

**[2006MOR/SAS]**

Moriyama and coworkers calculated hydrolysis constants for the polymeric hydrolysis species of the hexavalent actinides U, Np and Pu by using an electrostatic hard-sphere model. The semi-empirical model developed was calibrated against experimental uranium data. In this least-square fitting analysis routine, the effective charges of the central actinide ions are used over their formal charges. The effective charges were determined to be 2.22, 2.21 and 2.15 for $UO_2^{2+}$, $NpO_2^{2+}$ and $PuO_2^{2+}$, respectively, which are much smaller than the values previously reported in the literature. In fact, the values reported in this paper are even smaller than those reported by the same authors previously in [2002MOR/FUJ]. The difference originates from the source of ionic radii, depending on if they were determined as distances between atoms in crystals or in solution species. Another fact that may contribute to these differences is that the authors used octahedral aquo complexes, $AnO_2(H_2O)_4^{2+}$, as their reference species, which has been shown experimentally and theoretically to be less stable than the pentaaquo complex, $AnO_2(H_2O)_5^{2+}$. A total of 25 mono- and polynuclear hydrolysis species were calculated for U(VI), while the speciation of Np(VI) and Pu(VI) was limited to three solution species each, namely $NpO_2OH^+$ ($\log_{10}\beta^\circ$ = 9.09), $(NpO_2)_2(OH)_2^{2+}$ ($\log_{10}\beta^\circ$= 22.13), $(NpO_2)_3(OH)_7^-$ ($\log_{10}\beta^\circ$ = 52.68), $PuO_2OH^+$ ($\log_{10}\beta^\circ$ = 8.63), $PuO_2(OH)_2$(aq) ($\log_{10}\beta^\circ$ = 15.43), and $(PuO_2)_2(OH)_2^{2+}$ ($\log_{10}\beta^\circ$ = 20.15). No new experimental data are provided.

**[2006MOS/MAT]**

The heat of formation of $PuO_2^{2+}$ ions in the gas phase is calculated from experimental heats of formation of $PuF_4$(g), $PuF_6$(g) and $PuO_2$(g) and reaction enthalpies derived from DFT calculations. The heat of formation of $PuO_2^{2+}$(g) was calculated from 21 model reactions at 0 K with $PuF_4$(g), $PuF_6$(g) and $PuO_2$(g) as starting compounds, which all have established values for their heat of formations. The enthalpies of formation of other species involved in the chemical reactions are also well established.

The molecular structures of the compounds are optimised by applying the local density approximation and are used for calculating the reaction energetics with gradient-corrected functionals. The reaction energies are corrected for changes in zero-point vibrational energy to obtain the reaction enthalpies. The authors calculated the vibrational frequencies for $PuF_4$(g) (638, 232, 175 cm$^{-1}$), $PuO_2$(g) (828, 792, 109 cm$^{-1}$)

and $PuO_2^{2+}$(g) (1043, 1020, 218 $cm^{-1}$), and calculated the enthalpy of formation $\Delta_f H_m^o(PuO_2^{2+}, g)$ = (1750 ± 63) kJ·$mol^{-1}$ at 0 K.

The impact of relativistic effects is estimated by considering electron-electron interactions dominating over spin-orbit interactions in open shell configuration and favoring spin-orbit interactions in closed-shell configurations. While both methods provide close results for the reaction of $PuF_4$(g) and $PuF_6$(g), the $\Delta E$ values calculated with each model for reactions with $PuO_2$(g) are quite different with – 88 and – 4 kJ·$mol^{-1}$. Due to the large uncertainty of the $\Delta E$ value for reactions with $PuO_2$(g), the authors derive $\Delta_f H_m^o(PuO_2^{2+}, g)$ = (1750 ± 63) kJ·$mol^{-1}$ only from the reactions with $PuF_4$(g) and $PuF_6$(g). The data provided in this study are not included in the data selection by this review.

**[2006NEC/ALT]**

This study focuses on the determination of the activity coefficients for $Th^{4+}$ at 22 °C by solvent extraction methods. The authors compare the SIT ion-interaction parameters for tetravalent actinide ions and report $\varepsilon(Pu^{4+}, ClO_4^-)$ = (0.82 ± 0.07) kg·$mol^{-1}$ and $\varepsilon(Pu^{4+}, Cl^-)$ = (0.37 ± 0.05) kg·$mol^{-1}$. This calculation is based on the redox potential for the Pu(IV/III) couple, $E°(Pu^{4+}/Pu^{3+})$ = (1.047 ± 0.003) V, and the thermodynamic equilibrium constant, $\log_{10} K^o_{IV, III}$ = (17.69 ± 0.04), accepted by the NEA TDB for the one-electron transfer Reaction (A.541).

$$Pu^{4+} + e^- \rightleftharpoons Pu^{3+} \qquad \text{(A.541)}$$

**[2006REI/NEU]**

Reilly and Neu investigated the formation of monomeric and polynuclear hydrolysis species of $^{239}Pu(VI)$ at (25 ± 0.1) °C under argon atmosphere. Potentiometric titrations were performed with varying (1-10 mM) Pu(VI) concentrations in 0.1 M $NaNO_3$. The Pu source material contained 94 % $^{239}Pu$, 4 % $^{242}Pu$ and trace amounts of other Pu isotopes. The sample solutions were titrated with standardised 0.10 or 0.01 M NaOH to collect potentiometric data points in the pH range 2.7-8.4. Optical spectra of titrated solutions were measured simultaneously in the range 720-950 nm to monitor the shift of the Pu(VI) absorbance bands. A combination pH electrode was used to determine the pH and calibrated against known $H^+$ concentrations to obtain $p_cH$. The initial Pu(VI) concentration was measured spectroscopically with the absorbance at 830.5 nm and a molar extinction coefficient of 538 L·$mol^{-1}$·$cm^{-1}$. The $pK_{H_2O}$ of 13.78 was used in all calculations for 0.1 M $NaNO_3$ at 25 °C.

The potentiometric data were fit by using mono- and polynuclear hydrolysis products depending on the total Pu(VI) concentration. The potentiometric data at [Pu(VI)] ≥ 1 mM were best fit with only two solution species, $(PuO_2)_2(OH)_2^{2+}$ and

$(PuO_2)_2(OH)_4(aq)$, without the need for further solution species. From these data, the apparent formation constants were determined to be $\log_{10} {}^*\beta_{2,2} = -(7.79 \pm 0.20)$ and $\log_{10} {}^*\beta_{2,4} = -(19.3 \pm 0.5)$. The presence of two hydrolysis species was validated spectroscopically by the appearance of two absorption bands with increasing pH at 845 nm and 850 nm. The absorbance at 845 nm ($\varepsilon = 270\ L \cdot mol^{-1} \cdot cm^{-1}$) was assigned to $(PuO_2)_2(OH)_2^{2+}$ and the band at 850 nm was assigned to $(PuO_2)_2(OH)_4(aq)$. The authors used the same approach to determine the hydrolysis behaviour of Pu(VI) at $10^{-4}$ M Pu concentration. At these concentrations, no polynuclear species were observed to form and an absorbance band at 842 nm was assigned to $PuO_2OH^+$. Data at the low Pu concentrations were interpreted with solely monomeric solution species $PuO_2OH^+$ and $PuO_2(OH)_2(aq)$. The authors state that there was no evidence that supported the presence of $(PuO_2)_3(OH)_5^+$ or $(PuO_2)_4(OH)_7^+$.

The SIT was used to correct to zero ionic strength. Since no Pu(VI)-nitrate parameters were available, the authors used the ion-interaction parameters available for the U(VI) nitrate system:

$$\Delta\varepsilon_{1,1} = \varepsilon(UO_2OH^+, NO_3^-) + \varepsilon(H^+, NO_3^-) - \varepsilon(UO_2^{2+}, NO_3^-) = (0.34 \pm 1.40)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon_{1,2} = 2\varepsilon(H^+, NO_3^-) - \varepsilon(UO_2^{2+}, NO_3^-) = -(0.10 \pm 0.04)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon_{2,2} = \varepsilon((UO_2)_2(OH)_2^{2+}, NO_3^-) + 2\varepsilon(H^+, NO_3^-) - 2\varepsilon(UO_2^{2+}, NO_3^-) = (0.15 \pm 0.11)\ kg \cdot mol^{-1}$$

$$\Delta\varepsilon_{2,4} = 4\varepsilon(H^+, NO_3^-) - 2\varepsilon(UO_2^{2+}, NO_3^-) = -(0.20 \pm 0.07)\ kg \cdot mol^{-1}.$$

**[2006TSU/WAH]**

The bond distances and reduction potentials for the light actinide couples $AnO_2(H_2O)_5^{2+}/AnO_2(H_2O)_5^+$ with An = U, Np, Pu and Am were calculated in the gas phase from quantum chemical models at the MP2, CASPT2 and CCSD(T) levels including spin-orbit effects. A detailed review is given in the Uranium, App. A section.

**[2006WIL/ALM]**

Wilson and coworkers reported on the synthesis of three Pu(III) chlorides, cis-$Cs[PuCl_4(H_2O)_4](cr)$, and trans-$Cs_5[PuCl_4(H_2O)_4]Cl_4 \cdot 2H_2O(cr)$, and $(Et_4N)[PuCl_2(H_2O)_6]Cl_2 \cdot 2H_2O(cr)$ with chloride ligands coordinated to the Pu atom. The coordination of Pu(III) chloride in solid state compounds was explored by using single crystal X-ray diffraction. The three Pu(III) compounds were precipitated from concentrated hydrochloric acid solutions with varying amounts of CsCl and the presence of reducing agents to hold the trivalent oxidation state of plutonium. The compounds contained the bischloro cation, $PuCl_2(H_2O)_6^+$, and *cis*- and *trans*-

configurations of the tetrachloro anion, $PuCl_4(H_2O)_4^-$. No thermodynamic data on these compounds are reported.

**[2007GOU/SEI]**

[2007GOU/SEI] reported a photoelectron spectroscopy study of $PuO_2$ exposed to atomic oxygen to support the first-principles total-energy calculations of [2004KOR/VIT]. According to [2004KOR/VIT], strong oxidants such as atomic oxygen generated by α-radiolysis of water could lead to the formation of $PuO_{2+x}$, but only as transient surface species that transforms back to $PuO_2$ with release of molecular oxygen $O_2$.

[2007GOU/SEI] exposed thin $UO_2$ and $PuO_2$ films to atomic oxygen and probed them with UV photoelectron spectroscopy (UPS) using HeII excitation radiation (40.81 eV), and X-ray photoelectron spectroscopy (XPS) using non-monochromatic Mg-Kα and Al-Kα radiation, respectively. UPS probes about two atomic layers against ten atomic layers with XPS. Chemisorption on the surface with oxidation of the top layer was studied at low temperature ($T$ = 25 °C), while diffusion of surface oxygen into the lattice was investigated at high temperature ($T$ > 200 °C). An electron cyclotron resonance plasma source was used to generate the beam of atomic oxygen.

The UPS spectrum of $UO_2$ showed a broad band between 2 and 8 eV binding energy due to O-2p valence-band states and a peak at 2 eV due to U-$5f^2$ electrons. After exposure to atomic oxygen at 25 °C, the U-5f emission disappeared due to surface oxidation up to $UO_3$ (with the $5f^0$ configuration). This surface layer reduced back to $UO_2$ upon heating up to $T$ = 300 °C, however, showing that bulk diffusion is slow at low temperature. When exposed to atomic oxygen at high temperature, oxygen chemisorbtion occurred and was followed by bulk oxide formation to stable $UO_3$ as confirmed by the 4f XPS results.

When exposing $PuO_2$ to atomic oxygen at 25 °C, oxidation to $PuO_{2+x}$ occurred on the top surface as confirmed by UPS with the reduction of the Pu-$5f^n$ emission at 2 eV binding energy. Oxygen was adsorbed on the top surface which led to a symmetrical small peak at 6 eV binding energy superimposed on the O-2p band. This surface was reduced back to $PuO_2$ when heating to $T$ = 200 °C. However, by contrast with uranium, no chemisorbtion and bulk diffusion occurred when exposing to atomic oxygen at $T$ = 200 °C. This experimental observation supports the first-principles thermodynamic calculations of [2004KOR/VIT], who showed that $Pu_4O_9$ was unstable in the presence of atomic oxygen and decomposes back to $PuO_2$ while generating molecular oxygen (see Equations (A.526) and (A.527) of [2004KOR/VIT]). The results of [2007GOU/SEI] therefore exclude possible bulk oxidation of $PuO_2$. Only the outer surface can chemisorb extra oxygen, which is moreover released at 200 °C. This study

does not exclude the possible formation of oxy hydroxy compounds such as $Pu_4O_8OH$, however.

**[2007HAS]**

This paper follows a series of reports (see also [2005HAS], [2004HAS], [2002HAS/OVE]) that evaluate the reduction and disproportionation reactions of Pu in aqueous solutions. In this report the author is discussing the kinetics and mechanism of the disproportionation of Pu(IV) in acidic nitrate and perchlorate solutions claiming that experimental results published in the open literature do not support the commonly accepted reversible, bimolecular formation of Pu(V). Disproportionation data in nitric acid solutions were interpreted by following a dependence on $[Pu(IV)]^3$ and $[H^+]^{-3}$. Based on time-dependent speciation data the author claims that Pu(IV) disproportionates *via* the formation of a trimeric hydroxo-bridged species, $(PuOH)_3^{9+}$, to form $Pu^{3+}$ and $PuO_2^{2+}$. In the reverse reaction, Pu(IV) is generated via the protonation of $PuO_2^{2+}$ and hydrolysis of $Pu^{3+}$. The trimeric species $(PuOH)_3^{9+}$ is supposed to form by the combination of the Pu(III) products $Pu^{3+}$ and $PuOH^{2+}$ and the protonated Pu(VI) species $Pu(OH)_2^{4+}$. Pu(V) is a secondary product that only forms upon the reduction of Pu(VI). Equilibrium constants for the reactions:

$$3Pu^{4+} + 2H_2O \rightleftharpoons 2Pu^{3+} + PuO_2^{2+} + 4H^+ \quad \text{(A.542)}$$

$$Pu^{4+} + PuO_2^{+} \rightleftharpoons Pu^{3+} + PuO_2^{2+} \quad \text{(A.543)}$$

at $HNO_3$ concentrations of 0.060-0.5 M $HNO_3$ are calculated from measured Pu concentrations reported in the literature.

Table A-176: Experimental formation constants for the equilibria (A.542) and (A.543) calculated by Haschke from Pu(III), Pu(IV), Pu(V) and Pu(VI) concentrations as reported in the literature.

| Method | *I* /medium | $\log_{10}K_{IV,III/VI}$(A.542) | $\log_{10}K_{IV/V,III/VI}$(A.543) | Data source |
|---|---|---|---|---|
| spectr | 0.075M $HNO_3$ | – 2.05 | 0.77 | [1973COS/BIG] |
| spectr | 0.075M $HNO_3$ | – 3.34 | 0.60 | [1990TOT/BEL] |
| spectr | 0.10M $HNO_3$ | – 3.38 | 0.56 | [1973COS/BIG] |
| spectr | 0.10M $HNO_3$ | – 3.52 | 0.58 | [1990TOT/BEL] |
| spectr | 0.10M $HNO_3$ | – 3.15 | 0.54 | [1959ART/MED] |
| spectr | 0.20M $HNO_3$ | – 3.10 | 0.53 | [1959ART/MED] |
| spectr | 0.30M $HNO_3$ | – 3.39 | | [1959ART/MED] |
| spectr | 0.40M $HNO_3$ | – 3.74 | | [1959ART/MED] |
| spectr | 0.50M $HNO_3$ | – 4.22 | 0.0 | [1990TOT/BEL] |

Haschke claims that the thermodynamic model available does not properly describe the reaction mechanisms and steady-state behaviour of Pu. The redox chemistry of Pu is rather controlled by the kinetics and rates of hydrolysis, reduction

and disproportionation reactions. It is to note that the author uses data from graphical sources of reports from 1959, 1973 and 1990. The comparison between calculated and experimental oxidation state distributions in $HNO_3$ solutions at steady state revealed quite large discrepancies for Pu(III), Pu(IV) and Pu(VI).

**[2007NEC/ALT]**

In this report, Neck and coworkers review reported data on the solubility of Pu oxide and hydroxide solid phases in aqueous solution in the absence and presence of oxygen. This report is one of three publications [2007NEC/ALT], [2007NEC/ALT2], [2007NEC/ALT3] that address the formation and solubility behaviour of mixed-valent $PuO_{2+x}$(s) in aqueous solutions and the impact of colloid formation on overall Pu solubility. The authors discuss published data on Pu(IV) solubility data in the absence of carbonate and under different redox conditions, reiterating the calculations and conclusions outlined in [2007NEC/ALT2], [2007NEC/ALT3]. A compilation of equilibrium constants for redox reactions, solubility and hydrolysis reactions of Pu(III), (IV), (V) and (VI) as reported in the NEA TDB is provided. The standard molar Gibbs energies for U, Np and Pu oxides are compared by using the estimated values for Np and Pu oxides reported in [2007NEC/ALT2] and values selected in the NEA TDB. Based on the analogous chemistry and thermodynamic data trends of Np and Pu oxides, the authors disagree with the standard molar Gibbs energies for $PuO_{2.5}$(s) and $PuO_{2+x}$(s) reported by Haschke *et al.* ([2002HAS/ALL], [2002HAS/OVE]). The oxidation mechanism proposed by Hascke *et al.* is based on the water-catalysed oxidation of $PuO_2$(s) to form the mixed-valent oxide $PuO_{2+x}$(s) and hydrogen. However, the formation of hydrogen could not be justified with the thermodynamic values presented in this study and other mechanisms, *i.e.* radiolysis, are proposed to cause the oxidation reaction.

The redox potential is one of the key experimental parameter that greatly impacts the solubility behaviour of Pu. The authors propose to use the term (pe + pH) instead of the theoretical values of $\log_{10}P(O_2, g)$ and $\log_{10}P(H_2, g)$ calculated from measured redox potentials. The $E_h$-pH stability field of water is expressed by the equation $(pe + pH) = \log_{10}P(O_2, g) + 20.77 - 0.5 \log_{10} a_{H_2O}$. The upper stability boundary of water at $P(O_2, g) = 1$ bar is $pe = 20.77 - pH$ and the lower border at $P(H_2, g) = 1$ bar is given by $pe = - pH$. A redox-neutral expression is defined at (pe + pH) = 13.8. The SIT is used for ionic strength correction adopting some ion-interaction parameters from the analogous Am(III), Np(V) and U(VI). At reducing conditions, an interplay between $Pu(OH)_3$(s) and $PuO_2$(am, hyd) is discussed with $Pu(OH)_3$(s) only being stable up to redox conditions at $(pe + pH) = - (0.4 \pm 1.0)$.

The stability of $Pu(OH)_3$(s) and its transformation to $PuO_2$(am, hyd) is calculated to be outside the stability of water, implying that $Pu(OH)_3$(s) is not stable within the stability field of water. The estimated values are associated with a large

uncertainty of about one order of magnitude and improved measurements of the stability and solubility at reducing conditions are necessary to validate and refine the calculations in this report. Recent studies indicate that a Pu(III) solid phase may be stable within the stability field of water under very reducing conditions.

**[2007NEC/ALT2]**

This report is one of three publications [2007NEC/ALT], [2007NEC/ALT2], [2007NEC/ALT3] that discuss the formation and solubility behaviour of mixed-valent $PuO_{2+x}$(s) in aqueous solutions. Here, the authors review information available in the open literature and discuss the solubility of Pu(IV) under the control of the postulated mixed-valent Pu oxide, $PuO_{2+x}\cdot xH_2O$(s), at 20-25 °C. The formation of $PuO_{2+x}\cdot nH_2O$(s) relies on the premise that the Pu(V) concentrations present in reported Pu(IV) oxyhydroxide solubility studies are not consistent with the Reaction (A.544):

$$PuO_2\cdot xH_2O(s) \rightleftharpoons PuO_2^+ + e^- + xH_2O(l) \quad \text{(A.544)}$$

The authors claim that the solubility of Pu is rather controlled by the presence of a mixed-valent solid phase corresponding to the Reaction (A.545):

$$PuO_2\cdot nH_2O(s) + (x/2)O_2 \rightleftharpoons PuO_{2+x}\cdot xH_2O(s) \quad \text{(A.545)}$$

The mixed Pu(IV,V) solid phase can be formulated as $(Pu^{V})_{2x}(Pu^{IV})_{1-2x}O_{2+x}$(s, hyd) and is in equilibrium with Pu(IV) and Pu(V) in solution according to Reaction (A.546):

$$PuO_{2+x}\cdot nH_2O(s,hyd) + (2-3x)H_2O(l) \rightleftharpoons 2xPuO_2^+ + (1-2x)Pu^{4+} + (4-6x)OH^- \quad \text{(A.546)}$$

The standard Gibbs energy for $PuO_{2+x}\cdot nH_2O$(s) is obtained from the thermodynamic solubility constants of $PuO_{2.5}$(s, hyd) in $PuO_{2+x}\cdot nH_2O$(s) ($\log_{10}K^{o}_{sp} = -(14.0 \pm 0.8)$) and $PuO_2$(s, hyd) ($\log_{10}K^{o}_{sp} = -(58.33 \pm 0.52)$) in $PuO_{2+x}\cdot nH_2O$(s) and the standard Gibbs energies for $PuO_2^+$ ($-(852.65 \pm 2.87)$ kJ·mol$^{-1}$), $Pu^{4+}$ ($-(477 \pm 2.70)$ kJ·mol$^{-1}$), $OH^-$ ($-(157.22 \pm 0.07)$ kJ·mol$^{-1}$) and $H_2O$ ($-(237.14 \pm 0.04)$ kJ·mol$^{-1}$). The standard molar Gibbs energies of $PuO_2$(s, hyd) and $PuO_{2.5}$(s, hyd) are calculated from the solubility products according to (A.547) and (A.548), respectively.

$$\Delta_f G^{o}_m(PuO_2,s,hyd) = RT\ln K^{o}_{sp}(PuO_2,s,hyd) + \Delta_f G^{o}_m(Pu^{4+}) + 4\Delta_f G^{o}_m(OH^-) - 2\Delta_f G^{o}_m(H_2O,l) \quad \text{(A.547)}$$

$$\Delta_f G^{o}_m(PuO_{2.5},s,hyd) = RT\ln K^{o}_{sp}(PuO_{2.5},s,hyd) + \Delta_f G^{o}_m(PuO_2^+) + \Delta_f G^{o}_m(OH^-) - 0.5\Delta_f G^{o}_m(H_2O,l) \quad \text{(A.548)}$$

The standard molar Gibbs energy of formation of $PuO_{2+x}\cdot nH_2O$(s) with $x < 0.1$ is then given as:

$$\Delta_f G_m^o(PuO_{2+x}\cdot nH_2O) = 2x(\Delta_f G_m^o(PuO_{2.5}, s, hyd)) + (1-2x)\Delta_f G_m^o(PuO_2, s, hyd) = \\ = 2x(-(971.2 \pm 5.4)) + (1-2x)(-(965.5 \pm 4.0))\ kJ\cdot mol^{-1} \quad (A.549)$$

which is slightly lower than $\Delta_f G_m^o(PuO_2, s, hyd) = -(965.5 \pm 4.0)$ kJ·mol$^{-1}$.

The authors calculated a number of thermodynamic data for An(IV,V,VI) oxides and oxyhydroxides. For comparison with the An(IV) oxides, the authors converted $\Delta_f G_m^o$ values of An(VI) oxyhydroxides to data for the binary oxides $AnO_3$(s, hyd). From $\Delta_f G_m^o(PuO_2(OH)_2\cdot H_2O, cr) = -1442.4$ kJ·mol$^{-1}$ the value of $\Delta_f G_m^o(PuO_3, cr, hyd) = -968.1$ kJ·mol$^{-1}$ is derived; $\Delta_f G_m^o(PuO_{2.25}, cr) = -(995 \pm 3)$ kJ·mol$^{-1}$, $\Delta_f G_m^o(PuO_{2.5}, cr) = -(987 \pm 10)$ kJ·mol$^{-1}$ and $\Delta_f G_m^o(PuO_3, cr) = -(952 \pm 10)$ kJ·mol$^{-1}$ are estimated from pure and mixed valent An(IV,V,VI) oxides and oxyhydroxides. The standard molar Gibbs energies for the hydrated phase fractions in the mixed-valent $PuO_{2+x}\cdot nH_2O$(s) phase were calculated from auxiliary data in the NEA TDB for the anhydrous Pu oxides: $\Delta_f G_m^o(PuO_{2.25}, s, hyd) \geq -(968.4 \pm 4.7)$ kJ·mol$^{-1}$ and $\Delta_f G_m^o(PuO_{2.5}, s, hyd) > -(971.2 \pm 5.4)$ kJ·mol$^{-1}$. The $\Delta_f G_m^o$ for pure $PuO_{2.5}$(s, hyd) is estimated to be $-(965 \pm 7)$ kJ·mol$^{-1}$, which is slightly higher than the formal value of the $PuO_{2.5}$(s, hyd) fraction in the mixed solid phase $PuO_{2+x}\cdot nH_2O$(s). Since these data are estimates this review does not consider them for data selection.

Neck *et al.* also discuss the thermodynamic data reported by Haschke and Allen [2002HAS/ALL] for $PuO_{2+x}$(s) with $x = 0.05$-$0.5$ and discard their values of $\Delta_f G_m^o(PuO_{2.25}, s) = -1080$ kJ·mol$^{-1}$ and $\Delta_f G_m^o(PuO_{2.5}, s) = -1146$ kJ·mol$^{-1}$ as too negative. Neck *et al.* discard the claim of Haschke and Allen that the water-catalysed oxidation of $PuO_2$(s) produces $H_2$(g) because this reaction mechanism cannot be explained by experimental data.

**[2007NEC/ALT3]**

This report is one of three publications [2007NEC/ALT], [2007NEC/ALT2], [2007NEC/ALT3] that discuss the solubility and redox reactions of Pu(IV) oxide and the formation and solubility behaviour of mixed-valent $PuO_{2+x}$(s) in aqueous solutions. In this paper, experimental details are provided for the solubility studies performed to investigate the solubility behaviour of $^{242}$Pu(IV) at $(22 \pm 2)$ °C under air and argon atmosphere. Batch solutions were prepared under argon atmosphere with less than 10 ppm $O_2$ at pH ranging between 2.5 to 13 in 0.1 M $NaClO_4$. The solid phase was freshly precipitated with 1 M NaOH from 0.1 M $HClO_4$ and washed multiple times with water and 0.1 M NaOH. After equilibration for up to 104 days, aliquots were analysed after ultrafiltration (10 kD pore size). Liquid scintillation counting was used to determine the soluble Pu concentration, and the Pu oxidation states were analysed spectroscopically when the concentration was above $3 \times 10^{-6}$ M Pu. At lower Pu concentration, solvent

extraction with HPMBP was performed to determine the Pu(IV)/Pu(V) fractions. Unfiltered samples were counted to determine the total Pu concentration in solution, including colloidal particles. The pH was measured with a combination glass electrode and corrected for ionic strength effects to determine $p_cH$; the redox potential was measured with a combined Pt electrode and Ag/AgCl reference electrode corrected for the reference electrode potential. The solid phase was examined at the end of the experiments by using X-ray diffraction. Weak, broad bands characteristic for $PuO_2$(cr) suggested the solid to be amorphous and hydrated.

For their discussion, Neck *et al.* divide the solubility data into two sections with pH 3 as the boundary pH. At pH > 3 only Pu(V) was measured spectroscopically. The concentration of Pu(IV) at pH 4-8 is very low at $10^{-8}$-$10^{-10}$ M and therefore the measured data are highly scattered. The Pu(V) concentrations are explained with $\log_{10} K^{\circ}_{\mathrm{IVs,V}} = -(19.8 \pm 0.9)$ for the dissolution equilibrium:

$$\mathrm{PuO_2(am,hydr)} \rightleftharpoons \mathrm{PuO_2^+ + e^-} \qquad \text{(A.550)}$$

obtained with $\log_{10} K^{\circ}_{\mathrm{V,VI}} = -(15.82 \pm 0.09)$ in the NEA TDB.

The colloidal Pu fraction was determined to be steady at pH 8-13 between $10^{-7}$ and $10^{-10}$ M, about two orders of magnitude higher than the soluble concentration of Pu(IV). The colloid formation is described by $\log_{10} K^{\circ}_{\mathrm{IVs,coll}} = -(8.3 \pm 1.0)$ for the reaction:

$$\mathrm{PuO_2(am,hyd)} \rightleftharpoons \mathrm{PuO_2(coll,hyd)} \qquad \text{(A.551)}$$

From this equilibrium constant, the authors calculate $\Delta_f G^{\circ}_m$ ($PuO_2$, coll, hyd) = $-(918.1 \pm 7.0)$ kJ·mol$^{-1}$, $\Delta_f G^{\circ}_m$ ($PuO_2$, am, hyd) = $-(965.5 \pm 4.0)$ kJ·mol$^{-1}$ and $\log_{10} K_{\mathrm{IVcoll,V}} = -(11.4 \pm 1.3)$ in 0.1 M NaCl for the reaction:

$$\mathrm{PuO_2(coll,hydr)} \rightleftharpoons \mathrm{PuO_2^+ + e^-} \qquad \text{(A.552)}$$

At pH < 3, equimolar concentrations of Pu(III) and Pu(V) are present in solution. The Pu(III) concentration is consistent with $\log_{10} K^{\circ}_{\mathrm{IVs,III}} = (15.4 \pm 0.5)$ for the reductive dissolution reaction:

$$\mathrm{PuO_2(am,hydr) + e^- + 4H^+ \rightleftharpoons Pu^{3+} + 2H_2O(l)} \qquad \text{(A.553)}$$

At pH > 3, the Pu(V) concentration calculated from this constant are three to seven orders of magnitude lower than the experimentally observed total Pu concentrations. Comparing experimental solubility data under argon with trace amounts of oxygen with those measured under air atmosphere suggests that the solubility of $PuO_2$(am, hyd) and the formation of Pu(V) is related to the amount of oxygen present in the system. It is concluded that the oxygen is scavenged by the solid phase to form a mixed-valent $PuO_{2+x}$(s, hyd) solid phase. The mixed Pu solid phase is in equilibrium with Pu(IV) and Pu(V) and is described as $(Pu^{V})_{2x}(Pu^{IV})_{1-2x}O_{2+x-n}(OH)_{2n}$(s, hyd). Depending on the amount of oxygen traces available, the fraction of oxidised Pu in the

solid phase can vary between 0.5 % ($x = 0.003$) in this study and 10-12 % ($x = 0.05$-0.06) under air. The fractions of Pu(IV) and Pu(V) are calculated from the solubility products of the corresponding oxide in $PuO_{2+x}$(am, hyd) with $\log_{10} K^{o}_{sp}$ ($PuO_{2.5}$ in $PuO_{2+x}$(am, hyd)) = – (14.0 ± 0.8) for the reaction:

$$PuO_{2.5}(am, hydr) + 0.5H_2O(l) \rightleftharpoons PuO_2^+ + OH^- \quad \text{(A.554)}$$

The standard molar Gibbs energy of formation is calculated as a function of the oxidised fraction of Pu in $PuO_{2+x}$(s, hyd), $\Delta_f G^{o}_{m}$ ($PuO_{2+x} \cdot nH_2O$)) = [$2x$(– (971.2 ± 5.4) + (1–$2x$)(– (965.5 ± 4.0)] kJ·mol$^{-1}$. The free energy $\Delta_f G^{o}_{m}$ ($PuO_{2+x}$, cr) ≥ – 998 kJ·mol$^{-1}$ is estimated based on the fact that anhydrous $PuO_2$(cr) cannot be oxidised by oxygen without the presence of water.

**[2007REI/RUN]**

The solubility of Pu(VI) with $PuO_2CO_3$(cr) as the solubility-limiting solid phase was measured at 25 °C at varying carbonate concentrations and $I_m$ = 0.1-5.6 m. This study builds on the preliminary data reported in [2000REI/NEU]. $PuO_2CO_3$(cr) was precipitated at pH 7 under a $CO_2$ atmosphere and ozone to re-oxidise any radiolytically-reduced plutonium to Pu(VI). The precipitates were contacted with solutions of various NaCl concentrations and 5.6 m $NaClO_4$ solutions, with sodium hypochlorite added to the suspensions as holding agent for Pu(VI). The suspensions were purged with 100 % $CO_2$.

Initial and aged solid phases used in the experiments were characterised by using X-ray diffraction and diffuse reflectance spectroscopy and compared to the diffraction pattern of the isostructural solid phases $UO_2CO_3$(cr) and $NpO_2CO_3$(cr). pH measurements were performed with a glass electrode and ionic strength effects were determined with standards of known hydrogen concentration and ionic strength. The carbonate concentrations were calculated from the measured pH using the Pitzer formalism and confirmed with experimental data. The atmospheric pressure of a 100 % $CO_2$ atmosphere at elevated altitude was considered to be $\log_{10} P_{CO_2}$ = – 0.1192. The Pu oxidation state purity of the solutions was monitored throughout the experiment by using electronic absorption spectroscopy.

The authors discuss the difficulties of determining the solubility of Pu(VI) solid phases over a long period of time due to the instability of Pu(VI) in solution, changes in the solid phase and in solution speciation. Any solubility experiment of Pu(VI) is facing the challenge of maintaining Pu(VI) over the duration of the experiment and minimising reduction of Pu(VI) to lower oxidation states. The authors report that the rate of Pu(VI) reduction depends on pH and ionic strength. The reduction of Pu(VI) to lower oxidation state at low NaCl is reported to be significantly more rapid than in concentrated NaCl, presumably due to the formation of radiolysis products (*e.g.* hypochlorite) and the formation of Pu(VI) chloro complexes at high chloride

concentrations. To minimise Pu(VI) reduction, the authors enhanced the stability of Pu(VI) by addition of small amounts of sodium hypochlorite and used several batches of freshly prepared $PuO_2CO_3$(cr).

The solubility data are interpreted with the dissolution equilibrium (A.555):

$$PuO_2CO_3(cr) \rightleftharpoons PuO_2^{2+} + CO_3^{2-} \quad \text{(A.555)}$$

Spectroscopic data revealed that besides $PuO_2^{2+}$ a number of solution species are observed corresponding with the reduction of Pu(VI) and the chloride complexation of Pu(VI). The soluble $PuO_2^{2+}$ concentration is determined spectroscopically from the absorbance band of Pu(VI) at about 830 nm. The molar extinction coefficients of the $PuO_2^{2+}$ absorbance are obtained in $NaClO_4$ solutions of different concentrations and applied to NaCl solutions. The formation of Pu(V) is identified by the characteristic absorbance band at 569 nm. With increasing NaCl concentration additional bands are observed indicative of the formation of Pu(VI) chloride complexes in solution. Considering the sum of Pu(VI) species in solution $[Pu(VI)]_{tot} = [PuO_2^{2+}] + \Sigma[PuO_2Cl_x^{2-x}]$, the solubility of $PuO_2CO_3$(cr) in 5.6 m NaCl ($\log_{10}{}^{*}K_s$ (A.555) = – (14.07 ± 0.13)) is over one order of magnitude higher compared to the Pu solubility in 5.6 m $NaClO_4$ ($\log_{10}{}^{*}K_s$ (A.555) = – (15.26 ± 0.11)). The authors used the concentration of $PuO_2^{2+}$ to calculate apparent solubility products of $PuO_2CO_3$(cr). The SIT was used to extrapolate the apparent solubility products to zero ionic strength to obtain $\log_{10}K_s^{o}$ = – (14.82 ± 0.05) and $\Delta\varepsilon_{ij}$(A.555) = (0.11 ± 0.08) kg·mol$^{-1}$. The SIT parameter $\varepsilon(PuO_2^{2+}, Cl^-)$ = (0.19 ± 0.09) kg·mol$^{-1}$ was calculated from $\Delta\varepsilon_{ij}$ = (0.11 ± 0.08) kg·mol$^{-1}$ and $\varepsilon(Na^+, CO_3^{2-})$ = – (0.08 ± 0.03) kg·mol$^{-1}$. The authors provided individual concentrations of $PuO_2^{2+}$, $PuO_2^{+}$, and Pu(VI) chloro complexes, which can be used to calculate the formation constants of $PuO_2Cl^+$ and $PuO_2Cl_2$ (aq).

The spectroscopic evaluation of the speciation of Pu in this systems allowed the authors also to determine the equilibrium constant for the formation of Pu(VI) chloride complexes. The authors provided individual concentrations of $PuO_2^{2+}$, $PuO_2^{+}$, and Pu(VI) chloro complexes, which can be used to calculate the formation constants of $PuO_2Cl^+$ and $PuO_2Cl_2$(aq). From the absorbance at 838 nm for the $PuO_2Cl^+$ for the complex formed in NaCl systems, respectively, the authors calculate the thermodynamic equilibrium constant $\log_{10}\beta_1^{o}$ = (0.255 ± 0.029) according to the Reaction (A.556):

$$PuO_2^{2+} + Cl^- \rightleftharpoons PuO_2Cl^+ \quad \text{(A.556)}$$

The reported value of $\log_{10}\beta_1^{o}$ = (0.255 ± 0.029) is in very good agreement with the current NEA TDB selection, $\log_{10}\beta_1^{o}$ = (0.230 ± 0.030). The authors did not report the equilibrium constant for the second complex, $PuO_2Cl_2$(aq). The value of $\Delta\varepsilon_{1,1}$ = – (0.10 ± 0.02) kg·mol$^{-1}$ derived by Reilly and co-workers from the SIT plot using data up to 2.09 *m* NaCl can be combined with $\varepsilon(PuO_2^{2+}, Cl^-)$ = (0.19 ± 0.09) kg·mol$^{-1}$ from the solubility data and $\varepsilon(Cl^-, Na^+)$ = (0.03 ± 0.01) kg·mol$^{-1}$ from [2003GUI/FAN] to derive $\varepsilon(PuO_2Cl^+, Cl^-)$ = (0.12 ± 0.09) kg·mol$^{-1}$.

According to Equation (A.555) the solubility product of $PuO_2CO_3$(cr) is expressed by the equation:

$$K_{sp}(\text{A.555}) = [\,PuO_2^{2+}]\cdot[\,CO_3^{2-}\,] \tag{A.557}$$

This equilibrium can be monitored in non-complexing aqueous solutions (such as $NaClO_4$) of different ionic strengths, using the characteristic absorbance band of the $PuO_2^{2+}$(aq) ion at 830.6 nm. Applying the SIT, one can obtain the associated SIT parameter for Reaction (A.555):

$$\Delta\varepsilon_{ij}((\text{A.555}), NaClO_4) = \varepsilon(PuO_2^{2+}, ClO_4^-) + \varepsilon(Na^+, CO_3^{2-}) \tag{A.558}$$

Applying the SIT ion-interaction parameter $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.05)$ kg·mol$^{-1}$, we can derive from the Pu(VI) solubility data in $NaClO_4$ solutions the ion-interaction parameter $\varepsilon(PuO_2^{2+}, ClO_4^-)$. Unfortunately, only few solubility data of $PuO_2CO_3$(cr) have been reported as a function of perchlorate concentration. Thus, the NEA TDB adopted $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.46 \pm 0.05)$ kg·mol$^{-1}$ by analogy with $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol$^{-1}$, which was calculated in [1992GRE/FUG] from isopiestic data.

In the presence of chloride, however, the dissolved $PuO_2^{2+}$ ion interacts with chloride to form inner-sphere solution complexes, thus increasing the soluble concentration of Pu(VI). Depending on the NaCl concentration, Pu(VI) chloro complexes of general formula $PuO_2Cl_n^{2-n}$ may form and expand the dissolution reaction of $PuO_2CO_3$(cr) according to:

$$PuO_2CO_3(cr) \rightleftharpoons Pu(VI)_{tot} + CO_3^{2-} \tag{A.559}$$

with

$$[Pu(VI)_{tot}] = [PuO_2^{2+}] + \Sigma[PuO_2Cl_n^{2-n}] = [PuO_2^{2+}] + [PuO_2Cl^+] + [PuO_2Cl_2^o] + [PuO_2Cl_3^-] + [PuO_2Cl_4^{2-}] \tag{A.560}$$

The majority of solubility studies report total soluble concentrations of an actinide in its oxidation state. Measuring the dissolved Pu(VI) fraction in chloride-bearing solutions without differentiating between solution species results in a conditional solubility product ($^{\#}K_{sp}$) of $PuO_2CO_3$(cr), that in contrast to Equation (A.557) contains contributions of Pu(VI) chloride complexes:

$$^{\#}K_{sp}(\text{A.559}) = [Pu(VI)_{tot}]\cdot[CO_3^{2-}] = ([PuO_2^{2+}] + \Sigma[PuO_2Cl_n^{2-n}])\cdot[CO_3^{2-}] \tag{A.561}$$

The apparent solubility products $^{\#}K_{sp}$ of $PuO_2CO_3$(cr) at each NaCl concentration obtained from the total soluble concentration of Pu(VI) species increasingly differs from the corresponding $K_{sp}$ values due to the increasing solubilisation of Pu(VI) by chloride complexation. Spectroscopic measurements have shown that under the conditions and ionic strength applicable to the SIT only the two complexes $PuO_2Cl^+$ and $PuO_2Cl_2^o$(aq) play a major role (note that $\varepsilon(PuO_2Cl_2^o, Na^+) = \varepsilon(PuO_2Cl_2^o, Cl^-) = 0$):

$$^{\#}\Delta\varepsilon_{ij}(\text{A.559}) = \varepsilon(\text{Pu(VI)}_{tot}, Cl^-) + \varepsilon(Na^+, CO_3^{2-}) = \\ = \varepsilon(PuO_2^{2+}, Cl^-) + \varepsilon(PuO_2Cl^+, Cl^-) + \varepsilon(Na^+, CO_3^{2-}) \quad \text{(A.562)}$$

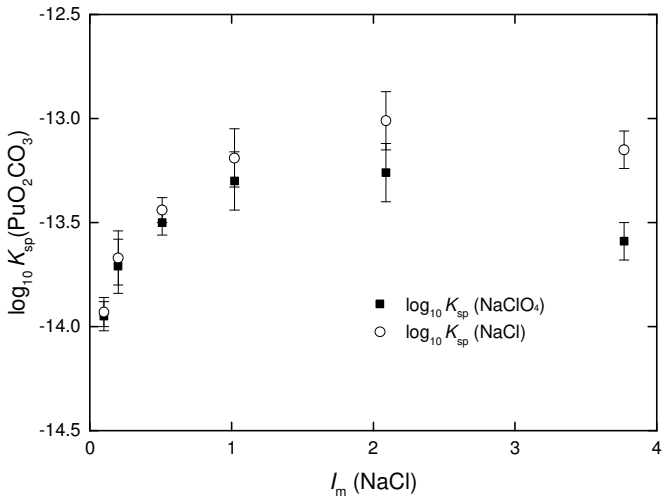
The ion-interaction parameters $\varepsilon(PuO_2^{2+}, Cl^-)$ and $\varepsilon(PuO_2Cl^+, Cl^-)$ cannot be derived independently from data collected in chloride solutions without quantifying speciation. Ciavatta calculated $\varepsilon(UO_2^{2+}, Cl^-) = (0.21 \pm 0.02)$ kg·mol$^{-1}$ without taking into account chloride complexes and Grenthe *et al.* [1992GRE/FUG] used $\varepsilon(UO_2^{2+}, X^-) = (0.46 \pm 0.03)$ kg·mol$^{-1}$ for the monovalent anions $Cl^-$, $ClO_4^-$ and $NO_3^-$. The spectroscopic determination of the concentrations of $PuO_2^{2+}$(aq) and Pu(VI) chloride complexes performed by [2007REI/RUN] enables the calculation of both $^{\#}K_{sp}$(A.559) and $K_{sp}$(A.555).

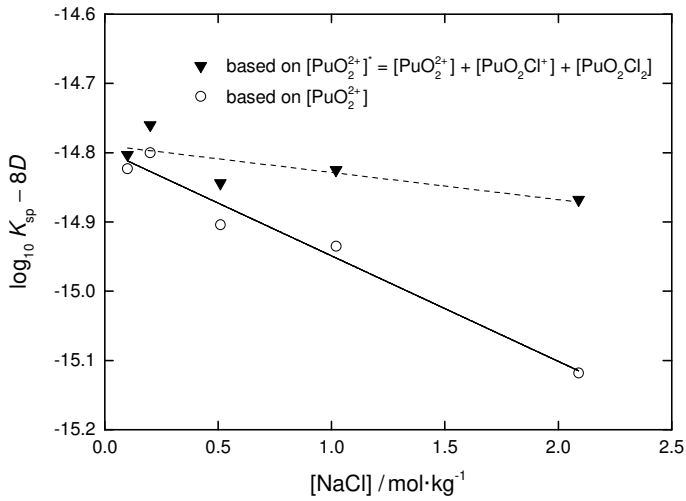
We re-evaluated the data in [2007REI/RUN] and calculated $\log_{10} K^{o}_{sp}$ (A.555) = – (14.80 ± 0.05) and $\Delta\varepsilon_{ij}$(A.555) = (0.15 ± 0.04) kg·mol$^{-1}$ from the reported soluble $PuO_2^{2+}$ concentrations determined spectroscopically. These results are in concert with those reported in [2007REI/RUN]. Using $\varepsilon(Na^+, CO_3^{2-})$ = – (0.08 ± 0.03) kg·mol$^{-1}$ we derive $\varepsilon(PuO_2^{2+}, Cl^-) = (0.23 \pm 0.04)$ kg·mol$^{-1}$. The thermodynamic solubility products obtained from both data sets, $\log_{10} {}^{\#}K^{o}_{sp}$ (A.559) = – (14.79 ± 0.06) and $\log_{10} K^{o}_{sp}$ (A.559), are identical, but $\Delta^{\#}\varepsilon_{ij}$(A.559) = (0.04 ± 0.05) kg·mol$^{-1}$ is quite different from $\Delta\varepsilon_{ij}$(A.555) due to the ionic strength-dependent Pu(VI) chloride complexation effect. Figure A-23 illustrates the identical thermodynamic solubility products but different ion interaction parameters. From this value and $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol$^{-1}$, we can calculate $\varepsilon(^{\#}PuO_2^{2+}, Cl^-) = (0.12 \pm 0.05)$ kg·mol$^{-1}$. The difference of $\Delta\varepsilon_{ij}$(A.559) – $\Delta^{\#}\varepsilon_{ij}$(A.555) = 0.11 kg·mol$^{-1}$ represents the contribution of the Pu(VI) chloro complexes and is equivalent to $\varepsilon(PuO_2Cl^+, Cl^-)$. The $\Delta\varepsilon_{ij}$ values are associated with high degree of variability depending on the number of data points selected for the iteration. Additional studies are needed to reduce the uncertainty of the ion-interaction parameters.

**[2007RUN/BRO]**

The authors synthesised and determined the single-crystal structure of a ternary Pu(IV) peroxo-carbonate solid state compound, $Na_6Pu_2(O_2)_2(CO_3)_6 \cdot 12H_2O$(cr), that contains discrete, dimeric $Pu_2(O_2)_2(CO_3)_6^{8-}$ anions. The structure contains ten-coordinate Pu atoms at a Pu-Pu distance of 3.528 Å and confirms the side-on coordination of peroxide groups sharing both Pu atoms. The diffuse reflectance spectrum of the crystals is compared with the electronic absorbance spectra of Pu(IV) in peroxide-containing carbonate solution. Both spectra exhibit a characteristic peak at 495.5 nm that is shifted from the well-known peak at 485.5 nm for the $Pu(CO_3)_5^{6-}$ complex, indicating a similar coordination of peroxide and carbonate in solution and solid state. No thermodynamic data are provided.

Figure A-23: (above) Conditional solubility products of $PuO_2CO_3$(cr) in NaCl solutions calculated from the $PuO_2^{2+}$ ion concentration determined spectroscopically (squares) and the total Pu(VI) concentration independent of solution speciation (circles). The differences in $\log_{10}K_{sp}$ are attributed to the contribution of $PuO_2Cl^+$ at [NaCl] ≥ 0.2 M and $PuO_2Cl_2$(aq) at [NaCl] ≥ 2M. (below) SIT plot illustrating the impact of Pu(VI) chloride complexation on $\Delta\varepsilon_{ij}$.



**[2007TAN/NIK]**

Tananaev *et al.* expands on the experimental studies on the formation of Pu(VII) and Pu(VIII) upon the oxidation of Pu(VI) in highly alkaline solutions as discussed in [2004NIK/GOG2]. Electrochemical studies of Pu(VI) in 2 M NaOH, analogous studies with Np(VI) in 1 M NaOH and 2 M LiOH, and redox reactions of ozonised Pu(VI) solutions with Fe(II) and Mn(VI) are used to discuss the formation of the highest oxidation states of plutonium in alkaline solutions. The reduction potentials in 2 M NaOH are estimated to be (0.68 ± 0.05) V *vs*. NHE for Pu(VII)/Pu(VI) and exceeding 0.90 V for the Pu(VIII)/Pu(VII) redox couple from electrochemical measurements. This value is identical to the data already reported in [2005NIK/GOG]. Analysis of spectroscopic data led to the estimation of the molar extinction coefficient of Pu(VIII) at 635 nm of about (2600 ± 400) $M^{-1}\cdot cm^{-1}$ and about 100 $M^{-1}\cdot cm^{-1}$ for Pu(VII) at 500-550 nm. The estimated spectroscopic parameters are calculated for Pu oxidation states without providing any details about the nature and structure of complexes present in solution. The authors estimate the yield of Pu(VIII) produced by ozonolysis or bulk electrolysis at 1.0 V (relative to Hg/HgO) in 2 M NaOH to be (15 ± 5) % of the total Pu concentration. No new thermodynamic data are provided in this study.

**[2007WAL/CHO]**

Walther and coworkers examined the spectroscopic features of the Pu(IV) hydrolysis products that are commonly used to measure species distributions and to determine stability constants. High Pu concentrations ($10^{-5}$-$10^{-2}$ M) in 0.5 M (H,Na)Cl solutions with $p_cH$ ranging between 0.3 and 2.1 are used to study the electronic absorption of $Pu(OH)_n^{4-n}$ solution species taking into account the potential Pu(IV) colloid formation. The authors claim that no colloidal or polymeric species larger than 5 nm were detected in the samples investigated by using laser-induced breakdown spectroscopy. The authors normalised the absorption spectra and subtracted a reference absorption spectrum of Pu(IV) to deconvolute spectra of five sample solutions containing multiple oxidation states and species.

In the absence of colloidal Pu(IV), the main absorbance band of $Pu^{4+}$ at 470 nm is found to be independent of pH. Thus, the authors assign all monomeric hydrolysis species expected to be present under the experimental conditions, $Pu(OH)_n^{4-n}$ with $n$ = 0-2, to the same wavelength and equal molar extinction coefficients. The authors claim that any changes to the absorption band at 470 nm are attributed to the formation of colloidal or polymeric Pu(IV) species, which causes the decrease of the Pu(IV) concentration, or redox reactions of Pu(IV). The spectral equality of Pu(IV) hydrolysis species proposed by Walther *et al.* is controversial and is in contrast to the common understanding that inner-sphere complexation alters the electronic absorbance features, such as reported in [2004YUS/FED]. Yusov and coworkers interpreted the spectral changes at pH 1-1.34 with the formation of $PuOH^{3+}$ and calculated the single

component spectrum. Although the analysis of both approaches is outside this review, the proposed spectral equality of Pu(IV) hydrolysis species proposed by Walther *et al.* has to be considered carefully based on concerns regarding the spectra analysis. Residual spectral features are remaining after the subtraction of the Pu(IV) reference spectrum, which are compared with the spectral characteristics of polymeric Pu(IV). However, the polymer reference spectrum in Figure 6b and d of this paper is slightly different from the spectra of colloidal Pu(IV) in 1 M $HClO_4$ and HCl at pH 1.8 in Figure 8 of the paper and neither match the residual features. The increasing slope of the residual at 450-600 nm with pH is indicative of erroneous background correction or the formation of Pu(IV) particles. Inconsistent background corrections are already apparent in the molar absorption spectra presented at 450-600 nm. The spectral equality of the Pu(IV) solution species $Pu^{4+}$ and $Pu(OH)_n^{4-n}$ with $n$ = 1 and 2 is reiterated in [2007YUN/CHO].

No new thermodynamic data are reported in this study.

**[2007XIA/FRI]**

This study investigates the complexation of Pu(IV) with sulfate using solvent extraction experiments at 25, 40 and 55 °C. The extraction experiment were performed with 0.05 M thenoyltrifluoroacetone (TTA) in toluene as the organic phase to extract Pu(IV) from 2 M $HClO_4$ solutions containing varying concentrations of sulfuric acid. A series of experiments were conducted in 2 M $HClO_4$ and in $HClO_4/H_2SO_4$ mixtures with varying amounts of $H_2SO_4$ at a constant $I_M$ = 2.0 M. The concentrations of $H_2SO_4$ ranged between $2.0 \times 10^{-3}$ M and $6.0 \times 10^{-2}$ M. Small amounts of 0.01 M $NaBrO_3$ were added to the aqueous phase as holding agent to maintain Pu(IV) during the experiment. To minimise hydrolysis of Pu(IV), the authors also used a low concentrated Pu(IV) ($1.3 \times 10^{-5}$ M) stock solution and re-purified the Pu(IV) stock solution after two weeks. The Pu oxidation state was checked during and after the experiment by measuring the distribution ratios of Pu aliquots from the stock solution and aqueous phase after the extraction into TTA-toluene. The nearly complete extraction of Pu into the organic phase suggested the presence of Pu(IV). The stoichiometry of the organic Pu(IV) complex was determined from the slope analysis (slope of about 4) of the plot $\log_{10}D$ *versus* $\log_{10}$ [TTA] according to Reaction (A.563):

$$Pu^{4+}(aq) + 4HTTA(org) \rightleftharpoons Pu(TTA)_4(org) + 4H^+ \qquad (A.563)$$

D is the distribution ratio expressed as $[Pu(TTA)_4(org)]/[Pu^{4+}(aq)]$. In the absence of sulfate, the authors determined the extraction equilibrium constants for (A.563) to be (7.08 ± 0.01) at 25 °C, (6.91 ± 0.01) at 40 °C and (6.63 ± 0.01) at 55 °C with the slopes varying between 4.07 and 4.10, close to the theoretical slope of 4. With the addition of sulfuric acid, the uptake of Pu(IV) into the organic phase decreased due to the coordination of Pu(IV) with the $HSO_4^-$ anion. When plotting the experimental data

$D_0/(D-1)$ *vs.* the concentration of free $HSO_4^-$, the authors could fit the distribution data and proposed the formation of the Pu(IV) sulfate complexes $PuSO_4^{2+}$ and $Pu(SO_4)_2(aq)$ in the aqueous phase:

$$Pu^{4+} + HSO_4^- \rightleftharpoons PuSO_4^{2+} + H^+ \quad \text{(A.564)}$$

$$Pu^{4+} + 2HSO_4^- \rightleftharpoons Pu(SO_4)_2(aq) + 2H^+ \quad \text{(A.565)}$$

The authors assumed the $[HSO_4^-]_{free}$ to be equal to the total concentration of $HSO_4^-$ since the concentration of the $Pu(SO_4)_n^{4-2n}$ complexes is negligible. The thermodynamic constants $\Delta G^\circ, \Delta H^\circ$ and $\Delta S^\circ$ were calculated from the apparent complex formation constants using the Van't Hoff equation assuming a constant complexation enthalpy over the temperature range investigated. Adopting values for the dissociation constants of $HSO_4^-$ from the literature ($pK_a$ = 1.07, 1.14, and 1.28 at $I_M$ = 2 M and 25, 40 and 55 °C, respectively) Xia *et al.* calculated the equilibrium constants $\log_{10}\beta_{1,1}$ (A.566) = $\log_{10}K_{1,1}$ (A.564) + $pK_a$ for Reaction (A.566) and $\log_{10}\beta_{1,1}$ (A.567) = $\log_{10}K_{1,2}$ (A.565) + 2$pK_a$ for Reaction (A.567).

$$Pu^{4+} + SO_4^{2-} \rightleftharpoons PuSO_4^{2+} \quad \text{(A.566)}$$

$$Pu^{4+} + 2SO_4^{2-} \rightleftharpoons Pu(SO_4)_2(aq) \quad \text{(A.567)}$$

The apparent equilibrium constants reported in this study were not corrected to $I$ = 0. The experimental methodology is very similar to that used in [2010XIA/RAO] to study the fluoride complexation of Pu(IV).

Table A-177: Equilibrium constants and thermodynamic data of Pu(IV) sulfate complexes reported in [2007XIA/FRI].

| $t$ /°C | Method | $I$ /medium | $\log_{10}\beta_{1,n}$ | $\Delta G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta S_m^\circ$ /J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|---|---|
| $Pu^{4+}+HSO_4^- \rightleftharpoons PuSO_4^{2+}+H^+$ | | | | | | |
| 25 | solv | 2.0 M $HClO_4$ | (2.71 ± 0.05) | – 15.5 | 11.2 | 89.6 |
| 40 | solv | 2.0 M $HClO_4$ | (2.79 ± 0.04) | – 16.7 | 11.2 | 89.3 |
| 55 | solv | 2.0 M $HClO_4$ | (2.87 ± 0.04) | – 18.2 | 11.2 | 89.6 |
| $Pu^{4+}+2HSO_4^- \rightleftharpoons Pu(SO_4)_2(aq)+2H^+$ | | | | | | |
| 25 | solv | 2.0 M $HClO_4$ | (4.59 ± 0.04) | – 26.2 | 5.1 | 104.8 |
| 40 | solv | 2.0 M $HClO_4$ | (4.66 ± 0.04) | – 27.9 | 5.1 | 105.4 |
| 55 | solv | 2.0 M $HClO_4$ | (4.58 ± 0.04) | – 28.8 | 5.1 | 103.1 |

**[2007YUN/CHO]**

Yun and coworkers investigate the hydrolysis of Pu(IV) in acidic 0.5 M HCl/NaCl solutions ($p_cH$ 0.3-2.5) at (23 ± 2) °C. The Pu oxidation states present in solutions that contained initially pure $10^{-5}$ to $4 \times 10^{-4}$ M $Pu(IV)_{tot}$ were examined by using electronic absorption spectroscopy and used to calculate redox potentials. The total Pu concentration in solution was measured by liquid scintillation counting. The calculated

$E_h$ potentials were compared with the experimental values obtained with a micro Pt-electrode and a micro Ag/AgCl reference electrode and corrected for the Ag/AgCl potential. The authors note a negligible drift in solutions without Pu(IV) colloids and an uncertainty of about ± 5 mV, while a slow drift of the potential is observed with time in the presence of colloids. This effect is explained by the potential adsorption of polymeric Pu(IV) species on the Pt electrode or contributing other redox reactions. The experimental values of $p_e = \log_{10} a_{e^-}$ are calculated from the equation $E_h = -(RT/F)\ln a_{e^-}$ and $p_e = 16.9\, E_h$ (in V) at 25 °C. The measured $p_e$ values were compared with those calculated from the redox equilibria and redox constants $\log_{10} K^{\circ}_{III/IV}$ (A.568) = – (17.69 ± 0.04), $\log_{10} K^{\circ}_{V/VI}$ (A.569) = – (15.82 ± 0.09), and $\log_{10} K^{\circ}_{IV(s)/V}$ (A.570) = – (19.78 ± 0.89) recommended by the NEA TDB:

$$Pu^{3+} \rightleftharpoons Pu^{4+} + e^- \qquad \text{(A.568)}$$

$$PuO_2^+ \rightleftharpoons PuO_2^{2+} + e^- \qquad \text{(A.569)}$$

$$PuO_2(am,hyd) \rightleftharpoons PuO_2^+ + e^- \qquad \text{(A.570)}$$

The $H^+$ concentration was measured with a combination glass electrode calibrated against standard pH buffers and 0.5 M HCl-0.01 M HCl/0.49 M NaCl solutions. The [$OH^-$] concentrations were calculated from $\log_{10}[H^+]$ and $\log_{10} K^{'}_{H_2O}$ = – 13.74 for 0.5 M NaCl. Sample solutions were kept in closed vials under air or under Ar with trace amounts of $O_2$. The spectroscopic evaluation of Pu oxidation state distribution relied on the fact that the absorbances for the $Pu^{3+}$, $PuO_2^+$ and $PuO_2^{2+}$ aquo ions are not changing in the $p_cH$ range of interest. However, intensity changes of the Pu(IV)(aq) absorbance at 470 nm in the pH range 0-2 are explained by the formation of Pu(IV) polymeric species and not by the formation of mononuclear Pu(IV) hydrolysis products. Laser-induced breakdown spectroscopy was used to detect polymeric/colloidal Pu(IV) species formed in solution. Thus, the 470 nm band, which was commonly used to determine the stability constants of $Pu(OH)_n^{4-n}$, contained absorbances of both $Pu^{4+}$ and $Pu(OH)_n^{4-n}$. The authors calculated the fraction of $Pu^{4+}$ from the spectroscopic value and the $Pu(OH)_n^{4-n}$ formation constants. Although chloride has no effect on the speciation for Pu(III, IV, V), about 15 % of the total Pu(VI) is attributed to the monochloro complex, $PuO_2Cl^+$. The fraction of colloidal or polymeric Pu(IV) species is calculated from the difference of the total Pu concentration and the sum of spectroscopically determined concentrations of $Pu^{3+}$, $PuO_2^+$, $PuO_2^{2+}$ and Pu(IV). After some weeks the oxidation state distribution and redox potentials reached constant values indicating a steady-state equilibrium, independent of the atmospheric conditions. A complex oxidation state distribution was measured with $Pu^{3+}$, $Pu^{4+}$ and $Pu(OH)_n^{4-n}$ as the predominant species at $p_cH < 1$, while at $p_cH > 1.5$ Pu(IV) colloids are in equilibrium with $Pu^{3+}$, $Pu^{4+}$ and $Pu(OH)_n^{4-n}$, $PuO_2^+$, and $PuO_2^{2+}$. By using the SIT and the NEA TDB recommended ion-interaction parameters the authors calculated apparent equilibrium and formation constants in 0.5 (H/Na)Cl: $\log_{10} K^{'}_{III/IV}$ (A.568) = – (16.55 ± 0.04), $\log_{10} K^{'}_{V/VI}$ (A.569) =

– (15.36 ± 0.09), $\log_{10} K'_{IV(s)/V}$ (A.570) = – (19.65 ± 0.89). The apparent formation constants $\log_{10}\beta'_{1,1} = 13.3$, $\log_{10}\beta'_{1,2} = 26.4$, $\log_{10}\beta'_{1,3} = 36.8$, and $\log_{10}\beta'_{1,4} = 44.3$ were calculated from the corresponding $\log_{10}\beta^{o}_{1,n}$ values selected in the NEA TDB.

The authors also calculated the hydrolysis constants from the measured pe values and the spectroscopically determined concentrations of $Pu^{3+}$ and Pu(IV)(aq) by combining Equation (A.568) and (A.571).

$$[Pu^{4+}] = [Pu(IV)(aq)]/(1+\Sigma\beta'_{1,n}[OH]^{-}) \quad \text{(A.571)}$$

By maintaining $\log_{10} K'_{III/IV}$ (A.568) = – (16.55 ± 0.04) constant, Yun *et al.* report both apparent and thermodynamic hydrolysis equilibrium constants for $Pu(OH)_n^{4-n}$ with $n$ = 1-3. The formation constant of $Pu(OH)_4(aq)$ was not determined because the analysis method used in this paper is only applicable to acidic conditions. The hydrolysis constants calculated in this paper are lower than the data selected in [2001LEM/FUG] and [2003GUI/FAN]. Although not measured in this paper, the authors also expect the selected value in the NEA TDB, $\log_{10}\beta^{o}_{1,4}$ = (47.5 ± 0.5), to be overestimated as well and calculate an upper limit of $\log_{10}\beta^{o}_{1,4} \leq 46.7$.

The vast majority of measured $p_e$ values overlap with the $p_e$ values calculated from $\log_{10} K'_{V/IV}$, but differ significantly from $p_e$ values calculated from the $\log_{10} K'_{III/IV}$. The authors base this difference on too large Pu(IV) hydrolysis constants used to calculate the fractions of $Pu^{4+}$. The authors also note that measured $p_e$ values in the presence of colloidal Pu(IV) (at pH > 2) are lower than those calculated from $\log_{10} K'_{III/IV}$ claiming adsorption of colloidal Pu(IV) species on the electrode surface. The authors do not mention that the measured $p_e$ value at $p_cH$ 2.03 matches very well the $p_e$ value calculated from $\log_{10} K'_{III/IV}$ and the colloidal fraction of 21.2 % at pH 2.03 was also present in solutions of lower pH, *e.g.* at pH ranging between 1.74 and 1.89. However, these solutions did not exhibit lower $p_e$ values. Thus, the impact of the presence of colloidal Pu(IV) on $p_e$ values is not clear from the presented data.

**[2007YUS/SHI]**

This is the first of a series of studies ([2007YUS/SHI], [2007YUS/SHI2], [2007YUS/SHI3], [2007YUS/SHI4]) conducted by Yusov and coworkers to study the behaviour of Pu in $K_{10}P_2W_{17}O_{61}$ solutions. This paper reports on the disproportionation reaction of $^{239}Pu(V)$ in the presence of 0.001-0.01 M $K_{10}P_2W_{17}O_{61}$ measured at pH 0.7-4.0 at 20 °C. Pu(V) was prepared from Pu(VI) by reduction with $H_2O_2$ and heating to 80-85 °C. In order to minimise changes in pH during the reaction, the experiments were carried out with at least fourfold excess of the ligand. The disproportionation reaction of Pu(V) was monitored spectroscopically of the time-dependent UV-vis-NIR absorption at 400-1300 nm. The weak electronic absorbances of the Pu(IV) complex at 650 (52 ± 3 $L \cdot mol^{-1} \cdot cm^{-1}$) and 1050 nm (72 ± 4 $L \cdot mol^{-1} \cdot cm^{-1}$) were used to estimate its concentrations. The intense absorbance at around 841 nm with the molar extinction

coefficients ranging at 405-445 $L \cdot mol^{-1} \cdot cm^{-1}$ was used to estimate the concentration of the Pu(VI) complex. Since the characteristics of the band at 841 nm varied with pH and other single-charged cations, the authors determined the band's extinction coefficient in the pH range 1-5. It is to note that the correct stoichiometry and charge of these complexes are uncertain because the $P_2W_{17}O_{61}^{10-}$ anions are known to interact with single-charged cations forming species of general formula $H_xK_yP_2W_{17}O_{61}^{(10-x-y)-}$ with $x$ = 6-7. No information was provided on the measurement of pH and $E_h$ of the experimental solutions.

After contacting Pu(V) with $K_{10}P_2W_{17}O_{61}$, the Pu(V) disproportionates into Pu(VI) and Pu(IV), which shows in the altered absorbance spectra. The accumulation of Pu(VI) was used to determine the disproportionation rates for Pu(V) according to $[Pu(V)] = [Pu(V)]_0 - 2\Delta A_{841nm}/\varepsilon_{841nm}$. The reaction is time-dependent and consumes hydrogen ions during the reaction. In analogy to Np(V), the authors suggest that the Pu(V) disproportionation follows a first-order reaction with respect to Pu(V) and nearly first-order to the concentration of the ligand: $\nu = k[Pu(V)][K_{10}P_2W_{17}O_{61}]^n$ where $n = (0.84 \pm 1)$. Using spectroscopic data collected at different temperatures, the authors evaluated the activation energy, entropy and enthalpy. The negative activation entropy suggests that the number of degrees of freedom decreases during the reaction. Although the reaction mechanism is not described in detail, the authors note a significant difference in the disproportionation of Np(V) and Pu(V). While Np(V) forms a metastable complex with an absorption at 1048 nm, a similar complex is not observed for Pu(V). The authors propose the protonation of the actinyl oxygen atom in the complex with $K_xP_2W_{17}O_{61}^{(10-x)-}$, which weakens the An-O bonds, to be a major step of the disproportionation reaction. Without providing further details, the authors calculate thermodynamic parameters, such as activation energy and enthalpy, for the Pu(V) disproportionation reaction at pH 2 ($E_a$ = 78.6 $kJ \cdot mol^{-1}$; $\Delta H^{\neq}$ = 76.1 $kJ \cdot mol^{-1}$; $\Delta S^{\neq}$ = – 40.7 $kJ \cdot mol^{-1}$) and pH 4 ($E_a$ = 64.2 kJ $mol^{-1}$; $\Delta H^{\neq}$ = 61.7 $kJ \cdot mol^{-1}$; $\Delta S^{\neq}$ = – 86.0 $kJ \cdot mol^{-1}$).

Due to the lack of details on the experimental quantification of experimental data, the thermodynamic data provided in this paper cannot be recommended.

**[2007YUS/SHI2]**

In this study, Yusov and coworkers examined the complex formation of hexavalent actinides (U, Np and Pu) with three heteropolyanions (HPA), $P_2W_{17}O_{61}^{10-}$, $SiW_{11}O_{39}^{8-}$, and $PW_{11}O_{39}^{7-}$, in the pH range – 0.3-5.5. The concentration of the $H^+$ concentration was calculated from the pH, which was measured with a glass electrode, or calculated from the volume of added acid (at $[H^+] > 0.1$ M). Although ionic strength effects are considered via $pH = -\log_{10}[H^+] + 0.15$ at $I$ = 1 M, the authors chose not to apply this correction factor because the addition of 0.1-1 M $Na^+$ did not change the pH meter readings more than 0.05 units at pH 2-3. This leads to slightly inaccurate $H^+$

concentrations when extracted from the pH measurements. The complexation of the actinide cations was monitored spectroscopically by the main electronic absorbances at 430, 608 and 1220 nm for Np(VI) and 830-840 nm for Pu(VI). The authors note that the presence of 0.01-0.02 M acid caused time-dependent changes in the absorption spectra due to the decomposition of the heteropolyanions, which required to collect the spectra immediately after sample preparation.

Complexation of An(VI) with the [HPA] ~ $10^{-4}$ M is observed at pH > 1. The stability of the An(VI) complexes with the HPAs decreases significantly at lower pH due to the protonation of the HPA. Changes in the intensities and positions of the An(VI) absorbances are interpreted with the coordination of hexavalent actinides with the heteropolyanions. The new absorbances at 841 nm for Pu(VI) and multiple absorbance peaks at 430-650 nm for Np(VI) were assigned to the formation of the 1:1 complexes $NpO_2^{2+}$ (HPA) and $PuO_2^{2+}$ (HPA). The protonation of the heteropolyanion results in shifting absorption maximum and molar extinction coefficient with pH. It is to note that the correct stoichiometry and charge of these complexes are uncertain because the $P_2W_{17}O_{61}^{10-}$ anions are known to interact with single-charged cations forming species of general formula $H_xNa_yP_2W_{17}O_{61}^{(10-x-y)-}$.

The authors estimated the potential influence of hydrolysis to be small and thus neglected its contribution for the complex stability constant calculations. Assuming complete complexation of An(VI) with HPA at pH $\geq$ 2.2, the authors calculated the apparent formation constants from the changes in the absorbance bands using the molar absorption coefficients for the An(VI)-HPA complexes. The complex formation is strongly dependent on pH and $Na^+/K^+$ concentration. At pH $\leq$ 1.5 and absence of $NaNO_3$, the stability follows the order $AnO_2(H_xPW_{11}O_{39})^{(5-x)-}$ > $AnO_2(H_xSiW_{11}O_{39})^{(6-x)-}$ > $AnO_2(H_xP_2W_{17}O_{61})^{(8-x)-}$ and complex stability trends U(VI) > Np(VI) > Pu(VI). In contrast to U(IV) which requires three deprotonations of the heteropolyanion, the complexation reaction of actinyl(VI) ions involves only two protons according to the following equation:

$$PuO_2^{2+} + H_3P_2W_{17}O_{61}^{7-} \rightleftharpoons PuO_2(HP_2W_{17}O_{61})^{7-} + 2H^+ \qquad \text{(A.572)}$$

Up to pH 5 one proton remains bound to the heteropolyanion. However, in the presence of alkali metal cations the proton may be replaced as illustrated by the dependence of the stability constant on the alkali metal ion concentration. By assuming the non-interference between deprotonation and complexation, the authors estimate the total stability constant for $PuO_2(HP_2W_{17}O_{61})^{7-}$ at $I$ = 1 M, $\log_{10}\beta_{tot}^{'} = \log_{10}\beta^{'} + \log_{10}k_1 + \log_{10}k_2 - 2pH$, where $\log_{10}\beta^{'}$ is the stability constant at low ionic strength and $\log_{10}k_1$ = 5.19 and $\log_{10}k_2$ = 4.00 are the first two deprotonation constants of the ligand. Given the uncertainties of estimated values and lack of details on experimental conditions, these data can be considered only as estimates for the complexation for An(VI) with heteropolyanions.

Table A-178: Formation constants for $PuO_2^{2+}$ with heteroployanions reported in [2007YUS/SHI2] (HPA = Heteropolyanion): $PuO_2^{2+} + HPA \rightleftharpoons PuO_2(HPA)$.

| Method | $I$ /medium | $\log_{10}\beta_1$ $P_2W_{17}O_{61}^{10-}$ | $\log_{10}\beta_1$ $SiW_{11}O_{39}^{8-}$ | $\log_{10}\beta_1$ $PW_{11}O_{39}^{7-}$ | Reference |
|---|---|---|---|---|---|
| spec | 0.1 M $HClO_4$ | (3.3 ± 0.3) | (3.5 ± 0.3) | (3.8 ± 0.3) | [2007YUS/SHI2] |
| spec | 0.2 M $HClO_4$ | (2.9 ± 0.3) | (3.1 ± 0.3) | (3.4 ± 0.3) | [2007YUS/SHI2] |
| spec | 0.5 M $HClO_4$ | (2.3 ± 0.3) | (2.5 ± 0.3) | (2.9 ± 0.3) | [2007YUS/SHI2] |
| spec | 1.0 M $HClO_4$ | (1.9 ± 0.3) | (2.2 ± 0.3) | (2.5 ± 0.3) | [2007YUS/SHI2] |
| spec | 2.0 M $HClO_4$ | (1.4 ± 0.3) | (1.9 ± 0.3) | | [2007YUS/SHI2] |

**[2007YUS/SHI3]**

The authors examined the complex formation between tetravalent lanthanides and actinides with the heteropolyanion $P_2W_{17}O_{61}^{10-}$ in 1 M $H^+$ or $Na^+$ solutions at pH 5.5. Yusov *et al.* discuss experimental potentiometric and spectrophotometric stability studies of U(IV) and Th(IV) and analyse published data for An(IV) (An = Np, Pu, Am and Cm) complexes with $P_2W_{17}O_{61}^{10-}$. Two complexes are suggested to form with tetravalent *f*-element ions, $AnP_2W_{17}O_{61}^{6-}$ and $An(P_2W_{17}O_{61})_2^{16-}$ with stability constants being dependent on pH due to the protonation of the ligand. It is to note that the correct stoichiometry and charge of these complexes are uncertain because the $P_2W_{17}O_{61}^{10-}$ anions are known to interact with single-charged cations forming species of general formula $H_xNa_yP_2W_{17}O_{61}^{(10-x-y)-}$. The complex $An(P_2W_{17}O_{61})_2^{16-}$ is about 20 orders of magnitude more stable in neutral solution than in acidic 1 M $H^+$ solution. Using the stepwise protonation constants for $P_2W_{17}O_{61}^{10-}$ at $I$ = 1 M, $\log_{10}K$ = 4.49, 3.75 and 2, the authors calculated an apparent stability constant $\log_{10}\beta_{1,2} = 37.7$ for the complex $Np(P_2W_{17}O_{61})_2^{16-}$ and $\log_{10}\beta_{1,2} > 36.3$ for $Pu(P_2W_{17}O_{61})_2^{16-}$ in 1 M $Na^+$ solutions (pH ~ 6) However, without providing any detailed justification the authors preferred a value of $\log_{10}\beta_2 = (35 \pm 2)$ for $Np(P_2W_{17}O_{61})_2^{16-}$ derived from direct measurements. The authors apparently estimated $\log_{10}\beta_2 = 15.6$ for $Np(P_2W_{17}O_{61})_2^{16-}$ and $\log_{10}\beta_2 > 14$ for $Pu(P_2W_{17}O_{61})_2^{16-}$ in 1 M $H^+$ by interpolating known metal complex stability constants as function of the ionic radii. This report lacks explanations on how data are calculated and why certain values are preferred over others. In the absence of more detailed information, the reported values can be considered only as estimates.

**[2007YUS/SHI4]**

In this paper, Yusov and coworkers evaluate the oxidation potentials of the An(IV)/An(III), An(V)/An(IV) and An(VI)/An(V) redox couples in the presence of $K_{10}P_2W_{17}O_{61}$. The oxidation potentials are calculated from the apparent complex stability data for An(III) and An(IV) complexes with $P_2W_{17}O_{61}^{10-}$ reported in [2007YUS/SHI3]. For the calculations of oxidation potentials, the authors adopted results from previous investigations of the solution speciation and complex formation in

these systems. For An(III) and An(IV), the complexes $AnP_2W_{17}O_{61}^{7-/6-}$ and $An(P_2W_{17}O_{61})_2^{17-/16-}$ were taken into account, while for An(V) and An(VI) only the 1:1 complex, $AnO_2P_2W_{17}O_{61}^{9-/8-}$, was considered. It is to note that the correct stoichiometry and charge of these complexes are uncertain because the $P_2W_{17}O_{61}^{10-}$ anions are known to interact with single-charged cations forming species of general formula $H_xNa_yP_2W_{17}O_{61}^{(10-x-y)-}$. The presence of the ligand has no impact on the An(VI)/(V) redox potentials in 1 M $HClO_4$. The fact that An(VI) is hydrolysed at neutral pH and complexation with $P_2W_{17}O_{61}^{10-}$ does not occur precludes the authors to report the oxidation potential for the An(VI)/An(V) couple in 1 M $Na^+$ solutions. The authors discuss uncertainties associated with the measurement of the An(IV)/An(III) couple due to the formation of a reduced form of the heteropolyanion and associated oxidation of An(III) to An(IV).

Table A-179: Calculated redox potentials in V for An redox couples in aqueous solutions containing $K_{10}P_2W_{17}O_{61}$.

| **Method** | ***I* /medium** | **U(IV)/(III)** | **U(V)/(IV)** | **U(VI)/(V)** | **Reference** |
|---|---|---|---|---|---|
| calc | 1 M $H^+$ | – 1.07 | 1.047 | 0.063 | [2007YUS/SHI4] |
| calc | 1 M $Na^+$ (pH~5) | – 1.6 | 1.09 | – | [2007YUS/SHI4] |
| **Method** | ***I* /medium** | **Np(IV)/(III)** | **Np(V)/(IV)** | **Np(VI)/(V)** | **Reference** |
| calc | 1 M $H^+$ | – 0.411 | 1.305 | 1.137 | [2007YUS/SHI4] |
| calc | 1 M $Na^+$ (pH~5) | – 0.9 | 1.27 | – | [2007YUS/SHI4] |
| **Method** | ***I* /medium** | **Pu(IV)/(III)** | **Pu(V)/(IV)** | **Pu(VI)/(V)** | **Reference** |
| calc | 1 M $H^+$ | < 0.416 | > 1.74 | 0.916 | [2007YUS/SHI4] |
| calc | 1 M $Na^+$ (pH~5) | – 0.1 | > 1.76 | – | [2007YUS/SHI4] |

**[2008ALT/NEC]**

The authors report the solubility of tetravalent hydrous metal oxide, $MO_2 \cdot xH_2O$(s) (M = Zr, Th, Pu), in alkaline 0.1 M-4.5 M $CaCl_2$ solution at (22 ± 2) °C. Th(IV) solubilities were measured at 0.2 M, 0.5 M, 1.0 M, 2.0 M and 5.0 M $CaCl_2$; Pu(IV) solubilities were determined in 1.0 M, 2.0 M and 4.0 M $CaCl_2$ solutions. Solid-liquid phase systems were equilibrated for 7-198 days under argon atmosphere. After ultrafiltration (10 kD pore size) or ultracentrifugation liquid scintillation was used to determine the soluble concentrations of Pu(IV). The solid phases were analysed by using X-ray diffraction, but the Th(IV) solid did not exhibit characteristic diffraction peaks illustrating its amorphous nature. The Pu(IV) solid phase contained about 0.5 % oxidised Pu and was designed as $PuO_{2+x}$(am, hyd). The pH was measured with a combination glass electrode and converted to $H^+$ concentration with correction values determined for chloride solutions.

As observed for Th(IV), the soluble Pu concentration increases from about $10^{-9}$-$10^{-10}$ M at $p_cH$ 8-11 to about $10^{-7}$ M at $p_cH \approx 12$. In the absence of spectrophotometric verification, the authors assumed the formation of $Ca_4[Pu(OH)_8]^{4+}$ in analogy with the ternary Th(IV) complex, which was previously verified to form with

EXAFS data. The solubility data were analysed including four data points at 0.5 M (0.51 m), 1.0 M (1.02 m), 2.0 M (2.11 m) and 4.5 M (5.26 m) $CaCl_2$ and corrected for ionic strength by using the SIT approach. The SIT regression for Th(IV) resulted in $\log_{10} K^{\circ}_{s,(4,1,8)} = (1.8 \pm 0.5)$ and $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-) = -(0.01 \pm 0.10)$ kg·mol$^{-1}$ for the dissolution reaction with An = Th:

$$An(OH)_4(am) + 4Ca^{2+} + 4OH^- \rightleftharpoons Ca_4[An(OH)_8]^{4+} \qquad (A.573)$$

The calculated ion-interaction coefficients for $Ca_4[Th(OH)_8]^{4+}$ was applied to $Ca_4[Pu(OH)_8]^{4+}$ and $\log_{10} K^{\circ}_{s,(4,1,8)} = -(2.0 \pm 0.5)$ was obtained for Pu. However, the ionic strengths of the solutions far exceed the validity range of the SIT (up to $I_m = 3.5$) and the data point at 4.5 M $CaCl_2$ clearly defines the slope of the SIT linear regression. The SIT plot including only conditional solubility constants determined in 0.5-2.0 M $CaCl_2$ solutions results in a value of $\log_{10} K^{\circ}_{s,(4,1,8)}$ closer to the one obtained by Pitzer and in a lower SIT coefficient, $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-) = (0.12 \pm 0.05)$ kg·mol$^{-1}$.

Applying the solubility product of $\log_{10} K^{\circ}_{sp} = -(58.3 \pm 0.5)$ for $PuO_2$(s, hyd), the formation constant $\log_{10} \beta^{\circ}_{1,8} = (56.3 \pm 0.7)$ is calculated for the equilibrium:

$$Pu^{4+} + 4Ca^{2+} + 8OH^- \rightleftharpoons Ca_4[Pu(OH)_8]^{4+} \qquad (A.574)$$

This value is in line with the data for Th(IV), $\log_{10} \beta^{\circ}_{1,8} = (49.6 \pm 0.6)$, which was obtained with $\log_{10} K^{\circ}_{sp} = -(47.8 \pm 0.3)$ for $ThO_2$(s, hyd). For further discussion on the solubility behaviour and speciation of Np(IV) and Pu(IV) in alkaline $CaCl_2$ solution see also [2010FEL/NEC].

**[2008BAL/CHA]**

The authors calculate the structures and vibrational frequencies of Pu(VI) carbonate complexes and examined their interactions with $Ca^{2+}$ cations using the density functional hybrid (DFT/B3LYP) and Møller-Plesset perturbation (MP2) methods. The calculated structure of $PuO_2(CO_3)_2^{2-}$ in the gas-phase contains two bidentate carbonate ligands in the equatorial plane around the O=Pu=O axial bonds. The computed structure does not contain any coordinated water molecule(s). This is in contrast to the observations in reported spectroscopic studies for the Pu(VI) biscarbonato complex, in which Pu(VI) coordinates a water molecule in aqueous solutions to form $PuO_2(CO_3)_2(H_2O)^{2-}$. Balasubramanian and Chaudhuri integrate a $Ca^{2+}$ cation and calculate the optimised structure of the neutral complex $CaPuO_2(CO_3)_2$. The $Ca^{2+}$ cation is centered between the two carbonate ligands in the equatorial plane bridging two carbonate oxygen atoms at a Ca-O distance of 2.178 Å. Placing three $Ca^{2+}$ cation in the equatorial symmetrically between the three bidentate carbonate ligands of the well-known $PuO_2(CO_3)_3^{4-}$ structure results in the proposed complex $Ca_3PuO_2(CO_3)_3^{2+}$. The Ca-O distance is calculated to be 2.245 Å. Although no thermodynamic data are presented in this study, the gas-phase calculations suggest possible interaction of $Ca^{2+}$

cations with the bridging carbonate-oxygen atoms in the equatorial coordination plane around the Pu atom. However, in the case of the Pu(VI) biscarbonate complex additional coordination of water molecule(s) can be expected to occur in aqueous systems.

**[2008GUE/CHA]**

[2008GUE/CHA] reported an extensive and critical review of the literature on the plutonium-oxygen system comprising phase diagram data, thermodynamic functions, oxygen chemical potential, oxygen partial enthalpies, as well as vapour pressure studies in the [$Pu_2O_3$ + $PuO_{2-x}$] and $PuO_{2-x}$ domains. Inconsistencies for the oxygen chemical potential and vaporisation data were identified. In addition, the authors reported a thermodynamic model for this system using the CALPHAD method where the Gibbs energies of the different phases were optimised by a least-squares minimisation procedure. The discussion is focused here on the results obtained for the thermodynamic functions of the plutonium oxide phases. The phase diagram data as reported in the literature and calculated by [2008GUE/CHA] and [2011GUE/DUP] (Figure 11-1 and 11-2) are presented in more detail in the main text (see also 11.2.2). The main features as suggested by [1990WRI] are well reproduced. A miscibility gap is calculated in the liquid state, although its extension could not be assessed thoroughly due to the lack of experimental data. The composition ranges of $PuO_{2-x}$ and $PuO_{1.61}$ are well reproduced, as well as the small miscibility gap in the $PuO_{2-x}$ phase. A good agreement is obtained between the optimised thermodynamic functions and those selected by [2001LEM/FUG], [2003GUI/FAN] and the present review as shown in Table A-180, except for the enthalpy of formation of $PuO_2$, which is 4 $kJ \cdot mol^{-1}$ lower than selected by [2001LEM/FUG], [2003GUI/FAN]. The relative error (0.4 %) remains acceptable, however.

$Pu_2O_3$ was treated as stoichiometric compound in the work of [2008GUE/CHA]. The recommended entropy value at 298.15 K is based on the measurements of Flotow *et al.* on $^{242}Pu_2O_3$ from 8 to 350 K [1981FLO/TET], as reported by [2001LEM/FUG], [2003GUI/FAN], [2014KON/BEN]. Since there are no measurements of the heat capacity values above 350 K, they were taken from the estimate by Glushko *et al.* [1982GLU/GUR], as selected by [2001LEM/FUG], [2003GUI/FAN]. The latter function is about 10 $kJ \cdot mol^{-1}$ higher at 2000 K than calculated in the work of [2014KON/BEN] and recommended in this review, however (Figure 11-5). The enthalpy of formation was derived in the literature from high temperature measurements of oxygen partial Gibbs energy [1987BES], [1966MAR/RAN] and partial enthalpy [1977CHE/DEA]. Both enthalpy and entropy values were optimised in the work of [2008GUE/CHA] and found in very good agreement with the data selected by [2001LEM/FUG], [2003GUI/FAN]. The model would need to be re-optimised to account for the newly recommended heat capacity

function of $Pu_2O_3$(cr), however. In addition, the model does not consider the phase transition between hexagonal A-type $Pu_2O_3$ and H-type structure at $T_{tr}$ = (2300 ± 50) K, as suggested by [2014KON/BEN] by analogy with the behaviour of the light lanthanide sesquioxides.

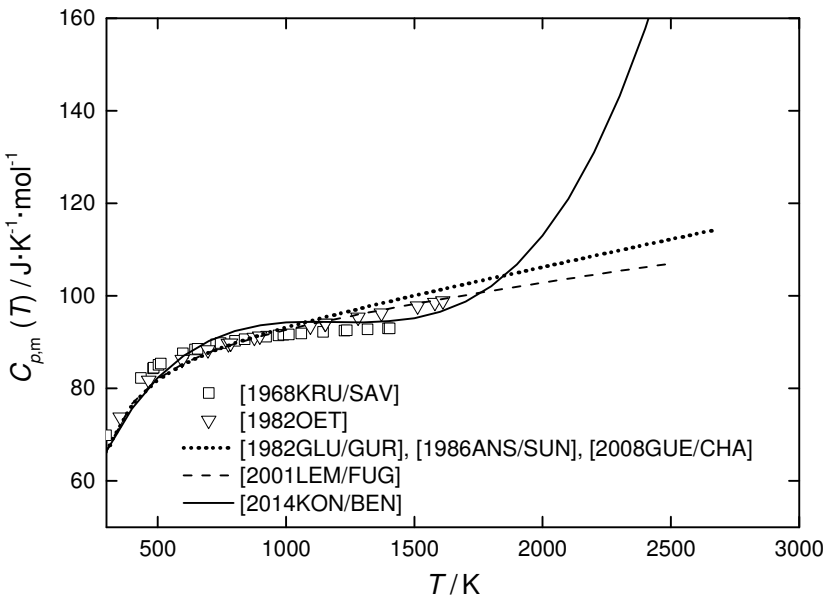
Table A-180: Optimised thermodynamic functions for the plutonium oxides [2008GUE/CHA] and comparison with literature data.

| Phase | $\Delta_f H_m^o$ (298.15 K) /kJ·mol$^{-1}$ | $S_m^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | $C_{p,m}^o$ (298.15 K) /J·K$^{-1}$·mol$^{-1}$ | Reference |
|---|---|---|---|---|
| $PuO_2$ | – 1060.3 | 66.13 | 66.25 | [2008GUE/CHA] |
| | – (1055.8 ± 1.0) | (66.13 ± 0.26) | (66.25 ± 0.26) | [2001LEM/FUG] |
| | – (1055.8 ± 1.0) | (66.13 ± 0.30) | 66.25 | [2014KON/BEN] |
| | – (1055.8 ± 1.0) | (66.13 ± 0.30) | (66.25 ± 0.30) | This review |
| $Pu_2O_3$ | – 1656.2 | 163.4 | 117 | [2008GUE/CHA] |
| | – (1656 ± 10) | (163.0 ± 0.6) | (117.0 ± 0.5) | [2001LEM/FUG] |
| | – (1647 ± 10) | (163.02 ± 0.65) | 116.98 | [2014KON/BEN] |
| | – (1656 ± 10) | (163.0 ± 0.6) | (117.0 ± 0.5) | This review |
| $PuO_{1.52}$ | – 838 | 80.4 | | [2008GUE/CHA] |
| | – (845 ± 10) | | | [2001LEM/FUG] |
| | – (845 ± 10) | | | This review |
| $PuO_{1.61}$ | – 867.2 | 81.2 | | [2008GUE/CHA] |
| | – (875.5 ± 10) | (83.0 ± 5) | (61.2 ± 5) | [2001LEM/FUG] |
| | – (875.5 ± 10) | (83.0 ± 5) | (60.2 ± 5) | This review |

Plutonium dioxide $PuO_{2-x}$ was modelled using the compound energy formalism in the work of [2008GUE/CHA] with the following sublattice model: $(Pu^{4+}, Pu^{3+})_1(O^{2-},Va)_2$. Only the enthalpy and entropy functions were optimised. The recommended entropy and heat capacity values at 298.15 K for $PuO_2$ are based on the measurements of Flotow *et al.* [1981FLO/TET] performed on $^{242}PuO_2$ and $^{244}PuO_2$ from 12 to 350 K [2001LEM/FUG], [2003GUI/FAN]. As the radiation effects are less important than for $^{239}PuO_2$, the latter measurements are more reliable than those of Sandenaw [1963SAN] and Kruger and Savage [1968KRU/SAV]. The optimised value is in very good agreement with the recommended data [2001LEM/FUG], [2003GUI/FAN]. The optimised value for the enthalpy of formation of $PuO_2$ deviates by 0.4 % from the value selected by [2001LEM/FUG], [2003GUI/FAN], however, which is based on the results of [1969JOH/DEV] obtained by oxygen combustion calorimetry starting from pure plutonium metal after careful analysis of the metal for

impurities and application of appropriate corrections. The heat capacity function used in the work of [2008GUE/CHA] for $PuO_2$ is the one recommended by [1982GLU/GUR], [1986ANS/SUN]. As seen in Figure A-24, this thermal function deviates slightly from the one recommended by [2001LEM/FUG], [2003GUI/FAN], which was calculated by refitting the values of Fink [1982FIN] to an extended Kelley polynomial. The difference amounts to ~ 3.4 $J \cdot K^{-1} \cdot mol^{-1}$ at 2000 K. The latter two equations do not account for the rapid increase in the heat capacity values above 1800 K due to oxygen Frenkel pair formation as suggested by [2014KON/BEN].

Figure A-24: Heat capacity function of face-centered cubic plutonium dioxide $PuO_{2.00}$.




$PuO_{1.61}$(cr) was modelled in the work of [2008GUE/CHA] using the compound energy formalism with the following sublattice model: $(Pu^{3+}, Pu^{4+})_2(O^{2-})_3(O^{2-},Va)_1$. There is no direct measurement of thermodynamic data for $PuO_{1.61}$. [2001LEM/FUG] estimated the enthalpy of formation and entropy values based on the oxygen potential measurements at high temperatures of [1966MAR/RAN], [1977CHE/DEA]. The optimised data in the work of [2008GUE/CHA] are in reasonable agreement with those values and within the assigned uncertainty ranges.

$PuO_{1.52}$ was treated as stoichiometric compound [2008GUE/CHA]. There is no direct measurement of the thermodynamic data for $PuO_{1.52}$. [2001LEM/FUG] estimated the enthalpy of formation based on the experimental work of [1977CHE/DEA] who

measured the enthalpy of combustion of an uncharacterised sample of $PuO_{1.57}$(cr) which was assumed to be a mixture of $PuO_{1.52}$(cr, bcc) and $PuO_2$(cr). [2008GUE/CHA] optimised both the enthalpy and entropy values of $PuO_{1.52}$(cr) for their assessment. The heat capacity function was taken from [2003KIN/UNO]. The optimised enthalpy of formation reported by [2008GUE/CHA] is in reasonable agreement with the result selected by [2001LEM/FUG].

The liquid phase is furthermore described using a ionic two-sublattice model: $(Pu^{3+})_P(O^{2-},Va^{Q-},PuO_2,O)_Q$ [2008GUE/CHA]. The melting enthalpy and entropy of the neutral combinations in this model, *i.e.,* $Pu_2O_3$, $PuO_2$, Pu and O were taken from [1982GLU/GUR], [1986ANS/SUN].

The gas phase is treated as an ideal mixture of (Pu, PuO, $PuO_2$, O, $O_2$, $O_3$) [2008GUE/CHA]. Using the Gibbs energy functions of the SGTE database for Pu(g), PuO(g), $PuO_2$(g), O(g), $O_2$(g), $O_3$(g) [1982GLU/GUR], [1986ANS/SUN], [2008GUE/CHA] calculated the vapour pressures in the [$Pu_2O_3$-$PuO_{2-x}$] domain, which showed that PuO(g) was the major vapour species, in good agreement with the studies of [1966ACK/FAI], [1968OHS/CIA], [1968MES], [1969BAT/REI]. In addition, the calculation of the congruent composition as a function of temperature was found in reasonable agreement with the literature [1973KEN], [1969BAT/REI], [1968MES], [1968OHS/CIA], [1966ACK/FAI]. The calculations showed that $PuO_2$(g) was the major vapour species above congruent plutonia, in good agreement with Kent [1973KEN], as opposed to [1969BAT/REI] who claimed it should be PuO(g). Significant deviations were found nevertheless for the partial pressures above the {$Pu_2O_3$-$PuO_{2-x}$} and $PuO_{2-x}$ systems, which pointed to the need for a re-assessment using experiments and/or calculations.

The study of [2008GUE/CHA] finally provides a sound basis for future studies on the Pu-O and higher order systems. The optimised thermodynamic functions for $PuO_{1.52}$ and $PuO_{1.61}$ cannot be retained in this review, however, as they are based on an optimisation using the CALPHAD method, and not on experimental measurements. We therefore retain the data selected by [2001LEM/FUG]. Nevertheless, the agreement being reasonable, this gives a higher degree of confidence on the latter data.

**[2009ALT/NEC]**

The authors report the solubility of hydrous $^{242}$Pu(IV) oxide, $PuO_2 \cdot xH_2O$(s), in $MgCl_2$ and $CaCl_2$ solution at (22 ± 2) °C under Argon atmosphere. Solubility experiments used hydrated $PuO_2$ as the initial solid phase, which contained about 5 % of oxidised Pu. Fe powder was added to the solid-liquid phase system to establish and to maintain reducing conditions. The samples were allowed to equilibrate up to 582 days and filtrated (10 kD) prior to the analytical measurements. The pH values were measured with a combination glass electrode and corrected for electrode junction potential and ionic

strength effect as a function of $MgCl_2$ and $CaCl_2$ concentrations. The redox potential was measured with a Pt electrode and corrected for the potential of the Ag/AgCl reference electrode. The redox potentials in the presence of Fe powder ranged between – 240 and – 450 mV, depending on the $p_cH$ and the $MgCl_2$ and $CaCl_2$ concentrations. In comparison, redox potentials in $CaCl_2$ solutions without the addition of Fe powder ranged between 100 and 300 mV. The dissolution of $PuO_2{\cdot}xH_2O(s)$ under reducing conditions was evaluated according to the reductive dissolution reaction:

$$PuO_2{\cdot}xH_2O(s) + e^- + 4H^+ \rightleftharpoons Pu^{3+} + (2+x)H_2O(l)$$

The experimental solubility data agreed with model calculations within the range of reported uncertainties for measurements and reported stability constants. The measured Pu concentration in 4 M $CaCl_2$ is raised by about 2-3 orders of magnitude compared to Pu concentrations reported in Ca-free solution (about $10^{-9}$-$10^{-10}$ M Pu after ultrafiltration at 1.5-2 nm, [2008ALT/NEC]). The difference of the experimental Pu concentration $\log_{10}[Pu] = -(9.7 \pm 0.5)$ (calc. $\log_{10}[Pu] = -10.1$) in 0.25 m $MgCl_2$ and $\log_{10}[Pu] = -(7.8 \pm 0.5)$ (calc. $\log_{10}[Pu] = -7.8$) in 3.87 m $MgCl_2$ reflect the ionic strength dependence of the Pu(III) stability constants. The solubility data in this study are interpreted with the formation of ternary Ca-Pu-OH complexes in solution. Solution complex stoichiometries and equilibrium constants have been adopted from studies with oxidation state analogs, *e.g.* Nd(III), Am(III), Cm(III), Th(IV) and Np(V). In the presence of Fe powder, Pu(III) (at $p_cH < 10$) and Pu(IV) (at $p_cH > 10$) dominated the solution speciation; in the absence of Fe powder, Pu(V) and Pu(IV) at $p_cH > 10$ are the main solution species. In concentrated $CaCl_2$ solution (3.5-4 M), ternary Ca-Pu(IV)-OH complexes were postulated that cause an increase of the Pu(IV) solubility at $p_cH$ 11-12. $Ca_4[Pu(OH)_8]^{4+}$ is proposed to be the dominant Pu(IV) solution species in analogy to the Th(IV) system. $Ca[Pu(OH)_3]^{2+}$, $Ca_2[Pu(OH)_4]^{3+}$, and $Ca_3[Pu(OH)_6]^{3+}$ were selected as prominent Pu(III) solution species. Using the Pitzer equations and associated ion-interaction parameters determined for the analogous Th(IV) system, the authors re-evaluated the data in [2008ALT/NEC] and report the thermodynamic equilibrium constant, $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)} = -(59.5 \pm 0.5)$, for the reaction:

$$Pu(OH)_4(s) + 4H_2O(l) + 4Ca^{2+} \rightleftharpoons Ca_4[Pu(OH)_8]^{4+} + 4H^+$$

It is to note that [2010FEL/NEC] also list the conditional equilibrium constant, $\log_{10}{}^{*}K^{\circ}_{s,(4,1,8)} = -(57.56 \pm 0.71)$ in 3.5 mol·$L^{-1}$ $CaCl_2$ , citing [2009ALT/NEC]. However, this conditional constant is not reported in [2009ALT/NEC].

**[2009SHI/BES]**

The reaction of Pu(VI) with $Fe(CN)_6^{3-}$ in NaOH was studied spectroscopically at room temperature:

$$Pu(VI) + Fe(CN)_6^{3-} \rightleftharpoons Pu(VII) + Fe(CN)_6^{4-} \qquad \text{(A.575)}$$

In > 8 M NaOH, $Fe(CN)_6^{3-}$ oxidises Pu(VI) to Pu(VII), while in more dilute NaOH solutions Pu(VII) is reduced to Pu(VI). The authors monitored the formation and reduction of Pu(VII) spectroscopically using its absorption band at around 635 nm. In 10.3 M NaOH, the oxidation of Pu(VI) to Pu(VII) followed a pseudo first-order law with a rate constant estimated as $k' = 1.16 \times 10^{-2}$ s$^{-1}$. The rate constant of the oxidation reaction of Pu(VI) with $Fe(CN)_6^{3-}$ to form Pu(VII) and $Fe(CN)_6^{4-}$ was calculated to be 1.29 L·mol$^{-1}$·s$^{-1}$, which increases to 2.4 and 3.3 L·mol$^{-1}$·s$^{-1}$ in 11.9 and 12.8 M NaOH, respectively. The potentials for the associated redox couples were estimated to be $E°'$(Pu(VII)/Pu(VI)) = 50-100 mV and $E°'$ ($Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$) to be close to 600 mV. The thermodynamic data provided in this study are generally estimated and cannot be considered for data selection by this review.

**[2009TKA/PRE]**

The reduction of Pu(IV) to Pu(III) in 1 M $HNO_3$ is investigated spectrophotometrically in the presence of various amounts of acetohydroxamic acid (HAHA). The solution speciation in 1 M $HNO_3$ at various concentrations of HAHA is assumed to be governed by the Pu(IV) nitrate complexes $Pu(NO_3)_2^{2+}$ and the Pu(III) complexes $Pu(NO_3)_2^{+}$, $Pu(NO_3)_3(aq)$, and $Pu(AHA)^{3+}$. The authors used thermodynamic constants for the corresponding equilibrium reactions reported in the literature and used the SIT to correct apparent constants to $I = 0$. The reduction of Pu(IV) to Pu(III) and its mechanism depends on the initial solution conditions, especially on the concentration of HAHA. The decomposition of the Pu(IV) complex $Pu(AA)^{3+}$ follows a second order reaction rate to form Pu(III). No new experimental and thermodynamic data are provided in this study.

**[2009TOP/AUP]**

See review in Chapter 16 (Appendix A, Np).

**[2009TOP/AUP2]**

See review in Chapter 16 (Appendix A, Np).

**[2010BRU/BOB]**

[2010BRU/BOB] reassessed the melting temperature of $PuO_2$ using an original experimental approach based on quasi-containerless fast laser heating technique and multi-wavelength pyrometry, yielding $T_{fus}$ = (3017 ± 28) K, a value about 300 K higher than reported in previous studies [2001CAR/YOD], [1967LYO/BAI], [1985ADA/AIT],

[2008GUE/CHA]. Their original experimental approach allowing to overcome traditional experimental limitations related to changing oxygen-to-metal ratio and sample containment interactions, gives a higher degree of confidence in the derived result. Their data are therefore retained in the present review. The experimental procedure and results are presented in more detail in [2011BRU/BOB].

**[2010CHO/JUN]**

Cho and coworkers investigated spectroscopically the stability of $^{242}$Pu(VI) hydrolysis species in 0.01 M $NaClO_4$ at (21 ± 2) °C. Samples with 0.1-0.12 mM Pu(VI) and pH between 3 and 8 were prepared under argon atmosphere. The pH was measured with a combination glass electrode filled with 3 M KCl, however, no details were given for the conversion to $p_cH$; the redox potential of the sample solutions was not measured. Based on the reported data, the authors calculated the $H^+$ concentration from the measured pH value. After different equilibration times up to 14 months, the soluble Pu(VI) concentration was measured by using liquid scintillation counting and electronic absorbance spectra were collected at 800-900 nm for Pu(VI) and 400-700 nm for Pu(III, IV, V). The molar absorption coefficients were measured as (546.8 ± 0.9) $M^{-1}\cdot cm^{-1}$ for Pu(VI) at 830.3 nm and (17.0 ± 0.2) $M^{-1}\cdot cm^{-1}$ for Pu(V) at 569 nm.

The authors monitored changes in the pH of the sample solutions and the long-term instability of Pu(VI) species over time. Sample solutions with initial pH of 5.62 changed to pH 5.33 after one month, and a solution with initial pH of 7.73 measured pH 5.89 after 14 months of equilibration time. The Pu(VI) species exhibited different stability behaviour that was strongly pH-dependent. At initial pH of 5.62, the $(PuO_2)_2(OH)_2^{2+}$ decomposes within one month and $PuO_2^+$ and $PuO_2^{2+}$ remain as solution species. At initial pH of 7.33, $PuO_2^{2+}$ is reduced to $PuO_2^+$, while the Pu(VI) hydrolysis product shows significantly higher stability and is present even after 14 months. The autoreduction of Pu(VI) to Pu(V) is explained to be caused by the redox conditions in the solutions rather than radiolytic effects of the $^{242}$Pu source.

The authors report the apparent stability constant $\log_{10}K'_{2,2} = -(7.34 \pm 0.22)$ for the equilibrium:

$$2PuO_2^{2+} + 2H_2O(l) \rightleftharpoons (PuO_2)_2(OH)_2^{2+} + 2H^+ \qquad \text{(A.576)}$$

which was converted to $\log_{10}K^{\circ}_{2,2} = -(7.08 \pm 0.22)$ by using the SIT. The ion-interaction parameters for the U(VI)-$ClO_4^-$ system were adopted for this calculation. The $\log_{10}K'_{2,2}$ value was averaged over three data determined at pH 5.20 ($\log_{10}K'_{2,2} = -7.09$), pH 5.62 ($\log_{10}K'_{2,2} = -7.45$), and pH 5.71($\log_{10}K'_{2,2} = -7.48$) in 0.01 M $NaClO_4$. The formation constant at the lower pH value appears to be inconsistent with the concordant formation constants at higher pH. This may be caused by the presence of some insoluble particulate at higher pH or the formation of additional species at low pH. The absorbance spectra exhibit a shift in the maximum of the broad absorbance at about 845

nm at pH 5.62 and 5.71, indicating the formation of different solution species. The authors assigned this broad band solely to $(PuO_2)_2(OH)_2^{2+}$. Other absorption bands were observed and suggested to belong to other Pu(VI) hydrolysis species, such as $PuO_2(OH)_2(aq)$, $(PuO_2)_2(OH)_4(aq)$ or $PuO_2(OH)_3^-$, but due to the absence of any experimental verification must be considered speculative. The formation of $PuO_2OH^+$ was not observed. The authors claim that the pH-dependent kinetic stability of Pu(VI) is associated with the formation of insoluble species. It is assumed that the insoluble species initially belonged to Pu(VI) hydroxide, which is unstable and reduced into polymeric or colloidal species or mixed-valent $PuO_{2+x}$(s, hyd). Unfortunately, the nature and quantity of those species was not determined in this study, which adds uncertainty in the reported data.

**[2010CHO/JUN2]**

Cho and coworkers studied spectroscopically the hydrolysis of hexavalent $^{242}Pu$ in 0.01 M $NaClO_4$ at (21 ± 2) °C. Samples were prepared under argon atmosphere with the pH ranging between 5 and 11. 1 mM NaOCl was added as oxidising agent to maintain Pu in its hexavalent oxidation state. The samples were analysed and spectroscopically investigated four days after sample preparation. The total Pu concentration was 50 μM in all experiments and the concentration of soluble Pu was measured after filtration through 10 kD pore size by using liquid scintillation counting. The pH was measured using a combination glass electrode filled with 3 M KCl. The redox potential was measured with a combination Pt electrode and Ag/AgCl reference electrode and corrected by 197 mV for the Ag/AgCl electrode potential at 25 °C.

Titration of the Pu(VI) solutions with NaOH resulted in the red-shift of the electronic absorbance of $PuO_2^{2+}$ at 830 nm. Three major absorption bands developed in the pH range 5-11. Absorbance maxima at 842 nm, 851 nm and 861 nm were assigned to the monomeric hydrolysis products $PuO_2OH^+$, $PuO_2(OH)_2(aq)$ and $PuO_2(OH)_3^-$, respectively. The molar absorption coefficients were determined by spectra deconvolution to be (546.8 ± 0.9) $L \cdot mol^{-1} \cdot cm^{-1}$ for $PuO_2^{2+}$, (272 ± 26) $L \cdot mol^{-1} \cdot cm^{-1}$ for $PuO_2OH^+$, and (436 ± 33) $L \cdot mol^{-1} \cdot cm^{-1}$ for $PuO_2(OH)_2(aq)$. Absorbances for polynuclear species, *i.e.*, 845 nm for $(PuO_2)_2(OH)_2^{2+}$, were not observed due to the low Pu concentrations. From slope analysis of the calculated species concentrations as a function of pH the authors determined the conditional formation constants $\log_{10}{}^*\beta_{1,n}$ for Reaction (A.577).

$$PuO_2^{2+} + nH_2O(l) \rightleftharpoons PuO_2(OH)_n^{2-n} + nH^+ \quad \text{(A.577)}$$

The SIT was used to correct for ionic strength effects, and due to the absence of Pu(VI) ion-interaction coefficients the ion-interaction coefficients for the analogous U(VI) species with $ClO_4^-$ were applied. The conditional formation constants of the mononuclear Pu(VI) hydrolysis products in 0.01 M $NaClO_4$, $\log_{10}{}^*\beta_{1,n}$ are calculated to

be – (5.8 ± 0.3) for $PuO_2OH^+$, – (13.4 ± 0.2) for $PuO_2(OH)_2(aq)$, and – (24.3 ± 0.8) for $PuO_2(OH)_3^-$.

**[2010FEL/NEC]**

See review in Chapter 16 (Appendix A, Np).

**[2010RAI/MOO]**

Rai and coworkers investigate the solubility and complexation of $^{239}Pu(III)$ in phosphate solution in the absence and presence of EDTA to develop a thermodynamic solubility model for Pu(III) and the solid phase $PuPO_4$(cr, hyd). The solubility experiments were conducted at (23 ± 2) °C under argon atmosphere. To maintain reducing conditions and Pu(III) in solution, hydrochinone ($4 \times 10^{-4}$ mol·L$^{-1}$) or $Na_2S_2O_4$ (0.01 mol·L$^{-1}$) was added to the experimental solutions. A number of experimental parameters were varied during the solubility experiments, including reaction time, pH (pH 1-12), $NaH_2PO_4$ ($10^{-4}$ mol·L$^{-1}$ to 1.0 mol·L$^{-1}$ at pH 2.5) and $Na_2H_2EDTA$ ($5 \times 10^{-5}$ mol·L$^{-1}$ to 0.256 mol·L$^{-1}$ at fixed $3.2 \times 10^{-4}$ mol·L$^{-1}$ phosphate and pH at 3.5, 10.6 and 12.6) concentrations. The pH of the suspensions was measured with a combination glass electrode and the $E_h$ was measured with a Pt combination $E_h$ electrode calibrated against quinhydrone buffers. After centrifuging and filtrating sample aliquots through 30 000 molecular weight limited filters (appr. 3.6 nm pore size), the total soluble Pu concentration was measured by using liquid scintillation counting. The fractions of Pu(III) and Pu(IV) were determined by solvent extraction with TTA/$KBrO_3$. However, the authors indicate that the TTA extraction method can include significant errors because Pu(III) can be extracted as Pu(IV), thus altering the actual fractions of Pu(III) and Pu(IV). A number of samples were selected for solution analysis using UV-vis-NIR absorbance spectroscopy and solid phase analysis with X-Ray diffraction. These analysis showed that Pu(III) is the predominant oxidation state in solution in equilibrium with a "not fully crystalline" $PuPO_4$ solid phase. The impact of EDTA was studied by adding $Na_2H_2EDTA$ to the phosphate-containing suspension and varying the pH between 1.3 and 13.

The solubility of $PuPO_4$(cr, hyd) was determined in $3.2 \times 10^{-4}$ mol·L$^{-1}$ $NaH_2PO_4$ at pH values ranging from about 1 to 12. The solubility of Pu(III) decreases from about pH 1 to about pH 6 and remains steady at pH ≥ 8 with a Pu concentration of about $10^{-10}$ mol·kg$^{-1}$. However, the concentration measurements in this pH range are constrained by the detection limit of the LSC and data reported in this pH range are questionable. At pH < 4, the Pu solubility decreases by about two orders of magnitude per pH unit and the data were interpreted according to the Reaction (A.578):

$$PuPO_4(cr, hydr) + 2H^+ \rightleftharpoons Pu^{3+} + H_2PO_4^- \qquad \text{(A.578)}$$

The authors used both the Pitzer formalism and the SIT to calculate conditional equilibrium constants and thermodynamic data. The calculated values are in reasonable agreement with those for the analogous Nd(III) and Am(III) phosphates reported by the same authors. Applying the Pitzer formalism, the Gibbs energy of reaction ($\Delta_f G_m^o /RT$) $PuPO_4$(cr, hyd) = – (703.454 ± 0.884) and the equilibrium constant $\log_{10} K^\circ$ = – (4.85 ± 0.38) were calculated for the dissolution Reaction (A.578).

In order to evaluate the coordination mechanism of Pu(III) with phosphate, the solubility of $PuPO_4$(cr, hyd) was tested at pH 2.5 in the presence of $10^{-4}$-1.0 mol·kg$^{-1}$ $NaH_2PO_4$. The suspensions were reacted for up to 76 days, though the solubility data appear to reach equilibrium within about five days. The Pu solubility exhibits a U-shaped curve where the Pu solubility decreases at $NaH_2PO_4$ concentrations below about 0.03 mol·kg$^{-1}$ according to (A.578), but increases at about [$NaH_2PO_4$] ≥ 0.03 mol·kg$^{-1}$. The authors used the Nd(III) phosphate system as a chemical analogue to evaluate the solution chemistry of Pu(III). However, applying $\log_{10}\beta^\circ = 2.78$ for the formation of $NdH_2PO_4^{2+}$ according to the equilibrium (A.579):

$$Pu^{3+} + H_2PO_4^- \rightleftharpoons PuH_2PO_4^{2+} \qquad \text{(A.579)}$$

the model overpredicts the solubility of Pu suggesting that the solution speciation of Nd(III) and Pu(III) is different. In contrast to other reports, the authors declare the interactions between Pu(III) and phosphate species to be very weak and changes in soluble Pu(III) at elevated $NaH_2PO_4$ concentration are explained solely by changing activity coefficients of solution species. Although acknowledging the limited viability of the solubility data measured at pH > 5 or 6, the authors estimated an upper limit for the equilibrium (A.580):

$$Pu^{3+} + PO_4^{3-} \rightleftharpoons PuPO_4(aq) \qquad \text{(A.580)}$$

Although this solubility study does not support the formation of $PuPO_4$(aq), the limiting $\log_{10} K^\circ \leq 14.4$ and ($\Delta_f G_m^o /RT$) $PuPO_4$(aq) ≥ – 680.382 was estimated based on the steady Pu concentrations at pH > 5. Since these values are obtained from Pu concentrations at the detection limit of the analytical method (liquid scintillation counting) used, these data can only be considered as highly uncertain upper estimates.

The authors interpreted the solubility trends with Pitzer ion-interaction parameters for the $Pu^{3+}/H_2PO_4^-$ ion couple ($\beta^{(0)}(Pu^{3+}, H_2PO_4^-) = 0.657$ kg·mol$^{-1}$) the SIT ion interaction parameter $\varepsilon(PuH_2PO_4^{2+}, Cl^-) = 0.00$ kg·mol$^{-1}$. The latter is highly uncertain due to the lacking sensitivity in respect to the analysis of the experimental data. It is to note that this study suggests that Pu(III) solubility data can be reasonably expressed by using only the $PuPO_4$(cr, hyd) solubility product and Pitzer ion-interaction parameter ($\beta^{(0)}(Pu^{3+}, H_2PO_4^-)$) or the SIT equilibrium constant for $PuH_2PO_4^{2+}$.

**[2010SMI], [2013SMI/CZE]**

[2010SMI] is the Ph.D. thesis of Smith that contains extensive information on the chemistry of uranium and plutonium in nitrate systems and their importance for analysing process streams in nuclear reprocessing systems. The following publication [2013SMI/CZE] is reviewed in detail in the Uranium App. A.

**[2010TOP/AUP]**

See review in Chapter 16 (Appendix A, Np).

**[2010XIA/RAO]**

Xia *et al.* studied the complexation of Pu(IV) with fluoride in 2.0 M $HClO_4$ (2.2 m at variable temperature) by solvent extraction at 25, 40 and 55 °C. The solvent extraction was performed with thenoyltrifluoroacetone (TTA) in toluene, with small amounts of sodium bromate $NaBrO_3$ introduced as holding agent for Pu(IV). The temperature was controlled in an aluminum reaction block with heat tape and thermocouples verified for the range – 200 to 250 °C. The Pu oxidation state was checked during and after the experiment by measuring the distribution ratios of Pu aliquots from the stock solution in TTA-toluene. The authors concluded that the extraction of Pu(IV) into the organic phase at the different temperatures is associated with a Pu(IV)-TTA complex according to Reaction (A.581):

$$Pu^{4+}(aq) + 4HTTA(org) \rightleftharpoons Pu(TTA)_4(org) + 4H^+ \qquad (A.581)$$

In the absence of fluoride, the authors determined the extraction equilibrium constants for (A.581) to be $(7.08 \pm 0.01)$ at 25 °C, $(6.91 \pm 0.01)$ at 40 °C and $(6.63 \pm 0.01)$ at 55 °C. Xia and coworkers verified the existence of Pu(IV) as the oxidation state maintained during the extractions at all temperatures and at varying TTA concentrations. The stoichiometry of the organic Pu(IV) complex was determined from the slope analysis (slopes 4.07-4.10 at 25, 40 and 55 °C) of the relationship $\log_{10}$ distribution ratio ($D$) *versus* $\log_{10}$[TTA]. A second test included the addition of $NaBrO_3$ to oxidise any fraction of Pu(III). The similar distribution ratios with and in the absence of $NaBrO_3$ confirmed the presence of Pu(IV). It also showed that the presence of $NaBrO_3$ had no significant impact on $D$ and Reaction (A.581).

With the presence of fluoride, the uptake of Pu(IV) into the organic phase decreases due to the coordination of Pu(IV) with fluoride. When plotting the experimental data $D_0/(D - 1)$ *vs.* [HF], the authors could fit the distribution data in the presence and absence of fluoride with a second-order polynomial and proposed the formation of the Pu(IV) fluoride complexes $PuF^{3+}$ and $PuF_2^{2+}$ in the aqueous phase:

$$Pu^{4+} + nHF \rightleftharpoons PuF_n^{4-n} + nH^+ \qquad (A.582)$$

with $n$ = 1 and 2.

The complexation of Pu(IV) with fluoride was observed to become stronger with increasing temperature. The equilibrium constants for Reactions (A.583) and (A.584) were calculated from $\log_{10}K_{1,n}$(A.582) and the dissociation constants of hydrofluoric acid at different temperatures.

$$Pu^{4+} + F^- \rightleftharpoons PuF^{3+} \quad \text{(A.583)}$$

$$Pu^{4+} + 2F^- \rightleftharpoons PuF_2^{2+} \quad \text{(A.584)}$$

The Van't Hoff equation was used to calculate thermodynamic properties of HF at 40 and 55 °C from the dissociation constant of HF, $\log_{10}\beta^\circ$ (HF, aq) = (3.180 ± 0.020), and $\Delta H_m^\circ$ (HF, aq) = (12.200 ± 0.300) kJ·mol$^{-1}$, at 25 °C. The SIT was used to correct the apparent equilibrium constants to $I$ = 0. Since the ion interaction parameters $\varepsilon_{ij}$ for the SIT are available only for 25 °C, the authors estimated the error associated with $\varepsilon_{ij}$ at other temperatures to be small and approximately constant when using $\varepsilon_{ij}$(25 °C) values for reactions at temperatures up to 100 °C.

Table A-181: Thermodynamic data for the dissociation reaction of hydrofluoric acid, $H^+ + F^- \rightleftharpoons HF(aq)$, for $I$ = 0 used in [2010XIA/RAO] and selected in [2001LEM/FUG]. The equilibrium constants at 40 and 55 °C were calculated from values at 25 °C using the Van't Hoff equation.

| $t$ /°C | $I$ /medium | $\log_{10}\beta_n^\circ$ | $\Delta G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta S_m^\circ$ /J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|---|
| 25 | 0 | (3.180 ± 0.020) | – (18.152 ± 0.114) | (12.200 ± 0.300) | (101.800 ± 1.077) |
| 40 | 0 | (3.28 ± 0.02) | | | |
| 55 | 0 | (3.38 ± 0.02) | | | |

Table A-182: Thermodynamic data of Pu(IV) fluoride complexes at $I$ = 0 reported in [2010XIA/RAO].

| $t$ /°C | $I$ /medium | $\log_{10}\beta_n^\circ$ | $\Delta G_m^\circ$ /kJ·mol$^{-1}$ | $\Delta H_m^\circ$ /kJ·mol$^{-1}$ | $\Delta S_m^\circ$ /J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|---|
| | | | $Pu^{4+} + F^- \rightleftharpoons PuF^{3+}$ | | |
| 25 | 2.0M $HClO_4$ | (8.86 ± 0.21) | – (50.56 ± 1.20) | (9.4 ± 5.0) | (201 ± 17) |
| 40 | 2.0M $HClO_4$ | (8.95 ± 0.20) | | | |
| 55 | 2.0M $HClO_4$ | (9.01 ± 0.20) | | | |
| | | | $Pu^{4+} + 2F^- \rightleftharpoons PuF_2^{2+}$ | | |
| 25 | 2.0M $HClO_4$ | (15.91 ± 0.21) | – (90.80 ± 1.20) | (15.0 ± 8.0) | (355 ± 27) |
| 40 | 2.0M $HClO_4$ | (16.02 ± 0.20) | | | |
| 55 | 2.0M $HClO_4$ | (16.15 ± 0.20) | | | |

The methods and data analysis described in this study are sound and reliable. However, the authors' illustration of experimental data is inconsistent with the reported ionic strength of 2.2 mol·kg$^{-1}$ $HClO_4$ claimed to persist in all samples. In Figure 1 of this paper, the authors plot $D_0/(D - 1)$ *vs*. [HF] including experimental data with [HF]

up to 3.0 mol·dm$^{-3}$. The discrepancy between [HF] ≤ 3.0 mol·dm$^{-3}$ and the claimed constant ionic strength of $I_m = 2.2$ mol·kg$^{-1}$ raises concerns about experimental parameter control and the application of appropriate ionic strength corrections.

**[2011BEN/POP]**

The enthalpy increment of $PuPO_4$(cr) has been measured using drop calorimetry in the temperature range from 530 K to 1386 K and the heat capacity by differential scanning calorimetry from 400 K to 1400 K. The $PuPO_4$(cr) sample was prepared by solid state reaction between $PuO_2$(cr) and $(NH_4)_2HPO_4$(cr) under nitrogen atmosphere at 1360 K. The recommended heat capacity of $PuPO_4$(cr) was determined based on both techniques as:

$$C^{\circ}_{p,\mathrm{m}}(T)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = 126.600 + 32.999\times10^{-3}(T/\mathrm{K}) - 1.9503\times10^{6}(T/\mathrm{K})^{-2}.$$

**[2011BRU/BOB]**

[2011BRU/BOB] investigated the melting behaviour of plutonium dioxide using a quasi-containerless fast laser heating technique and multi-wavelength pyrometry. The experimental melting temperature, *i.e.*, $T_{fus}$= (3017 ± 28) K, was found much higher than in previous studies [2001CAR/YOD], [1967LYO/BAI], [1985ADA/AIT], [2008GUE/CHA], *i.e.*, (2663 ± 40) K recommended by [2001LEM/FUG]. Such measurements are extremely challenging as both the change in the oxygen-to-metal ratio and the interaction with the containment material can affect the measurement: [2008KAT/MOR] who used a rhenium container material instead of tungsten found a melting temperature about 200 K higher than in previous studies. The latter measurement was not direct however, but based on the extrapolation of measurements on MOX samples with up to 60 % mol $PuO_2$ using an ideal solution model [2010BRU/BOB]. The quasi-containerless conditions in the study of [2011BRU/BOB] minimised undesired effects of reaction with the containment and/or changes in the O/Pu stoichiometry.

Five plutonium dioxide samples were prepared for the investigation in the form of disk-shaped samples of 8-9 mm in diameter and 4 mm in thickness. Sintering in $Ar/H_2$ atmosphere was applied to obtain dense materials, followed by heat treatment under air flow at 1423 K to adjust to the exact O/Pu = 2 stoichiometry. The latter stoichiometry was checked using thermogravimetry (TG) and X-ray diffraction (XRD) analyses. Selected samples were also characterised after the experiments using TG and XRD. The microstructure, homogeneity and purity were checked on both molten and unmolten areas after the experiment using Electron Probe Micro Analysis (EPMA) and Scanning Electron Microscopy (SEM).

The quasi-containerless conditions were achieved by heating with short heating pulses (60-200 ms) on a limited area (about 5 mm in diameter) on the sample surface:

the melted surface is surrounded by solid material in both the radial and axial directions [2010BRU/BOB]. In addition the sample was mounted in a small autoclave with inert atmosphere at pressures ranging from slightly above atmospheric to 400 MPa so as to limit vaporisation [2010BRU/BOB].

The pyrometer was operated at 652 nm and calibrated against a standard tungsten-ribbon lamp in the range 1800-2500 K in accordance with the International Temperature Scale of 1990. Beyond 2500 K, the validity of the calibration was checked by measuring the solidification radiance temperatures of Mo and W. The agreement with the tabulated values was better than ± 0.5 %. The results of the various determinations for five samples were well within 30 K, indicating a good repeatability. The suggested value $T_{fus}$= (3017 ± 28) K is retained in the present review. [2011BRU/BOB] moreover estimate the melting enthalpy of $PuO_2$(cr) as $\Delta_{fus}H_m^o(PuO_2, cr, T_{fus}) \approx 75\ kJ \cdot mol^{-1}$ using the approximation $\Delta_{fus}S_m^o \approx nR$ ($n$ being the number of atoms in the formula unit and $R$ the ideal gas constant) derived from a statistical-thermodynamic approach [1999PAP/LEB], [1967EPS]. This result is in good agreement with the value retained in the present review.

**[2011GOT/COL2]**

[2011GOT/COL2] reported Knudsen effusion mass spectrometry studies in the (Pu + O) system with the measurement of the partial pressures in the ($Pu_2O_3$-$PuO_{2-x}$) two-phase domain, near stoichiometric $PuO_{2.00}$, and at congruent vaporisation. The plutonium dioxide pellets used for the investigation were prepared using the sol-gel method followed by sintering at 1873 K in Ar/$H_2$ atmosphere (sample 1), yielding a stoichiometry of O/Pu = (1.834 ± 0.007) according to TGA analysis. A second sample of stoichiometry O/Pu ≈ 2.00 was obtained after heat treatment under air (sample 2). A biphasic sample ($Pu_2O_3$-$PuO_{2-x}$) (sample 3) was prepared from $PuO_{1.834}$ mixed with Pu metal by heating in a closed tantalum Knudsen cell up to 1800 K under vacuum. The excess Pu metal was subsequently removed by heating in an open Knudsen cell up to 2100-2200 K. The Knudsen measurements were performed in vacuum in tungsten, iridium, and tantalum cells, as well as in oxidative conditions in a YSZ/$ThO_2$ cell, at an ionisation energy of 40 eV. The program SIGMA [1990BON/HAS] was used to estimate the atomic ionisation cross-sections, while the additivity rule of Otvos and Stevenson [1956OTV/STE] was used for the ionisation cross-sections of molecular species.

Measurements were firstly performed in the $PuO_{2-x}$ phase field on sample 1 ($PuO_{1.834}$) in tungsten and iridium cells. The results in both type of cells were found in good agreement. The vapour phase was composed at 2230 K of 81 % $PuO_2$(g) and 19 % PuO(g), corresponding to an oxygen-to-metal ratio in the gas phase of O/Pu = (1.79 ± 0.02) using the ratio of the atomic flows between oxygen and plutonium as calculated from the Hertz-Knudsen relation [2001DUM/CHA]. The authors assigned the

same composition to their solid phase, supposing congruent vaporisation was attained. The latter interpretation must be adjusted, however. The attainment of the composition at congruent vaporisation supposes to wait a few hours until the steady state is reached. It seems that [2011GOT/COL2] have analysed the vapour composition directly after a heating ramp from 2000 to 2230 K, and it is not clear that the steady state was reached during their experiment. The composition at congruent vaporisation might therefore be overestimated in their work [2011GOT/COL2]. The plutonium dioxide sample was quenched after the Knudsen experiment and subsequently analysed by TG analysis, which yielded O/Pu = (1.824 ± 0.011), *i.e.*, rather close to the starting composition. The vapour pressure studies of Ohse and Ciani suggested a congruent composition O/Pu = 1.86 at 2000 K and O/Pu = 1.84 at 2200 K [1968OHS/CIA], [1968OHS]. It is clear that complementary studies are needed to confirm the value of the composition at congruent vaporisation. The measurements of [2011GOT/COL2] nevertheless allowed to solve the discrepancy in the literature on the vapour speciation above plutonia: Battles *et al.* [1969BAT/REI] reported that PuO(g) was the main vapour species above $PuO_{2-x}$, while Kent suggested it should be $PuO_2$(g) [1973KEN]. [2011GOT/COL2] therefore discarded the results of [1969BAT/REI].

The measurements in the two-phase field ($Pu_2O_3$-$PuO_{2-x}$) revealed that PuO(g) was the major vapour species, followed by Pu(g) and $PuO_2$(g), in good agreement with the results of Battles *et al.* [1969BAT/REI].

Finally, the measurements under oxygen flow performed on sample 2 (with an oxygen pressure *ca.* 100 Pa) were used to determine the sublimation enthalpy of $PuO_2$ while maintaining the sample as close as possible to the stoichiometric phase boundary O/Pu = 2.00. The $PuO_3^+$ species reported by Ronchi *et al.* [2000RON/CAP] was not observed under those highly oxidising conditions. Further studies are needed to determine if $PuO_3$(g) is an equilibrium vapour species. The second law and third law analyses of the data collected under oxygen flow yielded: $\Delta_{sub}H_m^o(PuO_2, cr, 298.15\ K) = (627 \pm 7)\ kJ \cdot mol^{-1}$ and $\Delta_{sub}H_m^o(PuO_2, cr, 298.15\ K) = (616 \pm 6)\ kJ \cdot mol^{-1}$, respectively. The agreement between the two values is reasonable. [2011GOT/COL2] observed a significant difference between the results under oxygen and vacuum, however, suggesting that the change in O/Pu ratio has an influence on the vaporisation equilibria. The second law value is retained in the present review. Combining with the enthalpy of formation of $PuO_2$(cr) [2003GUI/FAN], the enthalpy of formation of $PuO_2$(g) is derived as:

$$\Delta_f H_m^o(PuO_2, g, 298.15\ K) = -(428.0 \pm 20.0)\ kJ \cdot mol^{-1}.$$

**[2011GUE/DUP]**

In this paper presenting a CALPHAD model for the U-Pu-O-C system, [2011GUE/DUP] have slightly modified the CALPHAD model for the binary Pu-O

system [2008GUE/CHA] so as to improve the description of the miscibility gap in the fcc phase of $PuO_{2-x}$ and to account for the updated value of the melting temperature of $PuO_2$ measured by [2011BRU/BOB], *i.e.*, $T_{fus}$= (3017 ± 28) K. The calculated thermodynamic data deviate slightly from those reported by [2008GUE/CHA], however. In particular, the enthalpy of formation of $PuO_2$(cr), *i.e.*, $\Delta_f H_m^o$ ($PuO_2$, cr, 298.15 K) = – 1068.1 kJ·mol$^{-1}$ is about 12.3 kJ·mol$^{-1}$ lower than recommended in this review. The enthalpy of formation of $Pu_2O_3$(cr) is 3.4 kJ·mol$^{-1}$ lower than recommended in this review, *i.e.*, $\Delta_f H_m^o$ ($Pu_2O_3$, cr, 298.15 K) = – 1659.6 kJ·mol$^{-1}$. The entropy functions of $PuO_2$(cr) and $Pu_2O_3$(cr) are quasi unchanged, $S_m^o$ ($PuO_2$, cr, 298.15 K) = 66.56 J·K$^{-1}$·mol$^{-1}$ and $S_m^o$ ($Pu_2O_3$, cr, 298.15 K) = 163.3 J·K$^{-1}$·mol$^{-1}$.

**[2011RAI/YUI]**

Rai and coworkers review experimental solubility data of actinides, *i.e.* U, Np, Pu and Am, doped in glass and compare leachate data with the solubility of actinide and lanthanide oxide phases calculated by using the SIT. The thermodynamic data used for these solubility calculations were taken from the literature, including data for $PuO_{2.5}$(s) and $PuO_2$(am) selected in [2003GUI/FAN]. New data were developed for the Th(IV) phosphate system, but no new thermodynamic data are presented for Np or Pu. The value $\log_{10}K°$= 13.7 for the solid-solution equation:

$$M(OH)_3(ss) + 3H^+ \rightleftharpoons M^{3+} + 3H_2O(l) \qquad (A.585)$$

was reported with M representing a trivalent actinide or rare earth solid solution system (ss) with a mole fraction of the metal equal to 1. At a lower mole fraction $X_i$, the concentration of the trivalent actinide is expressed by $\log_{10}K°$= 13.7 + $\log_{10}X_i$.

From molecular modeling calculations the authors conclude that $PuSiO_4$(s) is not stable in a mixture of quartz and $PuO_2$(s). The initial solubility-controlling Pu(IV) oxide solids in or mixed with crushed glass may not be sufficiently stable in reducing environments of nuclear waste repositories and may transform to Pu(III) and upon leaching may form secondary Pu(III) solid phases.

**[2011RAO/TIA]**

Rao and Tian studied the hydrolysis of $^{242}$Pu(VI) at variable temperatures by using potentiometric, spectrometric and calorimetric methods. The concentration of Pu(VI) in the stock solution was determined by using liquid scintillation counting, α-spectrometry, and complexation of Pu(IV) with EDTA after complete electrochemical reduction of the Pu(VI). The OH concentration in the sample solutions was determined calorimetrically measuring the heat originated in acid/base titrations. The ionic strength was maintained at 1.0 M $NaClO_4$ at 298.15 K. Sample preparation

and titrations with $CO_2$-free NaOH were conducted under argon atmosphere. Potentiometric titrations were performed by using a combination glass electrode filled with 3 M KCl at $p_cH$ between 2.5 to 5.5 with Pu(VI) concentrations of 1-3 mM. It is to note that the pH measurements may have been affected by the potential precipitation of low-soluble $KClO_4$ at the liquid junction due to the high concentrations of $K^+$ ions in the electrode filling solution and perchlorate ions in the sample solutions. The initial Pu(VI) concentrations in the calorimetric titrations was between 1 and 5 mM. Laser-light scattering was used to determine if any precipitates had formed during the potentiometric titration. Electronic absorption spectra were collected for sample solutions with Pu(VI) concentrations ranging between $9 \times 10^{-5}$ and $1.7 \times 10^{-3}$ M.

For the potentiometric data analysis, the authors evaluated the state of equilibrium by performing forward and back-titrations. For the data analysis, potentiometric titration data to calculate the hydrolysis constants were limited to those where back and forward titrations overlapped, verifying the absence of colloidal or precipitate formation during the experiment. The potentiometric data at $p_cH < 5.5$ were best interpreted with a mixture of mono- and polynuclear hydrolysis species, namely $PuO_2OH^+$, $(PuO_2)_2(OH)_2^{2+}$ and $(PuO_2)_3(OH)_5^+$. The potentiometric data were used to calculate the enthalpy of Pu(VI) hydrolysis Reactions (A.586), (A.587), and (A.588):

$$PuO_2^{2+} + H_2O(l) \rightleftharpoons PuO_2OH^+ + H^+ \quad \text{(A.586)}$$

$$2PuO_2^{2+} + 2H_2O(l) \rightleftharpoons (PuO_2)_2(OH)_2^{2+} + 2H^+ \quad \text{(A.587)}$$

$$3PuO_2^{2+} + 5H_2O(l) \rightleftharpoons (PuO_2)_3(OH)_5^+ + 5H^+ \quad \text{(A.588)}$$

Spectrophotometric titrations with different Pu(VI) concentrations with NaOH up to pH 12 were conducted at 298.15 K. The spectroscopic data indicate that hydrolysis products form at $p_cH > 3$ with new absorption bands appearing at 840-860 nm. The provided data suggest that the first hydrolysis species, $PuO_2OH^+$, with a band at 842 nm is present at 0.09 and 0.19 mM $[Pu(VI)]_{tot}$, but does not form at 1.7 mM $[Pu(VI)]_{tot}$. At the higher Pu(VI) concentration the peak maximum of a band at 845 nm is slowly shifting to 849 nm with increasing $p_cH$. These observations suggest that $PuO_2OH^+$ does not form (or only form at trace levels) under the Pu(VI) concentrations used in the potentiometric titrations (1-3 mM).

The correlation between spectophotometric and potentiometric data shows two areas with different speciation: an "equilibrium region" with absorbances at 830 nm, and 840-850 nm and a "non-equilibrium region" with absorbances at 830, 850 and 868 nm. Based on the results from the potentiometric titrations the authors associate the absorbances in the equilibrium region with $PuO_2OH^+$, $(PuO_2)_2(OH)_2^{2+}$ and $(PuO_2)_3(OH)_5^+$, and the absorbances in the non-equilibrium region with higher hydrolysed species such as $PuO_2(OH)_4^{2-}$ and particulates. However, the authors note that the absorbance spectra in the equilibrium state could not be deconvoluted with the same three solution species, $PuO_2OH^+$, $(PuO_2)_2(OH)_2^{2+}$ and $(PuO_2)_3(OH)_5^+$, that were

used to analyse the potentiometric data. The authors imply that the spectra of $PuO_2OH^+$ and $(PuO_2)_2(OH)_2^{2+}$ are too similar to be deconvoluted. This is in contrast to the peak assignments reported in [1995PAS/KIM] [2010CHO/JUN2], and [2006REI/NEU] with the assignment of the absorbance band at 842 nm to $PuO_2OH^+$ and the absorbance at about 851 nm to $(PuO_2)_2(OH)_2^{2+}$. This internal inconsistency is of great concern and questions the validity of the speciation model used to analyse the potentiometric data. In the alkaline range, no absorbance features were observed which led the authors to suggest the formation of the centrosymmetric complex $PuO_2(OH)_4^{2-}$.

To correct for ionic strength, the authors converted data from molarity to molality scale and applied the SIT by using U(VI) ion-interaction parameters for the Pu(VI) system:

$$\Delta\varepsilon\ (\text{A.586}) = \varepsilon(PuO_2OH^+, ClO_4^-) + \varepsilon(H^+, ClO_4^-) - \varepsilon(PuO_2^{2+}, ClO_4^-)$$

$$\Delta\varepsilon\ (\text{A.587}) = \varepsilon((PuO_2)_2(OH)_2^{2+}, ClO_4^-) + 2\varepsilon(H^+, ClO_4^-) - 2\varepsilon(PuO_2^{2+}, ClO_4^-)$$

$$\Delta\varepsilon\ (\text{A.588}) = \varepsilon((PuO_2)_3(OH)_5^+, ClO_4^-) + 5\varepsilon(H^+, ClO_4^-) - 3\varepsilon(PuO_2^{2+}, ClO_4^-)$$

with $\varepsilon(PuO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol$^{-1}$, $\varepsilon(PuO_2OH^+, ClO_4^-) = \varepsilon(UO_2OH^+, ClO_4^-) = -(0.06 \pm 0.40)$ kg·mol$^{-1}$, and $\varepsilon((PuO_2)_3(OH)_5^+, ClO_4^-) = \varepsilon((UO_2)_3(OH)_5^+, ClO_4^-) = (0.45 \pm 0.15)$ kg·mol$^{-1}$. The potential errors introduced by the conversion of data at 298 K to other temperatures were estimated to be insignificant.

Table A-183: Thermodynamic properties of Pu(VI) hydroxide complexes $(PuO_2)_m(OH)_n^{2m-n}$ at various temperatures reported in [2011RAO/TIA].

| *m:n* | *T* /K | *I* /medium | $\Delta_f G_m^o$ /kJ·mol$^{-1}$ | $\Delta_f H_m^o$ /kJ·mol$^{-1}$ | $\Delta_f S_m^o$ /J·mol$^{-1}$·K$^{-1}$ |
|---|---|---|---|---|---|
| 1:1 | 283 | 1 M $NaClO_4$ | (34.26 ± 2.60) | | |
| 1:1 | 298 | 1 M $NaClO_4$ | (33.39 ± 2.8) | (35.0 ± 3.4) | (5 ± 15) |
| 1:1 | 313 | 1 M $NaClO_4$ | (32.67 ± 2.64) | | |
| 1:1 | 328 | 1 M $NaClO_4$ | (34.80 ± 3.02) | | |
| 1:1 | 343 | 1 M $NaClO_4$ | (34.10 ± 3.09) | | |
| 2:2 | 283 | 1 M $NaClO_4$ | (43.47 ± 0.70) | | |
| 2:2 | 298 | 1 M $NaClO_4$ | (44.01 ± 1.37) | (65.4 ± 1.0) | (72 ± 6) |
| 2:2 | 313 | 1 M $NaClO_4$ | (44.30 ± 1.26) | | |
| 2:2 | 328 | 1 M $NaClO_4$ | (43.16 ± 1.01) | | |
| 2:2 | 343 | 1 M $NaClO_4$ | (43.16 ± 1.31) | | |
| 3:5 | 283 | 1 M $NaClO_4$ | (115.57 ± 1.19) | | |
| 3:5 | 298 | 1 M $NaClO_4$ | (116.27 ± 1.26) | (127.7 ± 1.7) | (38 ± 7) |
| 3:5 | 313 | 1 M $NaClO_4$ | (117.50 ± 1.38) | | |
| 3:5 | 328 | 1 M $NaClO_4$ | (115.40 ± 1.38) | | |
| 3:5 | 343 | 1 M $NaClO_4$ | (115.29 ± 1.51) | | |

**[2011SHI/GOG]**

Shilov and coworkers evaluate published data on the stability of Pu(VI) and Pu(V) in acidic solutions. The authors base the reduction of Pu(VI) in acidic and neutral solutions

on radiolytic effects induced by the α-radiolysis of Pu and the radiolytic decomposition of water. The reduction of Pu(VI) results in the formation of a dimeric Pu(VI) species due to the combination of an excited and an unexcited Pu(VI) ion. This Pu(VI) dimer rapidly decomposes to Pu(V) and $H_2O_2$. The Pu(V) ions can be reduced in acidic and neutral solutions by hydrogen peroxide or disproportionate. In 0.5-7.6 M NaOH, the authors describe the disproportionation reaction of Pu(V) into Pu(VI) and Pu(IV) according to Equation (A.589):

$$2PuO_2(OH)_3(H_2O)^{2-} \rightleftharpoons PuO_2(OH)_4^{2-} + Pu(OH)_4(aq) + 2OH^- \quad \text{(A.589)}$$

No thermodynamic data are provided in this report.

**[2011SIL], [2011SIL2] and [2012SIL]**

In a series of papers Silver conducts mathematical evaluations to identify the first hydrolysis constant of Pu(IV) [2011SIL], to express the disproportionation of reactions of Pu [2011SIL2], and to develop criteria to evaluate the reliability of estimated hydrolysis constants. The authors use the double double-point (conditions where the concentrations of two sets of Pu oxidation states are equal) to estimate the hydrolysis constant. However, the estimation of the first hydrolysis constant of Pu(IV) based on the mathematical expressions of equilibrium equations still relies on several assumptions and accurate estimates of $[H^+]$. As a conclusion the author suggests that the first hydrolysis constant of Pu(IV) is closer to 0.035 than to 0.35. No experimental data are provided.

**[2012BEN/ZAO]**

The authors investigated the electronic structure, magnetic, dynamical and thermodynamic properties of NpN, PuN and AmN using ab initio pseudopotential and DFT methods. The complete review of this article is reported in the Appendix A for neptunium.

**[2012BUZ/CHU]**

Buz'ko and coworkers used the Density Functional Theory (DFT) to calculate the structures and binding energies of chloro complexes of Pu(III) and Pu(IV) of general formula $PuCl_n^{3-n}$ and $PuCl_n^{4-n}$ with $n$ = 2-8, respectively. The study suggests that a maximum coordination number of eight can be achieved in molten chloride, but the hexachloro species, $PuCl_6^{3-}$ and $PuCl_6^{2-}$, are determined to be the predominant complexes.

**[2012GOG/FED]**

Gogolev and coworkers evaluate the stability of Pu(VIII) and Pu(VII) in alkaline solutions. Ozone was used to oxidise 0.01-3 mM Pu(VI) in 1-16 M NaOH solutions at 0-25 °C. Ozonolysis of Pu(VI) at 0 °C produced Pu(VII), but did not result in the formation of the volatile compound $PuO_4$. The authors estimate the neutral complex $PuO_4$ to exist for only 0.1-0.2 sec in 1 M NaOH at 20 °C. Lower temperature increases the lifetime of Pu(VIII) and the ratio Pu(VIII)/Pu(VII) $\leq 0.05$ was observed at 0 °C. Because the Pu(VII) did not oxidise to Pu(VIII) in 1 M NaOH, the redox potential for the redox couple Pu(VIII)/Pu(VII) is estimated to be $\geq 1.15$ V *vs.* NHE. The half-lives of the Pu(VIII) solution species, $PuO_4(OH)_2^{2-}$ and $PuO_6^{4-}$, were estimated to be less than one second. No new thermodynamic data are provided in this study.

**[2012RIO/MIC]**

Monopositive An(V) and An(VI) (An = $^{238}U$, $^{237}Np$, $^{242}Pu$) ions were produced by gas phase electrospray ionisation (ESI) and trapped in a quadrupole ion trap mass spectrometer with collision induced dissociation capabilities. The experimental solutions contained about 180 μM of $AnO_2(ClO_4)_2$ and were adjusted to about pH 4. To model the impact of sequential water addition to the actinyl ions and their first hydrolysis step, DFT calculations in the gas phase are performed by using B3LYP hybrid functional and actinide core potentials. The main reaction for Np(VI) and Pu(VI) during the ionisation process is the reduction to $AnO_2^+$. Only a minor Pu fraction ($\leq 5$ %) remains in the hexavalent oxidation state in the form of $PuO_2OH^+$, while $NpO_2OH^+$ is not detected at all. In contrast, about 60 % of U(VI) is maintained in its oxidation state and forms the first hydrolysis product, $UO_2OH^+$.

The bare $AnO_2^+$ cations are exposed to water at about $10^{-6}$ Torr pressure to determine relative hydration kinetics and hydration number. After a ten second reaction time, the pentavalent actinides are coordinated with four water molecules in the equatorial plane to form $AnO_2(H_2O)_4^+$. The An(V) pentahydrates, $AnO_2(H_2O)_5^+$, are not observed experimentally, even after increasing the water pressure by a factor of two. The computed hydration energies and Gibbs free energies of hydration are exergonic with very similar $\Delta G°$ levels calculated for $AnO_2(H_2O)_4^+$ and $AnO_2(H_2O)_5^+$. However, the change in Gibbs energy for the formation of $AnO_2(H_2O)_5^+$ is nearly neutral and thus $AnO_2(H_2O)_4^+$ is slightly favored energetically. The first hydrolysis product contains three water molecules in the inner coordination sphere in $AnO_2OH(H_2O)_3^+$. The reaction free energies and Gibbs energy for the sequential hydration reactions of $AnO_2(H_2O)_{n-1}^+$ with $n$ = 1-5 and for the hydration reactions of the hydroxy complex $AnO_2OH(H_2O)_{n-1}^+$ with $n$ = 1-4 are calculated to be exergonic.

Table A-184: Calculated free energy at 0 K and Gibbs energy at 298 K for the sequential hydration reaction $AnO_2(H_2O)^+_{n-1} + H_2O \rightleftharpoons AnO_2(H_2O)^+_n$ reported in [2012RIO/MIC].

| | *An* | *T* /*K* | Method | *I* /medium | $\Delta E^o$ /kJ·mol$^{-1}$ | $\Delta_r G^o_m$ (298 K) /kJ·mol$^{-1}$ |
|---|---|---|---|---|---|---|
| *n = 1* | U | 298 | ESI/DFT | Gas phase | – 134 | – 109 |
| *n = 1* | Np | 298 | ESI/DFT | Gas phase | – 134 | – 104 |
| *n = 1* | Pu | 298 | ESI/DFT | Gas phase | – 133 | – 120 |
| *n = 2* | U | 298 | ESI/DFT | Gas phase | – 117 | – 81 |
| *n = 2* | Np | 298 | ESI/DFT | Gas phase | – 118 | – 82 |
| *n = 2* | Pu | 298 | ESI/DFT | Gas phase | – 118 | – 82 |
| *n = 3* | U | 298 | ESI/DFT | Gas phase | – 108 | – 72 |
| *n = 3* | Np | 298 | ESI/DFT | Gas phase | – 106 | – 70 |
| *n = 3* | Pu | 298 | ESI/DFT | Gas phase | – 104 | – 68 |
| *n = 4* | U | 298 | ESI/DFT | Gas phase | – 83 | – 45 |
| *n = 4* | Np | 298 | ESI/DFT | Gas phase | – 79 | – 46 |
| *n = 4* | Pu | 298 | ESI/DFT | Gas phase | – 74 | – 38 |

The effective charge of the actinide ions calculated in this study differ from the commonly accepted values. The charge values of 1.59 and 1.45 for Np and Pu in $NpO_2(H_2O)^+_4$, respectively, is quite lower than the generally accepted value of (2.2 ± 0.1) for pentavalent actinides in the aqueous phase reported by Choppin and Rao [1984CHO/RAO].

The authors also describe the formation of two peroxo adducts, $UO_2(O_2)(H_2O)^+_3$ and $UO_2(O_2)(H_2O)^+_2$. Those adducts were not formed for Np and Pu because their hexavalent oxidation state is not retained during the ionisation. The free energies at 298 K are predicted for the following reactions, but only the third reaction is observed for U:

$$UO^+_2(H_2O)_2 + O_2 \rightleftharpoons UO^+_2(O_2)(H_2O) + H_2O \quad \text{(A.590)}$$

$$\Delta_r G^o_m\,(298\ \text{K}) = 58\ \text{kJ·mol}^{-1}$$

$$UO^+_2(O_2)(H_2O) + 3H_2O \rightleftharpoons UO^+_2(H_2O)_4 + O_2 \quad \text{(A.591)}$$

$$\Delta_r G^o_m\,(298\ \text{K}) = -\,19\ \text{kJ·mol}^{-1}$$

$$UO^+_2(O_2)(H_2O)_2 + H_2O \rightleftharpoons UO^+_2(H_2O)_3 + O_2 \quad \text{(A.592)}$$

$$\Delta_r G^o_m\,(298\ \text{K}) = -\,35\ \text{kJ·mol}^{-1}$$

Bond distances and binding energies are calculated for optimised geometries in the ground state for both observed and hypothetical species of $AnO_2(H_2O)^+_n$, $AnO_2OH(H_2O)^+_n$ and $AnO^+_2(O_2)(H_2O)_n$ (An = U, Np).

This study is of interest from a coordination chemistry point of view, but the data reported by Rios *et al.* have not been considered for selection by this review.

**[2013DEL]**

The aging behaviour of Pu(IV) oxide, $PuO_2 \cdot xH_2O$, was studied in respect to the conditions present in alkaline tank wastes. Solid Pu(IV) oxide phases were prepared from Pu(IV) and Pu(VI) added to 1-15 M NaOH solutions and were equilibrated under air atmosphere at 18-24 °C. While the addition of Pu(IV) resulted in immediate precipitation of a green Pu(IV) oxide phase, experiments started from Pu(VI) initiated a solid phase transformation from a brown Pu(VI) oxide to a green Pu(IV) oxide. The solids are undergoing significant particle growth from about 1.9 nm to about 5 nm within about three years. The experiments that started from Pu(VI) produced larger particle sizes of up to about 9 nm in 1 M NaOH, which is explained by the radiolytic alterations of the initial Pu(VI) phases. Solubilities of $PuO_2$ fired at 400 °C and $PuO_2 \cdot xH_2O$ obtained from precipitation of Pu(IV) reached stability after about 800 days. No new thermodynamic data on $PuO_2 \cdot xH_2O$ are provided.

**[2013EKB/LAR]**

Ekberg and coworkers examined the structure and particle size of aged and freshly prepared Pu(IV) oxide by using EXAFS spectroscopy. Crystalline $PuO_2$ that is in contact with water exhibits a significant shortening of the Pu–O distances in the second coordination shell indicating that the Pu atoms in the surface of the $PuO_2$ particles become oxidised. The surface oxidation is distributed among the Pu atoms with the bulk $PuO_2$ structure remaining intact. Freshly prepared Pu(IV) polymers are found to be extremely small with 5-6 Pu atoms in each polymer. With time, these polymeric Pu clusters shrink down to 3-4 Pu atoms in each cluster with partial oxidation of Pu(IV) indicated by shorter Pu–O and Pu-Pu distances compared to $PuO_2$. No plutonyl bonds are present in the oxidised surfaces of the particles.

**[2013FEL/MOO]**

The reduction of $^{239}PuO_2$(am) by Fe(II) and the radioytical formation of Fe(III) hydroxide is discussed at (23 ± 2) °C. Suspensions of $PuO_2$(am) and 0.001 M $FeCl_2$ in 0.015 M NaCl were adjusted to pH 4-7 and aged in polypropylene and glass containers for up to 27 days. Hematite was added to the suspensions and the reactions monitored for up to 171 days. The pH measurements were conducted with semi-micro glass electrode and the $E_h$ was measured using a redox platinum electrode, which was calibrated with pH 4 and 7 quinhydrone buffer solutions. After centrifugation and filtration through 30 000 molecular weight cut-off filters, analysis of total soluble Pu

concentration was performed by using liquid scintillation counting, the Pu(III) fraction determination by TTA/$KBrO_3$ extraction, and the soluble Fe(II) fraction was determined spectroscopically at 562 nm using the ferrozine method. The hematite was treated with $NH_2OH{\cdot}HCl/HCl$ to remove any ferrihydrate and analysed for surface area and crystallinity. Scanning electron microscopy verified the presence of 1-2 μm hematite crystals. The solid Pu phase was examined by transmission electron microscopy and Pu $L_3$ XAFS spectroscopy.

The authors used data from the NEA TDB to derive $\log_{10}K = 15.7$ for the reductive dissolution reaction of $PuO_2$(am):

$$PuO_2(am) + 4H^+ + e^- \rightleftharpoons Pu^{3+} + 2H_2O(l) \qquad \text{(A.593)}$$

With the calculated activity coefficient of 0.28 for $Pu^{3+}$, the soluble equilibrium concentration of $Pu^{3+}$ (in molality) was predicted from the equation $\log_{10}[Pu^{3+}] = 16.26 - pe - 4pH$. However, the predicted Pu(III) concentrations were not in good agreement with the scattered experimental solubility data. Although still underestimating the Pu solubility by about one order of magnitude compared to experimental solubility data, a more reasonable prediction was obtained when calculating the soluble Pu concentration from the measured pH and the measured Fe(II) concentration in solution via $\log_{10}[Pu^{3+}] = \log_{10}[Fe^{2+}] - pH - 0.28$.

At pH > 4, oxidation of Fe(II) and the formation of amorphous $Fe(OH)_3$ was observed. The authors proposed the oxidation of Fe(II) in the presence of $^{239}Pu$ to be caused by radiolytic effects and the formation of oxidising free radicals, such as $OH^{\bullet}$ or $Cl^{\bullet}$. No new thermodynamic data were presented in this paper.

**[2013KIM/ASA]**

The behaviour of Pu(III) and Pu(IV) in 1-7 M $HNO_3$ is studied electrochemically and spectroscopically at 25 °C. A glassy carbon working electrode, Ag/AgCl reference electrode and Pt wire counter electrode are used for cyclic voltammetric studies in an electrochemical window between + 1.10 and + 0.30 V at various scan rates (0.05-0.20 $V{\cdot}s^{-1}$). A cathodic and a corresponding anodic peak in the cyclic voltammograms illustrate the quasi-reversible redox reaction between Pu(IV) to Pu(III) interpreted as the one-electron transfer Reaction (A.594):

$$Pu^{4+} + e^- \rightleftharpoons Pu^{3+} \qquad \text{(A.594)}$$

The formal redox potential $E°'$ is calculated from the $\Delta E_p/2$ values with $\Delta E_p = E_{pa} - E_{pc}$, measured at various nitric acid concentrations. With increasing scan rate the $\Delta E_p$ values increase with the scan rate, while the value $E°' = + 0.721$ V *vs.* Ag/AgCl in 1 M $HNO_3$ was found to be nearly independent from the scan rate. In contrast, the formal redox potential $E°'$ decreases with increasing nitric acid concentration. These changes in the redox potential with increasing nitric acid

concentration are associated with the formation of inner-sphere Pu(IV) and Pu(III) nitrate complexes and the electron transfer between those species.

The authors investigate the nitrate complexation of Pu(III) and Pu(IV) by using UV-vis-NIR absorbance spectroscopy. The electronic absorption spectra of Pu(IV) in nitric acid exhibited changes due to the interaction of Pu(IV) with nitrate to form inner-sphere solution complexes. The primary absorbances of Pu(IV) at 474 and 1068 nm shift to 480 and 1064 nm, respectively, and $Pu(NO_3)_n^{4-n}$ ($n$ = 1-3) in 1-4 M $HNO_3$ and $Pu(NO_3)_6^{3-}$ in higher concentrated nitric acid are proposed as the prominent Pu(IV) solution species. The Pu(III) solution spectra exhibited three characteristic peaks at 564 nm, 600 nm and 664 nm, but the individual species, assumed to be $Pu(NO_3)_n^{3-n}$ ($n$ = 1-3), could not be distinguished spectroscopically. Although the molar extinction coefficients of characteristic absorbance peaks of Pu(III) and Pu(IV) are presented, no detailed information about the speciation for either oxidation state is provided.

**[2013ODO/BYL]**

Odoh and coworkers studied the coordination of Pu ions with water and hydroxide by using Car-Parrinello molecular dynamics (CPMD) simulations. This method combines classical molecular dynamics with a density functional theory approach of the electronic structure and allows to include effects of the second coordination sphere. The structure of the $PuO_2^{2+}$ ion was optimised with five water molecules in the equatorial plane around the plutonyl axis, while $PuO_2^{+}$ binds only four water molecules. The tetraaquo structure, $PuO_2(H_2O)_4^{2+}$, was calculated to be about 10.68 kJ·mol$^{-1}$ higher in energy than the $PuO_2(H_2O)_5^{2+}$ ion, whereas the Pu(V) complex $PuO_2(H_2O)_4^{+}$ is 12.98 kJ·mol$^{-1}$ more stable than $PuO_2(H_2O)_5^{+}$. The O=Pu=O and Pu-$O_{eq}$ bond distances for both Pu(V) and Pu(VI) are in good agreement with published experimental results. The energy difference between the hydrated Pu(IV) species $Pu(H_2O)_8^{4+}$ and $Pu(H_2O)_9^{4+}$ is calculated to be very small with about 5.86 kJ·mol$^{-1}$ suggesting that both structures may be isoenergetic. However, ejection of the ninth water molecule within 6-8 psec of the simulation and the better agreement of calculated Pu-O bond lengths with experimental data favor the dominance of $Pu(H_2O)_8^{4+}$ in aqueous solution. The Pu(III) ion, $Pu(H_2O)_8^{3+}$, is calculated to be about 20.52 kJ·mol$^{-1}$ more stable than $Pu(H_2O)_9^{3+}$. However, the authors state that in aqueous solutions a dynamic interchange could occur between Pu(III) ions with seven, eight and nine coordinated water molecules with $Pu(H_2O)_8^{3+}$ as the most dominant species.

The authors used the energetics and coordination of the hydrated Pu ions to calculate the first hydrolysis constants. An entropic factor was applied for the metadynamic simulations to account for the possibility of any of the water molecules coordinated to Pu could be deprotonated. The free energy of the first hydrolysis of Pu(VI) resulted in 32.74 kJ·mol$^{-1}$ and a $pK_a$ of 5.70 at 300 K. The authors used $PuO_2(H_2O)_4^{+}$ to calculate the free energy of the Pu(V) hydrolysis to be 54.68 kJ·mol$^{-1}$

with a $pK_a$ of 9.51. The octahydrated Pu(IV) and Pu(III) ions were used to calculate the free energies (0.59 $kJ \cdot mol^{-1}$ for Pu(IV) and 38.23 $kJ \cdot mol^{-1}$ for Pu(III)) and the $pK_a$ values (0.17 for Pu(IV) and 9.13 for Pu(III)) for their first hydrolysis reactions.

The data reported in this study are of interest from a coordination chemistry perspective but are not considered for data selection by this review.

**[2013POM/TIW]**

Pomogaev and coworkers report quantum mechanical calculations to develop intermolecular force-field parameters for penta-and hexavalent actinide ions $AnO_2^+(aq)$ and $AnO_2^{2+}(aq)$, where An = U, Np, Pu and Am, and their interactions with water. A detailed review is given in the Uranium, App. A.

**[2013STE/WAL]**

Steppert and Walther investigated the Pu(VI) species distribution in aqueous solution at pH 4.5-5.3 by using nano-electrospray ionisation mass spectrometry. The solution pH was measured with a combination glass electrode after adjustment with $HNO_3$ and $NH_3$. Although the ionic strength was not well controlled, it had to be very low in order to avoid clogging of the ESI needle.

Due to the soft ionisation conditions, a wide range of water molecules are associated with the Pu species forming peak clusters of general formula, $[(PuO_2)_x(OH)_y(NO_3)_z]^{q+} \cdot (H_2O)_n$ with $x = 1\text{-}3$ and $n = 0\text{-}40$. The peak fit routine identified only singly and double charged Pu species in the spectra. Some peak clusters include the presence of nitrate, which is assumed not to be bound to Pu in its inner coordination sphere. The peak clusters at pH 4.5-4.8 were interpreted with the presence of $PuO_2^+$ (9.5-17.6 %), $PuO_2^{2+}$ (73.3-75.1 %), and the Pu(VI) hydrolysis products $PuO_2OH^+$ (3.8-4.1 %) and $(PuO_2)_2(OH)_2^{2+}$ (4.5-7.7 %). The species distribution matches well qualitatively the speciation calculated from stability constants in the NEA TDB. The solution at pH 5.3 is claimed to be saturated with respect to $PuO_2(OH)_2(s)$ and the solution speciation was dominated by $PuO_2^+$ (63.2 %); the fraction of soluble $PuO_2^{2+}$ (36.8 %) agrees well with the calculated value.

Prior to this study, the authors used this technique to examine the hydrolysis of U(VI) and obtained results that were in good agreement with published literature, confirming the presence of monomeric, dimeric and trimeric U(VI) hydrolysis products. In this very limited study (only four samples were measured), only monomeric and dimeric Pu species were observed; in contrast to the U(VI) hydrolysis study, no trimeric Pu species were observed within the detection limits. This study does not provide any new thermodynamic data.

**[2014BAN/BRE]**

Banik and coworkers tested the stabilisation of trivalent actinides, *i.e.*, U(III), Np(III) and Pu(III), in acidic solutions (HCl, $HClO_4$, $CF_3SO_3H$) up to pH 5.5 in the presence of three reducing agents, rongalite, hydroxylamine hydrochloride and acetohydroxamic acid. Hydroxylamine hydrochloride was established as the most effective redox holding agent that could effectively hold about 80 % of Pu(III) at pH below 5.5, while the Np(III) and U(III) aquo ions could only be stabilised below pH 2.5 and 1.0, respectively. No thermodynamic data are reported.

**[2014KAT/UCH]**

[2014KAT/UCH] reported the measurement of the linear thermal expansion of hypo-stoichiometric plutonium dioxide between 1673 K and 1923 K using dilatometry in a controlled oxygen partial pressure as a function of temperature and oxygen-to-metal ratio. Plutonium dioxide powder was pressed into a pellet for the experiments and sintered at 1973 K to 92 % TD. The oxygen partial pressure was controlled during the experiment with an $H_2/H_2O$ mixed gas atmosphere, and monitored with stabilised zirconia oxygen sensors. The O/M ratio of the investigated sample was calculated using the expression of Komeno *et al.* [2012KOM/KAT]:

$$x = [(163000\exp(\frac{-376\times10^3}{RT})P_{O_2}^{-1/2})^{-2} + ((66200\exp(\frac{-445\times10^3}{RT}))^{1/2}P_{O_2}^{-1/4})^{-2}]^{-1/2}$$

The thermal expansion measurements were subsequently performed for a constant O/M ratio (1.98, 1.95 and 1.92, respectively) for temperatures covering the range 1623-1923 K after attainment of equilibrium conditions. The linear thermal expansion (LTE) results showed a slightly higher thermal expansion for hypostoichiometric plutonium dioxide compared to $PuO_{2.00}$ [2014UCH/SUN]. The coefficients of thermal expansion (CTE) calculated at 1573 and 1923 K showed an increase with decreasing O/M ratio, with a maximum at about O/M = 1.95.

[2014KAT/UCH] subsequently estimated the various contributions to the heat capacity of $PuO_{2.00}$ and $PuO_{2-x}$ including the heat capacity at constant volume $C_v$ expressed using a Debye function, the dilatational term $C_d$, the Schottky term $C_{sch}$, and the excess term $C_{exc}$ due to oxygen Frenkel pairs formation. The dilatational term $C_d$ is equal to $C_d = \gamma\alpha T$ where $\gamma$ is the Gruneisen constant and $\alpha$ the thermal expansion coefficient. The Debye temperature and Gruneisen constant were approximated with that of $PuO_{2.00}$ as reported by [2000SER/ARA], *i.e.*, 420 K and 2.6, respectively. The calculation of $(C_v + C_d)$ using the experimentally determined equation for CTE showed that the effect of O/M on $(C_v + C_d)$ was negligible, with a deviation of 2 $J\cdot K^{-1}\cdot mol^{-1}$ for O/M = 2.00-192. The calculated data for $PuO_{2.00}$ were found 15 $J\cdot K^{-1}\cdot mol^{-1}$ lower than determined experimentally, however, based on the results of Oetting [1982OET]. This difference was attributed to the effect of a Schottky term with reference to the work of

Nakamura *et al.* for the estimation of its contribution using ab initio calculations [2010NAK/MAC]. In addition, [2014KAT/UCH] considered the effect of Oxygen Frenkel pairs formation which lead to a rapid increase of the heat capacity values above 1500 K as suggested by Konings and Benes [2013KON/BEN] by analogy with $UO_2$ and $ThO_2$. The authors showed that the estimation of ($C_v + C_d + C_{sch} + C_{exc}$) was consistent with the data of [1982OET]. However, they pointed to the need for further experimental and theoretical investigations to substantiate the existence of an excess component.

**[2014KON/BEN]**

[2014KON/BEN] performed a critical review of the thermodynamic data reported in the literature for $PuO_2$(cr) and $Pu_2O_3$(cr). Since the work of [2001LEM/FUG], [2003GUI/FAN], new experimental data considered in this article are the determination of the melting temperature of $PuO_2$ by Kato *et al.* [2008KAT/MOR] and Bruycker *et al.* [2010BRU/BOB], [2011BRU/BOB]. Because plutonium dioxide loses oxygen at high temperatures according to Reaction (A.595):

$$\mathrm{PuO_2(cr)} \rightleftharpoons \mathrm{PuO_{2-x}(cr)} + \frac{x}{2}\mathrm{O_2(g)} \qquad \text{(A.595)}$$

the determination of the melting temperature of stoichiometric $PuO_2$ is intricate and requires a high oxygen pressure as reported by [1970RIL]. The interaction with the containment material also affects the measurement: [2008KAT/MOR] who used a rhenium container material instead of tungsten found a melting temperature about 200 K higher than in previous studies. The value selected in the article by [2014KON/BEN] and retained in this review is the one obtained by Bruycker *et al.* [2010BRU/BOB], [2011BRU/BOB] who employed a quasi containerless laser melting technique and found $T_{fus}$ = (3017 ± 28) K.

The recommended entropy and heat capacity values at 298.15 K for $PuO_2$ are the same as in [2001LEM/FUG], and [2003GUI/FAN] but with slightly increased uncertainty. Those results are retained in this review:

$$S^{o}_{m}(PuO_2, cr, 298.15\ K) = (66.13 \pm 0.30)\ J\cdot K^{-1}\cdot mol^{-1},$$

$$C^{o}_{p,m}(PuO_2, cr, 298.15\ K) = (66.25 \pm 0.30)\ J\cdot K^{-1}\cdot mol^{-1}.$$

The enthalpy increment data reported in the literature for plutonium dioxide were refitted by [2014KON/BEN] based on the results of Kruger and Savage [1968KRU/SAV] from 298 to 1404 K, Ogard [1970OGA] from 1500 to 2715 K, and Oetting [1982OET] from 354 to 1611 K. Ogard's measurements suggest a rapid increase in $C^{o}_{p,m}$ above 2370 K attributed to partial melting of $PuO_2$ through interaction with the tungsten container [1982OET], [1982FIN], [2001LEM/FUG]. A similar increase was observed in the heat capacities of $ThO_2$, $UO_2$, and $ZrO_2$, and was attributed to the formation of oxygen Frenkel pairs at high temperatures. The heat capacity

function selected by [2001LEM/FUG] was calculated by refitting the values of Fink [1982FIN] to an extended Kelley polynomial. In the latter analysis the measurements of Ogard above 2370 K were given zero weight. [2014KON/BEN] refitted all the experimental data including those of Ogard which were given a lower weight in the range 2470-2640 K. The fitted enthalpy increment (see Figure 11-3 in the main text) and derived heat capacity function (see Figure 11-5 in the main text) are in reasonable agreement with the experimental data and include the upward trend associated with the formation of Frenkel pairs on the oxygen lattice. This heat capacity equation is selected in the present review:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{PuO_2},\mathrm{cr},T) = 35.2952 + 0.15225T - 129.255\times10^{-6}T^{2} + 36.289\times10^{-9}T^{3} - 3.47593\times10^{5}T^{-2} \quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Note that there is a typing error in the equation reported by [2014KON/BEN], which was corrected here.

There are no data on the heat capacity or enthalpy of liquid $PuO_2$ except for a single enthalpy measurement by [1970OGA]. In the review of [2014KON/BEN], the enthalpy of fusion was estimated considering that the entropy of fusion was the same as for $UO_2$ (24 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$). The reported result is in error, however, and we have recalculated:

$$\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}(\mathrm{PuO_2},\mathrm{cr},T_{\mathrm{fus}}) = (72.5 \pm 6)\ \mathrm{kJ\cdot mol^{-1}}.$$

While [2001LEM/FUG] recommended $C^{\circ}_{p,\mathrm{m}}(\mathrm{PuO_2}, \mathrm{l}, T) = 131\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, [2014KON/BEN] selected $C^{\circ}_{p,\mathrm{m}}(\mathrm{PuO_2}, \mathrm{l}, T) = 70\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ based on the data for $UO_2$(l), which shows a decrease from about 120 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ near the melting point to about 84 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 4500 K. The estimation of [2014KON/BEN] is accepted in this review.

Regarding $Pu_2O_3$(cr), [2014KON/BEN] assume that the hexagonal type-A rare earth sesquioxide in space group $P\bar{3}m$l transforms to a H-type structure at $T_{tr}$ = (2300 ± 50) K by analogy with the behaviour of the light lanthanide sesquioxides although there is no experimental evidence for this transition. The latter was not considered in the review by [2001LEM/FUG], [2003GUI/FAN]. There are no measurements of the heat capacity or enthalpy increment of $Pu_2O_3$(cr) at high temperatures. The heat capacity function recommended by [2014KON/BEN] was estimated by comparison with the actinide and lanthanide oxides, yielding values about 10 $\mathrm{kJ\cdot mol^{-1}}$ lower than calculated by [1967IAE], [1982GLU/GUR], [2001LEM/FUG] as shown in Figure 11-5 in the main text. The present review selects the data of [2014KON/BEN], *i.e.*,

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Pu_2O_3},\mathrm{cr},T) = 130.6670 + 18.4357\times10^{-3}T - 1.70530\times10^{6}T^{-2} \quad \mathrm{J\cdot K\cdot mol^{-1}}.$$

The melting temperature of H-type $Pu_2O_3$(cr) was estimated as $T_{\mathrm{fus}}$ = (2352 ± 10) K based on the data of [1970RIL] after correction to ITS-90

[2014KON/BEN], which is also selected in this review. This is slightly lower than recommended by [2001LEM/FUG], [2003GUI/FAN], *i.e.*, $T_{fus}$ = (2358 ± 25) K based on the data of Chikalla *et al.* [1964CHI/MCN], and rather low compared to the lanthanide sesquioxides and $Am_2O_3$ as mentioned by [2014KON/BEN].

While the enthalpy of fusion of A-$Pu_2O_3$(cr) was estimated as $\Delta_{fus}H_m^o(A-Pu_2O_3, cr, T_{fus})$ = (113 ± 20) kJ·mol$^{-1}$ by [2001LEM/FUG], and [2003GUI/FAN], Konings *et al.* [2014KON/BEN] considered the effect of the $A \rightarrow H$ transition at (2300 ± 50) K and suggested:

$$\Delta_{tr}H_m^o(\text{A-Pu}_2\text{O}_3 \rightarrow \text{H-Pu}_2\text{O}_3) = (32 \pm 10)\ \text{kJ·mol}^{-1},$$

$$\Delta_{fus}H_m^o(\text{H-Pu}_2\text{O}_3, \text{cr}, T_{fus}) = (71 \pm 10)\ \text{kJ·mol}^{-1}.$$

The latter values are selected in this review.

The heat capacities of H-$Pu_2O_3$(cr) and $Pu_2O_3$(l) were estimated by [2014KON/BEN] as:

$$C_{p,m}^o(\text{H-Pu}_2\text{O}_3, \text{cr}, T) = 165\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$C_{p,m}^o(\text{Pu}_2\text{O}_3, \text{l}, T) = 179\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

Those values are accepted in this review for scoping calculations.

As there are no direct measurements reported on the enthalpy of formation of $Pu_2O_3$(cr), the latter was estimated in the literature based on the assessment by Markin and Rand [1966MAR/RAN] of the oxygen potential measurements of Markin *et al.* [1964MAR/BON] in the region between $PuO_{1.5}$ and $PuO_2$ as discussed in details in the reviews by [1990COR/KON], [1982GLU/GUR], [2001LEM/FUG], [2014KON/BEN]. The analysis refers to reaction:

$$2\text{Pu}_2\text{O}_3(\text{cr}) + \text{O}_2(\text{g}) \rightleftharpoons 4\text{PuO}_2(\text{cr}) \qquad \text{(A.596)}$$

[2014KON/BEN] suggested $\Delta_f H_m^o$ ($Pu_2O_3$, cr, 298.15 K) = – (1647 ± 10) kJ·mol$^{-1}$, which is somewhat more negative than reported by [1982GLU/GUR], *i.e.*, $\Delta_f H_m^o$ ($Pu_2O_3$, cr, 298.15 K) = – (1670 ± 20) kJ·mol$^{-1}$, and [2001LEM/FUG], *i.e.*, $\Delta_f H_m^o$ ($Pu_2O_3$, cr, 298.15 K) = – (1656 ± 10) kJ·mol$^{-1}$. The enthalpy of formation as reported by [2014KON/BEN] was based on the thermodynamic assessment of [2008GUE/CHA], which gives a consistent description of the phase diagram and oxygen potential data, by combining the Gibbs energy of Reaction (A.596) derived from the thermodynamic model [2008GUE/CHA], together with the selected enthalpy and entropy values for $PuO_2$(cr), $Pu_2O_3$(cr) and $O_2$(g). Applying the same approach to the optimised thermodynamic data reported by [2011GUE/DUP], we find $\Delta_f H_m^o$ ($Pu_2O_3$, cr, 298.15 K) = – 1635 kJ·mol$^{-1}$, which deviates rather significantly from the previously reported data. The present review prefers to retain the assessment by [2001LEM/FUG] which is based solely on experimental measurements, rather than the assessment by [2014KON/BEN] which is based on a combined approach {CALPHAD

optimisation + experimental data}. The enthalpy of formation of $Pu_2O_3$(cr) was subsequently re-assessed in this review to account for the newly determined heat capacity functions of $PuO_2$(cr) and $Pu_2O_3$(cr) at high temperatures. The analysis described in detail by [2001LEM/FUG] was repeated, yielding $\Delta_f H_m^o$ ($Pu_2O_3$, cr, 298.15 K) = – (1656 ± 10) kJ·mol$^{-1}$ in very good agreement with [2001LEM/FUG]. The results are listed in Table 11-11 of the main text. As detailed in [2001LEM/FUG], the values of the Gibbs energies are preferred to the enthalpies given by Markin and Rand [1966MAR/RAN].

It can be noted in Table 11-11 that the agreement with the experiment is in fact improved compared to the work of [2001LEM/FUG], which gives further confidence for the consistency of the recommended functions for $PuO_2$(cr) and $Pu_2O_3$(cr). We therefore retain:

$$\Delta_f H_m^o (Pu_2O_3, \text{cr}, 298.15\ \text{K}) = -(1656 \pm 10)\ \text{kJ·mol}^{-1},$$

which is also in very good agreement with the value optimised by [2008GUE/CHA], and in good agreement with that optimised by [2011GUE/DUP].

Based on the same data, [2001LEM/FUG] evaluated the thermodynamic functions of $PuO_{1.61}$(cr, bcc) for the following reactions:

$$100/11 Pu_2O_3(\text{cr}) + O_2(\text{g}) \rightleftharpoons 200/11 PuO_{1.61}(\text{cr, bcc}) \qquad \text{(A.597)}$$

$$0.39 Pu_2O_3(\text{cr}) + 0.22 PuO_2(\text{cr}) \rightleftharpoons PuO_{1.61}(\text{cr, bcc}) \qquad \text{(A.598)}$$

This analysis was re-assessed here to account for the newly recommended thermodynamic functions for $Pu_2O_3$(cr) and $PuO_2$(cr). The heat capacity of $PuO_{1.61}$(cr, bcc) was estimated by [2001LEM/FUG] using the weighted sum of $Pu_2O_3$(cr) and $PuO_2$(cr). Considering the newly determined functions, the recommended equation for $PuO_{1.61}$(cr, bcc) is:

$$C_{p,m}^o(PuO_{1.61}, \text{bcc}, T) = 58.7251 + 40.6849\times10^{-3}T - 2.84361\times10^{-5}T^2 + 7.98358\times10^{-9}T^3 - 7.41537\times10^{5}T^{-2}\ \text{J·K}^{-1}\text{·mol}^{-1}$$

A very good agreement between experimental and re-assessed values is obtained for $\Delta_r G_m$ (1600 K), $\Delta_r G_m$ (1100 K) and $\Delta_r G_m$ (573 K). The enthalpy of formation and entropy values selected in [2001LEM/FUG] are therefore retained:

$$\Delta_f H_m^o (PuO_{1.61}, \text{bcc}, 298.15\ \text{K}) = -(875.5 \pm 10.0)\ \text{kJ·mol}^{-1}$$

$$S_m^o (PuO_{1.61}, \text{bcc}, 298.15\ \text{K}) = (83.0 \pm 5.0)\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

**[2015BYK/RAI]**

[2015BYK/RAI] reported the synthesis and structural characterisation by X-ray diffraction of the phases forming in the Na-Pu-O system at 400 °C and 700 °C. The phases forming are numerous with oxidation states varying between (IV) and (VII).

[2015BYK/RAI] obtained those phases by mixing plutonium oxide and sodium oxide in varying ratios under argon or oxygen flow. The phases forming at 700 °C are $Na_3PuO_4$ orthorhombic in space group *Fmmm*, $Na_5PuO_5$ monoclinic in space group *C2/m*, β-$Na_4PuO_5$ tetragonal in space group *I4/m,* $Na_5PuO_6$ monoclinic in space group *C2/m*, and $Na_2PuO_3$ which shows partial ordering with the coexistence of a rhombohedral phase in space group $R\bar{3}m$ and a monoclinic phase in space group *C2/c*. The phases forming at 400 °C are cubic of the NaCl type (in space group $Fm\bar{3}m$), with cell parameters $a$ = 4.73 Å for the syntheses under oxygen and $a$ = 4.77 Å for the syntheses under argon. It was not possible to conclude on the exact stoichiometry of the latter phases, however.

**[2015SMI]**

In her PhD thesis, [2015SMI] reported the structural and thermodynamic investigations of the Na-Np-O and Na-Pu-O systems. Most of the data were published in separate articles [2015SMI/RAI], [2015SMI/HEN], [2015SMI/HEN2]. In addition, [2015SMI] measured the low temperature heat capacity of $Na_5NpO_6$(cr) and $Na_5PuO_6$(cr). The review of those measurements is reported in the Appendix A for uranium.

**[2015SMI/RAI]**

[2015SMI/RAI] reported for the first time the synthesis and structural characterization of α-$Na_3NpO_4$(cr) and α-$Na_3PuO_4$(cr) using X-ray diffraction and $^{237}$Np Mössbauer spectroscopy. The complete review of this article is reported in the Appendix A for neptunium.

**[2016CHO/YOU]**

Cho and co-workers studied the hydrolysis behaviour of Pu(III) under reducing conditions in 0.1 M $NaClO_4$. The authors prepared a Pu(III) stock solution by reducing Pu(IV) adsorbed on anion-exchange resin and eluted with 9 M HCl/0.1 M HI solution. The anion exchange separated 99.9 % $^{241}$Am from the plutonium, which was confirmed by quantitative analysis using liquid scintillation counting and gamma-spectroscopy. The Pu solution contained a mixture of $^{242}$Pu (86.5 %), $^{238}$Pu (12.3 %) and $^{239/240}$Pu (1.2 %). After further purification of the Pu(III) stock solution with repeated evaporation in concentrated $HClO_4$, Pu(III) was prepared electrochemically in 0.1 M $HClO_4$ on a platinum electrode at – 0.2 V *vs.* an Ag/AgCl reference electrode. The electrolysis was performed in an argon atmosphere glovebox at 25 °C. Coulometric titrations were conducted in 20 mL (H/Na)$ClO_4$ solutions containing Pu(III) concentrations ranging between $10^{-5}$ and $5 \times 10^{-4}$ M Pu(III) at pH 1.9-3.7. After applying a constant current to reduce hydrogen ions, the current was turned off and the

pH was measured using a conventional glass electrode calibrated against pH buffer solutions. The $H^+$ ion concentration was calculated as the sum of the measured pH and $\log_{10}\gamma_{H+} = 0.095$ in 0.1 M $NaClO_4$ derived with the ion-interaction coefficient $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol$^{-1}$. After ultrafiltration (10 kDa), the total Pu concentration was determined by liquid scintillation counting. At high Pu concentration $Pu(OH)_3(s)$ precipitated. The solid phase was separated and examined by X-ray diffraction under argon atmosphere to avoid oxidation. Solution speciation was studied by using absorption spectroscopy with a 100 cm liquid waveguide capillary (LWCC), while laser-induced breakdown detection (LIBD) was applied to detect the formation of colloidal particles.

The utilisation of a 100 cm LWCC enables to study the solution speciation at much lower Pu concentrations in solution. The authors determined the molar extinction coefficients for the characteristic absorbance bands at 601 nm ((37.7 ± 1.0) L·mol$^{-1}$·cm$^{-1}$) for Pu(III), 470 nm ((48.9 ± 0.9) L·mol$^{-1}$·cm$^{-1}$) for Pu(IV) and used the data reported in [2010CHO/JUN] for the Pu(V) band at 569 nm ((17.0 ± 0.2) L·mol$^{-1}$·cm$^{-1}$). At pH 5.93, 6.17 and 6.34 and low Pu concentrations, only dissolved Pu(III) species were observed, while at pH 6.52 and 6.78 the formation of colloidal Pu species was indicated by an increase in the LIBD probability. The absorbance at 601 nm was used to calculate the concentration of $Pu^{3+}$ in solution. The potential presence of other oxidation states besides Pu(III) was found to be below the detection limit and thus was neglected for spectra analysis and thermodynamic calculations. There appears to be a small discrepancy between spectroscopic data and LSC data at pH values below 4.5 where only the $Pu^{3+}$ exist in solution. The reported species distribution in Figure 6 of the paper shows a minor (0-4 %) amount of $PuOH^{2+}$ present, although only $Pu^{3+}$ should be present under these conditions.

When increasing the pH from 5.93 to 6.78, the shape and position of the characteristic Pu(III) absorption bands do not change, although a slight decrease in the intensity is observed. The authors explained the decrease in absorbance intensity with the decrease in $[Pu^{3+}]$, based on the premise that the difference in $[Pu(III)]_{tot}$ are due to non-absorbing Pu(III) hydrolysis species. The fact that the normalisation of the measured Pu(III) absorbance bands in the region 500-700 nm (*ca.* 570 nm, 601 nm and 665 nm) do not show any changes of the intensity ratios, also suggesting the observed absorbance is related to the same absorbing solution species, namely $Pu^{3+}$.

The coulometric and spectroscopic data from 20 samples were used to determine solution speciation and equilibrium constants for the hydrolysis reaction:

$$Pu^{3+} + H_2O(l) \rightleftharpoons PuOH^{2+} + H^+ \qquad \text{(A.599)}$$

and the solubility product of the obtained solid phase:

$$Pu(OH)_3(am) + 3H^+ \rightleftharpoons Pu^{3+} + 3H_2O(l) \qquad \text{(A.600)}$$

The equilibrium Reaction (A.599) was verified by the slope of 1.02 for the correlation between $\log_{10}(\Sigma[\mathrm{Pu(OH)}_n^{3-n}]/[\mathrm{Pu}^{3+}])$ *vs.* $-\log_{10}[\mathrm{H}^+]$. This is consistent with the formation of $\mathrm{PuOH}^{2+}$ as the only Pu(III) hydrolysis product besides $\mathrm{Pu}^{3+}$. Of concern is the large scattering in Figure 5 of the paper with up to a full unit of the logarithmic Pu(III) species concentration ratio at a given value of $-\log_{10}[\mathrm{H}^+]$.

Cho and coworkers used data from 20 samples to determine the equilibrium constant for Reaction (A.599), $\log_{10}{}^{*}K_{1,1} = -(6.62 \pm 0.25)$, which was extrapolated to $\log_{10}{}^{*}K^{\circ}_{1,1} = -(6.18 \pm 0.25)$ by using the SIT ion-interaction parameters $\varepsilon(\mathrm{Pu}^{3+}, \mathrm{ClO}_4^-) = (0.49 \pm 0.05)$ kg·mol$^{-1}$ and $\varepsilon(\mathrm{PuOH}^{2+}, \mathrm{ClO}_4^-) = \varepsilon(\mathrm{AmOH}^{2+}, \mathrm{ClO}_4^-) = (0.39 \pm 0.04)$ kg·mol$^{-1}$ reported in [2001LEM/FUG] and [2003GUI/FAN].

Two data sets were used to determine the solubility product of the solid phase assumed to be $\mathrm{Pu(OH)_3(am)}$ in 0.1 M $\mathrm{NaClO_4}$. The concentration of $\mathrm{Pu}^{3+}$ at pH 6.29-6.90 was determined spectroscopically and was used to calculate the conditional solubility product according to Reaction (A.600), $\log_{10}{}^{*}K_{s,0} = (15.15 \pm 0.53)$. In a second set of experiments at pH 6.50-8.43, the authors calculated the $[\mathrm{Pu}^{3+}]$ from the total concentration of soluble Pu determined by LSC and the hydrolysis constant $\log_{10}{}^{*}K_{1,1} = -(6.62 \pm 0.25)$ determined in this work. The resulting conditional constant, $\log_{10}{}^{*}K_{s,0} = (15.28 \pm 0.51)$, is very similar to the value obtained from the spectroscopic approach. The average value over all solubility data is reported as $\log_{10}{}^{*}K_{s,0} = (15.23 \pm 0.50)$ in 0.1 M $\mathrm{NaClO_4}$, which is extrapolated to zero ionic strength $\log_{10}{}^{*}K^{\circ}_{s,0} = (14.58 \pm 0.50)$. It is to note that the second data set was obtained at pH values that far exceeded the conditions used to determine the first hydrolysis constant. It can be expected that at pH above 7-9 additional hydrolysis products besides $\mathrm{PuOH}^{2+}$ form and thus contribute to the solution speciation. Under these circumstances, applying only the first hydrolysis constant of Pu(III) is incorrect. Using only solubility data at pH $\leq 7$ from both sets, the conditional solubility product is $\log_{10}{}^{*}K_{s,0} = (15.06 \pm 0.46)$, which is $\log_{10}{}^{*}K^{\circ}_{s,0} = (14.41 \pm 0.46)$ extrapolated to zero ionic strength.

**[2016SMI/MAR]**

[2016SMI/MAR] reported for the first time the structural refinement of $\mathrm{Na_2PuO_3}$, monoclinic in space group *C2/c*, and revealed the existence of isostructural $\mathrm{Na_2NpO_3}$. The authors reported XANES measurements at the U-$L_{III}$, Np-$L_{III}$, Pu-$L_{III}$ edges of the following phases: α-$\mathrm{Na_2UO_4}$, α-$\mathrm{Na_2NpO_4}$, $\mathrm{Na_3NpO_4}$, $\mathrm{Na_4NpO_5}$, $\mathrm{Na_5NpO_6}$, $\mathrm{Na_2PuO_3}$, $\mathrm{Na_4PuO_5}$, and $\mathrm{Na_5PuO_6}$. No thermodynamic data are reported in this work.

# Discussion of selected references for Americium

**[1992GIB/HAI]**

In this differential thermal analysis study of Np, Am alloys and their pure elements the authors have indicated much lower transition temperatures for the alloys of the latter elements. The metal was prepared by reduction of the dioxide with 200-400 ppm cation impurity, while anionic impurities were not considered. Two samples were used to measure the transition from *fcc* to *bcc* and only one sample was subjected to melting point determination studies. A heating rate of 10 $K \cdot min^{-1}$ was used. Transition temperatures for *fcc* to *bcc* and *bcc* to liquid were found to be (1337 ± 5) K and (1431 ± 8) K respectively and their corresponding enthalpies of transition and fusion are 2300 $J \cdot mol^{-1}$ and 4900 $J \cdot mol^{-1}$. A small peak was found at (1031 ± 5) K presumed to be the *dhcp* to *fcc* transition with a very small transition enthalpy of 350 $J \cdot mol^{-1}$. The authors reported that high vapor pressures and melting temperatures lead to vaporization or creep during the investigations, so that sample instabilities limited their experimental capabilities.

**[2001KON]**

The standard entropies of the trivalent oxides, fluorides and chlorides of the actinide elements from U to Cf have been estimated by a semi-empirical method in which the total entropy is described as the sum of a lattice entropy and an excess entropy. The latter represents the distribution of the electrons over their various energy levels, including the contribution due to the splitting of the ground state term by the crystalline field. This is, in fact, the method already adopted within the other reviews of this series

[1992GRE/FUG], [1995SIL/BID], [2001LEM/FUG], as well as in earlier reviews (for example [1976FUG/OET]) to estimate the entropies of some aqueous actinide ions.

For the solids, this approach was verified by calculations on the iso-electronic lanthanide(III) compounds, for which most entropies have been determined experimentally. For the trihydroxides, trifluorides and trichlorides, the deviations from the model are about 1-2 %; the deviations are a little larger for the sesquioxides owing to the presence of two sites of different symmetry in the crystal.

For the actinides, the lattice contribution has been calculated from the known entropies of $Pu_2O_3$(cr), $UF_3$(cr), $PuF_3$(cr) and $UCl_3$(cr), and is assumed to decrease slightly as the atomic number of the actinide element increases, as in the lanthanide series. It should be noted, however, that the experimental standard entropies of $UF_3$(cr) and $UCl_3$(cr) have been increased by $R\cdot\ln 2$, to allow for the fact that the experimental measurements (rather incompletely documented by Cordfunke *et al.* [1989COR/KON]) probably did not extend to low enough temperatures to include the antiferromagnetic transition between 0 and 10 K. The excess contributions for the trichlorides were calculated from the well-known energy levels in these compounds, but those for the trifluorides and sesquioxides are less well established.

The important conclusion from this study is that the entropy values previously estimated for ionic Am solids, especially those containing Am(III), are most likely too large. This is because the ground level of Am(III) is $^7F_0$ and is non-degenerate, while the first excited $^7F_1$ level is at *ca.* 2750 $cm^{-1}$ above the ground state, and therefore does not contribute significantly to the standard entropy at 298.15 K. The excess entropy term is thus zero for Am(III) compounds, resulting in standard entropies notably smaller than those for the corresponding U and Pu compounds.

**[2001KON2]**

This paper deals with a review and critical assessment of the properties of curium and curium oxides, which is supplemented by estimates in trends of the lanthanide and actinide series as performed in [2001KON] and in subsequent papers by Konings *et al.* [2003KON], [2005KON/MIT]. The paper includes figures for trends in entropy, melting temperature, thermal conductivity for elemental actinide and lanthanides, which covers the experimental (estimated for thermal conductivity) information for americium. Similarly the lattice heat capacities for lanthanide sesquioxides and $PuO_2$(cr) is reviewed.

**[2003KON]**

In this paper the heat capacities of the three allotropes of Americium are estimated by including harmonic ($C_{har}$), dilation ($C_{dil}$), electronic ($C_{ele}$) and magnetic ($C_{mag}$)

contributions. Previous estimates reviewed in [2003GUI/FAN] do not clearly indicate which heat capacity terms are evaluated in their estimates, as high temperature studies have yet to be performed. The main factors affecting the heat capacity other than the harmonic contribution, is the magnetic term, which becomes important above 300 K, where the population of the excited states becomes important; the electronic and dilation terms are negligible. The heat capacities for the α-Am (*dhcp*) and β-Am (*fcc*) phases are quite similar, as only the dilation term changes in the β phase, due to a smaller molar volume, compared to the low temperature phase. The high temperature (γ-Am) allotrope is assumed to have a *bcc* structure as it is analogous with the lanthanide series, but a determination of the structure is not available. The heat capacity is therefore deduced by interpolation from the lanthanide (La-Gd) and actinide (U, Pu) series, which include mainly lattice contributions (Gd) and some electronic contributions (La, U, Pu). The argument is that the heat capacity of Gd (*bcc*) is close to the Dulong-Petit limit and therefore does not include a significant excess term. Given the $f^0$ electronic configuration of La, there can be no $C_{mag}$ contribution and therefore the excess is due solely to the $C_{ele}$. The heat capacity of γ-Am is then taken as the summation of $C_{lat} + C_{ele} + C_{mag}$, where the latter is calculated in the same way as for α-Am. A similar approach was taken for the heat capacity of liquid Am, using the same data for the magnetic term [1992CAR]. Additionally, the selected transition enthalpies are revised in this paper compared to [1995SIL/BID] although no new experiments have been performed since then (see Table A-185). While the enthalpies measured for the α → β transition are in good agreement, the latter two transition enthalpies are scattered. This paper addresses the discrepancy by evaluating the trends in transition entropies for lanthanide and actinide metals. The authors concluded that the previously selected values from [1967WAD/WOL] provide a better fit to the trend of tetravalent actinides which are considerably higher than the trivalent lanthanide series. The values of [1992GIB/HAI] are selected by this paper since they agree well with trends of trivalent actinide and lanthanide metals.

Table A-185: Transition enthalpies of Am(cr).

| | $\Delta_{trs}H^{o}_{m}$ /kJ·mol$^{-1}$ | | |
|---|---|---|---|
| Reference | α → β | β → γ | $\Delta_{fus}H^{o}_{m}$ /kJ·mol$^{-1}$ |
| [1967WAD/WOL] | | 5.9 | 14.4 |
| [1977SEL/KOS] | (0.34 ± 0.08) | (3.8 ± 0.4) | (8.0 ± 1.3) |
| [1992GIB/HAI] | (0.35 ± 0.25) | (2.3 ± 0.9) | (4.9 ± 1.5) |
| Selected | **(0.34 ± 0.10)** | **(3.8 ± 0.4)** | **(8.0 ± 2.0)** |

**[2003SHI]**

Shilov studied the reduction of Am(IV) in aqueous solutions containing $KHCO_3/K_2CO_3$ in the pH range, $8.5 < pH < 10.5$ using spectrophotometry and suggests a mechanism for this reaction that involves formation of an intermediary, [Am(IV)*][Am(IV)], where

Am(IV)* is a thermally excited species. The intermediate then reacts to form 2Am(III) and $H_2O_2$. There is no experimental evidence for the formation of thermally excited states of this type and the present review does not find the proposed mechanism plausible — reduction as a result of α-radiolysis seems more likely. There are no thermodynamic data in the paper.

**[2003THI/KON]**

A thermodynamic model is assessed using the experimental data identical to those used by [2003GUI/FAN]. The hypo-stoichiometric dioxide is represented as a solid solution of $AmO_2$ and a lower oxide $Am_aO_b$, where a and b are fit through a relation of the Gibbs energy of formation deduced from oxygen partial pressure data. The partial pressure is given as $\ln p^*_{(O_2)} = A + B/T - s\ln(x)$ where $s = 2/(2a-b)$ and $x$ also contains information on the partial molar Gibbs energies. Fitting the available pressure data it was found that $3.53 < x < 4.34$, with the stoichiometric coefficient $s$ taken as 4, and considering various ratios of $b/a$ or the ratio oxygen to metal, O/M. The two main compositions are $Am_{5/4}O_2$ and $Am_2O_3$ or $AmO_{3/2}$. Given these $a/b$ values, the initial pressure expression is fit as a function of temperature and deviation in composition of $AmO_{2-x}$. In the fit a set of thermodynamic parameters including the enthalpy and entropies of the equilibrium reaction as well as the solute and solvent interaction are derived for the minor oxides considered. An expression for the oxygen partial pressure as a function of temperature and composition is derived and compared to experimental data. Both models agree well with experiment, although $Am_2O_3$ provides a slightly better statistical representation. However, $Am_{5/4}O_2$ has a more physical representation for the $AmO_{2-x}$ composition of the phase diagrams. The following standard thermodynamic values are obtained:

$$\Delta_f H^o_m(AmO_2, 298.15\ K) = -(932.3 \pm 3.0)\ kJ\cdot mol^{-1}$$

$$S^o_m(AmO_2, 298.15\ K) = (77.8 \pm 5)\ J\cdot K^{-1}\cdot mol^{-1}$$

$$C^o_{p,m}(AmO_2, T) = 66.8904 + 19.1123\times10^{-3}T - 4.6356\times10^{-6}T^2 - 0.548830\times10^{6}T^{-2}\ J\cdot K^{-1}\cdot mol^{-1}$$

$$C^o_{p,m}(AmO_2, 298.15\ K) = 66.00\ J\cdot K^{-1}\cdot mol^{-1}.$$

**[2004KON]**

The heat capacities of actinide oxide, fluorides and chlorides are evaluated in order to extend the studies of [2001KON] and [2001KON2]. The work extends beyond the previously evaluated trihalides [2001KON2] and includes the An(IV) halide complexes. A reassessment of the actinide dioxide excess entropy and heat capacity terms is also performed. In this process the experimental values included a residual excess term, in addition to the excess values due to the crystal field energy levels. The difference

between $S_{exp} - S_{exs(f)}$ does not equal the previously chosen value of $S_{lat}$ as previously suggested from the equation $S_{tot} = S_{lat} + S_{exs}$. Therefore an additional residual entropy term is included. The values of $PaO_2$ and $AmO_2$ are extrapolated from the experimental values ($S_{exp} - S_{exs(f)}$) of $UO_2$, $NpO_2$ and $PuO_2$, which exhibit a linear trend. The extrapolated value for $AmO_2$ was found to be less than the original $S_{lat}$ based on $ThO_2$, which does not include residual entropy term. The authors consider the previous estimate of the lattice entropy to be overestimated for $AmO_2$ and therefore the total entropy is lowered from $S^o_m(AmO_2, 298.15\ K) = (77.7 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}$ in [2003GUI/FAN] to the accepted value by the authors of $S^o_m(AmO_2, 298.15\ K) = (75.5 \pm 3)\ J \cdot K^{-1} \cdot mol^{-1}$.

**[2004LUO/MIL]**

Luo and Millero have used ion-exchange to determine the equilibrium constants for $LnF^{2+}$ and $LnF_2^+$, where Ln are various rare earth elements. For the present review only Eu(III) and Nd(III) system are of interest because they can be used as analogues for Am(III) and Cm(III). Luo and Millero report equilibrium constants that refer to an ionic strength of 0.025 M that we will discuss, but they have also used the Pitzer approach to calculate the equilibrium constants at zero ionic strength. The equilibrium constants at $I = 0.025$ M have been measured in the temperature range 278-318 K and used to determine the enthalpies of reaction. Extrapolation of $\log_{10}\beta$ ((A.601), $I = 0.025$ M) and $\log_{10}\beta$ ((A.602), $I = 0.025$ M) to $I = 0$ has been conducted in this review considering only the Debye-Hückel term in the SIT approach. The reported data for the Eu(III) and Nd(III) systems are given in Table A-186 for Reactions (A.601) and (A.602).

$$Ln^{3+} + F^- \rightleftharpoons LnF^{2+} \qquad \text{(A.601)}$$

$$Ln^{3+} + 2F^- \rightleftharpoons LnF_2^+ \qquad \text{(A.602)}$$

Table A-186: Equilibrium constants and reaction enthalpies reported in [2004LUO/MIL] at $I = 0.025$ M for the formation of $LnF^{2+}$ and $LnF_2^+$ complexes with Ln = Nd(III) and Eu(III). Extrapolation of $\log_{10}\beta_n$ to $I = 0$ conducted in this review considering only the Debye-Hückel term of the SIT approach.

| Reaction | Ln | $\log_{10}\beta_n$ | $\log_{10}\beta^o_n$ | $\Delta_r H_n$ /kJ·mol$^{-1}$ |
|---|---|---|---|---|
| (A.601) | Nd | (3.29 ± 0.01) | (3.68 ± 0.01) | (9.38 ± 0.44) |
| | Eu | (3.72 ± 0.01) | (4.11 ± 0.01) | (8.19 ± 0.42) |
| (A.602) | Nd | (5.66 ± 0.05) | (6.31 ± 0.05) | (20.25 ± 0.55) |
| | Eu | (6.11 ± 0.01) | (6.76 ± 0.01) | (18.6 ± 1.2) |

The equilibrium constants are in good agreement with the ones for the Cm(III) and Am(III) systems. The enthalpies of reaction are consistent with the ones from [2010SKE/PAN].

This review finds the reported uncertainty in both the equilibrium constants and the enthalpies of reaction unrealistic. In the analysis of the ion-exchange data, Luo and Millero have not taken the sorption of $EuF^{2+}$ on the cation exchanger into account, which will result is a systematic error and we therefore suggest that an uncertainty of 0.10 log units is more realistic. The enthalpy of reaction has been determined over a rather short temperature range, this fact together with the unrealistically small errors in the equilibrium constants results in underestimation of the uncertainty in $\Delta_r H_n$. This review considers an uncertainty a factor of 5 larger than those reported as more realistic.

This review notes that the chemistry, including equilibrium constants and enthalpies of reaction, is very similar in the Eu(III), Nd(III), Am(III) and Cm(III) systems.

**[2004VER/AME]**

This is a review of studies that are discussed in more detail in following publications. The authors make a case for $Am(CO_3)_3^{3-}$ as the limiting complex, but the present review is not convinced about the arguments for reasons discussed in [2005VER/VIT]. The authors also present data for sulfate complexes of Eu(III) and La(III) obtained by using ESI-MS (electrospray-mass spectroscopy); they report the formation of $EuSO_4^+$ and $Eu(SO_4)_2^-$ from experiments where the highest sulfate concentration is about 0.5 M but no equilibrium constants are provided. Data using ESI-MS were obtained using La(III) and suggest that the method is useful for determination of the stoichiometry of complexes, a more detailed study is reported in [2005VER/AME].

**[2004NIK/GOG]**

Nikolov *et al.* have studied the Reactions (A.603) and (A.604) using spectrophotometry in 1-3 M NaOH.

$$2Pu(VI) \rightleftharpoons Pu(V) + Pu(III) \qquad (A.603)$$

$$Am(III) + Am(V) \rightleftharpoons 2Am(IV) \qquad (A.604)$$

They report rates of reduction of Am(VI) (about 20 % /h) in 2 M NaOH and conclude that water is the reducing agent with radiolysis making only a minor contribution. Nikolov *et al.* have also studied the oxidation of Am(III) by $K_3Fe(CN)_6$ that results in the formation of Am(IV) or Am(V) depending upon the concentration of NaOH. Measurement of the formal redox potential in 1 M NaOH, $E_{form} = 0.7$ V *vs.* NHE, as compared to the standard potential $AmO_2^{2+}$ / $AmO_2^+$ selected in [1995SIL/BID] is a result of formation of much stronger hydroxide complexes for Am(VI) than Am(V). As the detailed speciation is not known the formal potential can only be used to make this qualitative statement of the chemistry.

**[2004NIK/GOG3]**

Nikonov *et al.* have studied oscillations in americium systems where solutions of Am(III) hydroxide are oxidized by ozone. The oscillations are followed using spectrophotometry and seems to follow a radical mechanism that is discussed in some detail. There is no thermodynamic information in this study.

**[2005KON/MIT]**

By studying the thermodynamics of monoclinic $Gd_2O_3$ sesquioxide, the systematic interpretation of the lanthanide sesquioxide series was revisited and refined. Most notably the standard entropy at room temperature based on the lattice energy was not found to vary linearly across the lanthanide series and the entropies of the monoclinic and triclinic sesquioxides were found to be systematically higher than the cubic structures. Therefore, the lattice entropy was split into two linear components and the data were revisited for consistency. Americium and plutonium sesquioxide both have a triclinic $Ln_2O_3$ structure, and their lattice entropies were adjusted to be parallel with the lanthanide series, resulting in a slightly higher estimate than before.

**[2005NIK/GOG2]**

Nikonov *et al.* discuss redox properties of Am(IV), in particular for preparative purpose in alkaline media. An example is the preparation of $Am(OH)_4(s)$ from $Am(OH)_3(s)$, using ozone as the oxidant. The disproportionation Reaction (A.605) is discussed, but there are no thermodynamic data reported.

$$2\mathrm{Am(IV)} \rightleftharpoons \mathrm{Am(III)} + \mathrm{Am(V)} \qquad \text{(A.605)}$$

**[2005PAN/KIM]**

Panak *et al.* have used laser fluorescence spectroscopy, TRLFS, to study complex formation between Cm(III) and silicate at room temperature in 0.03 M NaCl. The key problem in this study is the identification of the silicate speciation at different values of pH, where the concentration of polysilicates increases with increasing pH and total concentration of Si. Panak *et al.* have explored the pH range 1.5-9.0 using three different total concentrations of Si, $2.7 \times 10^{-4}$ - $9.6 \times 10^{-4}$ M, a concentration range below the solubility of silica and where monomeric silicate species are predominant. The total concentration of Cm(III) in these experiments was about $10^{-7}$ M. In a separate series of experiments, the authors investigated the formation of solid Cm(III) silicate and identified a separate emission peak for the solid.

The complex formation takes place at pH > 4 and data from 6.2 < pH < 8.3 were used to extract information for the constitution and equilibrium constant(s) of the complexes formed using peak deconvolution of the fluorescence spectra. The reported equilibrium constant for Reaction (A.606) in 0.03 M NaCl is $\log_{10}\beta_1$ = (7.32 ± 0.08), or for Reaction (A.607), $\log_{10}{}^{*}\beta_1$ = – (2.34 ± 0.10).

$$Cm^{3+} + SiO(OH)_3^- \rightleftharpoons CmSiO(OH)_3^{2+} \quad \text{(A.606)}$$

$$Cm^{3+} + Si(OH)_4(aq) \rightleftharpoons CmSiO(OH)_3^{2+} + H^+ \quad \text{(A.607)}$$

Extrapolation of these constants to zero ionic strength using SIT gives $\log_{10}\beta_1^{o}$ = (7.74 ± 0.08) and $\log_{10}{}^{*}\beta_1^{o}$ = – (2.07 ± 0.10).

Spectroscopic data reported in [2005PAN/KIM] show a large overlap between the fluorescence peak for $CmSiO(OH)_3^{2+}$, denoted Cm-silicate I, and a second peak denoted Cm-silicate-II. From the analysis of the concentration of the second peak, Panak *et al.* conclude that it is not due to the formation of $Cm(SiO(OH)_3)_2^+$, but they were not able to determine the nature of this species. The present review notes that the peak of Cm-silicate-II is non-Lorenzian, suggesting that it might be a result of overlap of two or more peaks, however, this does not seem to have an influence on the analysis of the intensity changes due to Cm-silicate-I, and the present review accepts the analysis and equilibrium constant proposed by Panak *et al.* The value of $\log_{10}\beta_1^{o}$ is in good agreement with a previous experimental data by Jensen *et al.*, [1996JEN/CHO], on the Eu(III)-silicate system studied by liquid-liquid extraction and fluorescence spectroscopy that report $\log_{10}\beta_1^{o}$ = (7.93 ± 0.20). However, the identification of $Eu(SiO(OH)_3)_2^+$ in the latter study is not consistent with the observations by Panak *et al.* A study by Wadsak *et al.* [2000WAD/HRN] (reviewed in [2003GUI/FAN]), made by liquid-liquid extraction of the Eu(III) silicate system in the pH range 3.0-3.8, resulted in the equilibrium constant $\log_{10}{}^{*}\beta_1$ = – (2.16 ± 0.04) in 0.2 M $NaClO_4$ and $\log_{10}{}^{*}\beta_1^{o}$ = – (1.60 ± 0.04) at zero ionic strength. This review notes that according to both the studies of Jensen *et al.* and Panak *et al.* there should be no significant formation of silicate complexes in this pH range.

**[2005SAN/MAR]**

Handbook of Atomic Spectra data of elements including americium, which was used to calculate the thermal functions of Am(g).

**[2005SED/KON]**

[2005SED/KON] reported *ab initio* calculations of the enthalpies of formation of the actinide mononitrides AnN(cr) (An = Ac, Th, Pa, U, Np, Pu, Am). The review is given in the Uranium, App. A section.

**[2005VER/AME]**

Vercouter *et al.* discuss the use of Ln(III) as models for Am(III) and Cm(III) using the La(III) and Eu(III) sulfate system. For this purpose they have both made an extensive review of previous studies and obtained new experimental data based on TRLFS in the Eu(III) and electro-spray mass spectroscopy (ESI-MS) in the La(III) study. The TRLFS study follows the standard protocol, while they have used an improved technique in the ESI-MS study, the details of which are well described. From an experimental point of view this is a very satisfactory study. The experimental data refer to a temperature of (296 ± 1) K, using test solutions with 0.04-2.0 m $Na_2SO_4$ and a hydrogen-ion concentration between 0.02 and 0.05 M. The TRLFS data have been analysed by fitting the experimental molar fluorescence intensities to a function that includes both the equilibrium constants and the molar fluorescence intensity of $Eu^{3+}$, $EuSO_4^+$ and $Eu(SO_4)_2^-$, where only the value for $Eu^{3+}$ can be determined in a separate experiment. In fittings of this type one is invariably faced between correlations between the equilibrium constants and the molar fluorescence intensity—this effect has not been explored by Vercouter *et al.* Thermodynamic data reported in the TRLFS study are given in Table A-187, where $\log_{10}K_2$ refers to the reaction

$$EuSO_4^+ + SO_4^{2-} \rightleftharpoons Eu(SO_4)_2^- \qquad \text{(A.608)}$$

Table A-187: Equilibrium constants, $\log_{10}\beta_1$ and $\log_{10}K_2$ for the Eu(III) sulfate complexes obtained using TRLFS.

| Ionic medium | Ionic strength | $\log_{10}\beta_1$ | $\log_{10}K_2$ |
|---|---|---|---|
| | $I \rightarrow 0$ | (3.78 ± 0.06) | (1.5 ± 0.2) |
| $H_2SO_4/HClO_4$ | 0.02-0.04 | 2.90-3.06 | 1.21-1.26 |
| $Na_2SO_4/NaClO_4$ | 0.50-0.59 | 1.71-1.76 | 0.82-0.88 |
| $Na_2SO_4/NaClO_4$ | 0.60-0.70 | 1.67-1.72 | 0.70-0.82 |
| $Na_2SO_4/NaClO_4$ | 0.91 | 1.62 | 0.62 |
| $Na_2SO_4/NaClO_4$ | 1.91-2.10 | 1.35-1.37 | 0.86-0.91 |
| $Na_2SO_4/NaClO_4$ | 1.51-1.62 | 1.41-1.43 | 0.75-0.78 |

The range of the reported constants is presumably a measure of their uncertainty, but according to the experience of this review the uncertainty is larger. Based on the conditional constants in Table A-187, Vercouter *et al.* have made an extrapolation to zero ionic strength, the procedure is described in detail. The difficulty in this extrapolation lies in the estimate of the ion interaction terms involving the ions with positive charge that includes interacions with $SO_4^{2-}$, $HSO_4^-$ and $ClO_4^-$. Here the interaction term $\varepsilon(Eu^{3+}, SO_4^{2-})$ is estimated using a Pitzer parameter, but it is not clear how this is done and how sensitive the extrapolation is to errors in this quantity. Based on these comments, the present review finds the reported uncertainty too low and suggests ± 0.2 and 0.4 $\log_{10}$ units in $\log_{10}\beta_1$ and $\log_{10}K_2$, respectively.

The ESI-MS study is important from a methodological point of view, and provides interesting chemical information on the constitution of the complexes formed in the ionization process, in particular on the number of coordinated water molecules. The data demonstrate the formation of $LaSO_4(OH_2)_n^+$ complexes and suggest an equilibrium constant of $\log_{10}\beta_1 = (3.5 \pm 0.3)$ and $\log_{10}\beta_1 = (4.4 \pm 0.3)$ in two separate experiments and speculate about the reason for the "too high" value in one of them. The importance of this study is its methodological aspects, but it is not accurate enough as a method for determination of equilibrium constants.

The present review considers $\log_{10}\beta_1^o = (3.8 \pm 0.2)$ and $\log_{10}K_2^o = (1.5 \pm 0.4)$ as reasonable values for the formation of $EuSO_4^+$ and $Eu(SO_4)_2^-$. The difference between the Eu(III) and Cm(III) data for formation of $M(SO_4)_2^-$ is surprisingly large and part of this might be related to the difficulty to use SIT because of the large number of interaction coefficients that are required in the study by Vercouter *et al.*

**[2005VER/VIT]**

Vercouter *et al.* have studied the relative stability of $M(CO_3)_2^-$ and $M(CO_3)_3^{3-}$, M = Am(III), Cm(III) over the temperature range 283 to 353 K, based on measurements of the equilibrium constant, $K_3$(A.609):

$$M(CO_3)_2^- + CO_3^{2-} \rightleftharpoons M(CO_3)_3^{3-} \qquad \text{(A.609)}$$

Cm(III) is often used as model for Am(III) and this study allows a possibility to test the accuracy of this model. The Cm(III) study was made using TRLFS in 3 M $NaClO_4$; this is a well-tested standard method where the measured fluorescence intensity provides information on the complexes formed when the carbonate concentration is varied. The total concentration of Cm(III) is orders of magnitude smaller than that of carbonate, which means that the free carbonate concentration can be calculated from the hydrogen ion concentration of the test solutions. The analysis of the experimental data can either be made by peak-deconvolution of the emission spectra, which gives a direct information on the relative concentrations of the complexes, or by fitting of the experimental fluorescence intensity, $F_{\text{mes},\lambda}$, using Equation (A.610), where $F_{3,\lambda}$ is the molar fluorescence intensity of $Cm(CO_3)_3^{3-}$ that can be determined in test solutions with high concentration of carbonate. $F_{2,\lambda}$ is the fluorescence intensity of $Cm(CO_3)_2^-$, that has to be fitted together with $K_3$.

$$\frac{F_{\text{mes},\lambda}}{[\text{Cm}]_T} = \frac{F_{2,\lambda} + F_{3,\lambda}K_3[CO_3^{2-}]}{1 + K_3[CO_3^{2-}]} \qquad \text{(A.610)}$$

The accuracy of the fitted constants may be affected by the correlation between $F_{2,\lambda}$ and $K_3$, a point that has not been discussed by Vercouter *et al.*; this is, however a less serious problem than in systems where both $F_{3,\lambda}$ and $K_3$ have to be fitted. It had been of interest to investigate if peak deconvolution had resulted in the same result. The

plot of the measured fluorescence at a given wavelength as a function of the free carbonate concentration provides a more direct information of the stoichiometry of the reaction and the corresponding equilibrium constant (Figure 1b in the publication) and clearly demonstrates that one carbonate is involved in the reaction and that the corresponding equilibrium can be obtained at the location of the inflexion point of the curve. The present review accepts the analysis of Vercouter *et al.* that the equilibrium they have studied involves only two complexes and the resulting equilibrium constant, $\log_{10}K_3$(A.609) = (2.08 ± 0.10). However, their data can be described either the one in Reaction (A.611) or (A.612). The stoichiometry of the limiting complex is discussed in [2003GUI/FAN] that conclude, based on the studies by Fanghänel *et al.* ([1998FAN/WEG2]), that $Cm(CO_3)_4^{5-}$ is formed at very high carbonate concentrations, up to 6 molal. We have listed the relevant equilibrium constants for Cm(III)/Am(III) carbonato complexes in Table A-188.

$$M(CO_3)_2^- + CO_3^{2-} \rightleftharpoons M(CO_3)_3^{3-} \quad \text{(A.611)}$$

$$M(CO_3)_3^{3-} + CO_3^{2-} \rightleftharpoons M(CO_3)_4^{5-} \quad \text{(A.612)}$$

Table A-188: Equilibrium data for the Am(III)/Cm(III)-carbonate system from [2003GUI/FAN], where the reported uncertainties are those assigned in the original publications.

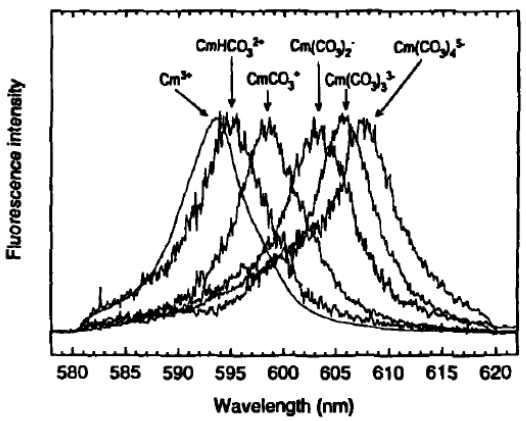
| Reaction: $An(CO_3)_2^- + CO_3^{2-} \rightleftharpoons An(CO_3)_3^{3-}$ | | | | | | |
|---|---|---|---|---|---|---|
| An | Medium | $T$/K | Method | $\log_{10}K_3$ | $\log_{10}K_3^o$ | Reference |
| Cm | 1.0 M NaCl | 298 | TRLFS | (2.91 ± 0.15) | (2.09 ± 0.15) | [1998FAN/WEG2] |
| Cm | 0.01-6 m NaCl | 298 | TRLFS | | | |
| | I = 0 | | | | 2.00 | [1999FAN/KON] |
| Am | I = 0 | rt | sol | | 2.9 | [1990FEL/RAI] |
| Am | 0.1 M NaCl | 294 | sol | (1.80 ± 0.26) | (1.4 ± 0.3) | [1994GIF] |
| Am | 4 M NaCl | 294 | sol | (2.24 ± 0.25) | (0.9 ± 0.3) | [1994GIF] |
| Am | 5 M NaCl | 295 | sol | (3.2 ± 0.5) | (2.0 ± 0.5) | [1994RUN/KIM] |
| Am | $I$ = 0 | 298 | review | | (2.9 ± 0.5) | [1995SIL/BID] |
| An | Medium | $T$/K | Method | $\log_{10}K_3$ | $\log_{10}K_3^o$ | Reference |
| Am + Cm | $I$ = 0 | 298 | review | | (2.2 ± 0.7) | [1998NEC/FAN], [1999FAN/KON] |
| Am + Cm | $I$ = 0 | 298 | review | | (2.1 ± 0.8) | [2003GUI/FAN] |
| Reaction: $An(CO_3)_3^{3-} + CO_3^{2-} \rightleftharpoons An(CO_3)_4^{5-}$ | | | | | | |
| An | Medium | $T$/K | Method | $\log_{10}K_4$ | $\log_{10}K_4^o$ | Reference |
| Cm | 1.0 M NaCl | 298 | TRLFS | (1.0 ± 0.2) | | [1998FAN/WEG2] |
| Cm | 0.01-6 m NaCl | 298 | TRLFS | | | |
| | $I$ = 0 | | | | – 2.16 | [1999FAN/KON] |

This review has looked into the study by Fanghänel *et al.* [1998FAN/WEG2] where the Cm(III)-carbonate system was studied in 1 M NaCl, at 298 K using TRLFS. The

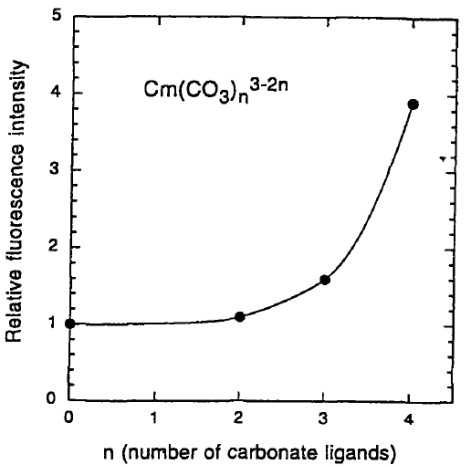
emission spectra and emissions intensities reported in [1998FAN/WEG2] are shown in Figure A-25(a and b). The wavelength shift and the pronounced increase in intensity at the highest carbonate concentration is a strong indicator for the formation of a new complex, $Cm(CO_3)_4^{5-}$, but no equilibrium constant for this complex was selected by the present reviewers.

Figure A-25: TRLFS data reported in [1998FAN/WEG2]: (a) Single component spectra of Cm(III) species, scaled to the same intensity for better visualization. (b) Relative fluorescence intensity of the different Cm(III) species. (Reprinted with permission from *Radiochim. Acta*, **1998**, *82* , 47. Copyright (1998) De Gruyter).

(a)



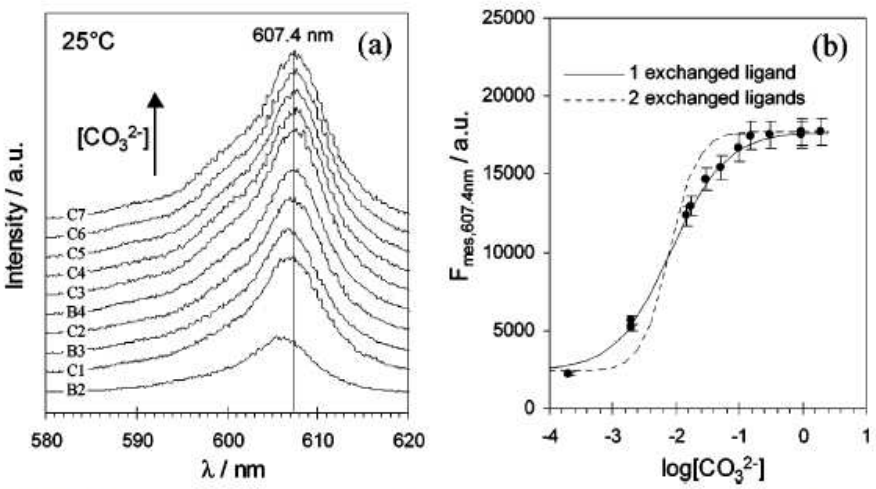

(b)



The fluorescence spectrum in [2005VER/VIT] is shown in Figure A-26 (a), together with the sigmoid curve typical in systems with a single equilibrium reaction Figure A-26 (b). This curve also shows that Vercouter *et al.* have studied test solutions with a carbonate concentration of 1 and 2 M, somewhat higher than the concentrations used in [1998FAN/WEG2] where the complex $Cm(CO_3)_4^{5-}$ was identified.

Vercouter *et al.* report $\log_{10} K_3^\circ = (2.08 \pm 0.10)$; $\Delta_r G_m$ (A.611) = – (11.5 ± 0.2) kJ·mol$^{-1}$; $\Delta_r H_m$ (A.611) = (12.2 ± 2.3) kJ·mol$^{-1}$; $\Delta_r S_m$ (A.611) = (79 ± 8) J·K$^{-1}$·mol$^{-1}$, all in 3 M $NaClO_4$. The data from Fanghänel *et al.* [1998FAN/WEG2] indicate the formation of $Cm(CO_3)_4^{5-}$, but the life-time measurements by Vercouter *et al.*, $\tau = (197 \pm 10)$ µs in 1 M $Na_2CO_3$, are not consistent with the formation of this complex as the use of the Kimura relation [1994KIM/CHO2] suggests that the complex contains (2.5 ± 0.5) coordinated water.

Figure A-26: Influence of carbonate concentration on the speciation of Cm(III) in $NaHCO_3$-$Na_2CO_3$ solutions with $I$ = 3 M and 298 K, as reported in [2005VER/VIT]. (a) fluorescence spectra; (b) fluorescence intensities at 607.4 nm, the wavelength of the maximum intensity for $Cm(CO_3)_3^{3-}$ (as defined in [2005VER/VIT]), over $\log_{10}[CO_3^{2-}]$. Curves in Figure A-26 (b) were adjusted considering the exchange of 1 (solid line) and 2 (dashed line) ligands in the complex formation reaction. (Reprinted with permission from *Inorg. Chem.*, **2005**, *44* (16), 5833. Copyright (2005) American Chemical Society).



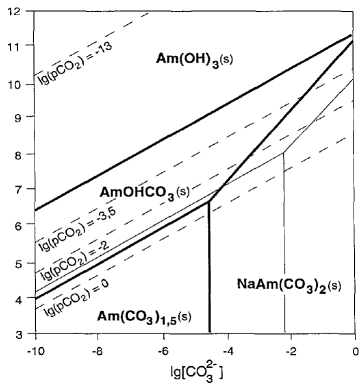

The speciation and the equilibrium constants in the Am(III) carbonate system are far from clear as illustrated in Table A-188. One reason is that all studies are based on solubility experiments, which require careful consideration of the composition of the

solid phase, in this case $AmOHCO_3(s)$, $Am_2(CO_3)_3(s)$ and $NaAm(CO_3)_2(s)$, and possible phase transformations, which may be kinetically constrained. One notes that no complex beyond $Am(CO_3)_3^{3-}$ has been suggested/identified. Vercouter *et al.* have reviewed published data on the composition and relative stability of solid phases formed in the Am(III)-carbonate system, $AmOHCO_3(s)$, $Am_2(CO_3)_3(s)$ and $NaAm(CO_3)_2(s)$ and conclude that the two latter are stable phases, depending on the concentration of carbonate and $Na^+$. $AmOHCO_3(s)$ does not seem to be stable in these systems but may form as a metastable phase as suggested by Felmy *et al.* [1990FEL/RAI].

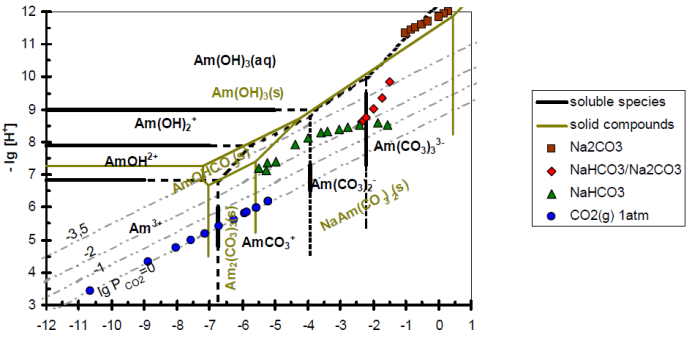
The data in the thesis of Giffaut [1994GIF] were reanalysed in [2003GUI/FAN], where the proposal of Giffaut that $AmOHCO_3(s)$ was the solubility limiting phase in 4 M NaCl was questioned. Vercouter *et al.* agree with this in their more detailed analysis of the data reported by Giffaut. A comparison of the predominance diagrams in Figure A-27 illustrates the differences between both interpretations, the predominance areas of the different solids are vastly different.

Figure A-27: Predominance diagram of Am(III) as calculated in (a) [1994GIF] (Reprinted with permission from ANDRA. Copyright (1994)) and (b) [2004VER/AME] (Reprinted with permission from the first author. Copyright (2004)).

(a)




(b)



The very large difference in the predominance field of $AmOHCO_3(s)$ in the two figures is clearly seen. The x-axis shows $p[CO_3^{2-}]$ and we note that there is extensive information at high concentrations of carbonate, where we should expect the formation of $Am(CO_3)_4^{5-}$. This review notes that the assignment of equilibrium constants, based on solubility data is problematic in the absence of accurate solid phase characterization, and has therefore not accepted the analysis in [2005VER/VIT]. We have also evaluated how the equilibrium constants for the formation of $AmCO_3^+$, $Am(CO_3)_2^-$ and $Am(CO_3)_3^{3-}$ compared with the corresponding Cm-complexes. The values of the stepwise constants at zero ionic strength are listed below for Am and Cm:

$$\log_{10} K_1^o(\text{Am}) = (8.00 \pm 0.40);\ \log_{10} K_1^o(\text{Cm}) = (8.00 \pm 0.40)$$

$$\log_{10} K_2^o(\text{Am}) = (4.60 \pm 0.30);\ \log_{10} K_2^o(\text{Cm}) = (4.80 \pm 0.30)$$

$$\log_{10} K_3^o(\text{Am})\ \text{(varying from 0.90 to 2.90)};\ \log_{10} K_3^o(\text{Cm}) = (2.10 \pm 0.20)$$

The large variation in $\log_{10} K_3^o$ for the americium system may well be due to both experimental problems and the neglect of $Am(CO_3)_4^{5-}$.

From the reported equilibrium constants, $\log_{10} K_1^o$ and $\log_{10} K_2^o$, this review confirms that Cm(III) is a good model for Am(III) and that the equilibrium constants for the former may be used as proxy for the latter. Hence, this review retains the selected value in [2003GUI/FAN] $\log_{10} K_3^o = (2.10 \pm 0.20)$ for the formation of $Am(CO_3)_4^{5-}$. No value is selected for $\log_{10} K_4^o$ either for the Am(III) or the Cm(III) system.

**[2005VER/VIT2]**

Vercouter *et al.* [2005VER/VIT2] studied the complexation of Eu(III) with carbonate by both TRLFS and by examining the solubility of $NaEu(CO_3)_2{\cdot}5H_2O(cr)$ at 296 K. Emphasis was placed on identifying the limiting carbonate complex of Eu(III). Interestingly, the results were different for $Na^+$ containing solutions than for those containing $K^+$. The difference was attributed to a different hydration state for $Na^+$ as compared to $K^+$. $Eu(CO_3)_4^{5-}$ was favoured as the limiting complex in $K^+$ solutions and $Eu(CO_3)_3^{3-}$ in $Na^+$ containing solutions. The solubility constant for the reaction $NaEu(CO_3)_2{\cdot}5H_2O(cr) + CO_3^{2-} \rightleftharpoons Na^+ + Eu(CO_3)_3^{3-} + 5H_2O(l)$ was determined to be $\log_{10} K_s = -(4.20 \pm 0.20)$. Activity coefficients in the $Na^+$ containing electrolyte were calculated by using the SIT formalism.

Although this study deals with Eu(III) not Am(III), the results are applicable to Am(III)-$CO_3$ system as discussed in the main text.

**[2005WAN/FEL]**

Wang *et al.* [2005WAN/FEL] have investigated interactions between Eu(III) and Cm(III) in systems where there are high total amounts of amorphous silica present and in the Eu(III) systems also $Eu(OH)_3(s)$. The fluorescence spectra of the supernatant solutions have been measured and demonstrate that interactions between Eu(III)/Cm(III) and silicate take place, but these data do not provide information on the composition of the species formed, or on equilibrium constants. The authors have used Si-NMR to determine the speciation of silicate at pH = 12 and this information is important for the interpretation of data designed to determine equilibrium constants. For example, at pH = 12 and a total concentration of silica of $3.4 \times 10^{-4}$ M, the concentration of $SiO(OH)_3^-$ is $2.8 \times 10^{-4}$ M and of $SiO_2(OH)_2^{2-}$ $1.4 \times 10^{-5}$ M while the concentration of polymers is negligible. This result is based on available equilibrium constants and estimated Pitzer interaction parameters. The dominance of monomers over polymers is demonstrated by the Si-NMR data.

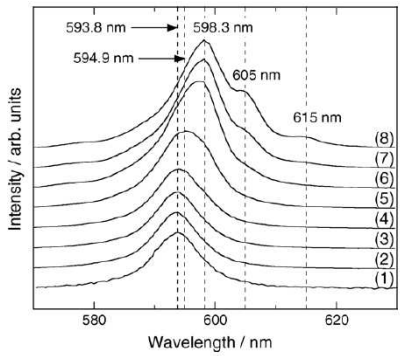
**[2006ARI/KIM]**

Arisaka *et al.* have studied complex formation in the Cm(III)-chloride system in LiCl solutions with concentrations between 0-14 M, at 298 K, using TRLFS, and they compared the data with those in the analogous Eu(III) system [2002ARI/KIM]. The speciation in the Cm(III) system was based on peak deconvolution of the fluorescence spectrum and on estimates on the number of coordinated water molecules based on fluorescence life-times in the different test solutions. Arisaka *et al.* point out that these two methods not always give concordant results and provide a plausible explanation for this.

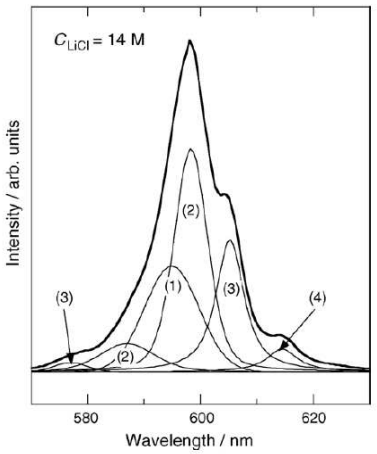
The point of main interest for the present reviewers is the speciation in Figure A-28 (a), derived from the fluorescence spectra in Figure A-28 (b). The accuracy of this procedure is not obvious and the claim by Arisaka *et al.* for the formation of four complexes, $CmCl_n^{3-n}$, $n$ = 1-4, where the complex $CmCl_4^-$ is based on the life-time measurements, is not accepted.

Figure A-28: Emission spectra of Cm(III) reported in [2006ARI/KIM]: a. in LiCl solutions 0 M (1), 1 M (2), 4 M (3), 6 M (4), 8 M (5), 10 M (6), 12 M (7) and 14 M (8); b. in a 14 M LiCl solution, including the peak deconvolution, with $CmCl^{2+}$ (1), $CmCl_2^+$ (2), $CmCl_3(aq)$ (3) and $CmCl_4^-$ (4). (Reprinted with permission from *J. Alloys Compd.* **2006**, 408-412, 1307-1311. Copyright (2006) Elsevier).

(a)




(b)




Arisaka *et al.* have plotted the number of coordinated chloride ions as a function of the water activity in Figure A-29, where one notes the large decrease in water activity with increasing LiCl concentrations; these data can therefore be compared with those in [2014SKE/FRO], where the water activity changes as a result of increasing temperature.

Figure A-29: Average chloride coordination number, $N_{Cl}$, reported in [2006ARI/KIM] for the Cm(III) and Eu(III) chloride systems as a function of water activity in the test solutions used. (Reprinted with permission from *J. Alloys Compd.* **2006**, 408-412 , 1307-1311. Copyright (2006) Elsevier).

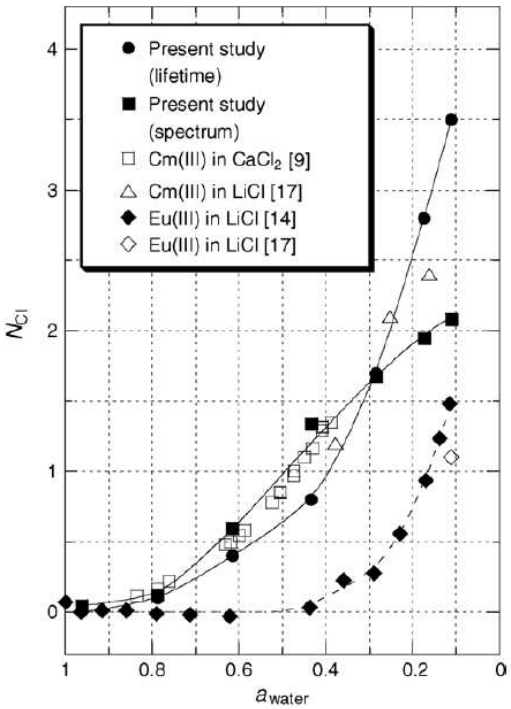



Figure A-29 shows an important difference between the Cm(III) and Eu(III) systems, which is difficult to explain on chemical grounds. The main conclusions by the present review is that the experimental data in [2006ARI/KIM] only provides qualitative information on the formation of chloride complexes, but no information on equilibrium constants.

**[2006PAT/CHO]**

Pathak and Choppin [2006PAT/CHO] have studied complex formation between Cm(III), Eu(III) and U(VI) and silicate over the temperature range 278-318 K in 0.2 M $NaClO_4$ by using liquid-liquid extraction with bis(2-ethylhexyl)phosphoric acid (HDEHP). The experiments were made at a constant $-\log_{10}[H^+]$ of 3.40 for Cm(III) and 3.15 for Eu(III) by varying the total concentration of silicate. From the concentration dependence of the distribution of Eu(III) and Cm(III) between the organic and aqueous phases, they determined the equilibrium constant for formation of $Eu/CmSiO(OH)_3^{2+}$ .

Conditional equilibrium constants reported for Reactions (A.613) and (A.614) at different temperatures are shown in Table A-189. The corresponding Gibbs energy, enthalpy and entropy of reaction are summarized in Table A-190.

$$Eu^{3+}/Cm^{3+} + SiO(OH)_3^- = Eu/CmSiO(OH)_3^{2+} \quad \text{(A.613)}$$

$$UO_2^{2+} + SiO(OH)_3^- = UO_2SiO(OH)_3^+ \quad \text{(A.614)}$$

Table A-189: Conditional equilibrium constants, $\log_{10}\beta_1$, reported in [2006PAT/CHO] for the formation of $UO_2SiO(OH)_3^+$ and $Eu/CmSiO(OH)_3^{2+}$ complexes in 0.20 M $NaClO_4$ as a function of temperature.

| Ion | 278 /K | 288 /K | 298 /K | 308 /K | 318 /K |
|---|---|---|---|---|---|
| $UO_2^{2+}$ | (6.78 ± 0.01) | (6.82 ± 0.01) | (6.87 ± 0.02) | (6.92 ± 0.02) | (6.99 ± 0.02) |
| $Cm^{3+}$ | (7.67 ± 0.01) | (7.77 ± 0.01) | (7.83 ± 0.02) | (7.91 ± 0.03) | (8.07 ± 0.02) |
| $Eu^{3+}$ | (7.61 ± 0.02) | (7.67 ± 0.01) | (7.79 ± 0.01) | (7.86 ± 0.03) | (7.93 ± 0.01) |

Table A-190: Thermodynamic functions reported in [2006PAT/CHO] for the formation of $UO_2^{2+}$, $Cm^{3+}$ and $Eu^{3+}$ silicate complexes in 0.20 M $NaClO_4$ and 298 K.

| Metal ion | $\Delta_r G_m$ /kJ·mol$^{-1}$ | $\Delta_r H_m$ /kJ·mol$^{-1}$ | $\Delta_r S_m$ /J·K$^{-1}$·mol$^{-1}$ |
|---|---|---|---|
| $UO_2^{2+}$ | – (39.2 ± 0.1) | (8.3 ± 0.7) | (159.5 ± 2.3) |
| $Cm^{3+}$ | – (44.7 ± 0.1) | (15.8 ± 2.0) | (203.0 ± 6.4) |
| $Eu^{3+}$ | – (44.4 ± 0.1) | (14.5 ± 1.0) | (197.7 ± 3.2) |

The present reviewers consider the estimated uncertainties in Table A-189 and Table A-190 as too small and have instead used 0.05 for $\log_{10}\beta_1$, ± 0.3 kJ·mol$^{-1}$ for $\Delta_r G_m$, 3.0-4.0 kJ·mol$^{-1}$ for $\Delta_r H_m$ and ± 10 J·K$^{-1}$·mol$^{-1}$ for $\Delta_r S_m$. We also note that the thermodynamic data for the Eu(III) and Cm(III) are in very good agreement, confirming that both are good models for Am(III). $\log_{10}\beta_1$ has been extrapolated using SIT to zero ionic strength to give $\log_{10}\beta_1^o = (8.65 \pm 0.05)$ and $\Delta_r G_m^o = -(49.4 \pm 0.3)$ kJ·mol$^{-1}$. Enthalpy values have been extrapolated to $I = 0$ as described in the Appendix A for uranium (see entry [2006PAT/CHO]), resulting in $\Delta_r H_m^o = (18.6 \pm 4.0)$ kJ·mol$^{-1}$ for Cm(III) and in $\Delta_r H_m^o = (17.3 \pm 3.0)$ kJ·mol$^{-1}$ for Eu(III).

**[2007THA/SIN]**

Thakur *et al.* have studied the complex formation between Am(III), Cm(III) and Eu(III) and $SiO(OH)_3^-$ using liquid-liquid extraction with di-(2-ethylhexyl) phosphoric acid (HDAHP) at 298 K and pH = 3.50, over a range of ionic strengths (0.2 to 1.0 M $NaClO_4$). The authors also investigated polymerization of the silicate solutions as function of the total concentration of silica, pH and temperature and noted that polymerization increased with the ionic strength, the total concentration of silica and

temperature. Of main interest for the present review is that the amount of polymer is about 94 % in 1 M $NaClO_4$ at a total silicate concentration of 0.002 M, but only 74 % in 0.20 M $NaClO_4$ at the highest total concentration used, 0.02 M. Unfortunately, Thakur *et al.* have not indicated to which data these equilibrium constants (Table A-191) refer. For this reason the present review has only considered the data at the lowest ionic strength, 0.20 M, where the amount of polymer is smallest.

The reaction studied is

$$M^{3+} + SiO(OH)_3^- \rightleftharpoons MSiO(OH)_3^{2+} \quad \text{(A.615)}$$

To calculate the equilibrium constant $\log_{10}\beta_1$, it is necessary to know the dissociation constant of $Si(OH)_4(aq)$, where Thakur *et al.* used, $pK_1 = 9.58$. The present review has used the value selected in the NEA TDB, $pK_1^o = (9.81 \pm 0.02)$, and recalculated this to $I = 0.20$ M obtaining $pK_1$ ($I = 0.20$ M) = (9.54 ± 0.02).

Table A-191: Conditional equilibrium constants, $\log_{10}\beta_1$, for formation of $MSiO(OH)_3^{2+}$, M = Am(III), Cm(III) and Eu(III) at different ionic strength as reported in [2007THA/SIN]. The values at $I = 0$ have been calculated in this review from the conditional constants in 0.20 M $NaClO_4$ using SIT.

| $I$ (M, $NaClO_4$) | Am(III) $\log_{10}\beta_1$ | Cm(III) $\log_{10}\beta_1$ | Eu(III) $\log_{10}\beta_1$ |
|---|---|---|---|
| 0.20 | (8.02 ± 0.10) | (7.78 ± 0.08) | (7.81 ± 0.11) |
| 0.50 | (7.86 ± 0.09) | (7.59 ± 0.10) | (7.62 ± 0.08) |
| 0.75 | (7.70 ± 0.11) | (7.42 ± 0.09) | (7.43 ± 0.12) |
| 1.00 | (7.67 ± 0.12) | (7.37 ± 0.13) | (7.38 ± 0.13) |
| 0.00 | (8.84 ± 0.10) | (8.60 ± 0.08) | (8.63 ± 0.11) |

The equilibrium constants for the formation of $MSiO(OH)_3^{2+}$, agree within their estimated uncertainty, confirming the close similarity in the chemistry of Am(III), Cm(III) and Eu(III). This review notes that the equilibrium constant for Am(III) differs significantly form the value selected in [2003GUI/FAN], $\log_{10}\beta_1^o = (8.13 \pm 0.18)$.

**[2007YUS/SHI4]**

Yusov *et al.* have studied redox reactions and their variation among the actinide elements by using solutions containing the heteropolytungstate, "$K_{10}P_2W_{17}O_{61}$". As a result of the high negative charge of the anion $P_2W_{17}O_{61}^{10-}$, this is easily protonated but can also form strong complexes with actinides in their various oxidation states. As a result, the measured formal potentials are strongly dependent on pH and the constitution and equilibrium constants of the complexes formed. There is no information of this type in the paper and the formal potentials cannot provide thermodynamic data of use for the present review.

**[2007YUS/SHI3]**

Equilibrium constants for the complex formation between the heteropolyanion ($P_2W_{17}O_{61}^{10-}$) and several tetravalent and trivalent ions were determined in 1 M ionic strength solutions. New experimental data are presented for U(IV), Th(IV), Ce(IV)/Ce(III), Pr(III), and Tb(III). Published data on the equilibrium constants of Np(IV), Pu(IV), Am(IV), and Cm(IV) are analysed and the stability of these actinides with $P_2W_{17}O_{61}^{10-}$ is also estimated. No thermodynamic data can be selected from this study.

**[2008NIS/ITO]**

[2008NIS/ITO] report for the first time the measurement of the enthalpy increments of AmN(cr) using twin-drop calorimetry in the temperature range 354-1071 K. The complete review of this article is reported in the Appendix A for neptunium.

**[2008NIS/TAK]**

Thermal diffusivity measurements are performed for $AmO_{2-x}$, with initial O/Am = 1.9. However, at the reduction under vacuum between 573-873 K in the first measurements resulted in a final O/Am = 1.73. A general trend of decreasing thermal diffusivity and conductivity with increasing temperature is established. The two properties are related by $\lambda = \alpha C_p \rho$, where the variables $\lambda, \alpha, C_p, \rho$ correspond to thermal conductivity, thermal diffusivity, specific heat capacity and bulk density, respectively. The specific heat capacity is taken from the original review by [1995SIL/BID] and remained unchanged in [2003GUI/FAN].

**[2008OTO/AKA]**

The oxygen potential of $AmO_{2-x}$ was measured for $0.50 < x < 0.019$ at $T = 1333$ K using EMF with the following galvanic cell:

$$Pt/AmO_{2-x}/Y_2O_3\text{-}ThO_2/air, Pt$$

$^{241}AmO_2$ pellets were prepared by sintering pressed powder for six hours at 1600 K in air, followed by a one hour heat treatment at 1333 K in artificial air to control the oxygen to metal ratio. XRD measurements indicated the fluorite-type structure, common in actinide dioxides and with a lattice parameter that is in agreement with literature values. Coulometric titrations were carried out to change the stoichiometry at 1333 K using a 0.25 mA current for ten min. The values of $x$ were independently determined for three samples using thermogravimetric measurements, were $AmO_{2-x}$ samples were oxidized to obtain the $AmO_2$ stoichiometry. Oxygen potential

measurements were taken up to six hours after the coulometric titration, providing a detailed analysis of the oxygen potential with respect to $x$ in $AmO_{2-x}$ ranging from 0.01 to 0.5. The most notable findings is the observation of a two phase region between $Am_9O_{16}$ and $AmO_{2-x}$, where the oxygen potential is constant at $\mu(O_2) = -204.7$ kJ·mol$^{-1}$ between $0.22 < x < 0.23$ and a second two phase region at $0.30 < x < 0.31$, where $\mu(O_2)$ is constant at $-244.2$ kJ·mol$^{-1}$ where *FCC* and $Am_7O_{12}$ phases are present. Neither of these have previously been reported or confirmed in literature. However, there are analogous Ce compounds ($Ce_9O_{16}$ and $Ce_7O_{12}$), which exist at much higher oxygen potentials than measured here. The phase boundary between hexagonal and cubic (A + C) is found to be at $x = 0.33$, compared to $x = 0.4$ for the proposed phase diagram by [2003THI/KON] and the miscibility gap proposed by [1970SAR/ZAM] is shifted to higher stoichiometry of $x = 0.19$ instead of extended to $x = 0.32$. The *bcc* C'-type phase exists over a wider composition range than [2003THI/KON]. Most of these phase relations are similar to the analogous Ce-O system, which suggests the stable structures of the new americium phases and their phase boundaries discussed in [2008OTO/AKA]. However, these data are not yet confirmed.

**[2008RAB/ALT]**

The authors examined the hydroxide complexes of Cm(III) in alkaline solutions containing $CaCl_2$ at (295 ± 2) K by TRLFS. Two types of experiments were conducted: (1) one type with varying [$CaCl_2$] (0.1-3.5 M) at nearly constant $-\log_{10}[H^+]$ (~ 11.7); (2) the other type with varying $-\log_{10}[H^+]$ (10.8-11.9) at three constant concentrations of $CaCl_2$ (1.0, 2.5, and 3.5 M), corresponding to 1.02, 2.68, and 3.91 m, and contributing to the ionic strengths of 3.06, 8.04, and 11.73 m, respectively.

In comparison with the experiments with mixtures of 5 M NaCl/NaOH ([NaOH] = 1, 3, and 4 M) where the fluorescence was very weak, the experiments in $CaCl_2$ solutions, showed the fluorescence emission of Cm(III) to be significantly enhanced and new emission peaks appeared at 607.5, 609.9, and 614.7 nm when the concentration of $CaCl_2$ was at or above 1 M (*i.e.*, $I \geq 3.06$ m) and $-\log_{10}[H^+]$ was in the region of 10.8-11.7.

In conjunction with previous fluorescence studies [1994FAN/KIM] and the experiments in NaCl/NaOH solutions, this study assigned the emission peaks at 593.8, 598.8, and 603.5 nm to free $Cm^{3+}$, $Cm(OH)^{2+}$, and $Cm(OH)_2^+$, respectively, the new peaks observed only in $CaCl_2$ solutions in this study, were assigned to $Cm(OH)_3(aq)$ (607.5 nm), $Cm(OH)_4^-$ (609.9 nm), and $Cm(OH)_6^{3-}$ (614.7 nm). Fitting the fluorescence data with a model that includes these species resulted in conditional equilibrium constants for these species in $CaCl_2$ solutions, as shown in Table A-192.

Table A-192: Step-wise conditional equilibrium constants reported in [2008RAB/ALT] for the formation of the complexes $Cm(OH)_3(aq)$, $Cm(OH)_4^-$ and $Cm(OH)_6^{3-}$ in alkaline 1.02 to 3.91 m $CaCl_2$ solutions.

| Reaction | Conditional equilibrium constant, $\log_{10}K$ ($\pm 2\sigma$) [(a)] | | |
|---|---|---|---|
| | $[CaCl_2]$ = 1.02 m<br>$I$ = 3.06 m | $[CaCl_2]$ = 2.68 m<br>$I$ = 8.04 m | $[CaCl_2]$ = 3.91 m<br>$I$ = 11.73 m |
| $Cm(OH)_2^+ + H_2O(l) \rightleftharpoons Cm(OH)_3(aq) + H^+$ | – (10.5 ± 0.5) | – (10.3 ± 0.3) | – (9.9 ± 0.3) |
| $Cm(OH)_3(aq) + H_2O(l) \rightleftharpoons Cm(OH)_4^- + H^+$ | – (10.8 ± 0.4) | – (11.3 ± 0.3) | – (11.8 ± 0.3) |
| $Cm(OH)_4^- + 2H_2O(l) \rightleftharpoons Cm(OH)_6^{3-} + 2H^+$ | – (23.6 ± 0.4) | – (22.8 ± 0.3) | – (22.2 ± 0.3) |

(a) In the fitting, the reaction $CmOH^{2+} + H_2O(l) \rightleftharpoons Cm(OH)_2^+ + H^+$ was included in the model. Its equilibrium constant was considered to be identical with that for the reaction $NdOH^{2+} + H_2O(l) \rightleftharpoons Nd(OH)_2^+ + H^+$ that was obtained by a solubility study [2009NEC/ALT]: $\log_{10}K$ = – (9.1 ± 0.5), – (9.9 ± 0.5), and – (10.5 ± 0.5), for $CaCl_2$ solutions of 1.02 m, 2.68 m, and 3.91 m, respectively.

Because the conditional equilibrium constants were obtained at very high ionic strengths, it is not possible to extrapolate and calculate accurate equilibrium constants at infinite dilution using SIT. Attempts to do so results in unreasonable ion interaction parameters, as the authors pointed out in the paper. Furthermore, the authors pointed out that, even if the equilibrium constants at $I = 0$ could be obtained from these data, they would not be applicable to the "Ca-free ionic media", because the absence of the emission peaks at 607.5, 609.9, and 614.7 nm in NaCl/NaOH media (with $I$ as high as 5 M) suggests that these species, $Cm(OH)_3(aq)$, $Cm(OH)_4^-$, and $Cm(OH)_6^{3-}$ did not form under these conditions. Accordingly, Rabung *et al.* suggested the formation of ternary $Ca_p$-$Cm_q$-$OH_r$ complexes in alkaline $CaCl_2$ solutions and corresponding equilibrium constants, as derived also from [2009NEC/ALT]:

$$Ca^{2+} + Cm^{3+} + 3H_2O(l) \rightleftharpoons Ca[Cm(OH)_3]^{2+} + 3H^+ ;\ \log_{10}{}^*\beta^o_{1,1,3} = -26.3$$

$$2Ca^{2+} + Cm^{3+} + 4H_2O(l) \rightleftharpoons Ca_2[Cm(OH)_4]^{3+} + 4H^+ ;\ \log_{10}{}^*\beta^o_{2,1,4} = -37.2$$

$$3Ca^{2+} + Cm^{3+} + 6H_2O(l) \rightleftharpoons Ca_3[Cm(OH)_6]^{3+} + 6H^+ ;\ \log_{10}{}^*\beta^o_{3,1,6} = -60.7$$

[2008RAB/ALT] and [2009NEC/ALT] also reported SIT and Pitzer ion interaction coefficients for the proposed $Ca_p$-$Cm_q$-$OH_r$ ternary complexes. The equilibrium constants and associated ion interaction coefficients provide a consistent interpretation of both Cm(III) spectroscopic data [2008RAB/ALT] and $Nd(OH)_3(s)$ solubility [2009NEC/ALT] in alkaline $CaCl_2$ solutions.

The present review concludes: (1) the spectroscopic experiments in [2008RAB/ALT] were carefully conducted by taking reasonable precautions to reduce colloidal phases from the test solutions; (2) the interpretation of the fluorescence spectra in $CaCl_2$ solutions of high $-\log_{10}[H^+]$ using the model including the higher hydrolysis species, $Cm(OH)_3(aq)$, $Cm(OH)_4^-$, and $Cm(OH)_6^{3-}$, is acceptable; and (3) the enhancement of fluorescence intensity in the presence of $CaCl_2$ could imply the interactions between $Ca^{2+}$ and the anionic species such as $Cm(OH)_4^-$ and $Cm(OH)_6^{3-}$.

However, the present reviewers have concerns on several issues: (1) The limitation of SIT in such solutions of high ionic strengths and the circular reasoning in the re-evaluation of the constants raises questions on the accuracy of the equilibrium constants. (2) The stoichiometry of the ternary Ca-Cm-OH complexes is based on assumptions and analogy to tetravalent systems that is questionable. Direct experimental determination of the stoichiometry may be difficult, but theoretical calculations may provide valuable information to verify or refute the proposed stoichiometries. (3) The appearance of additional emission bands and the significant enhancement of emission intensities in $CaCl_2$ solutions, but not in NaCl systems even at high concentrations of $OH^-$ and $Cl^-$, needs additional model testing in addition to the interactions involving $Ca^{2+}$. For example, the effect of outer-sphere vs. inner-sphere complex formation on fluorescence intensity and lifetime could contribute to the observations. (4) As the following estimation by the present review indicates, the complexation between $Ca^{2+}$ and $Cm(OH)_3(aq)$ is extremely weak and invoking the ternary complex, $Ca[Cm(OH)_3]^{2+}$, may be unnecessary in order to interpret the solubility data in $CaCl_2$ solutions.

Using the selected values of $\log_{10}{}^{*}\beta_3^{\circ}$ for Am(III) hydrolysis in [2003GUI/FAN] for the Cm(III) system,

$$Cm^{3+} + 3H_2O(l) \rightleftharpoons Cm(OH)_3(aq) + 3H^+ ;\ \log_{10}{}^{*}\beta_3^{\circ} = -26.2$$

and combining this reaction with the formation of $Ca[Cm(OH)_3]^{2+}$ from [2008RAB/ALT],

$$Ca^{2+} + Cm^{3+} + 3H_2O(l) \rightleftharpoons Ca[Cm(OH)_3]^{2+} + 3H^+ ;\ \log_{10}{}^{*}\beta_{1,1,3}^{\circ} = -26.3$$

we obtained

$$Ca^{2+} + Cm(OH)_3(aq) \rightleftharpoons Ca[Cm(OH)_3]^{2+} ;\ \log_{10}{}^{*}\beta_{1,1,3}^{\circ} = -0.1$$

Based on the above discussions, this review does not accept the formation constants of the ternary Ca-Cm-OH complexes from [2008RAB/ALT] and [2009NEC/ALT].

**[2009NEC/ALT]**

The authors conducted extensive solubility studies with $Nd(OH)_3(s)$ in NaCl, $MgCl_2$, and $CaCl_2$ solutions and re-analysed previous solubility data on $Am(OH)_3(s)$ from [1991VIT/TRA] in conjunction with the data for Cm(III) in a TRLFS study [2008RAB/ALT]. Neck *et al.* demonstrated that, by including the formation of ternary Ca-M(III)-OH complexes, the solubility of $Nd(OH)_3(s)$ in concentrated $CaCl_2$ solutions could be adequately described. A model including equilibrium constants of the formation of the ternary complexes, $Ca[Cm(OH)_3]^{2+}$, $Ca_2[Cm(OH)_4]^{3+}$ and $Ca_3Cm[(OH)_6]^{3+}$, and the associated Pitzer ion-interaction parameters was developed.

However, based on the detailed discussions under [2008RAB/ALT] in Appendix A, this review does not accept the equilibrium constants of the formation of the ternary Cm(III) complexes and associated SIT or Pitzer parameters from [2008RAB/ALT] and [2009NEC/ALT].

Using SIT to re-analyse the solubility data in 0-10 M KOH from [1991VIT/TRA] that were not considered in previous reviews, Neck *et al.* developed the equilibrium constant for the formation of $Am(OH)_4^-$ species as $\log_{10}{}^*\beta_4^o = -(40.7 \pm 0.7)$ with associated SIT parameters $\varepsilon(K^+/Na^+, Am(OH)_4^-) = -(0.03 \pm 0.05)$ [2009NEC/ALT].

Although the model including the $Am(OH)_4^-$ species is able to describe the increase of $[Am(III)]_{total}$ in highly alkaline solutions where $[OH^-] \geq 3$ M, this review does not accept the corresponding equilibrium constant from [2009NEC/ALT] for the following reasons: (1) The use of SIT to analyse the data in solutions of very high ionic strength is questionable, and (2) the presence of $Am(OH)_3(s)$ as solid phase controlling the solubility in this highly alkaline solution was not confirmed experimentally, and thus the formation of ternary K-Am(III)-OH solid phases cannot be ruled out in the solubility study by [1991VIT/TRA].

**[2009SKE/PAN]**

Skerencak *et al.* [2009SKE/PAN] studied the complexation of Cm(III) with nitrate by TRLFS over a wide range of nitrate concentration (0.1-4.6 m) and over a temperature range of 298-473 K at a Cm(III) concentration of $10^{-7}$ M. A decrease in the fluorescence intensity was noted with increasing temperature. The stability constants for the first complex averaged $(1.31 \pm 0.06)$ across the temperature range 298-348 K. At higher temperature the stability constants for the $CmNO_3^{2+}$ complex increased significantly, although the uncertainty also increased (see Table A-193). Spectroscopic observations in [2009SKE/PAN] revealed the formation of the complex $Cm(NO_3)_2^+$, which is only significant at temperatures greater than 373 K. Equilibrium constants reported by Skerencak *et al.* for the second complex $Cm(NO_3)_2^+$ are also summarized in Table A-193.

Based on the temperature variation of $\log_{10} K_n^o$, Skerencak *et al.* calculated the corresponding enthalpies, entropies and heat capacities of reaction. Values for the SIT parameters as a function of temperature were also reported. This review notes that the temperature variation of $\Delta\varepsilon$ is small, less than 10 % of the value at 298 K. This review considers the study by Skerencak *et al.* of high quality, and the thermodynamic quantities reported by the authors are used in the selection of the Am(III)-nitrate system.

Table A-193: Stepwise formation constants reported in [2009SKE/PAN] for the formation of $CmNO_3^{2+}$ and $Cm(NO_3)_2^+$ species as a function of temperature.

| $T$ /K | $\log_{10} K_1^o$ | $\log_{10} K_2^o$ |
|---|---|---|
| 278 | (1.28 ± 0.07) | – (0.50 ± 0.05) |
| 288 | (1.26 ± 0.06) | – (0.47 ± 0.01) |
| 298 | (1.29 ± 0.06) | – (0.36 ± 0.10) |
| 323 | (1.30 ± 0.03) | – (0.30 ± 0.10) |
| 348 | (1.38 ± 0.05) | – (0.08 ± 0.17) |
| 373 | (1.58 ± 0.18) | – (0.07 ± 0.12) |
| 393 | (1.71 ± 0.30) | (0.07 ± 0.12) |
| 413 | (1.94 ± 0.18) | (0.17 ± 0.12) |
| 433 | (1.99 ± 0.24) | (0.19 ± 0.16) |
| 453 | (2.03 ± 0.18) | (0.54 ± 0.21) |
| 473 | (2.04 ± 0.24) | (0.80 ± 0.27) |

**[2009MIN/TAK]**

[2009MIN/TAK] reported the measurement of the thermal expansion, heat capacities, thermal diffusivities, and oxygen potentials of neptunium, plutonium, and americium nitrides and oxides using high temperature X-ray diffraction, drop calorimetry, and the laser-flash method, and electromotive force method, respectively. The complete review of this article is reported in the Appendix A for neptunium.

**[2009SOB]**

A model to analyze an equation of state (EOS) for the determination of thermodynamic properties is implemented and compared to available literature data. Thermophysical properties such as heat capacity, thermal expansion coefficient and the bulk modulus are studied. The Helmholtz free energy as a function of temperature and volume is used to model the equation of state. The model used a microscopic statistical approach that includes ground state, phonon and electronic contributions to the EOS. The input parameters for the localized 5f-electron levels used in the electronic contribution to the free energy are those listed by [2004KON]. Their values for the heat capacity are in agreement with those of the model in [2003THI/KON]. No new experimental data are produced.

**[2010KON/BEN]**

No new experimental data on the americium metallic phase is presented in this review. However a reevaluation of the transition enthalpies leads the authors to reject the previous selected values in [1995SIL/BID], which were based on the studies of [1967WAD/WOL]. The significantly lower values of [1977SEL/KOS], which were more in agreement with trends in the actinide and lanthanide series presented in the

review, are selected. The selected heat capacity values for Am are based on the estimates by [2003KON] as no experimental data is available.

**[2010PHI/VER]**

This study is of interest because it describes lanthanide(III) carbonate systems that have been investigated using solubility and laser fluorescence measurements. Even if it does not provide experimental data on carbonate complexes of trivalent actinides, it sheds light on the stoichiometry of the complexes formed, more specifically on changes in stoichiometry that result from the variation in the ionic radii. As a result of the decrease of the ionic radii from $La^{3+}$ to $Lu^{3+}$, it is often found that the coordination number of the $Ln^{3+}$ elements decreases from nine in the first half of the lanthanide series, to eight for the second half. There is also information that there are equilibria between 8- and 9-coordination, where the species with 9-coordination is predominating for the ions with the larger ionic radii and 8-coordination for the ones with smaller radii. An interesting example is offered by the $Ln^{3+}$(aq) ions, where data for $Eu^{3+}$ has demonstrated equilibrium between $Eu(OH_2)_9^{3+}$ and $Eu(OH_2)_8^{3+}$. Philppini *et al.* find the same pattern for carbonate complexes; the limiting complex has the stoichiometry $Ln(CO_3)_4^{5-}$ for Ln = La and Nd, and $Ln(CO_3)_3^{3-}$ for M = Eu and Dy.

The solubility experiments have been made using $NaLn(CO_3)_2(s)$ and varying the carbonate concentration and the TRLFS by using sufficiently low Eu(III)/Tb(III) concentrations to avoid precipitation. The experiments are carefully made, ensuring that no phase transformation takes place during the experiment and the same care has been taken in the analysis of the data. Philippini *et al.* use their data in a discussion of the constitution of the limiting complex in the Am(III)/Cm(III) carbonate system and claim that their results, with $Eu(CO_3)_3^{3-}$ as the limiting complex, support a stoichiometry $An(CO_3)_3^{2-}$ for both Am and Cm. However, in [2005VER/VIT2], Vercouter *et al.* demonstrate very clearly that $Eu(CO_3)_4^{5-}$ is formed when using $KEu(CO_3)_2(s)$ in the solubility measurements and it is difficult to argue that such a change in the ionic medium should result in changes in the constitution of the complex. This review concludes that $Eu(CO_3)_4^{5-}$ is the limiting complex at $-2 < p[CO_3^{2-}] < 0.3$, and we were surprised to see that this result in [2005VER/VIT2] was not commented in [2010PHI/VER]. This general features of the chemistry of the Ln(III) and An(III) elements, apart from their redox properties, are very similar in the 4f and 5f elements. One example is their very similar equilibrium constants for a given ligand, another is the variation in the coordination number with the ionic radius of the $Ln^{3+}$-ions. Because of the similar chemistry it is difficult to argue that there should be a change in the ionic radius dependent coordination between the 4f and 5f elements. As the ionic radii of the $An^{3+}$ ions are larger than those of their $Ln^{3+}$ analogues one would expect that $Am^{3+}$ is more prone to form $Ln(CO_3)_4^{5-}$ than the corresponding $Eu^{3+}$ complex. Our analysis of the stoichiometry of the limiting complex in the Cm(III) carbonate system

[2005VER/VIT], shows very clearly that the limiting complex is $Cm(CO_3)_4^{5-}$, not surprising because its ionic radius is larger than that of $Eu^{3+}$.

**[2010SKE/PAN]**

Skerencak *et al.* have made a detailed study of the complex formation of Cm(III) with fluoride by TRLFS across the temperature range 293-363 K in $NaClO_4$ solutions of different concentration. The experimental method and the data analysis are detailed and of high quality. The stepwise equilibrium constants for Reactions (A.616) and (A.617), $\log_{10}K_1$ and $\log_{10}K_2$ were extrapolated to zero ionic strength using SIT. The corresponding values $\log_{10}K_1^\circ$, $\log_{10}K_2^\circ$ and ion-interaction terms, $\Delta\varepsilon_n$, are reported in Table A-194.

$$Cm^{3+} + F^- \rightleftharpoons CmF^{2+} \quad \text{(A.616)}$$

$$CmF^{2+} + F^- \rightleftharpoons CmF_2^+ \quad \text{(A.617)}$$

Table A-194: Equilibrium constants, $\log_{10}K_1^\circ$ and $\log_{10}K_2^\circ$ and the corresponding ion interaction factor, $\Delta\varepsilon$, for formation of $CmF^{2+}$ and $CmF_2^+$ from [2010SKE/PAN].

| $T$ /K | $\log_{10}K_1^\circ$ (mean) | $\Delta\varepsilon_1$ /kg·mol$^{-1}$ | $\log_{10}K_2^\circ$ (mean) | $\Delta\varepsilon_2$ /kg·mol$^{-1}$ |
|---|---|---|---|---|
| 293 | (3.56 ± 0.07) | – (0.13 ± 0.01) | (2.20 ± 0.84) | – (0.11 ± 0.20) |
| 303 | (3.65 ± 0.07) | – (0.12 ± 0.01) | (2.35 ± 0.69) | – (0.17 ± 0.08) |
| 313 | (3.69 ± 0.10) | – (0.13 ± 0.01) | (2.60 ± 0.55) | – (0.19 ± 0.05) |
| 323 | (3.74 ± 0.16) | – (0.14 ± 0.01) | (2.78 ± 0.47) | – (0.18 ± 0.04) |
| 333 | (3.82 ± 0.09) | – (0.13 ± 0.01) | (2.95 ± 0.41) | – (0.16 ± 0.03) |
| 343 | (3.87 ± 0.07) | – (0.14 ± 0.01) | (3.09 ± 0.26) | – (0.14 ± 0.02) |
| 453 | (3.94 ± 0.07) | – (0.14 ± 0.01) | (3.23 ± 0.25) | – (0.13 ± 0.01) |
| 363 | (3.98 ± 0.06) | – (0.14 ± 0.01) | (3.34 ± 0.21) | – (0.13 ± 0.01) |

$\log_{10}K_1^\circ = (3.60 \pm 0.07)$ and $\log_{10}K_2^\circ = (2.3 \pm 0.7)$ at 298 K, are within the reported uncertainty equal to the selected value for $AmF^+$, $\log_{10}K_1^\circ = (3.40 \pm 0.40)$ and for $AmF_2^+$, $\log_{10}K_1^\circ = (2.4 \pm 0.4)$ selected in [2003GUI/FAN], these values are therefore retained in the present review.

The enthalpies of reaction for Reactions (A.616) and (A.617) have been calculated from the temperature dependence of the equilibrium constants, assuming, $\Delta_r H_1$ and $\Delta_r H_2$ to be independent of temperature. The thermodynamic data from [2010SKE/PAN] are given in Table A-195 and we consider these values reliable.

Table A-195: Thermodynamic data for formation of $CmF^{2+}$ and $CmF_2^+$ from [2010SKE/PAN].

| | $Cm^{3+} + F^- \rightleftharpoons CmF^+$ | $CmF^{2+} + F^- \rightleftharpoons CmF_2^+$ |
|---|---|---|
| $\log_{10} K_n^o$ (293 K) | (3.56 ± 0.07) | (2.20 ± 0.84) |
| $\log_{10} K_n^o$ (363 K) | (3.98 ± 0.06) | (3.34 ± 0.21) |
| $\Delta_r G_m^o$ (293 K) /kJ·mol$^{-1}$ | – (20.54 ± 0.39) | – (13.22 ± 4.71) |
| $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | (12.09 ± 2.15) | (33.01 ± 14.33) |
| $\Delta_r S_m^o$ /J·K$^{-1}$·mol$^{-1}$ | (109.48 ± 6.55) | (155.14 ± 41.59) |

**[2011MOL/BRE]**

Moll *et al.* [2011MOL/BRE] investigated the complexation of Cm(III) with phosphate in 0.1 M $NaClO_4$ solutions using TRLFS. Spectra were collected after an equilibration time of ten minutes. The formation of a first phosphate complex was identified by a red shift in the spectra and an increase in luminescence intensity. These spectral characteristics were attributed to the species $CmH_2PO_4^{2+}$.

At high pH with added phosphate the spectra were interpreted by taking account of the formation of a $CmHPO_4^+$ complex as well as the formation of Cm(III) phosphate colloids. Moll *et al.* reported $\log_{10}\beta^o$ (A.618) = (22.02 ± 0.13) and $\log_{10}\beta^o$ (A.619) = (18.56 ± 0.80) for the reactions

$$Cm^{3+} + 2H^+ + PO_4^{3-} \rightleftharpoons CmH_2PO_4^{2+} \quad \text{(A.618)}$$

$$Cm^{3+} + H^+ + PO_4^{3-} \rightleftharpoons CmHPO_4^+ \quad \text{(A.619)}$$

The corresponding equilibrium obtained using the NEA selected values for the protonation of $PO_4^{3-}$ are, $\log_{10} K^o$ (A.620) = (2.46 ± 0.13) and $\log_{10} K^o$ (A.621) = (6.20 ± 0.80). These are the predominant reactions under the experimental conditions used by Moll *et al.*

$$Cm^{3+} + H_2PO_4^- \rightleftharpoons CmH_2PO_4^{2+} \quad \text{(A.620)}$$

$$Cm^{3+} + HPO_4^{2-} \rightleftharpoons CmHPO_4^+ \quad \text{(A.621)}$$

This review considers the value of $\log_{10} K^o$ (A.620) reported in [2011MOL/BRE] to be reliable and it is also consistent within the rather large uncertainty ranges from the one selected in previous reviews, $\log_{10} K^o$ (A.620) = (3.00 ± 0.50). The experimental data from Moll *et al.* provide evidence for the formation of $Cm(HPO_4)^{2+}$. However, this review does not select any thermodynamic quantity for this complex from the data in [2011MOL/BRE] due to the formation / co-existence of Cm(III)-phosphate compounds / colloids in this pH region, as also reported by the authors.

This review notes that the solubility product calculated in Moll *et al.* for amorphous Cm(III) phosphate colloids was obtained in very short-term experiments with equilibration time of about 10 minutes. The value of $\log_{10} K_{s,0}^o(CmPO_4 \cdot xH_2O(am))$ = – 20.1 reported by the authors in not selected in this review but provided for information only.

**[2011NIS/ITO]**

Nishi *et al.* measured the enthalpy increments of cubic $AmO_2$ from 335 to 1081 K and that of hexagonal $AmO_{1.5}$ between 335 and 1086 K using a twin-type drop calorimeter. The americium used to prepare these samples was high purity containing Am-243 (0.58 % non-radioactive impurity, 99.49 % of the Am was Am-243). The measured lattice parameters were in agreement with published values for the stoichiometric phases. The samples were enclosed in platinum containers, and the weights were 78.8 mg $AmO_2$ in 498.77 mg Pt and 61.77 mg $AmO_{1.5}$ in in 357.64 mg Pt. The results were fitted to a Maier-Kelly type of polynomial to derive the heat capacity The heat capacities were fitted to the following equations with errors of ± 3.3% and ± 5.1% respectively:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{AmO_2}, T) = 88.240 + 1.3150\times10^{-3}T - 3.4227\times10^{6}T^{-2} \quad \mathrm{JK^{-1}\cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Am_2O_3}, T) = 70.067 + 3.6068\times10^{-3}T - 2.4144\times10^{6}T^{-2} \quad \mathrm{JK^{-1}\cdot mol^{-1}}\ .$$

**[2011RAO/TIA2]**

Rao and Tian [2011RAO/TIA2] used TRLFS to examine the complexation of nitrate with Cm(III). Experiments were conducted at an ionic strength of 1.0 M $Na(ClO_4/NO_3)$ across the temperature range 283-358 K. An isopiestic point was observed at 594 nm indicating that there were two emitting Cm(III) species in solution. The emission peak at 592 nm was assigned to the $Cm^{3+}$ ion and the peak at 596 nm to the $CmNO_3^{2+}$ complex. Equilibrium constants reported in [2011RAO/TIA2] for Reaction (A.622) at $T$ = 283-358 K are summarized in Table A-196. SIT parameters were also calculated and reported to be largely independent of temperature, with $\Delta\varepsilon = -(0.01 \pm 0.02)$ kg·mol$^{-1}$ as an average obtained within the investigated temperature range 283-358 K. Thermodynamic quantities reported in [2011RAO/TIA2] for the complex $CmNO_3^{2+}$ are considered reliable by this review.

$$\mathrm{Cm^{3+} + NO_3^- \rightleftharpoons CmNO_3^{2+}} \qquad \text{(A.622)}$$

Table A-196: Equilibrium constants reported in [2011RAO/TIA2] for the formation of the $CmNO_3^{2+}$ complex as a function of temperature.

| $T$ /K | $\log_{10}K^{\circ}$(A.622) |
|---|---|
| 283 | (1.18 ± 0.04) |
| 298 | (1.16 ± 0.04) |
| 313 | (1.16 ± 0.04) |
| 328 | (1.15 ± 0.04) |
| 343 | (1.16 ± 0.04) |
| 358 | (1.17 ± 0.04) |

**[2012BEN/ZAO]**

The authors investigated the electronic structure, magnetic, dynamical and thermodynamic properties of NpN, PuN and AmN using *ab initio* pseudopotential and DFT methods. The complete review of this article is reported in the Appendix A for neptunium.

**[2013KON/BEN]**

New experimental heat capacity data by [2011NIS/ITO] were discussed in this review article dealing with americium oxides. A model for the Am-O phase diagram is reported by [2003THI/KON] and improved by [2011GOT/COL], using the data of [2011NIS/ITO] and their vaporization behavior from [2011GOT/COL3]. The data by [2011NIS/ITO] is accepted in [2013KON/BEN], although a higher value for the constraint at $C^{o}_{p,m}$ ($AmO_2$, 298.15 K) is set to 64.3 $J \cdot K^{-1} \cdot mol^{-1}$ as derived by [2004KON] provides at better fit of the trends in the lanthanide and actinide oxides and also accounts for experimental error due to the encapsulation of the samples in a platinum container. The standard entropy value from [2004KON] is accepted here, which leads to a slight decrease in the Gibbs energy of formation selected by the review, although still within the initial experimental error. Additionally for the $Am_2O_3$ sesquioxide, a slight adjustment is made to the standard entropy based on a more sound theoretical evaluation of the lanthanide series analogue in [2005KON/MIT] that slightly increases the lattice contribution to the entropy due to structural differences. The fitted heat capacity data of [2011NIS/ITO] also included a correction for the room temperature values as is done in $AmO_2$.

**[2013POV/FIL]**

The electronic heat capacity of americium is calculated at low temperatures (0-400 K) using a molar Gibbs thermodynamic potential model, which includes a Debye function coupled with density functional approximations (LDA + U + SO) and a temperature independent term. The electronic heat capacity is described by an electron free energy portion, a one electron contribution accounting for spin-fluctuations, and a magnetic anharmonic term. The electron free energy term is dominant up until about 100 K, whereafter the latter two terms become more important up to 300 K. The total specific heat is calculated with the $C_{lat}$ and compared to experimental [1980HAL/LEE]. The calculated values from the model are in agreement with experimental findings up to 140 K, after which the calculated values range from 1.3-3.4 % higher than in the work of [1980HAL/LEE], which is attributed to a neglect of the low temperature heat capacity in the experimental data.

**[2013SKE/PAN]**

Skerencak *et al.* have studied complex formation in the Cm(III) sulfate system using TRLFS. Two series of experiments were performed, one where the total concentration of sulfate was varied between 0.006 and 0.365 m at a constant ionic strength ($I_m$ = 2 m), and the second where test solutions at two different total concentration of sulfate, 0.05 and 0.2 m, respectively were studied at different ionic strength, $I_m$ = 1.0, 2.0. 3.0 and 4.0 m. There is a pronounced shift in the emission spectrum towards longer wavelength with increasing temperature, reflecting the formation of stronger complexes, including $Cm(SO_4)_3^{3-}$, which can only be identified at a sulfate concentration of 0.144 m and a temperature of 473 K. The reported equilibrium constants at different temperatures are shown in Table A-197.

Table A-197: Stepwise equilibrium constants, $\log_{10}K_n^o$, $n$ = 1-3 reported in [2013SKE/PAN] at different temperatures for the formation of $Cm(SO_4)_n^{3-2n}$ complexes obtained by SIT extrapolation from the experimental data at $I_m$ = 1-4 m.

| $T$ /K | $\log_{10}K_1^o$ | $\log_{10}K_2^o$ | $\log_{10}K_3^o$ |
|---|---|---|---|
| 298 | (3.45 ± 0.13) | (1.12 ± 0.44) | – (1.17 ± 1.23) |
| 323 | (3.77 ± 0.15) | (1.37 ± 0.57) | (0.12 ± 0.59) |
| 348 | (4.47 ± 0.28) | (1.56 ± 0.37) | – (0.18 ± 0.65) |
| 373 | (5.03 ± 0.72) | (1.96 ± 0.37) | (0.40 ± 0.52) |
| 393 | (5.61 ± 0.52) | (2.18 ± 0.40) | (0.90 ± 0.41) |
| 413 | (6.19 ± 0.60) | (3.01 ± 0.19) | (1.17 ± 0.34) |
| 433 | (6.50 ± 0.69) | (3.20 ± 0.15) | (1.61 ± 0.34) |
| 453 | (7.03 ± 0.80) | (3.37 ± 0.17) | (2.11 ± 0.26) |
| 473 | (7.55 ± 0.91) | (3.51 ± 0.09) | (2.37 ± 0.23) |

From the temperature dependence of the equilibrium constants Skerencak determined the molar enthalpies and heat capacities of reaction for the formation of the different complexes, these data are shown in Table A-198, where the results obtained by assuming both a constant and a temperature dependent enthalpy of reaction are shown. This review accepts these values for the complexes $CmSO_4^+$ and $Cm(SO_4)_2^-$, although the uncertainty in the heat capacity of reaction is seriously underestimated and we estimate an uncertainty of at least 50 $J \cdot K^{-1} \cdot mol^{-1}$. Spectroscopic observations in [2013SKE/PAN] provide evidence on the formation of the complex $Cm(SO_4)_3^{3-}$ at elevated temperature and high sulfate concentrations. Minor molar fractions of this species (< 0.05) are formed at $T \leq 348$ K and the sulfate concentrations studied by Skerencak *et al.*, and accordingly this review does not select any thermodynamic quantity for this complex.

Table A-198: Reaction enthalpy, entropy and heat capacity reported in [2013SKE/PAN] for the stepwise formation of $Cm(SO_4)_n^{3-2n}$ complexes with $n$ = 1-3.

| | $n$ = 1 | $n$ = 2 | $n$ = 3 |
|---|---|---|---|
| Van't Hoff | | | |
| $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | (40 ± 4) | (30 ± 6) | (62 ± 7) |
| $\Delta_r S_{m.\,298\,K}^o$ /J·K$^{-1}$·mol$^{-1}$ | (68 ± 5) | (79 ± 7) | (186 ± 9) |
| Ext. Van't Hoff | | | |
| $\Delta_r H_m^o$ /kJ·mol$^{-1}$ | (40 ± 4) | (30 ± 6) | – |
| $\Delta_r S_{m.\,298\,K}^o$ /J·K$^{-1}$·mol$^{-1}$ | (68 ± 5) | (79 ± 7) | – |
| $\Delta_r C_{p,m}^o$ / J·K$^{-1}$·mol$^{-1}$ | (280 ± 12) | (150 ± 15) | – |

Measurements of the fluorescence life-time may provide information of the number of coordinated water molecules and in this way indirect information on the number of coordinated sulfate ions and their mode of coordination, uni- or bidentate. However, the authors have not discussed this point.

**[2014KON/BEN]**

This review article discusses the heat capacity and entropy data for $AmO_2$ and $Am_2O_3$. The complete review of this article is reported in the Appendix A for uranium.

**[2014SKE/FRO]**

Skerencak-Frech *et al.* have used Cm(III) fluorescence spectroscopy to study complex formation in the Cm(III) chloride system in the temperature range 298-473 K and also studied the structure om Am(III) chloride complexes using EXAFS. The experimental details are clearly outlined as are the methods used to analyse the data. The group has extensive experience of the fluorescence method and has designed state-of-the-art equipment for the high-temperature experiments. We accept their data and will only make a few comments. The observation that the stability of the complexes increase with increasing temperature can be related to the large decrease in dielectric permittivity of water with increasing temperature, a similar effect is often found at room temperature in non-aqueous solvents. The change in the emission spectrum is small at room temperature, which makes it impossible to obtain a value of the equilibrium constant(s). The complex $CmCl^{2+}$ does not contribute significantly to the total emission even at higher temperature and no information on the equilibrium constant can therefore be obtained. The situation is different for $CmCl_2^+$ which contributes significantly from 373 K and upwards, which makes it possible to calculate the equilibrium constant at 298 K. The contribution of $CmCl_3$(aq) to the emission spectrum is small, but sufficiently large to support the formation of this uncharged species.

The present review accepts the equilibrium constant $\log_{10}\beta_2^o$ at 298 K reported by Skerencak-Frech *et al.* that is obtained from the temperature dependence of $\log_{10}\beta_2$ .

EXAFS data obtained in solutions with [$Cl^-$] of 3 m do not show any evidence of coordination of chloride and the equilibrium constant, $\log_{10}\beta_1^o = (0.24 \pm 0.03)$, selected in [2003GUI/FAN] would result in a conditional equilibrium constant in 3 m chloride, equal to $\log_{10}\beta_1$ (3 m $Cl^-$) $\approx -1.4$, that results in the presence of about 10 % $CmCl^{2+}$ in the test solution; the selected value of $\log_{10}\beta_1^o = 0.24$ is thus consistent with the EXAFS data.

**[2014TIA/SHU]**

Tian and Shuh [2014TIA/SHU] studied the complexation of americium(III) with nitrate in 1 M $HNO_3$-$HClO_4$ using spectrophotometry at temperatures ranging between 283 and 358 K. The authors used the shift exhibited in the main absorbance at 503 nm and changes in the absorbance intensity to propose the formation of the 1:1 complex, $AmNO_3^{2+}$. The authors only used the 503 nm band to determine equilibrium constants at the various temperatures, although the absorbance spectrum of the $AmNO_3^{2+}$ complex has two maxima at about 504 nm and 508 nm. Tian and Shuh used the SIT to calculate $\log_{10}K_1^o = (1.13 \pm 0.06)$ and the Van't Hoff plot to determine $\Delta_r H_m^o = (2.0 \pm 0.5)$ kJ·mol$^{-1}$, and $\Delta_r S_m^o = (9.5 \pm 3.0)$ J·K$^{-1}$·mol$^{-1}$ at 298 K.

**[2015HER/GAO]**

Herm *et al.* studied the solubility of $Nd(OH)_3$(s) and TRLFS of Cm(III) in alkaline, dilute to concentrated NaCl, $MgCl_2$ and $CaCl_2$ solutions containing varying concentrations of nitrate. All experiments were performed at $T = (295 \pm 2)$ K. The results indicated an increase in the solubility of $Nd(OH)_3$(s) in highly concentrated $Mg(NO_3/Cl)_2$ electrolytes. The authors noted that $Mg^{2+}$ may form a ternary complex with curium and nitrate and proposed the species, $Mg[CmNO_3OH]^{3+}$ and $Mg[CmNO_3(OH)_2]^{2+}$. These results indicate a possible interaction between $Mg^{2+}$ and the Cm-OH-$NO_3$ species in these solutions, however it remains unclear why such an interaction is observed only in the presence of $Mg^{2+}$ and not in analogous solutions containing $Ca^{2+}$. The proposed ternary Mg(II)-An(III)/Ln(III)-OH-$NO_3$ complexes form only at $Mg(NO_3/Cl)_2$ concentrations $\geq$ 2.8 m, which are far beyond the applicability of SIT. The Pitzer model reported by the authors explains well solubility and spectroscopic observations, but is not considered in this review for the selection of thermodynamic data.

**[2015HIN/ALT]**

This is one of the few studies involving the complexation of the Am(III) analogs Nd(III) and Cm(III) with borate species. The investigators were unable to determine the stoichiometry of Cm(III)-borate species that formed although there was evidence for at least two species in their TRLFS measurements. The solubility studies of the Am(III) analogue Nd(III) did not show any increase in the solubility of $Nd(OH)_3(s)$ in the presence of borate, but did indicate that the presence of borate at high concentration ($\geq 0.16$ M) could induce solid phase formation. The observed solubilities were similar to those for a well-defined $Nd(B_9O_{13}(OH)_4)(cr)$ solid phase. No thermodynamic data is provided in this study.

# Discussion of selected references for Technetium

**[1978BOY]**

The authors reported gravimetric isopiestic water activity measurements in binary $NaTcO_4$ and $NaReO_4$ solutions compared with aqueous binary sodium perchlorate solutions to concentrations of about 8.5 m. There was an error in the mathematical data interpretation, identified by [1991RAR/MIL]. This correction is accepted in the present review, see detailed data evaluation of [1991RAR/MIL].

**[1978BOY2]**

Both osmotic and mean activity coefficients were obtained for aqueous pertechnetic acid and perrhenic acid solutions using careful gravimetric isopiestic measurements of water activities. By comparison with Raman spectroscopy data the authors have shown that both $HTcO_4$ and $HReO_4$ remain entirely ionized up to concentrations of 6 M while condensation and hydration may occur at higher concentrations. More recent data in mixed $H_2SO_4/HTcO_4$ solutions [2010POI/WEC] have confirmed that pertechnetate remains completely dissociated in $H_2SO_4$ concentrations of up to 8 M, corresponding to water activities of 0.26. Formation of $TcO_3(OH)(H_2O)_2(aq)$ occurs at higher concentrations. However, the evaluations of [1991RAR/MIL] indicate that published smoothed values of the osmotic coefficients and mean molal activity coefficients are substantially in error. Re-analyses of the data of [1978BOY2] gave a good fit (see detailed data evaluation of [1991RAR/MIL]). This review accepts the experimental data of [1978BOY2] with its mathematical representation given by [1991RAR/MIL].

**[1979GRA/DEV]**

Using a mercury electrode, the authors studied the electrochemical reduction of pertechnetate in acidic (pH l-3.5), nearly neutral (pH 3.5-10) and alkaline media (pH > 10) with 0.5 M KCl-HCl and 0.5 M $NaHSO_4$-$Na_2SO_4$ as the supporting electrolyte. In acid media, formation of metallic Tc and dissolved Tc(III) were observed. The coulometric reoxidation of Tc(III) lead in a one electron step to a compound with a UV spectrum of a non-colloidal brown Tc(IV) complex, similar to that described as $[Tc(OH)_2(SO_4)_2]^{2-}$ by [1976SPI/KUZ] with an absorption peak at 500 nm. However, the structure of the complex of [1976SPI/KUZ] has been questioned by [2002VIC/OUV], [2003VIC/FAT] and a polymer species of Tc(IV) was identified

instead. The authors showed for acid sulfate media in the pH range 1.6-3.25 that $E_{1/2}$ changed linearly with pH:

$$E_{1/2}\,(\mathrm{V}) = (0.286 \pm 0.033) - (0.123 \pm 0.013)\ \mathrm{pH}.$$

The $E_{1/2}$ value was obtained at total Tc concentration of $6 \times 10^{-4}$ M, which in the stability range for Tc(IV) is supersaturated with respect to $TcO_2$(am). The authors therefore interpreted the data using the equation:

$$TcO_2\,(\mathrm{am}) + 2H^+ + e^- \rightleftharpoons TcO^+ + H_2O(\mathrm{l}) \qquad (A.623)$$

and

$$E = 0.319 - 0.1182\,\mathrm{pH} - 0.0591 \log_{10}[TcO^+]$$

However, no precipitate was observed in this pH range, indicating that precipitation may take longer than the duration of the experiment.

The paper is discussed in the main text of [1999RAR/RAN] to fix a bounding value for $\Delta_f G^\circ$ of $Tc^{3+}$ but no detailed evaluation in Appendix A of [1999RAR/RAN] has been provided. A review was also provided by [1983RAR]. We agree with the reviewer that in this pH region, reduction of Tc(III) to Tc(0) leads to $Tc^{3+}$ as the dominant aqueous species. The reviewer proposed to replace Reaction (A.623) by $Tc^{3+} + H_2O(\mathrm{l}) \rightleftharpoons TcO^{2+} + 2H^+ + e^-$, thus explaining the one-electron step in reduction and the consumption of two protons. From the $E^\circ$ value of 0.319 V, the CODATA values for $H_2O$ and the thermodynamic data of [1983RAR] for $TcO^{2+}$ and its correction in [1999RAR/RAN] a minimum value of $\Delta_f G^\circ_m\,(Tc^{3+}) > 89.6\ \mathrm{kJ \cdot mol^{-1}}$ was proposed [1999RAR/RAN]. The character "minimum value" stems from the fact that for $TcO^{2+}$ also only a minimum value for the Gibbs energy of formation was given in the review of [1999RAR/RAN]. However, [1999RAR/RAN] only proposed this minimum value tentatively and did not recommend it due to uncertainties in the hydrolysis scheme of Tc(III).

An almost identical $E^\circ$ value of 0.32 was deduced in the present review by analysing the work of [2009VON], which might support the selection of this value as the standard potential. However, the present review does not confirm the presence of $TcO^{2+}$. Instead of the monomer, we prefer formation of dimers of the type $Tc_2O_2(OH)_2^{2+}$ as the dominant solution complexes of Tc(IV), leading to the reaction:

$$Tc_2O_2(OH)_2^{2+} + 6H^+ + 2e^- \rightleftharpoons 2Tc^{3+} + 4H_2O(\mathrm{l})$$

The dependency of the $E$ value on pH and Tc(III) concentration for this reaction would correspondingly be:

$$E = 0.319 - 0.177\,\mathrm{pH} - 0.0295 \log_{10}[Tc^{3+}]$$

The pH dependency is steeper than that reported by the authors. The minimum value of $\Delta_f G^\circ\,(Tc^{3+})$ derived by [1999RAR/RAN] is also only valid in the proposed

speciation model. With the speciation model and the associated thermodynamic data presented in the present review, a lower $\Delta_f G_m^o (Tc^{3+})$ value is obtained:

$$\Delta_f G_m^o (Tc^{3+}) = (71.193 \pm 11.237)\ kJ \cdot mol^{-1}$$

At neutral pH the reduction of Tc(VII) results in the formation of Tc(IV), in the form of solid $TcO_2(am)$, according to the overall reaction:

$$TcO_4^- + 2H_2O(l) + 3e^- \rightleftharpoons TcO_2(am) + 4OH^-$$

The authors' Figure 8 clearly shows different $E_h$/pH diagrams for dissolved $TcO(OH)_2(aq)$ and precipitated $TcO_2(am)$. In the present work it is clear that the $TcO_2(am)$ solubility is much lower. The authors used a solubility of $10^{-5}$ M to provide a link between the $E_h$/pH diagram with precipitated $TcO_2(am)$ and a subsequent slow hydrolysis of $TcO^{2+}$ to form $TcO(OH)^+$ and $TcO(OH)_2(aq)$. However, as $TcO^{2+}$ is not stable in the studied pH range it is very unlikely that it is formed. It is more likely that hydrolysed Tc(IV) species form directly by oxidizing $Tc^{3+}$ in the given pH range without initial formation of unhydrolysed $TcO^{2+}$.

**[1991MEY/ARN2]**

This paper has been reviewed already in [1999RAR/RAN]. Because of the necessary re-evaluation of hydrolysis data in the present review, by consideration of more recent solubility data, in particular in [2015YAL], an updated evaluation became necessary. The paper summarises the results of several reports from Oak Ridge National Laboratory, USA [1986MEY/ARN], [1987MEY/ARN], [1988MEY/ARN], [1989MEY/ARN] where Tc(IV) oxide was prepared by precipitation upon purified sand with hydrazine, or by electrodeposition on a platinum mesh electrode in acidic or basic solutions.

The authors determined a hydration number between 1.38 and 2.1 for solids prepared from acidic and basic solutions. No characterisation was given for the precipitated solids. An average value of 1.9 water molecules for deposition from acid and 1.5 water molecules for deposition from basic solution can be obtained, but when studying the solubility of this oxide over a wide pH range (1-10) no clear difference in $\log_{10} K_s$ with the water content of the solid can be observed.

The concentrations of the total technetium and Tc(IV) (after separation of $TcO_4^-$ by solvent extraction) concentrations in the equilibrated solutions over the solid oxide were determined daily by liquid scintillation counting of $^{99}Tc$. Extraction to determine Tc(VII) was done with tetraphenylarsonium chloride in chloroform. It is remarkable that the amount of Tc(VII)/Tc(IV) ratio was always large, and that data were ignored only if the Tc(VII)/Tc(IV) ratio was smaller than 200, despite using a controlled atmosphere box with less than 1 ppm $O_2$. Solutions with pH values between 0 and 10 containing HCl and NaCl as inert electrolytes, sometimes containing $NaHCO_3$ and

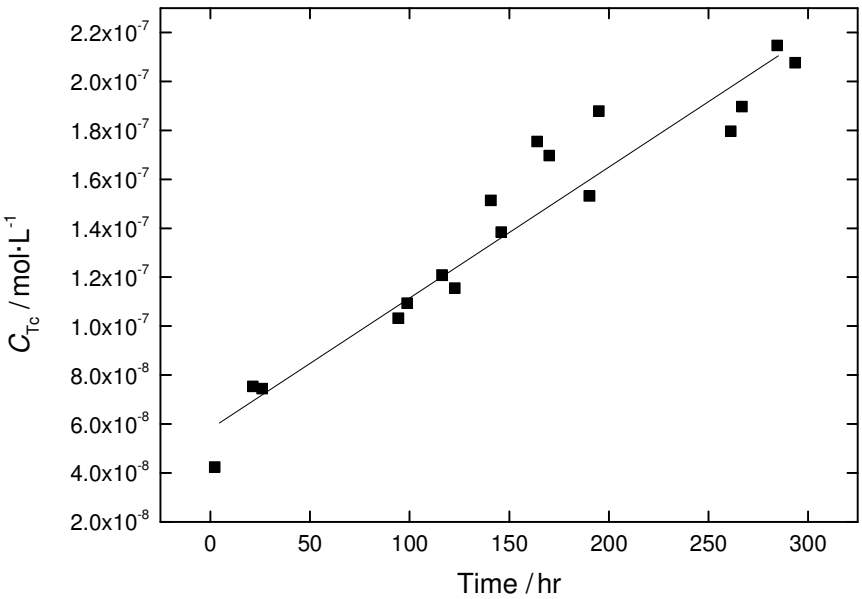
$Na_2CO_3$, have been used. The Tc solubility is not strongly dependent on the ionic strength and the chloride concentration in near-neutral solutions of 0.05 to 2.6 M NaCl.

The review of [1999RAR/RAN] has accepted the presentation of the authors, indicating that solubility measurements of $TcO_2 \cdot nH_2O$(am) in 0.1 M HCl at a fixed applied potential show a gradual increase of both Tc(IV) and Tc(VII) concentrations until a steady value was obtained after about 12 days ([1991MEY/ARN2], Figure 1). However, the establishment of steady state is only suggested based in a graphical presentation in a semi logarithmic plot. In the present review a re-evaluation of Figure 1 of [1991MEY/ARN2] was performed, presenting the digitized data in linear plot. This shows that no steady state has been reached and that the concentration has continued to rise in this low pH test, demonstrating that no equilibrium was reached. Under low pH conditions, [2004POI], [2006POI/FAT2] also report a slow achievement of equilibrium and clearly show that slow polymerisation in aqueous solution is responsible for the slow kinetics at pH < 1.5. Kinetic control of apparent solubility data at low pH is also confirmed by the solubility data of [2004HES/XIA] for the pH range 1-3, showing a slope of – 2 when approaching solubility equilibrium from oversaturation and a slope of – 1 when approaching it from undersaturation. The reinterpretation of the data of [2004HES/XIA] in the present Appendix A shows an increase of concentrations with time at pH < 1 and, after an initial rise, a decrease with time for pH values larger than 2.

[1999RAR/RAN] stated that the data interpretation in strongly acidic solutions is doubtful, due to potential presence of chloride complexation, and only an upper value for the stability of $TcO^{2+}$ can therefore be deduced from the data. However, [1999RAR/RAN] considered the first protonation reaction of $TcO(OH)_2$(aq) well established, and, based on the three points at pH values 3.01, 2.16 and 1.27 ([1991MEY/ARN2], Figure 3) a stability constant $\log_{10}\beta$ of (2.5 ± 0.3) was deduced for the reaction $TcO(OH)_2(aq) + H^+ \rightleftharpoons TcO(OH)^+$. Because equilibrium has not been reached, the present review does not accept this interpretation.

No kinetic data exists in the more alkaline pH range (predominance of $TcO(OH)_3^-$), but consistency with other published solubility data in this pH range [2007LIU/YAO], [2015YAL], [2016YAL/GAO] indicates that equilibrium has been achieved.

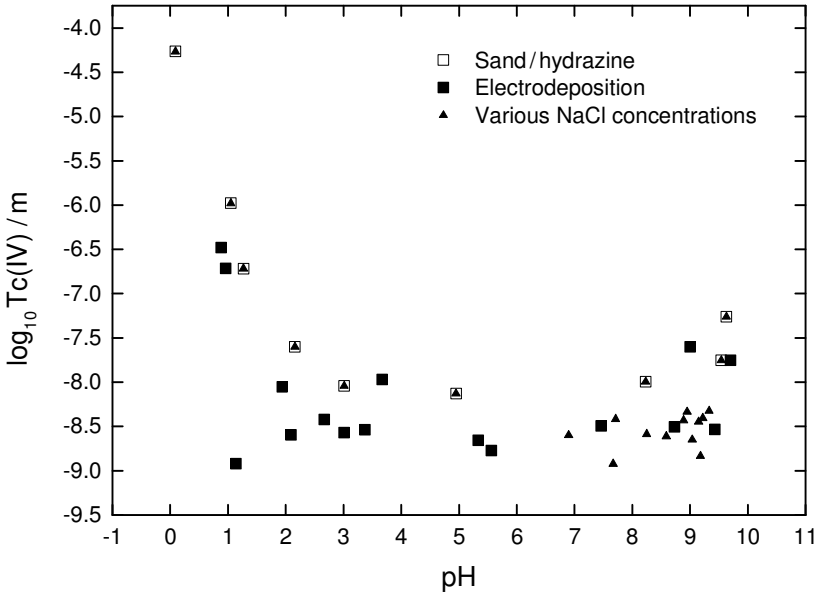
Figure A-30: Reinterpretation of the time dependence of solubility data of $TcO_2 \cdot nH_2O$(am) of Figure 1 of [1991MEY/ARN2] in 0.1 M HCl. Reported data in semi-log form indicate equilibrium after 300 hours.




Equilibrium was reached after 50 hours (Figure 2 of [1991MEY/ARN2]) at pH 9.27, as indicated by constant Tc(IV) concentrations. Under these conditions $TcO(OH)_2$(aq) is the dominant hydrolysis species. The present review accepts the data of [1991MEY/ARN2] as equilibrium values, in the range where $TcO(OH)_2$(aq) is dominant.

Disregarding kinetic constraints of the data in the low pH range, an analysis of the data of [1991MEY/ARN2] using a model with dimeric species is presented as follows: Figure A-31 shows the pH dependency of solubility data obtained both with tetravalent Tc hydrated oxide formed by electrodeposition or by hydrazine on sand. Triangles correspond to solubility experiments performed as a function of NaCl concentration using $TcO_2 \cdot nH_2O$(am) formed with hydrazine/sand.

Figure A-31: Presentation of solubility data of $TcO_2 \cdot nH_2O$(am) of [1991MEY/ARN2].




The data were interpreted either by the model of [1999RAR/RAN] or by a model using a bi-charged cationic dimer hydrolysis species instead of $TcO^{2+}$ and $TcO(OH)^{+}$ as developed in the present review. Table A-199 shows the resulting constants and their uncertainties:

Table A-199: Comparison of stability constants obtained by the interpretation of solubility data of [1991MEY/ARN2] by either the hydrolysis model of the present review considering the presence of a $2^{+}$-charged dimer hydrolysis species or by the model of [1999RAR/RAN].

| | electro-deposited | σ | hydrazine | σ | hydrazine | σ | all data | σ |
|---|---|---|---|---|---|---|---|---|
| Present review | | | I = 0 | | all I ≤ 2 | | | |
| $\log_{10}K_s$ ($TcO(OH)_2$(aq)) | – 8.48 | 0.18 | – 8.02 | 0.11 | – 8.49 | 0.13 | – 8.46 | 0.13 |
| $\log_{10}K$ ( $Tc_2O_2(OH)_2^{2+}$ ) | 11.56 | 0.51 | 12.01 | 0.29 | 13.02 | 0.34 | 2.22 | 0.34 |
| $\log_{10}K$( $TcO(OH)_3^-$ ) | – 9.23 | 0.58 | – 9.22 | 0.25 | – 9.29 | 0.37 | – 9.31 | 0.39 |
| Model [1999RAR/RAN] | | | | | | | | |
| $\log_{10}K_s$($TcO(OH)_2$(aq)) | – 8.52 | 0.23 | – 8.19 | 0.38 | – 8.58 | 0.17 | – 8.55 | 0.17 |
| $\log_{10}K$($TcO(OH)^+$) | 2.08 | 0.45 | 3.15 | 0.45 | 3.54 | 0.26 | 2.78 | 0.29 |
| $\log_{10}K$( $TcO(OH)_3^-$ ) | – 9.12 | 0.62 | – 8.99 | 0.67 | – 9.12 | 0.4 | – 9.15 | 0.42 |

The solubility data where fitted either individually for each set (electrodeposited, hydrazine/sand with and without data in order to assess the impact of NaCl on solubility up to $I = 2$ M) and as well all data together. The data were insensitive to the potential presence of $TcO^{2+}$, hence no constant could be obtained. The data show that there is no statistical reason to treat each dataset separately, the uncertainties are similar when all data are analysed together, whichever method of solid preparation is used. The uncertainties for the hydrolysis model of [1999RAR/RAN] are similar to those of a model with a dimeric $2^+$-charged cationic hydrolysis species. Nevertheless, as expected from the non-equilibrium conditions in the low pH region, the derived stability constants for the dimer are lower than those selected in the present review. No data are available that might indicate whether data in the low pH regime are governed by the presence of polymeric or monomeric species. Also, based on uncertainty analyses, data are non-conclusive as to whether mono- or bi-charged hydrolysis species are dominant in the acid range. The solubilities of the Tc(IV) oxide from different precipitates lie between $10^{-9}$ and $10^{-8}$ M for solutions with pH > 2 . The average value of 23 solubilities measured between pH values 5 and 9.5 (*i.e.*, the pH range in which no side reactions such as protonation or deprotonation of $TcO(OH)_2(aq)$ occur) is $(3.6 \pm 2.1) \times 10^{-9}$ M, excluding high concentration values between pH 9 and 10. We include this value in the statistical evaluation for the solubility of $TcO_2 \cdot nH_2O(am)$. The high constant determined for $TcO(OH)_3^-$ is a result of the exclusion of four high concentration data-points between pH 9 and 10. Other data at the same pH do not show any increase. One of the four data points is at pH 9 and corresponds to freshly precipitated material (the only data point on the alkaline side with freshly formed solid), hence this data cannot be used to constrain the fit. Other high values at pH 9.7 concerns experiments at 0.01 M $NaHCO_3$ or in carbonate containing groundwater. Carbonate complexation increases solubility at pH 9.7 according to the model of this review by only 0.01 $\log_{10}$ units. High Tc concentrations may also result as equilibrium values from the possible existence of $TcO_4^-$. Indeed, the authors accepted all data with high excess concentrations of Tc(VII) except those in which Tc(VII) concentrations are more than 200 times higher than Tc(IV). Liquid-liquid extraction may not be entirely effective if concentration differences of the two oxidation states are very high. Considering that the other data of [1991MEY/ARN2] indicates that the solubility does not increase at pH 9-10, the present review does not give any weight to these high concentration data points, a decision which is the same as that of the authors.

In summary, only stability constants for $TcO(OH)_2(aq)$ where derived from the data of [1991MEY/ARN2] to constrain a hydrolysis model for Tc(IV).

**[1997KON/NEC]**

In a very carefully study, the authors made gravimetric isopiestic vapor pressure experiments with aqueous $NaTcO_4$, mixed $NaTcO_4$-NaCl, and NaCl reference solutions

(Tantalum cups, temperature accuracy 0.05 °C, four-fold repetition, concentration uncertainty to 0.2 %). The paper was already discussed in [2003GUI/FAN]. In the following, some additional aspects are discussed.

The osmotic coefficients of the binary and ternary solutions are used to evaluate Pitzer parameters. The results of the authors for $NaTcO_4$ agree excellently with the data of [1978BOY] recalculated by [1991RAR/MIL] with the maximum deviation of 0.2 %. This confirms as well the high quality of the experimental data of [1978BOY]. The authors claim that their binary Pitzer parameter agrees slightly better to the results than the one of [1991RAR/MIL], which is only true for experiments with maximum $NaTcO_4$ concentrations of 7.3278 m studied in the present study, while the [1991RAR/MIL] data agree better to the overall experimental range until concentrations of 8.5 m. This review recommends using the Pitzer parameters of the study of [1991RAR/MIL] or the derived SIT interaction parameters of the joint dataset.

The solubility of $CsTcO_4$ is determined in 0-7.4 m CsCl and in 0-5.6 m NaCl solutions. The caesium pertechnetate was prepared by precipitation, neutralizing an aqueous $Cs_2CO_3$ solution with $HTcO_4$ leading to the formation of a white precipitate, which was recrystallized in water. No additional characterisation of the solid was reported. The results of the solubility measurements were reproducible with a precision of ± 2 %. A solubility constant of $\log_{10} K_s^\circ (CsTcO_4) = -(3.622 \pm 0.02)$ was obtained from an overall fit of solubility data both in NaCl and CsCl solutions. Activity coefficients for $TcO_4^-$ in CsCl solutions can be obtained from the reported solubility data. Together with Pitzer parameters for $Cs^+$-$TcO_4^-$ derived from solubility experiments and for $Na^+$-$TcO_4$ derived from isopiestic data, this solubility constant describes well experimental solubility data from 0 to 7 m with 0.5 % of accuracy [1997KON/NEC]. The solubility constant is, within the error range similar to the value $-(3.65 \pm 0.13)$, recommended in [1999RAR/RAN], the solubility constant of $CsTcO_4$ recommended by [1997KON/NEC] that was included in Table V-36 of [1999RAR/RAN] and also included in their evaluation of $\log_{10} K_s^\circ$, even though the data of [1997KON/NEC] was not evaluated in the review. The present review retains this selected value, considering the fact that the solid of [1997KON/NEC] was not further characterised.

The solubility data of the authors were used in the present review to derive SIT parameters. SIT interaction parameters $\varepsilon_1$ and $\varepsilon_2$ for CsCl were obtained from the mean activity coefficients reported by [1972HAM/WU]. Only up to a concentration of 2 m, the SIT model describes well the published data and up to 5 m, deviations between model and data remained less than 10 %. The obtained interaction parameters for $Cs^+$-$Cl^-$ were $\varepsilon_1 = (0.058 \pm 0.001)$ kg·mol$^{-1}$ and $\varepsilon_2 = (0.067 \pm 0.002)$ kg·mol$^{-1}$.

Figure A-32: Mean activity coefficient of CsCl: comparison of [1972HAM/WU] data with model data using SIT theory. Fit by concentration dependent $\varepsilon(Cs^+, Cl^-)$ = – (0.058 ± 0.001) + (0.067 ± 0.002) log(m).

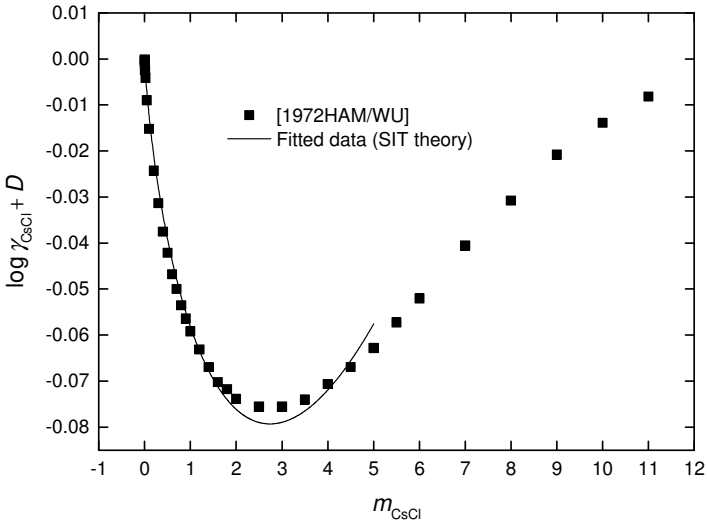
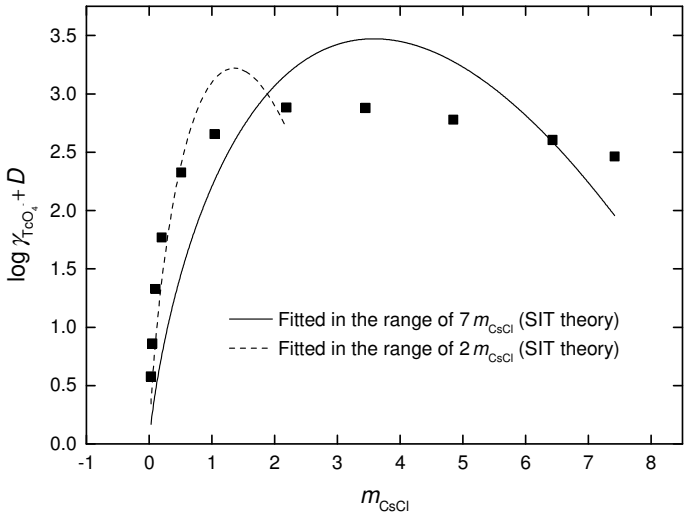



Figure A-33: Single ion activity coefficient for $TcO_4^-$ in CsCl solutions and comparison to two SIT model curves for validity ranges to either 2 or 7 m CsCl.

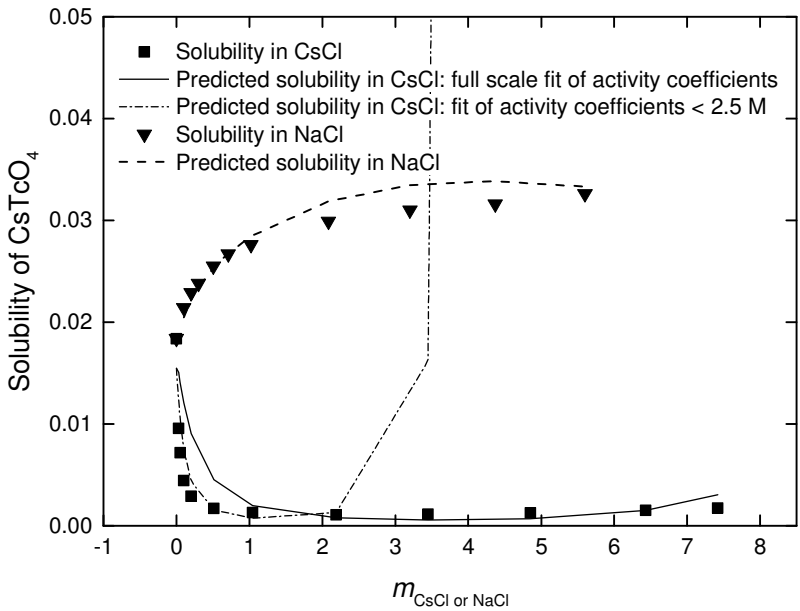


Using the equation $\log_{10} m_{CsTcO_4} = 1/2\,(\log_{10} K_s^o - \log_{10}\gamma_{Cs^+} - \log_{10}\gamma_{TcO_4^-})$ with the solubility constant and the single ion activity coefficient for $Cs^+$ in CsCl, one obtains the single ion activity coefficient for $TcO_4^-$ in CsCl. Interaction coefficients $\varepsilon_1$ and $\varepsilon_2$ for $TcO_4^-$ were obtained by fitting these data.

The quality of the fit is low in the entire concentration range (up to 7.5 m), demonstrating the limits of SIT theory for this type of data. A better fit was obtained when the concentration range was limited to 2.2 m.

For the interaction $Cs^+$-$TcO_4^-$ in the concentration range < 7 m, $\varepsilon_1 = (2.206 \pm 0.290)$ kg·mol$^{-1}$ and $\varepsilon_2 = -(2.231 \pm 0.372)$ kg·mol$^{-1}$ and for the concentration range < 2.2 m, $\varepsilon_1 = (3.098 \pm 0.259)$ kg·mol$^{-1}$ and $\varepsilon_2 = -(5.471 \pm 0.823)$ kg·mol$^{-1}$. If higher accuracy is needed for the overall concentration range, the Pitzer data of the authors must be used.

Figure A-34: Comparison of solubility data of $CsTcO_4$ in either CsCl or NaCl solutions with model curves using SIT theory.




The new set of SIT parameters can then be used to assess the solubility of $CsTcO_4$ in CsCl. As expected, it was not possible to obtain a reasonable representation of solubility data for the whole concentration range. If the SIT parameter for the whole concentration range were used, the representation of solubility data at low CsCl

concentration is not good but the interaction coefficients derived for the limited concentration range results in predicted solubility at higher concentrations that is meaningless. Better solubility data representation was obtained for $CsTcO_4$ solubility in NaCl solutions. In this case the SIT interaction coefficients derived from the joint data set of isopiestic data of the present author and of [1991RAR/MIL] were used (see Appendix "ionic strength corrections"). No fit to solubility data of $CsTcO_4$ solubility in NaCl solutions was performed.

Due to the limitation of the SIT theory in this system, no interaction coefficient is selected for $Cs^+$-$TcO_4^-$.

**[1998NEC/KON2]**

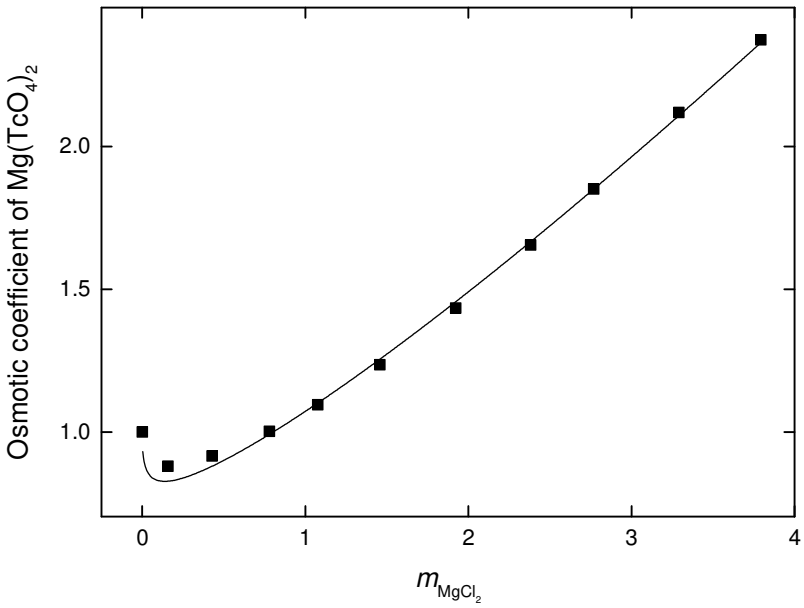
This is a combined isopiestic and solubility study. The paper was already discussed in [2003GUI/FAN]. Here some additional data are derived. The authors used very carefully performed (tantalum cups, temperature accuracy 0.05 °C, four-fold repetition, concentration uncertainty to 0.2 %) gravimetric isopiestic vapour pressure experiments at 25 °C with $Mg(TcO_4)_2$ solutions and with ternary mixtures containing various combinations of $NaTcO_4$, $Mg(TcO_4)_2$, NaCl, $MgCl_2$, $Na_2SO_4$, and $MgSO_4$. The osmotic coefficients of the binary solutions are used to evaluate the binary Pitzer parameters $\beta(0)$, $\beta(1)$, and $C(0)$ for $Mg(TcO_4)_2$. The binary parameters for $KTcO_4$ and $Ca(TcO_4)_2$ are evaluated from solubilities of $KTcO_4$ in KCl and $CaCl_2$ solutions, respectively. Pitzer mixing parameters are obtained from either osmotic coefficients or solubilities in the corresponding ternary mixtures.

Using the isopiestic data (osmotic coefficients) of the $Mg(TcO_4)_2$ system, SIT interaction parameters were obtained from a fit given in Figure A-35.

The quality of the fit is reasonable for high concentrations but significant deviations occur at low concentrations. The interaction parameters for $Mg^{2+}$- $TcO_4^-$ were $\varepsilon_1 = (0.082 \pm 0.015)$ kg·mol$^{-1}$ and $\varepsilon_2 = (0.167 \pm 0.016)$ kg·mol$^{-1}$.

For solubility studies, solids where carefully prepared, in order to avoid the formation of carbonates and to control the degree of hydration. The solubility of water free $KTcO_4$ was determined in 0-4.5 m KCl, in 0-4.65 m $MgCl_2$, in 0-4.36 m $CaCl_2$ and 0-0.617 $K_2SO_4$ solutions. The solubility measurements had an uncertainty of ± 0.25 %. A solubility constant of $\log_{10} K_s^o (KTcO_4) = -(2.239 \pm 0.013)$ was obtained from the fit to the solubility data in KCl solutions. Activity coefficients for $TcO_4^-$ in KCl solutions can be obtained from the reported solubility data using an $\varepsilon(K^+, Cl^-)$ value of 0 [2003GUI/FAN].

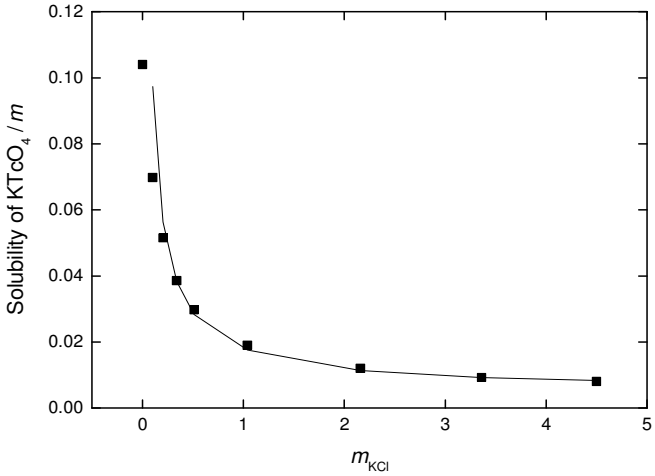
Figure A-35: Osmotic coefficients of $Mg(TcO_4)_2$ in $MgCl_2$ solutions and comparison to model data using SIT theory.




Using the equation $\log_{10} m_{KTcO_4} = 1/2\,(\log_{10} K_s^{\circ} - \log_{10} \gamma_{K^+} - \log_{10} \gamma_{TcO_4^-})$ with the solubility constant and the ion activity coefficient for $K^+$ in KCl, we obtain the ion activity coefficient for $TcO_4^-$ in KCl (see Appendix B). Application of these data to the solubility curve is shown in Figure A-36.

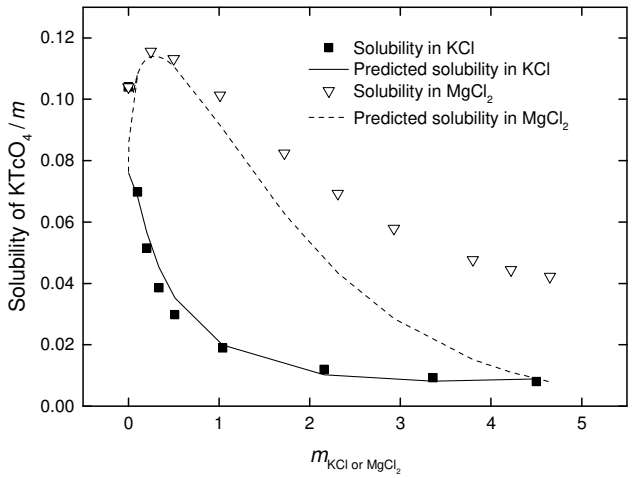
The quality of the fit over the whole concentration range (up to 4.5 m) is very good. If higher accuracy is needed in the entire overall concentration range, the Pitzer data of the authors should be used.

Figure A-36: Solubility of $KTcO_4$ in KCl solutions as function of concentration and comparison to model curves using the SIT theory.




The new set of SIT parameters can then be used to assess the solubility of $KTcO_4$ in KCl and $MgCl_2$ (Figure A-37).

Figure A-37: Solubility of $KTcO_4$ in either KCl or $MgCl_2$ solutions as function of molality. Comparison of experimental data with model curves obtained by using the SIT theory.



It is not surprising that there is a good representation of solubility data in KCl (the SIT coefficients where derived from these solubility data), while the agreement for solubility data in $MgCl_2$ solutions is only satisfactory up to about 1 m; presumably the SIT parameters obtained from osmotic coefficients are not sufficiently reliable (low concentration data show significant deviation). For this reason, only interaction parameters for $K^+$-$TcO_4^-$ are recommended in this review.

**[1999BEN] and [2000BEN/FAT]**

The authors studied the speciation and the redox reactions of technetium both in chloride and in carbonate medium. The experiments were conducted under $N_2$ atmosphere in degassed solutions. The progress of reduction was followed by variation of distribution ratios of Tc using liquid extraction with tetraphenylarsoniumchloride, TPACl and in some cases by UV-visible and Raman spectroscopy. In chloride medium (1 M HCl) the concentration ratio of $TcO_4^-$/Tc(IV) was determined in the presence of the redox couple Fe(III)/Fe(II), which has a very well-known redox potential. No absorption bands of Tc(V) in form of $TcOCl_5^{2-}$ (at 229 and 295 nm) were observed and since $Fe^{2+}$ in 1 m HCl is not capable to reduce Tc(VII) to Tc(III) the author concluded that Tc(VII) has been reduced to Tc(IV). The concentrations of technetium were varied between $10^{-11}$ and $10^{-4}$ M ($10^{-11}$ M using $^{99m}$Tc and $10^{-6}$ and $10^{-4}$ M using $^{99}$Tc). The effect of kinetics on the reduction reaction has been followed in some experiments up to 200 hours. Different ratios $[Fe^{3+}]/[Fe^{2+}]$ between 0.014 and 333 have been used to reduce $TcO_4^-$ in HCl. The potentials fixed by these ratios varied between 0.590 and 0.849 V *vs*. SHE. At a constant Fe(III)/Fe(II) ratio of 0.014, the reduction rate increased with increasing $Fe^{2+}$ concentrations. The reduction rate also increased at increasing $H^+$ concentrations. If the reaction time is sufficiently long, reduction can become complete at this Fe(III)/Fe(II) ratio for equilibrium times longer than 80 hours and at Fe(II) concentrations smaller than 0.01 M. Equilibrium was not attained in 50 hours in solutions of $10^{-11}$ M Tc at Fe(III)/Fe(II) ratios of unity but it appears to be attained (constant concentration of remaining Tc(VII) between 50 and 200 hours, Figure 3-5 of the authors) for Tc concentrations of $10^{-6}$ M and Fe(III)/Fe(II) ratios of 5. Dissolved oxygen strongly slowed down the reduction rate. In the absence of equilibrium, the author concluded that the corresponding $E°$ values were underestimated.

At 1 m HCl, the author observed a pseudo-equilibrium between spectroscopically identified $TcCl_6^{2-}$ and an unidentified Tc(IV)(aq) species at a concentration ratio 0.8. This was interpreted as an equilibrium $TcCl_6^{2-} \rightleftharpoons TcCl_5^- + Cl^-$ corresponding to an equilibrium constant of 1.25. As the species in this experiment were not characterisatised, the present review does not accept this value. In fact, neither $TcCl_6^{2-}$ nor $TcCl_5^-$ are stable under these conditions (see Figure IV-3 in [2004POI]). Equilibrium times are probably too short. Necessary equilibrium times are longer than ten days and equilibrium values are influenced by light [2004POI], [1998BEN/FAT].

**[2003VIC/FAT]**

The authors studied Tc(IV) chemistry in mixed chloride/sulfate acidic media under inert gas. Reduced samples were stored in an inert gas box with $O_2 < 5$ ppm. Two methods were employed: either the Tc(IV) chemistry was studied with $K_2TcCl_6$ as starting material, or by reduction of Tc(VII) at a large surface platinum electrode. Starting from $TcCl_6^{2-}$, in 3 M $Cl^-$ solutions and for pH lower than 0.6, $TcCl_5^-$ was the dominant solution complex of Tc(IV) . The authors observed the formation of polymer species at higher pH, although the reaction is very slow (3000 hours). The substitution of the $Cl^-$ ions of $TcCl_6^{2-}$ in various media ($Cl^-$, $SO_4^{2-}$, $TFMS^-$) at various pH or the electroreduction of pertechnetate ions in the same media led to a common Tc(IV) species characterised by a UV-visible absorption peak at 500 nm. A species with this absorption peak was already observed by [1976SPI/KUZ], formed during the electroreduction of dissolved Tc(VII) at a platinum electrode in aqueous $H_2SO_4$. [1976SPI/KUZ] assigned the stoichiometry $Tc(SO_4)_2(OH)_2^{2-}$ to this complex. However, Vichot *et al.* [2003VIC/FAT] have shown that the species with an absorption at 500 nm is a polymer. A good fit of spectral changes from $TcCl_5^-$ to the polymer with increasing pH was obtained both with a polymer nuclearity of 2 and 3 (see Figure 3 of the authors). The authors argued that the fit is better for a trimer than a dimer, but the present review cannot see a significant difference between the two, in addition no uncertainty analyses has been presented by the authors.

The authors looked at additional evidence for a trimer rather than a monomer by analysing the pH variation for the oxidation of the polymeric species by $H_2O_2$. However, this pH variation does not only depend on the nuclearity but also on the number of OH groups in the polymer species and we do not accept this additional evidence.

Vichot *et al.* also speculated on the reasons why trimeric Tc(IV) oxo-complexes, rather than dimeric ones are formed, as in the compounds or complexes already prepared, are present in sulfate solutions. Indeed many compounds are known containing $Tc(\mu\text{-}O)_2Tc$ dimers, where additional ligands which surround the Tc(IV) are strong polydentate complexing agents such as oxalate [1990ALB/AND]; 1,4,7-triazacyclononane [1989LIN/DEW] or ethylene diamine tetra-acetate [1981BUE/AND]. These species have characteristic UV absorption peaks at 500 nm. However, the authors rejected the dimer hypothesis due to analogy with stable $Mo_3O_4^{4+}$ complexes and the observation in literature [1987COL/WIL] of formation of stable trimeric species such as $(AsPh_4)_2Tc(C_2O_4)_3$. [2004POI] has shown that the reported EXAFS spectrum corresponds to $Tc(\mu\text{-}O)_2Tc$ bridges like in $TcO_2{\cdot}nH_2O$(am), which is incompatible with a $Tc_3O_4^{4+}$ structure. Hence, the present review considers the data of the authors as further evidence for the existence of a dimeric species of the type $Tc_2O_2(OH)_2^{2+}$ as deduced principally from solubility data.

Vichot *et al.* used capillary electrophoresis to determine the neutral character of the polymer species, which is inconsistent with the solubility data discussed in the present review.

At pH 0 and 3 M $Cl^-$, $TcCl_5^-$ is the dominant species. At higher pH it transforms to another species. Based on analogy to structures of solids, the authors assigned it the stoichiometry $TcCl_5(OH)^{2-}$. However, the present review considers this assignment as speculative. According to more recent data of [2004POI], [2006POI/FAT2], the monomer chloride complexes are polymerising at higher pH and give $Tc_2OCl_{10}^{4-}$ with the equilibrium constant $\log_{10}K\ (I = 3\text{M}) = (4.67 \pm 0.07)$ for the reaction $2TcCl_5^- + H_2O(l) \rightleftharpoons Tc_2OCl_{10}^{4-} + 2H^+$. After a further pH increase, species having UV spectra with the 500 nm band are obtained. These species are Tc(IV) polymers with Tc-O-Tc bonds. An equilibrium constant $K = [Tc_3O_4^{4+}]\cdot[Cl^-]^{15}\cdot[H^+]^5/[TcCl_5(OH)^{2-}]^3 = 10^{9.53}$ has been determined for the reaction

$$3TcCl_5(OH)^{2-} \rightleftharpoons Tc_3O_4^{4+} + 15Cl^- + 5H^+$$

from the spectroscopic analyses of the reactions at different pH. Temperature was not reported and is presumably room temperature. The transition between the chloride complexes and the trimeric hydrolysis species was observed at pH 1.4 in a 3 M NaCl solution. For comparison, [2004POI] observed this transition at pH 1.1 and the hydrolysis and chloride complexation model used in the present review, calculates a pH of transition of 0.8 in 3 M NaCl.

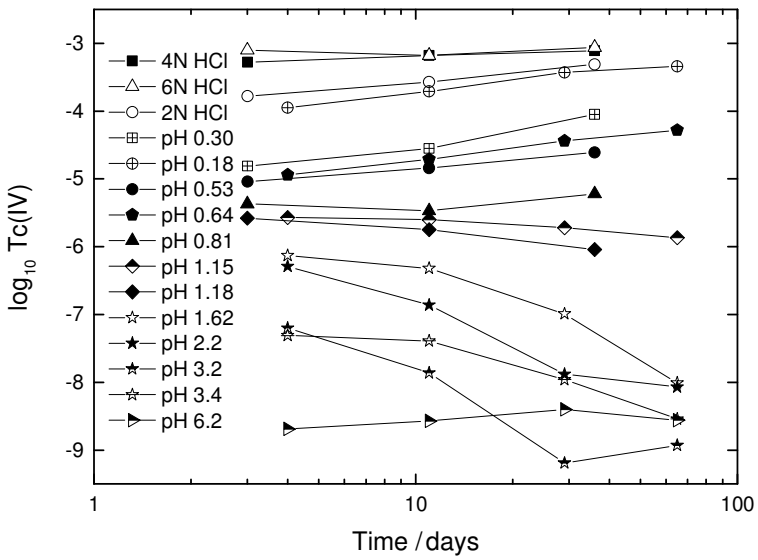
**[2004HES/XIA]**

The authors performed solubility studies of $TcO_2\cdot nH_2O$(am) both from over and under-saturation and using equilibrations between 3 and 66 days. Most data were collected for 11 days. Variables studied were pH and chloride concentration. Experiments were performed in an inert gas box and hydrazine was used to obtain reducing conditions, although a few experiments were performed using $Eu^{2+}$ as reductant. All experiments showed presence of Tc(VII) which was removed by solvent extraction prior to Tc(IV) analyses. Solid phases were characterised by XRD. A thermodynamic model was developed that included chemical potentials of the Tc(IV)-chloro species and Pitzer ion-interaction parameters for Tc(IV) hydrolysed species with bulk electrolyte. The paper provided UV spectroscopic analyses of the experimental data, however, assignment of peaks and spectra to the various hydrolysis species has been done by first identifying the dominance range of a given species from the model of [1999RAR/RAN]. Hence, the spectroscopic analyses do not provide an independent check of solution speciation. In fact, the spectrum with a peak at 329 nm was assigned by the authors to $TcO^{2+}$, while by EXAFS and UV spectroscopy, [2004POI] has shown that this spectrum belongs to a polymer of the type $Tc_nO_y^{(4n-2y)+}$. Again, in solutions between $pC_{H+} = 0.1$ and 1.1 and

$Cl^-$ concentrations between 1 and 2.5 M the authors observed the formation of $TcCl_4(aq)$, identified by spectrum with a peak at 350 nm. However, in about the same range of pH and concentration of chloride and Tc, [2004POI] identified both $Tc_nO_y^{(4n-2y)+}$ and $Tc_2OCl_{10}^{4-}$. The latter species also has a peak at 350 nm. In summary, in contrast to the identification of $TcCl_6^{2-}$, which is well-known, this review does not accept the assignment of spectra to species $TcO^{2+}$ and $TcCl_4(aq)$ given by the authors.

A kinetic analysis of the data in 0.02 m hydrazine is shown in Figure A-38. This analysis shows that most data collected are non-equilibrium values. Eleven days of experiment is not always sufficient to obtain equilibrium. We can distinguish various kinetic regimes with respect to attainment of equilibrium.

Figure A-38: Kinetic analysis of solubility data of $TcO_2 \cdot nH_2O$(am) by [2004HES/XIA] in 0.02 m hydrazine.




(1) In very acidic conditions (6 M HCl), constant concentrations are established rapidly. However, it is unlikely that these are equilibrium concentrations since final concentrations of Tc(IV) were about 1 mM, whereas the total starting concentration in the reactors was about 2 mM and where about 35 % of the dissolved Tc was identified as Tc(VII). This review suggests that these data might be controlled by complete dissolution and partial oxidation of the quantity of Tc(IV) added.

(2) In the pH range between 4 M HCl and pH 0.8, solution concentrations continue to rise with time without reaching an equilibrium value. Similarly, data of [2006POI/FAT] and our new interpretation of the data of [1991MEY/ARN] in this pH range demonstrate a very slow increase of the solution concentration, probably governed by polymerisation kinetics of hydrolysis species. None of these data can be used to constrain solubility models.

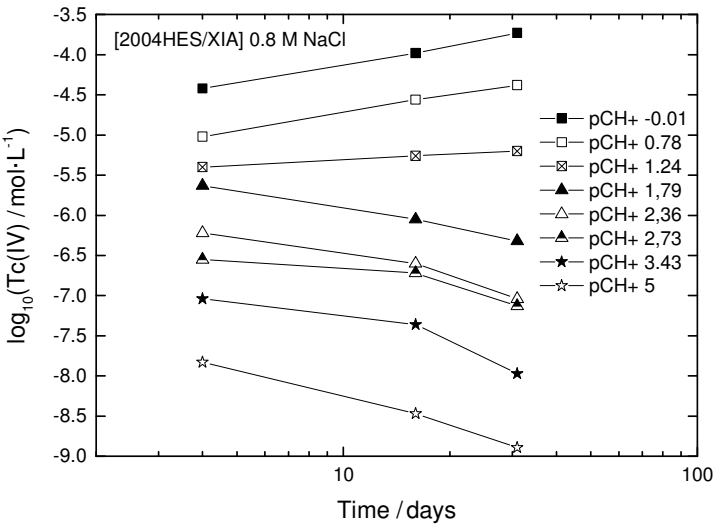
(3) At pH 1.1 to pH 1.2 solution concentrations decrease with time without reaching an equilibrium value. Also these data cannot be used to constrain solubility data.

(4) Between increasing concentrations for pH < 0.8 and decreasing concentration > pH 1.1 one can expect a domain of constant concentration at about pH 1 of $\log_{10}C = -5.5$.

(5) At pH between 3.2 and 6.2, 66 days are sufficient to achieve final equilibrium concentration values of $\log_{10}Tc(IV) = -(8.69 \pm 0.23)$.

(6) At all pH values between 1.1 and 3.2, equilibrium is approached from oversaturation (decreasing concentrations) despite the designation of the tests as undersaturation tests. This may be due to rapid dissolution of very fine particles (effect of particle size) and slow recrystallization, corresponding to some type of Oswald ripening process.

Figure A-39: Kinetic analysis of solubility data of $TcO_2 \cdot nH_2O$(am) by [2004HES/XIA] in 0.8 M NaCl.



At 0.8 M, 2.5 M and 5 M NaCl the evaluation of the evolution of solution concentrations with time is shown in Figure A-39 - Figure A-41.

Figure A-40: Kinetic analysis of solubility data of $TcO_2 \cdot nH_2O$(am) by [2004HES/XIA] in 2.5 M NaCl.

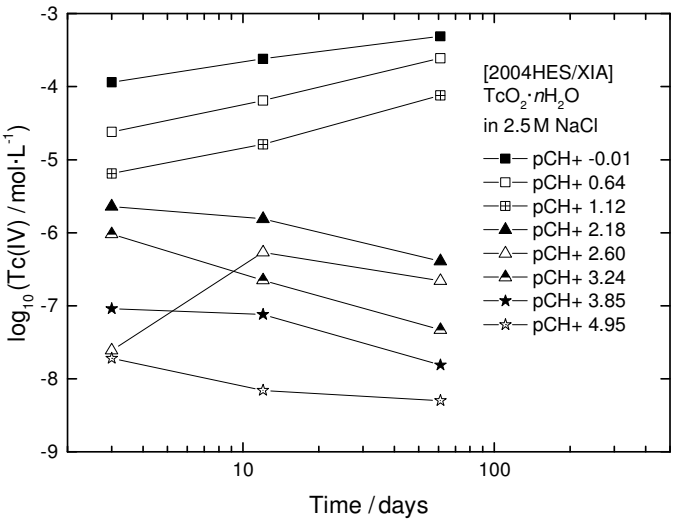
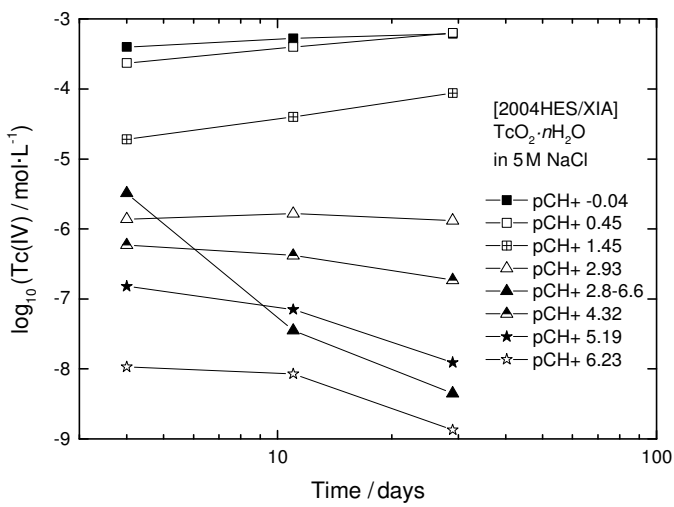



Figure A-41: Kinetic analysis of solubility data of $TcO_2 \cdot nH_2O$(am) by [2004HES/XIA] in 5 M NaCl.



The data in Figure A-38 to Figure A-41 show clear concentration changes with time indicating that solubility equilibrium is not attained. The data below pH 1.3 (0.8 M NaCl), below pH 1.2 (2.5 M NaCl), or below pH 1.5 (5 M NaCl) show an increase in concentration of Tc with time, whereas data above pH 1.7 (0.8 M NaCl), above pH 2.1 (2.5 M NaCl) or above pH 2.8 (5 M NaCl) show a decrease. The present evaluation shows that the rate of establishment of solubility equilibrium is slower at higher ionic strength than at lower one.

Only the data at pH 2.93 in 5 M NaCl indicate achievement of constant concentration, but since concentrations either rise or fall both at higher and at lower pH, the present review consider the behaviour at pH 2.93 to correspond to a steady state between between increasing polymer formation in solution and Oswald ripening of the solid phase, rather than to an equilibrium state. Looking at the concentration trends in the figures, one is tempted to discard all data from the overall analyses since they are kinetically controlled. However, comparison to other data in the present review indicates that it may be useful to study the short term and long term data in separate analyses. Indeed, $\log_{10} K_s^o$ values obtained from data for longer times, are within reported uncertainties, rather similar to data from other authors, obtained for similar time periods. There seems to be only little change of the Tc(IV) solubility between 24 and 180 days. Therefore, both short (6 days) and long term data were used for slope analyses (equilibrium concentration as function of pH) in order to identify limiting solution complexes in the two time regimes. Slopes in short term tests were lower than – 1, which does not match any model of hydrolysis complex formation.

Results from experiments approaching solubility equilibrium from oversaturation are shown in Figure A-42. Again all data have not achieved equilibrium because the concentrations continue to decrease, often with a slope smaller than – 1. The only conclusion that can be taken from this diagram is that final concentrations remain larger than equilibrium concentrations, hence, that $\log_{10} K_s$ values for $TcO(OH)_2 \cdot nH_2O$ are smaller than – 8.70 (three final values for pH > 3.3). The design of the study where equilibrium was approached from either over- or undersaturation was thought as a method to prove achievement of equilibrium. However, as has been shown in Figure A-38 for the pH range of Figure A-43 in low ionic strength solutions, solution concentration of Tc(IV) decrease also in the so-called undersaturation experiments. Hence, in both cases equilibrium is reached from the same direction. Combining with the data from Figure A-38, we can conclude that $\log_{10} K_s$ values are equal or smaller to (8.70 ± 0.23).

Figure A-42: Solution concentrations in short term tests (11-16 days) as a function of pH and ionic strength. Slopes are lower than – 1.

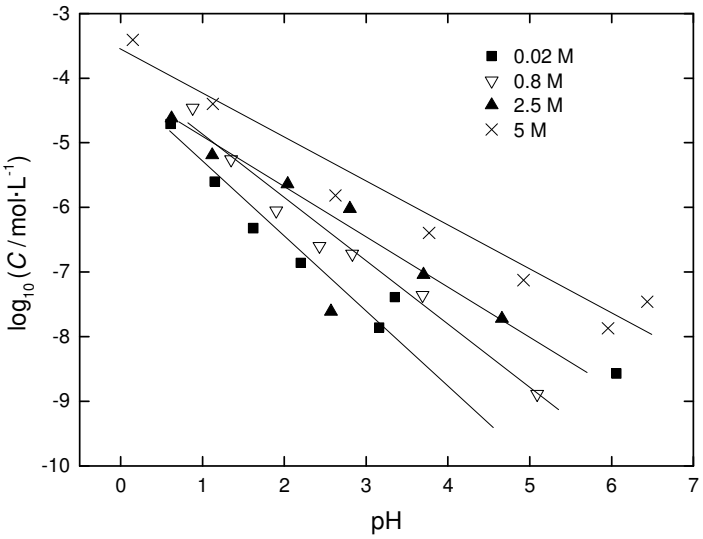
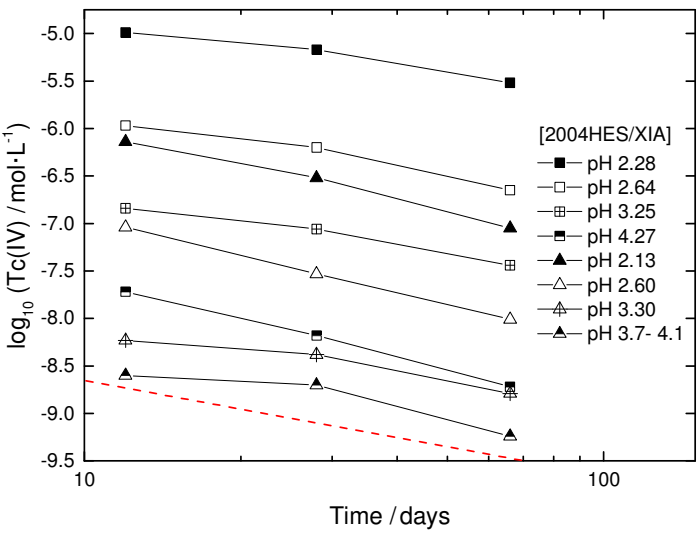



Figure A-43: Results from oversaturation experiments: The dashed line corresponds to a constant rate decrease in solution concentrations



This review does not accept the interpretation for the formation of chloro complexes used by the authors. Hence, we also reject the values for the standard molar Gibbs energy of formation obtained both for $TcCl_4$ and $TcCl_6^{2-}$. Additionally, the stability constants for formation derived from these values for either $TcCl_6^{2-}$ or $TcCl_4$(aq) ($\log_{10}\beta_6^o = 1.38$; $\log_{10}\beta_4^o = 5.66$) are inconsistent, as they imply that $TcCl_6^{2-}$ can only be formed in presence of $TcCl_4$(aq) with a $Cl^-$ activity > 138. At 6 m HCl the mean activity coefficient of HCl is only 3.2 [1972HAM/WU], which is insufficient to allow predominance of $TcCl_6^{2-}$, using these stability constants. In contrast to the experimental observations, $TcCl_6^{2-}$ should form only in 10 m HCl. Hence, one or both stability constants are erroneous. [2004HES/XIA] state that $\beta_4^o$ is highly uncertain. Our analysis shows that the peak assignment in the spectra to $TcCl_4$(aq) was erroneous. The presence of this peak is indicative of presence of polymeric species which are not taken into account in the analyses. However, the present review does not accept the value for $\beta_6^o$ as it is inconsistent with the observation [2004POI] of kinetic instability of $TcCl_6^{2-}$ at 3 m (Na,H)Cl solutions. On the other hand, the peak assignment in the UV spectrum is accepted for this species, hence, $TcCl_6^{2-}$ may have been present in the experiments of the authors. Indeed this species is expected and observed in the data at 6 M HCl of the authors and as well at very acidic 5 M Cl solutions.

To interpret pH dependency of solubility data at high chloride solutions, the authors suggested as solubility limiting phase the formation of $TcCl_4$(am) mixed with $TcO_2{\cdot}xH_2O$(am) at highly acidic solutions. Even if the XRD and EXAFS analyses of the solid phases show the presence of two discrete amorphous Tc compounds at HCl concentrations lower and higher than 0.5 M, the identification of $TcCl_4$(am) remains speculative, since no chemical analysis of the solid phase has been done. This review does not follow the interpretation of the authors.

In conclusion, considering the large effect on rate of the solubility data of the authors, only the long-term data are used in the overall comparison with the data from other authors. The weight of these data in the overall evaluation is relatively low since uncertainties are very high.

**[2004POI]**

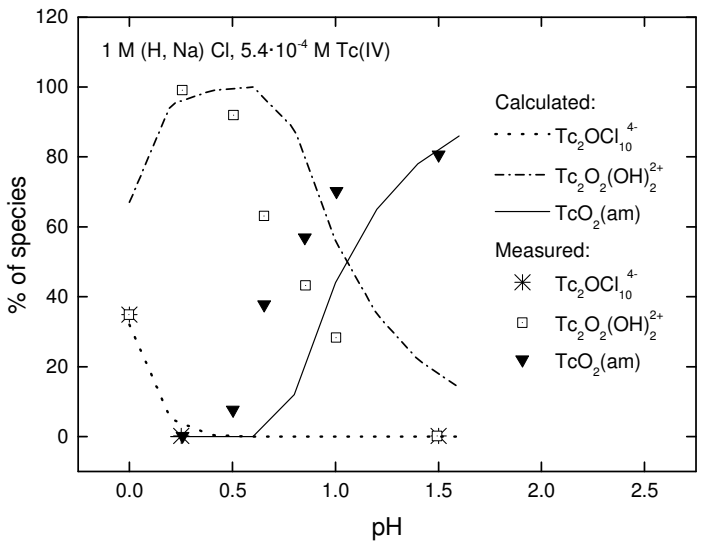
The author studied the formation of $Tc_nO_y^{(4n-2y)+}$ proposed by [2002VIC/OUV] starting from $TcCl_6^{2-}$ solutions in 1 and 3 M NaCl. In a first hydrolysis step $TcCl_5(H_2O)^-$ was formed photochemically. $TcCl_5(H_2O)^-$ condensed by forming linear $Tc_2OCl_{10}^{4-}$ as confirmed by EXAFS. Hydrolysis and cyclisation of this molecule leads to $Tc_nO_y^{(4n-2y)+}$. The data of the author indicate that with increasing pH and prior to transformation to $Tc_nO_y^{(4n-2y)+}$, $Tc_2OCl_{10}^{4-}$ may transform to $Tc_2OCl_{10-x}^{4-x}$, but no data on the value of *x* were provided.

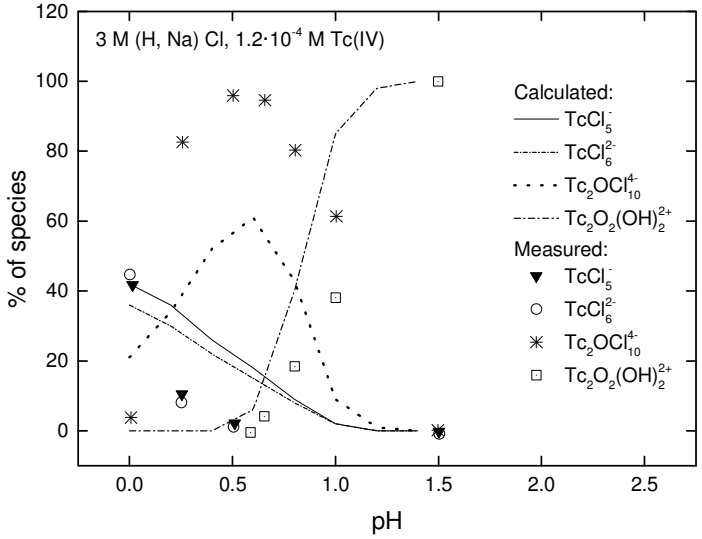
The XANES study, carried out on the complexes $TcCl_6^{2-}$, $TcCl_5(H_2O)^-$, $Tc_2OCl_{10}^{4-}$ and $Tc_nO_y^{(4n-2y)+}$ shows a correlation between the displacement of the absorption edge and the partial charge on the Tc-atom. This partial charge information was used in order to understand the condensation process of Tc(IV).

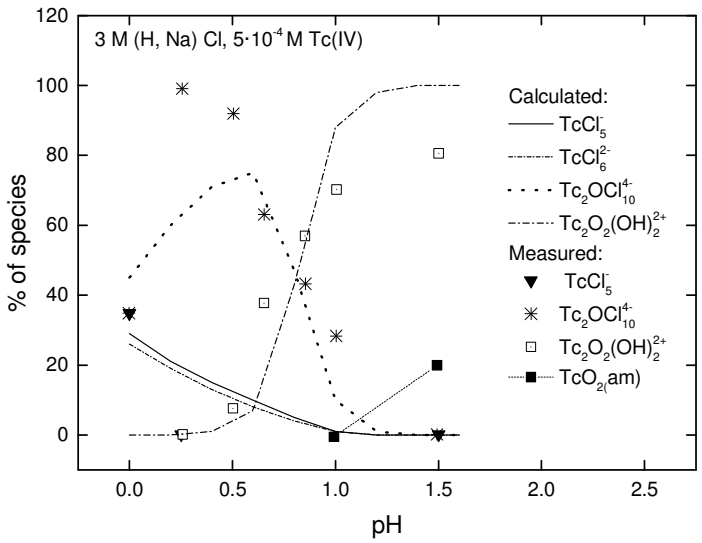
Using UV-Vis spectroscopy, test solutions obtained after equilibrium times up to nine months were analyzed using deconvolution techniques, in order to prepare speciation diagrams of Tc(IV) to distinguish between $TcCl_6^{2-}$, $TcCl_5(H_2O)^-$, $Tc_2OCl_{10}^{4-}$, $Tc_nO_y^{(4n-2y)+}$ and precipitated $TcO_2$(am) in the pH range between 0 and 1.5 in 1 and 3 M NaCl and Tc concentrations of $1.2 \times 10^{-4}$ and $5 \times 10^{-4}$ M. The concentration ratios in the diagrams where used in the present review to obtain conditional equilibrium constants between $Tc_2OCl_{10}^{4-}$ and $Tc_nO_y^{(4n-2y)+}$ at two ionic strengths and between $TcCl_5^-$, $TcCl_5(H_2O)^-$ and $Tc_2OCl_{10}^{4-}$ in 3 M NaCl. In this analysis $Tc_nO_y^{(4n-2y)+}$ has been identified as $Tc_2O_2(OH)_2^{2+}$, consistent with the hydrolysis scheme of the present review. The uncertainties in the derived equilibrium constants are presented in the main text of this review.

Figure A-44 shows the distribution diagrams spectroscopically determined by [2004POI] in 1 and 3 M (H,Na)Cl compared to the calculated species distribution using the thermodynamic data of the present review.

Figure A-44: Distribution diagram for speciation of Tc(IV) in 1 and 3 M (H,Na)Cl solutions at low pH.

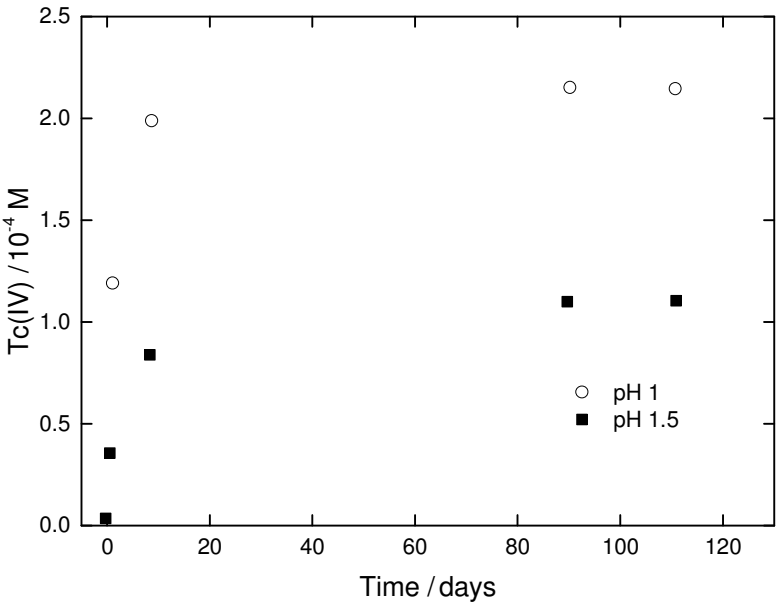





The author also studied the dissolution of $TcO_2$(am, hyd) between pH 0 and 1 after 115 days equilibration in 3 M NaCl and the resulting solubility at pH 1 and pH 1.5; in addition the evolution with time of the concentration of $Tc_nO_y^{(4n-2y)+}$ was studied, see Figure A-45.

Figure A-45: Time dependence of the Tc(IV) concentration during dissolution of $TcO_2$(am) between pH 1 and 1.5.




In the pH range studied, only $Tc_2OCl_{10}^{4-}$ and $Tc_nO_y^{(4n-2y)+}$ were formed. No other Tc(IV) species was observed. Solubility at 3 M NaCl at pH 1 was about 100 times higher as observed by [1991MEY/ARN]. Predicted solubilities with the model in the present review and using $TcO_2$(am, hyd) as solid phase are $3.6 \times 10^{-4}$ M for pH 1 and $2 \times 10^{-5}$ M for pH 1.5, the data were not used to constrain the solubility model since no solid phase characterisation has been performed.

**[2005LUK/BUC]**

The authors studied the reduction of pertechnetate in the presence of simulated radioactive waste using $Na_2S$ and addition of dry grout (consisting of 46 % type F fly ash, 46 % blast furnace slag, BFS, and 8 % Portland cement) sealed in cuvettes made either of oxygen permeable polystyrene or impermeable polypropylene. By the addition of sulfide, either CaS in BFS or as $Na_2S$, resulted in reduction of $TcO_4^-$ to a lower-valent technetium sulfide species, thought to be similar to $TcS_2$, while in alkaline solution $Tc_2S_7$ was formed. The resulting Tc(IV) sulfide was characterised by extended X-ray absorption fine structure (EXAFS) spectroscopy, showing the formation of

triangular clusters of Tc(IV) centres linked together through a combination of disulfide and sulfide bridges as a $Tc_3(\mu^3\text{-}S)(S_2)_3S_6$ core similar to the one in $MoS_3$. From this EXAFS model, the stoichiometry of $TcS_x$ is then $Tc_3S_{10}$, which is presumably the compound generally referred to as "$Tc_2S_7$". It is a Tc(IV) compound, which is consistent with its Tc K-edge absorption energy, 6.5 eV below that of $TcO_4^-$, clearly showing absence of Tc(VII) in $Tc_2O_7$. No thermodynamic data can be derived from this study.

**[2006POI/FAT], [2006POI/FAT2], [2006POI/FAT3] and [2006POI/FAT4]**

These publications contain data and discussions of results that have already been presented in the PhD thesis [2004POI]—see the corresponding Appendix A entry.

**[2007LIU/YAO]**

The work describes solubility experiments of Tc(IV) in granitic groundwater both in aerobic and anaerobic waters. The solubility was studied from oversaturated conditions where an initial Tc(VII) solution of $3 \times 10^{-6}$ M was reduced by $SnCl_2$. Excess of Tc(VII) (Tc(VII)/Tc(IV) ratios of 20 were reported) was removed from the solution by solvent extraction using tetraphenylarsonium. Equilibration times prior to the solid/solution separation were between two and four months, as stated in the conclusions by the authors, or three to seven months, as stated in the main text. Solution and precipitate were separated by ultrafiltration or by centrifugation. However, the molecular weight cutoff of 10000 $g \cdot mol^{-1}$ is not sufficient to filter off nanosized small colloids which typically have a diameter [2004SEK/NAR] of only 2-3 nm. Despite of this, the results from ultrafiltration and centrifugation were similar. Tc(IV) was measured after separation of Tc(VII) by tetraphenylarsonium in chloroform. Tc(VII) was always present in large excess. No significant differences were found in solubility values between aerobic and anaerobic solutions. This may seem surprising at a first glance, but it is expected that the degree of oxidation only changes the ratio of Tc(VII) to Tc(IV), and only Tc(IV) was reported. The solubility was independent of the pH between 2 and 11, corresponding to a solubility constant of $\log_{10} K_s^o = -(8.6 \pm 0.3)$.

The similar pH dependency of the solution concentrations as those of [1991MEY/ARN] indicates that the results are meaningful, even though the hydrolysis model (presence of $TcO(OH)^+$ and $TcO^{2+}$) used to explain increase of solubility in the pH < 2 range has not been accepted. Data at pH 0 with Tc(IV) concentrations of about $10^{-7}$ M were not accepted here, since the low initial total Tc(IV) concentration ($3 \times 10^{-6}$ M) and the potentially large excess of Tc(VII), may result in too low Tc concentration in order to reach the solubility limits. Sorption on the reaction vessel may have further reduced the apparent solubility. Another consequence of the low initial Tc concentration is that the quantity of precipitated solid phase must have been very small.

As a consequence, the particle size of the precipitates is probably very small, as the mass of Tc allowed to precipitate is small (<< $3 \times 10^{-6}$ M).

All experimental data except those at pH 0 were included in an overall fit of solubility data of $TcO_2 \cdot nH_2O$(am). This indicates the dominance of a polymer species controlling the aqueous solubility under these very acidic conditions. While the data of [2007LIU/YAO] agree with the choice of a solubility controlling polymeric aqueous species, the derived stability constants are much lower than those at higher ionic strength. This indicates that monomeric species might control the solubility under low ionic strength acidic conditions.

The solubility of Tc(IV) has been observed to be slightly increased by $Na_2CO_3$ addition up to 0.01 mol·$L^{-1}$ or higher. However, data modelling clearly showed that this increase in Tc(IV) solubility can be explained entirely by the increase in pH and the formation of $TcO(OH)_3^-$. Therefore, no thermodynamic data for Tc carbonate complexes can be derived from the experimental data.

**[2007WAR/ALD]**

The authors studied the solubility of $TcO_2$(am) formed by reduction of ammonium pertechnetate ($NH_4TcO_4$) solutions in the concentration range $1.8 \times 10^{-6}$ to $1.0 \times 10^{-10}$ mol·$dm^{-3}$ using $SnCl_2$ or $FeSO_4$ as reducing systems. The solubility measurements in this study were restricted to highly alkaline solutions, the pH range of about 11.8 to about 14.4. The reductant was added to the solution of heptavalent Tc at a given pH in solid form: 0.7 g $SnCl_2$(s) powder or 0.7 g $FeSO_4$(s). The solution was equilibrated for at least one week. These equilibrium times are too short as has been shown in the present analyses in particular of the data of [2004HES/XIA], times longer than 25 days are necessary. The mixture was filtered using a 0.22 μm cellulose membrane syringe filter. The solubility was independent of pH for values lower than 13.5. Solutions reduced with Fe(II) have lower solubilities than solutions reduced with Sn(II) for pH values larger than 12.3. For pH values lower than 13.5, solubility values are similar to literature values. The $\log_{10} K$ for the formation of $TcO(OH)_3^-$ is $-(21.6 \pm 0.3)$ according to the chemical reaction $TcO_2 \cdot nH_2O(s) \rightleftharpoons TcO(OH)_3^- + H^+ + (n-2)H_2O(l)$ with $K = [TcO(OH)_3^-] \cdot [H^+]$. This result supports a lower stability of the anionic species than that of Eriksen *et al.* in 1992 [1992ERI/NDA].

No explanation is provided for the lower solubility in alkaline solutions when compared to the data of Eriksen *et al.* [1992ERI/NDA] and the different solubility values in presence of either $SnCl_2$ or $FeSO_4$ was explained by potential scavenging of Tc by a solid Fe(II) of Fe(III) phase. One may add that also $SnCl_2$ addition may lead to the formation of solid precipitates ($SnO_2$, etc.). However, the total quantities of Tc in these experiments are rather low and the sorption may decrease the Tc concentrations to

values lower than required by solubility constraints. No solid phase characterisation was performed. Considering the short equilibration times, the possibility of sorption or scavenging, and the non-explained differences when using Fe(II) or Sn(II) as reductant led this review to give zero weight to the data.

**[2008TUM/GER]**

The authors studied by spectrophotometry dissolved peroxides of technetium produced by the reaction of Tc(IV) with hydrogen peroxide in solutions of anhydrous concentrated (16 M) sulfuric acid. In the absence of hydrogen peroxide, Tc(IV) is stable and no oxidation is observed. $TcO_2 \cdot 1.51H_2O$(s) dried at 150 °C, was added to the concentrated acid resulting in total Tc concentrations between $10^{-3}$ and $10^{-4}$ M. Due to the low water activity, the decomposition of extremely unstable intermediate technetium(V) and (VI) peroxo complexes was suppressed.

Spectral data were taken between 400 and 1000 nm. A shoulder at 400 nm was indicative of Tc(IV), interpreted as monomeric $TcO^{2+}$. No data were provided to confirm the speciation of Tc(IV) at highly concentrated $H_2SO_4$.

The rate of formation and decomposition of Tc(V) and Tc(VI) peroxides was found to be independent of the initial hydrogen peroxide concentration. The technetium peroxide species were stable for as long as 400 minutes, allowing determining their spectral characteristics and the rate parameters for its formation and decomposition. Solutions of technetium peroxo- complexes become blue-violet and decompose to release oxygen. No thermodynamic data could be derived for these metastable peroxide species.

**[2009ALL/ALL]**

The redox potential Tc(VII)/Tc(IV) was measured by potentiometric techniques in the pH range 7.0-10.0, for total carbonate concentration of 0.3, 0.6, and 0.7 M. Tc(IV) was added to the system by re-oxidation of a blue Tc(III) carbonate solution synthesised at a potential of – 600 mV versus the Ag/AgCl (saturated KCl) electrode. Assuming that $TcO_4^-$ is the only Tc(VII), the results indicate the presence of the two monomeric hydroxide-carbonate complexes of Tc(IV) recommended in the review of [1999RAR/RAN]. The hydrolysis equilibrium between these two complexes ($Tc(CO_3)(OH)_2(aq) + H_2O(l) \rightleftharpoons Tc(CO_3)(OH)_3^- + H^+$), with $-\log_{10}[H^+]_{1/2}$, is – (8.69 ± 0.20), which is consistent with the value – (8.3 ± 0.6) calculated from the data of [1999RAR/RAN]. The standard potentials are (733 ± 44) mV/SHE and (575 ± 60) mV/SHE for the redox couples $TcO_4^-/Tc(CO_3)(OH)_2(aq)$ and $TcO_4^-/Tc(CO_3)(OH)_3^-$. The corresponding equilibrium constants from $TcO(OH)_2$(aq) are $\log_{10}K$ = (19.8 ± 0.5) and $\log_{10}K$ = (10.5 ± 0.5), to be compared with the values (19.3 ± 0.3) and (11.0 ± 0.6)

respectively proposed by [2003GUI/FAN]. The monomeric character of the Tc(IV) complexes is verified in this study.

The authors claimed that carbonate complexes dominate when the partial pressure of $CO_2(g)$ is $> 10^{-1.1}$ atm, without specifying the pressure below which the carbonate complexes become insignificant. This is true at neutral pH but it is clear in hyperalkaline conditions that the anionic Tc(IV) carbonate complex stays dominant for partial pressures as low as 0.0003 atm.

Based on slope analysis of electrochemical potentials as a function of pH, the authors wanted to show that no precipitation of $TcO_2$(am) occurred in their experiments. Indeed, precipitation at equilibrium would have given a slope (plotting $E$ as a function of $\log_{10}[Tc(IV)]_T$) of zero, which would have made it impossible to use the potentiometric data for the analyses of carbonate complexation. However, using the Tc(IV) carbonate speciation model of the authors together with the hydrolysis model of the present review, we find that Tc(IV) speciation was largely dominated by carbonate complexes, but the solutions are supersaturated with respect to freshly precipitated $TcO_2 \cdot nH_2O$(am) ( $\log_{10} K_s^o < 10^{-7.6}$). The quantity of precipitated $TcO_2 \cdot nH_2O$(am) may be low compared to dissolved Tc(IV) and may not correspond to equilibrium. Hence, the slopes may not be strongly influenced by precipitation, but this cannot be ascertained. In the absence of an analysis of $Tc_{tot}$ concentrations at the end of the experiment, the influence of precipitation cannot be quantified. In consequence, even though the slope analysis reflects carbonate speciation of Tc(IV), we cannot exclude that they are not also influenced by precipitation. For this reason no weight is given to the data. The authors quoted Paquette *et al.* [1985PAQ/LAW], who did not observe any precipitation in their electrochemical studies in bicarbonate media for a Tc(IV) concentration of about $10^{-4}$ M, quoting that [1999RAR/RAN] explained this behaviour of Tc(IV) by the hydration number of $TcO_2 \cdot nH_2O$(am), modifying Tc(IV) solubility. The present review does not confirm this statement, since even with of a $\log_{10} K_s^o = -7.6$ for a slightly aged $TcO_2 \cdot nH_2O$(am) strong precipitation is predicted. This indicates that the studied system is a non-equilibrium system. The comparison of the carbonate complexation data of the authors to the data of [2003GUI/FAN] shows good agreement, but we cannot use these data neither for an independent check of the data of [2003GUI/FAN], nor for a reduction of the uncertainty of the selected thermodynamic values.

**[2009VON]**

The study concerns the effect of the redox potential, acidity and Tc concentration on the speciation of technetium-99 in non-complexing acidic 1-9 M trifluoromethanesulfonic acid (HTFMS) media. HTFMS was used as it is a very strong acid and even less complexing than perchlorate. Focus was on Tc(IV) chemistry and in particular the stability of the polymer species. Pertechnetate was reduced electrochemically to Tc(III),

which was then allowed to re-oxidize by traces of oxygen to Tc(IV) and Tc(VII) at free potential in inert atmosphere. Reduction and re-oxidation were followed by UV-vis spectroscopy.

An attempt was made to refine the Pourbaix diagram of technetium in an acidic medium by deconvolution of the UV-vis spectra obtained at equilibrium between the polymer and pertechnetate. In 1 M HTFMS and for concentrations higher than $10^{-4}$ M in technetium, the re-oxidation of the reduced species shows the formation of a polymer form with characteristic UV-visible bands at 250, 320 and 495 nm. The UV-vis spectrum of the polymer is similar to that of [2001VIC] assigned to $Tc_nO_y^{(4n-2y)+}$ but the molar extinction coefficient of the authors is 2-3 times higher, attributed to the fact that in [2001VIC] extinction coefficients were determined based on the total Tc concentration in solution, while in this study account is taken to the model of nuclearity of the polymer (2 or 3) and correcting for the presence of Tc(III). The tetravalent state of the polymer (instead of a mixed Tc(IV)-Tc(III)) state was confirmed by redox titration. By comparison to molybdenum, the nuclearity of the polymer was estimated at 2 but there remain high uncertainties in this value.

Again in HTFMS 1 M and at Tc concentrations less than $5 \times 10^{-4}$ M, the reduction of $TcO_4^-$ leads directly to the formation of monomer $Tc^{3+}$ without any characteristic UV-vis band. However, starting with Tc concentrations of $2 \times 10^{-4}$ M, with increasing Tc concentration, Tc(III) polymerises to a species with characteristic UV-vis bands at 238, 290 nm and 460-480 nm. Already at Tc concentrations of $8.5 \times 10^{-4}$ M the reduction only results in formation of Tc(IV) polymers and no trivalent Tc is formed. The results of [2014CHO/CZE] are partially inconsistent with the authors spectroscopic result, but the acidity of the solutions used by [2012CHO/CZE] (4 M $H_2SO_4$) was much higher than in experiments performed by the author.

In 6 M HTFMS the reduction of pertechnetate to Tc(III) depends on the Tc concentration and proceeds either *via* Tc(V) and the Tc(IV) polymer, or at Tc concentrations higher than $2 \times 10^{-4}$ M only via Tc(IV). The Tc(III) was partly in form of a polymer with a characteristic band at 460-480 nm. In 9 M HTFMS, Tc(VII) is not stable and autoreduces to Tc(V). The Tc(IV) polymer is formed only at high Tc concentration.

Using the measured potentials and the concentrations of pertechnetate and of Tc(IV) polymer determined by spectral deconvolution of the re-oxidized solutions, apparent standard potentials of Tc(VII)/Tc(IV) polymer were determined as (0.751 ± 0.062) V SHE for 1 M HTFMS, (0.77 ± 0.029) V SHE for 3 M HTFMS and 0.614 and 0.989 V at 6 M HTFMS. However, to obtain a standard potential consistent with this review, the conditional values determined have to be corrected for water activity and activity coefficients. Also, the stoichiometry of the Tc(IV) polymer used in this review is $Tc_2O_2(OH)_2^{2+}$ and not $Tc_nO_y^{(4n-2y)+}$. Activities of solution species have been calculated using SIT theory and the ion interaction parameters in Appendix B or

those determined in the present review. SIT interaction parameters for cations with trifluoromethane sulfonate anion are not known but were assumed to be similar to the ones with chloride ions. Water activities $a_{H_2O}$ in 1 M to 6 M HTFMS solutions have been calculated using the molarity/molality conversion given by the authors and the Pitzer model with ion interaction parameters for HTFMS from [2004DAS] valid until 4.5 m and extending its use with large uncertainties to 11 m HTFMS. The SIT theory was used to calculate pH values of these acids:

1 M HTFMS, 1.088 m: $a_{H_2O}$ 0.959, pH= 0.029

3 M HTFMS: 3.898 m, $a_{H_2O}$ 0.804, pH = – 0.872

6 M HTFMS: 10.998 m, $a_{H_2O}$ 0.258, pH – 2.701 (with a large but unquantified uncertainty)

Data in 6 M HTFMS were not taken into account, both due to the difficulties using SIT in very high ionic strength solutions and because the speciation of Tc(IV) may change at this high concentration [2013DEN]. Using the presumed equilibrium reaction:

$$10H^+ + 2TcO_4^- + 6e^- \rightleftharpoons Tc_2O_2(OH)_2^{2+} + 4H_2O(l) \qquad (A.624)$$

and the corresponding measured potential $E$ and measured concentrations of $TcO_4^-$ and of the polymer of Tc(IV)

$$E = E^0 + \frac{2.3026RT}{6F}\cdot(\log_{10}\frac{[TcO_4^-]^2[H^+]^{10}}{[Tc_2O_2(OH)_2^{2+}]a_{H_2O}^4} + \log_{10}\frac{\gamma_{TcO_4^-}^2\gamma_{H+}^{10}}{\gamma_{Tc_2O_2(OH)_2^{2+}}})$$

The parameters used are summarised in Table A-200.

Table A-200: Parametrisation used in the evaluation of the authors' data for the Tc(VII)/Tc(IV) equilibrium.

| m(HTFMS) | a($H_2O$) | pH | ΔE(meas.) | σ(E, meas.) | Tc (tot) m | Tc(VII)/(IV) meas. | $\log_{10}\gamma$(Tc(VII)) | $\log_{10}\gamma$ (Tc(IV),dimer) | E° |
|---|---|---|---|---|---|---|---|---|---|
| 1.09 | 0.959 | 0.03 | 0.67 | 0.026 | 9E-05 | 0.528 | – 0.154 | – 1.416 | 0.700 |
| 1.09 | 0.959 | 0.03 | 0.713 | 0.028 | 9,5E-05 | 0.204 | – 0.154 | – 1.416 | 0.754 |
| 1.09 | 0.959 | 0.03 | 0.742 | 0.029 | 9,8E-05 | 0.21 | – 0.154 | – 1.416 | 0.782 |
| 1.09 | 0.959 | 0.03 | 0.68 | 0.027 | 0.00019 | 0.05 | – 0.154 | – 1.416 | 0.730 |
| 1.09 | 0.959 | 0.03 | 0.728 | 0.029 | 0.00048 | 0.05 | – 0.154 | – 1.416 | 0.774 |
| 3.90 | 0.804 | – 0.63 | 0.723 | 0.029 | 0.0001 | 0.448 | 0.038 | – 3.120 | 0.666 |

Using the SIT parameters from this review (Appendix B), a mean value of $E°(TcO_4^-/Tc_2O_2(OH)_2^{2+}) = (0.735 \pm 0.088)$ V is obtained. This value is in good agreement with the value of (0.731 ± 0.011) V, which can be obtained directly from the thermodynamic data for Reaction (A.624), derived from solubility studies in the present review. The comparison demonstrates the agreement with the present interpretation of

solubility data of tetravalent Tc in the low pH region using a model with a bi-charged dimer hydrolysis species.

The study allows also derivation of thermodynamic data for Tc(III). Slope analyses by [2009VON] of reduction reactions with pH have given "$Tc^{3+}$" as most likely stoichiometry. This agrees also with the absence of a pH dependence of the reduction of Tc(III) to Tc(0) reported by [1978GRA/ROG]. Conditional standard potentials for reduction of the Tc(IV) polymer to $Tc^{3+}$ were reported. The conditional standard potential was determined in 1 and 6 M HTFMS combining electrochemical reduction and deconvoluted UV-vis spectroscopy. No correction for ionic strength and water activity was performed by the author.

Taking the equilibrium reaction:

$$Tc_2O_2(OH)_2^{2+} + 2e^- + 6H^+ \rightleftharpoons 2Tc^{3+} + 4H_2O \qquad (A.625)$$

and the corresponding measured potential E and measured concentrations of $Tc^{3+}$ and of the polymer of Tc(IV), one can determine the standard potential for (A.625) by:

$$E = E^0 + \frac{2.3026RT}{2F}\cdot(\log_{10}\frac{[Tc_2O_2(OH)_2^{2+}][H^+]^6}{[Tc^{3+}]^2 a_{H_2O}^4} + \log_{10}\frac{\gamma_{Tc_2O_2(OH)_2^{2+}}\gamma_{H+}^6}{\gamma_{Tc_{3+}}^2})$$

Ion interaction parameters for $Tc^{3+}$ are not known. The element with a trivalent ionic radius most similar to $Tc^{3+}$ is $Cr^{3+}$ with known interaction parameter $\varepsilon(Cr^{3+}, Cl^-)$ value of 0.3 kg·mol$^{-1}$. Therefore, this value was also used for $Tc^{3+}$. It should be mentioned that this interaction parameter varies only little between other trivalent ions for ionic radii between that of $Al^{3+}$ ($\varepsilon$ = 0.33 kg·mol$^{-1}$) and of $Am^{3+}$ ($\varepsilon$ = 0.23 kg·mol$^{-1}$).

Only two measured conditional standard potentials are given, one for 1 M and one for 6 M HTFMS. The data calculated as 0.21 V in 6 M HTFMS could not be used due to high uncertainties in the speciation model in HTFMS at high HTFMS concentration (see [2013DEN]) and strong uncertainties of SIT theory at this high ionic strength. After correcting for water activity and activity coefficients one obtains a value of (0.32 ± 0.04) V for 1 M HTFMS (1.088 m).

Table A-201: Parameters used in the evaluation of the data of the authors for the Tc(IV)/Tc(III) equilibrium.

| m(HTFMS) | a($H_2O$) | pH | ΔE (measured) | σ(E, measured) | Tc (tot) m | $\log_{10}$(Tc(IV)/ Tc(III)$^2$) | $\log_{10}\gamma$ (Tc(III)) | $\log_{10}\gamma$ (Tc(IV), dimer) | E° |
|---|---|---|---|---|---|---|---|---|---|
| 1.088 | 0.959 | 0.029 | 0.472 | 0.017 | 1.86E-04 | 3.73 | – 1.54 | – 1.41 | 0.32 |

The calculated potential is:

$$E°(Tc_2O_2(OH)_2^{2+}/Tc^{3+}) = (0.32 \pm 0.02)\ V.$$

Together with the thermodynamic constants of the Tc(IV) dimer determined in this study, this standard potential allows to obtain:

$$\Delta_f G^o_m(Tc^{3+}) = (71 \pm 11)\ kJ \cdot mol^{-1}$$

This is smaller than the value of 89.6 $kJ \cdot mol^{-1}$ calculated from the equilibrium $TcO^{2+}/Tc^{3+}$, tentatively accepted as lower limit by the review of [1999RAR/RAN], without selecting this value (see discussion in the Appendix A entry for [1979GRA/DEV]).

The study also confirms absence of monomer hydrolysis species of Tc(IV) for Tc concentrations as low as $10^{-5}$ M even in non-complexing very strong acid solutions (up to 9 M HTFMS). However, recent data of [2013DEN] show that complexation by triflate ions occurs in these solutions, indicating that in the absence of corresponding stability constants, these high ionic strength solutions cannot be used in the present review to constraint the thermodynamic model.

**[2010POI/WEC]**

The authors studied the molecular structure and spectroscopic properties of Tc(VII) species at 12 M $H_2SO_4$ by NMR, UV-visible and XAFS spectroscopy. Experimental results using EXAFS and density functional calculations show the formation at 12 M $H_2SO_4$ of "$HTcO_4$" with the formula $TcO_3(OH)(H_2O)_2(aq)$. In contrast, at 6 M $H_2SO_4$, $TcO_4^-$ remains stable. No technetium heptoxide or sulfato- complexes were detected up to 12 M acid concentration. NMR spectroscopy made it possible to follow the protonation of pertechnetate. Transformation of $TcO_4^-$ to "$HTcO_4$" starts at 8 M and is terminated at 12 M. A good fit of the experimental data was obtained with $pK_a$ of – 4.9 and the equation:

$$\log_{10}([HTcO_4]/[TcO_4^-]) = pK_{HTcO_4} - H_0$$

where $H_0$ is the Hammet acidity of $H_2SO_4$. However, based on the EXAFS data of the authors, the correct reaction should be:

$$TcO_4^- + H^+ + 2H_2O(l) \rightleftharpoons TcO_3(OH)(H_2O)_2(aq)$$

Hence, in contrast to the approach of the authors, water activity needs to be taken into account explicitly, to obtain meaningful thermodynamic constants:

$$\log_{10}([TcO_3(OH)(H_2O)_2]/[TcO_4]) = pKa_{HTcO_4} - H_0 + 2\log_{10} a_{H_2O}$$

Since water activity varies strongly with acid strength, a new fit of the original experimental data would be required. However, the formation of $HTcO_4$ occurs only at very high $H_2SO_4$ concentration, outside of the range of applicability of the SIT theory. Therefore, no thermodynamic constant is proposed in the present review.

**[2011MAU/POI]**

The authors studied the reduction of $2.2 \times 10^{-2}$ M ammonium pertechnetate by sodium borohydride containing 0.1 M NaOH followed by addition of concentrated acetic acid. An X-ray amorphous black precipitate forms which was separated from the solution by centrifugation. A large number of analytical techniques both for the solid precipitate and the reduced solution was used. The UV-visible spectra of the reduced solutions exhibit bands at 350 and 500 nm, which may indicate the formation of polymeric Tc(IV) acetate species. Addition of 12 M HCl to the solution led to $TcCl_6^{2-}$ formation, as shown by its characteristic UV-Vis spectrum. XAFS and XANES measurements show that the precipitate contains dimeric species with a $[Tc(\mu\text{-}O)_2Tc]^{3+}$ core structure and coordinated acetate ligands, consistent with the formation of a mixed valence Tc(III)/Tc(IV) precipitate. No thermodynamic data can be derived from this study. No pH value was reported but from the reported quantity of added concentrated acetic acid one can conclude that it was insufficient to acidify the initial strongly alkaline solution. The formation of mixed Tc(III)/Tc(IV) precipitates was not considered in the present review. Further studies are necessary to identify the corresponding thermodynamic data.

**[2011MAU/POI2]**

The authors studied the coulometric reduction of 0.01 M and $2 \times 10^{-3}$ M pertechnetate in 1 M $H_2SO_4$ and the electrodeposition of metallic Tc on a smooth gold foil electrode with an area of 0.25 $cm^2$, using a 3 M $Cl^-$ Ag/AgCl reference electrode. Solutions were not deaerated during reduction. A constant current density of 1.0 A/$cm^2$ was applied at a potential of – 2.0 V, leading to significant hydrogen evolution. Deposits were characterised by XRD, XAFS and SEM/EDS, indicating the presence of hexagonal Tc metal in all samples and absence Tc-O scattering. No Tc(IV) or Tc(VII) was detectable on the cathode. The total deposited quantity of Tc was determined by LSC counting. UV-Vis spectroscopy of solution samples showed after electrodeposition, the characteristic absorbance near 500 nm corresponding to hydrolysed polymer Tc(IV) produced during the deposition of Tc metal.

**[2012CHO/CZE]**

The authors studied the electroreduction of relatively large concentrations of pertechnetate ions (1.19 mM) at 0.5 to 4 M $H_2SO_4$, by combining electrochemical (CV, RRDE) and spectroelectrochemical UV-vis (Au-OTE) techniques. A Hg, $Hg_2SO_4$|0.5 $H_2SO_4$ reference electrode was used and liquid junction potentials were corrected.

The spectroscopic evaluation identified as soluble reduction products a dimeric Tc(IV) with $Tc(\mu\text{-}O)_2Tc^{4+}$ structure in the potential range 0.59-0.53 V, characterised by a band at 502 nm and at lower reduction potential probably polymeric mixed oxidation

species, Tc(III,IV), with $[Tc(\mu\text{-}O)_2Tc]^{3+/4+}$ bonds and an absorption band at 670 nm. The authors suggested the formation of $TcO^{2+}$, based on a small absorption band at 410 nm, assigned to $TcO^{2+}$, based on the Tc(IV) band observed by [2008TUM/GER] in anhydrous concentrated $H_2SO_4$. However, [2008TUM/GER] did not assign unambiguously the peak at 400 nm to $TcO^{2+}$ since they did not measure spectra below 400 nm. Data in non-complexing media [2009VON] indicate absence of important quantities of $TcO^{2+}$ even in strongly acidic media at lower total Tc concentrations (0.1 mM) than in this work. Therefore, the present review takes no account of the potential presence of $TcO^{2+}$. The absorption band at 410 nm might as well be part of the spectrum of the mixed valance Tc(III/IV) species, thus explaining the isosbestic point in the authors' Figure 8. The results indicate the existence of mixed chemical and electrochemical pathways for the generation of Tc(IV) species, which can later be reduced to mixed valence Tc(III,IV) dimers.

The peaks and the shape of the cyclic voltammograms in the pertechnate reduction depend strongly on scan rates, indicating kinetic controls. This allowed determination of the activation energy, $(12.56 \pm 1.14)$ kJ·mol$^{-1}$ for the reaction where the dimer of Tc was formed in 4 M $H_2SO_4$.

Using scan rates between 20 and 200 mV/s, half wave potentials (*vs.* SHE) have been obtained as a function of temperature both for pertechnetate reduction to Tc(IV) and for the reduction of Tc(IV) to Tc(III):

Table A-202: Half wave potentials (*vs*. SHE) as a function of temperature reported for pertechnetate reduction to Tc(IV) and for the reduction of Tc(IV) to Tc(III) (scan rates of cyclic voltammograms between 20 and 200 mV/s).

| T /K | $E_{1/2}$(VII/IV) /V | $E_{1/2}$(IV/III) /V |
|---|---|---|
| 284 | 0.697 | 0.512 |
| 293 | 0.689 | 0.508 |
| 303 | 0.686 | 0.506 |
| 313 | 0.680 | 0.502 |

These half wave potentials were determined from the peak positions recorded in oxidising and reducing direction in the cyclic voltammogram. No analyses of uncertainties have been provided. To obtain an estimate of these, the present review, digitized a voltammogram using Origin8 to fit the peaks. This procedure gave an uncertainty of 0.007 V in the peak position, hence, the uncertainty in the $E_{1/2}$ value, determined by the position of two peaks is 0.014 V.

Assuming full reversibility, standard potentials may be obtained from these values. However, as deduced from the dependency of the peak on scan rate, the peak

number 1 (reduction of Tc(VII) to Tc(IV)) appears to be irreversible or "quasi reversible". This would mean that a standard potential cannot be obtained. Indeed, using spectrophotometric data, the authors suggested the formation of solid precipitates. However, no solid state characterisation techniques were used to validate this hypothesis. Peak 4 was then interpreted by the authors as re-oxidation of Tc(IV) to Tc(VII). Formation of deposits on the gold electrode is a likely hypothesis, considering the high total Tc concentrations used in this study. However, as according to spectroscopic data, soluble Tc(IV) is probably in dimeric form, the kinetic step might also be associated to the rate of polymerisation if this is slower than the scan rates.

To obtain standard potentials one needs to consider the nature of dominant solution complexes as well as the activity coefficients of reacting species and the water activity. As Tc(IV) species, the present review uses the hypothesis of formation of $Tc_2O_2(OH)_2^{2+}$ in accordance to solubility studies. No information on the stoichiometry of the mixed (III/IV) valence species is available, but one may make the hypothesis that the stoichiometry can be deduced from the dimeric tetravalent species, simply reducing one of two Tc atoms. This would give the composition $Tc_2O_2(OH)_2^{+}$.

One needs to know the ratio of the diffusion coefficients of the oxidized and the reduced species in the analysis, where the authors assumed that the diffusion coefficients for oxidizing and reduced species are similar. This may, however, not be the case if the redox reaction is associated with the formation of dimers. The larger ion size of these species will lead to a lower diffusion coefficient. By comparing compilations of ionic diffusion coefficients, this review estimates that the ratio of diffusion coefficient related to different ionic radius will most likely be smaller than a factor of 2. Using the equation:

$$E_{1/2} = E^{\circ *} + \frac{RT}{2n\mathrm{F}} \ln\left(\frac{\mathrm{D_{Red}}}{\mathrm{D_{ox}}}\right)$$

we estimate a maximum error in the standard potential of 7 mV which might be attributed to uncertainties in the diffusion coefficient/ratio.

Using the following equation for the oxidation of $TcO_4^-$ to Tc(IV)

$$E = E^{\circ} + \frac{2.3026RT}{6\mathrm{F}} \left(\log_{10} \frac{[TcO_4^-]^2[H^+]^{10}}{[Tc_2O_2(OH)_2^{2+}]a_{H_2O}^4} + \log_{10} \frac{\gamma_{TcO_4^-}^2 \gamma_{H+}^{10}}{\gamma_{Tc_2O_2(OH)_2^{2+}}}\right)$$

a mean value for $E^{\circ}$(TcVII/IV) may be estimated from the $E_{1/2}$ values at 293 K as 0.57 V (SHE) but as stated above, due to the partially irreversibility of the reaction and due to the unknown activity coefficients of $Tc_2O_2(OH)_2^{2+}$ in sulfate media, this value is not accepted by the present review.

**[2013DEN]**

The author studied the speciation of technetium at strongly acidic medium, specifically in trifluoro-methane-sulfonic acid (HTFMS) and sulfuric acid. The redox behaviour of Tc in these media was investigated in the absence and presence of α radiation. The speciation was analysed by UV and by XAS spectroscopy.

In the absence of α radiation and in the absence of a reductant, the spectrophotometric results indicate that pertechnetate ions are not stable in solutions of HTFMS above 4 M, where formation of tetravalent $Tc_nO_y^{(4n-2y)+}$ is observed: $Tc_2O_2(H_2O)_4(TFMS)_4$. The rate of reduction of pertechnetate ions depends on the initial concentration of Tc(VII) and on the acidity. In 5 M HTFMS complete reduction takes many months. XAS analysis indicates the formation of a cyclic dimer of Tc(IV) complexed to triflate ligands and formulated as $Tc_2O_2(CF_3SO_3)_4(H_2O)_4$. This compound contains linear to Tc-O-Tc units at increased HTFMS concentrations.

Between 4 M and 11.15 M HTFMS and under radiation, Tc(VII) was unstable both in the form of $TcO_4^-$ and $TcO_3(OH)(H_2O)_2$. The adjustment of EXAFS signals and DFT calculations, showed the formation of $Tc_2O_2(H_2O)_4(TFMS)_4$.

In 98 % or higher concentrated HTFMS, pertechnetic acid is stable in absence of radiation, but reduces to Tc(V) in its presence. The formal oxidation state + 5 was confirmed by XANES spectroscopy. From the adjustment of the EXAFS signal and DFT calculations, we considered both structures $[OTc(F_3CSO_3)_2(H_2O)_2]^{2+}$ and $[OTc(F_3CSO_3)_2(OH)_2]^-$ where the ligands triflates are coordinated in monodentate mode with Tc.

**[2013FAN/ANI]**

The reduction of Tc(VII) by FeS nano-particles was studied with variable S/Fe ratios. Up to a ratio of 0.056 reduction rates increased with S/Fe ratio and it decreased for S/Fe ratios > 0.224. The formed solid phase was characterised by XRD, XPS, Mösbauer and EXAFS spectroscopy. EXAFS spectroscopy showed that increased reduction rates where associated with the formation of Tc-sulfide phases, principally $TcS_2$. With S/Fe ratios < 0.022, the dominant solid phase of Tc(IV) formed was $TcO_2$, while increased S/Fe ratios leads to increased $TcS_2/TcO_2$ ratios. No thermodynamic data could be obtained from this work since no data on solution speciation where presented.

**[2013FER/KER]**

The authors studied the synthesis of $TcS_2$ by reaction at 45 °C in a sealed tube of $K_2TcCl_6$ and $H_2S$ gas in sulfuric acid. A black X-ray amorphous solid was formed. EDX

analyses confirmed the stoichiometry and XANES analyses confirmed the tetravalent state of Tc. No thermodynamic data can be derived from this work.

**[2013KOB/SCH]**

The reduction of Tc(VII) probably to Tc(IV) was studied as a function of time for up to 328 days in the pH range 2-13 at 22 °C by adding different reducing agents to a solution of $1 \times 10^{-5}$ mol $l^{-1}$ of Tc(VII) in a 0.1 M NaCl background electrolyte under inert Ar atmosphere. Reducing agents were either dissolved or in suspension. The solutions were pre-equilibrated for several weeks prior to the Tc addition. The technetium oxidation state of the aqueous species was characterised by a solvent extraction of Tc(VII) from 10 kD filtered solutions in chloroform/tetraphenyl-phosphonium chloride (TPPC). For Tc sorbed to Fe minerals, XANES and EXAFS spectra were obtained.

The redox transformation processes follow $E_h$-pH conditions in solution, described by the equation:

$$TcO_4^- + 3e^- + 4H^+ \rightleftharpoons TcO_2 \cdot xH_2O(\text{coll, hyd}) + (2-x)H_2O(l)$$

with a pH depending potential which may be described by

$$pe = (\log_{10} K^\circ + \log_{10}([TcO_4^-] \cdot \gamma_{TcO_4^-}) - 4\,pH - ((2-x)\log_{10} a_{H_2O})/3$$

where $TcO_2 \cdot xH_2O$(coll, hyd) corresponds to a solid or colloidal particle. The experimentally derived $E_h$ for this equation is about 100 mV lower than the equilibrium value calculated with ionic strength correction from the standard redox potential for a $TcO_4^-/TcO_2 \cdot 1.6H_2O$(s) electrode recommended by [1999RAR/RAN]. This was explained by formation of a hypothetical $TcO_2 \cdot nH_2O$(am) which might be nanoparticulate. It is well known that solubility increases with decrease in particle size at nanometric scales. Alternatively, the authors suggested redox kinetics as explanation. The reduction rate was observed to depend on the distance to the calculated stability line in the $E_h$/pH diagram. In general Tc(VII) is reduced whenever the redox potentials measured in solution are below the boundary line at which reduction of $TcO_4^-$ should start to occur. Slow reduction of Tc(VII) to Tc(IV) was observed when the redox potential in the system was slightly below this line, while the reaction was fast at redox potentials much lower the line. Such behaviour would be expected if reduction kinetics is controlled by the thermodynamic affinity.

In Fe(II) containing systems, also surface mediation affects the rate of reduction. The EXAFS spectra of Tc adsorbed on magnetite, siderite and mackinawite did not show the pre-edge peak at around 21 050 eV typical for Tc(VII), suggesting complete reduction of Tc(VII) to Tc(IV). Data indicate incorporation of Tc(IV) in the magnetite structure.

The observation of the authors for the dependence of reduction rates on the distance from the boundary line in the $E_h$/pH diagram indicated a complex rate control.

**[2013POI/BUR]**

The authors studied the speciation of Tc(VII) in $HClO_4$ and $HNO_3$, using $^{99}$Tc NMR, UV-Vis and XAFS spectroscopy. The speciation depends on the concentration and strength of the acid. Pertechnetic acid, $HTcO_4$, forms above 8 M $HClO_4$ while in concentrated $HNO_3$, due to the low degree of dissociation of $HNO_3$, the pertechnetate anion is still the predominant species. EXAFS spectroscopy shows that the structure of $HTcO_4$ in $HClO_4$ can be described as $TcO_3(OH)(H_2O)_2$ which is similar to the one reported [2010POI/WEC] for $H_2SO_4$ concentrations larger than 7 M. In concentrated perchloric acid, $^{99}$Tc NMR and UV-Vis measurements are consistent with the formation of $HTcO_4$.

Using the equation $\log_{10}([HTcO_4]/[TcO_4]) = pKa_{HTcO4} - H_0$, where $H_0$ is the Hammett parameter in perchloric acid ( $H_0 = -\log_{10}(a_{H^+}\,\gamma_{TcO_4^-}/\gamma_{HTcO_4})$ ), a $pK_a$ of – 6.1 is determined for the protonation of $TcO_4^-$ in $HClO_4$. However, no comparison of experimental and calculated data is provided, justifying the quality of the derived constant. Also no error analysis is given. Activity coefficient corrections in the Hammet acidity function are not consistent with SIT theory, but the representation of activity coefficients in the Hammet functions should ideally allow interpreting the $pK_a$ value as a standard state $pK^\circ$ value. However, the $pK_a$ value is different in concentrated sulfuric acid (– 4.9) [2010POI/WEC], indicating that this simple interpretation seems to be invalid. Based on the EXAFS data of the authors, the correct reaction should be:

$$TcO_4^- + H^+ + 2H_2O(l) \rightleftharpoons TcO_3(OH)(H_2O)_2(aq)$$

Hence, in contrast to the approach of the authors, water activity needs to be taken into account explicitly, to obtain meaningful thermodynamic constants:

$$\log_{10}([TcO_3(OH)(H_2O)_2]/[TcO_4^-]) = pKa_{HTcO_4} - H_0 + 2\log_{10}a_{H_2O}$$

Since water activity varies strongly with acid strength, it seems impossible to correct the data without a new fit of the original experimental data.

**[2013POI/WEC]**

The authors studied the reaction between $HTcO_4$ and MeOH in 13 M $H_2SO_4$ using $^{99}$Tc NMR, UV-visible and X-ray absorption fine structure (XAFS) spectroscopy. $HTcO_4$ dihydrate forms above 8 M $H_2SO_4$ and is the predominant species above 13 M $H_2SO_4$. In 6 M $H_2SO_4$ no reaction was observed but in 13 M $H_2SO_4$, $HTcO_4$ was reduced by methanol to a green species, whose oxidation state was determined as Tc(V) using titration with cerium(IV). This result was confirmed by EXAFS analysis. Absence of

Tc(VII) was confirmed by UV-vis and NMR spectroscopy while EPR spectroscopy demonstrated absence of Tc(IV). Methanol was oxidized to formic acid. The Tc(V) complex showed absorption band at 190 nm, 255 nm and 695 nm. EXAFS analyses is consistent with the stoichiometry of $TcO(HSO_4)_2(H_2O)_2(OH)$ and/or $[TcO(HSO_4)_3OH]^-$ and DFT calculations shows that these complexes are stable and calculated bond distances agree to those measured by EXAFS.

**[2013POI/WEC2]**

The authors studied the reaction of $2.6 \times 10^{-4}$ M $KTcO_4$ solutions with hydrogen peroxide at 3 to 12 M $HNO_3$ using UV/Vis analyses. For $HNO_3$ concentrations of more than 7 M and $H_2O_2$ concentrations of 4.25 M, red solutions are obtained with a band at 500 nm, attributed to Tc(VII) peroxo species. No reaction occurs at $H_2O_2$ concentrations of 0.1 M. Calculated spectra using TD-DFT at the B3LYP/SDD level of theory were compared to the experimental spectrum and the results are consistent with the presence of diperoxo pertechnetic acid, *i.e.*, $TcO(O_2)_2(H_2O)(OH)$. The red solutions were highly unstable and decomposed exothermically in the course of five minutes with vigorous release of oxygen. No thermodynamic data can be derived from this study.

**[2014CHO/CZE]**

The authors studied the electroreduction of pertechnetate ions in 0.5 to 4 M $H_2SO_4$ using rotating disc gold electrodes. Evaluation of the aqueous speciation during reduction was followed by using optically transparent thin layer spectro-electrochemical cells (Au/RVC-OTTLE). The experiments allowed calculation of redox standard potentials for $Tc_2O_2^{3+}$/TcO(OH)(aq) system, which was found to be equal to 0.255 V *vs*. Ag, AgCl (KCl sat.) no uncertainty was estimated. The identification of the species $Tc_2O_2^{3+}$ apparently was based on spectroscopical similarity to spectra identified by [2011MAU/POI], however, in this paper a band at 500 nm was mentioned as indicative of the formation of a polymeric Tc(IV) complex with acetate and no clear spectral band at 500 nm is shown. Mixed Tc(III)/Tc(IV) valence states are reported in [2011MAU/POI] for the precipitate and not for the solution. In consequence, the present review does give no weight to the identification of the aqueous mixed Tc(III)/Tc(IV) solution species.

**[2014CHO/CZE2]**

The authors studied the electrochemical reduction of the $5 \times 10^{-4}$ M pertechnetate ions in (0.5-4 M) sulfuric acid solutions using an optically transparent thin layer spectroelectrochemical (RVC-OTTLE) cell. Soluble Tc(III), $TcO^{2+}$ and $[Tc(\mu\text{-}O)_2Tc]^{3+/4+}$ species with absorption bands at 420-450, 400, and 502 nm,

respectively, were found to be formed during the reduction of pertechnetate ions. The monooxotechnetium(IV) $TcO^{2+}$ ions can be electrooxidized at potentials lower than 0.6 V *versus* Ag, AgCl(sat.) (0.799 V SHE) while dimeric structures of Tc, $[Tc(\mu\text{-}O)_2Tc]^{3+/4+}$, are oxidized to pertechnetate ions at potentials higher than 0.8 V versus Ag, AgCl(sat.) (0.999 V SHE).

**[2014FER]**

The author studied the formation of both aqueous sulfide species and solid phases of Tc, using UV spectroscopy, XAS spectroscopy combined with DFT calculations of structure models. In solution $TcO_3S^-$ was observed as a sufficiently stable complex formed in the reaction of $(Bu_4N)TcO_4$ and $(Me_3Si)_2S$ with a ratio Tc:S = 1:200 in acetonitrile. This compound is redox sensitive and undergoes a fast reduction and/or polymerisation reaction. Sulfur/oxygen exchange lead to formation of aqueous sulfide species, which polymerised in solution. It is possible that $TcO_3S^-$ underwent reduction and/or polymerisation into a technetium oxo-sulfide species.

In 3, 6, 9 and 12 M $H_2SO_4$ solution the presence of polymeric species containing the Tc-O-Tc unit coordinated to sulfate, water and/or hydroxide ligands was observed. In the 15 M $H_2SO_4$ solution a monomeric compound was formed in which the central technetium atom is surrounded by sulfate, water and/or hydroxide ligands. The species contained the $Tc_2(\mu\text{-}O)_2$ units coordinated to monodentate sulfate, water and/or hydroxide ligands. The mechanism of polymerization was described as successive reduction of $Tc^{VII}O_3(H_2O)_2(OH)$ to $Tc^{V}O(HSO_4)_3(OH)^-$ and to Tc(IV) complexes (*i.e.*, $Tc(HSO_4)_2(H_2O)(OH)_2$ and $Tc_2O(HSO_4)_4(H_2O)_2(OH)_2$). Those oxosulfide and sulfate complexes started to polymerise and formed colloids.

The author reinvestigated also the chemistry of $Tc_2S_7$ and $TcS_2$ in sulfuric acid-hydrogen sulfide solutions. There remained uncertainties in the stoichiometry of $Tc_2O_7$ because the solid contained impurities. XANES spectra showed that there was no presence of Tc(VII) in this solid. Reactions from different oxidation state technetium compounds lead to the most thermodynamically stable technetium (IV) sulfide compound, $TcS_2$. However, no thermodynamic data could be determined from this study.

**[2015GER/SHI]**

The authors studied the formation of technetium sulfides by reacting Tc(VII) with $Na_2S$. Brown aqueous sulfides were formed with an absorbance at 450 nm at pH between 8 and 12 both in buffered and non-buffered solutions. The proposed reaction is:

$$TcO_4^- + 5H_2S \rightleftharpoons TcS_2 + 3S^0 \rightleftharpoons TcS(S_2)_2^-$$

However, the proposed speciation for this reaction was not analysed in this study but was only deduced from the one by [2005LUK/BUC]. In the latter, only structural and no thermodynamic data were reported, making it impossible to obtain any thermodynamic data from the present study. The concentration of truly dissolved Tc was dependent on the $Na_2S$ concentration. An X-ray amorphous precipitate was formed with a Tc:S ratio of 2 to 6.67. Solubility of Tc sulfide between three and five days was evaluated for different [$Na_2S$] by separation of colloidal particles with 5 kD membranes. EXAFS analyses support the structure of the technetium sulfide reported by [2005LUK/BUC]. Colloids are reported to have the composition $Tc_3S_{13}$, which in the present review would be considered as a polynuclear complex rather than a colloid. For $Na_2S$ concentrations higher than 0.05 M the formation of colloids was observed described by the general formula ($[Tc_3(\mu^3\text{-}S)(\mu^2S_2)_3(S_2)_{3/3}]_n$) (there seems to be an error in the formula, as it is quoted in [2016GER/OBR] as $[Tc_3(\mu^3\text{-}S)(\mu^2S_2)_3(S_2)_{(3n-1)/n}]_n$) . The equation describing Tc(IV) sulfide solubility was given as $-9 \times 10^{-5}\text{Ln}[Na_2S] - 2 \times 10^{-5}$ M. The stoichiometry $Tc_3S_{10}$ was given for the solubility controlling solid previously described as $Tc_2S_7$. No thermodynamic data could be obtained from the experimental solubility data. The colloidal solutions of the technetium sulfide formed were found to be rather stable. Similar stability of the Tc sulfide colloids has been observed for solutions described by Saiki *et al.* [2003SAI/FUK].

**[2015MOE/ABI]**

The authors measured the water activity, mean activities and osmotic coefficients for aqueous $HTcO_4$ solutions at $T$ = 298.15 K from molality m = 1.4 to 8.32 mol·kg$^{-1}$. The used water activity meter has higher uncertainties than those obtained in typical gravimetric isopiestic apparatus like the one used in [1978BOY2]. Density variations at $T$ = 298.15 K are also established. The limiting partial molar volume was measured as (43.67 ± 5.00) cm$^3$·mol$^{-1}$. Due to the high uncertainties, this value is not significantly different from the value of 47.1 of [1987NEC/KAN] or 48.1 cm$^3$·mol$^{-1}$ of [1992LEM/SAL].

For concentrations below 4 m, very good consistency is observed with osmotic coefficients that were measured by [1978BOY2] and recalculated by [1991RAR/MIL]. For higher concentrations, clear deviations are observed, explained by the authors by the observation of [1978BOY2] of coloration of the high concentrated solutions, interpreted by the authors as a change in solution speciation due to potential presence of $Tc_2O_7$ formation. On the other hand, no discussion of the coloration or its absence was reported for the authors own data. Equal weight is given to the present data and those of [1978BOY2].

**[2015POI/GER]**

The authors observed the formation of two peroxo complexes as a function of acidity and hydrogen peroxide concentration: blue species (band in the region 500-800 nm) of Tc(VII) in solutions of 0.17 M $H_2O_2$ and $H_2SO_4$ concentrations > 9 M, with bands increasing at 13 and 18 M $H_2SO_4$. No such species were observed at lower $H_2SO_4$ concentration. The data are interpreted by formation of Tc(VII) peroxo complexes exhibiting bands at 520 and 650 nm. UV-visible spectra are different at 13 and 18 M $H_2SO_4$, indicating different number of peroxo ligands. Various hypotheses can be formulated, the blue species can either be a Tc(VII) peroxosulfate complex, a Tc(VII) monoxo or tri-peroxo complex. The effect of $H_2O_2$ concentration on solution speciation was studied at 6 M $H_2SO_4$ and 0.34 mM Tc(VII), with $H_2O_2$ concentrations of 0.38 to 8.5 M. At concentrations above 2.12 M $H_2O_2$, red complexes were formed with a single band centred at 500 nm. These complexes are similar to those reported in [2013POI/WEC2] for > 7 M $HNO_3$, consistent with the presence of $TcO(O_2)_2(H_2O)(OH)$. $^{99}Tc$ NMR spectra were consistent with symmetries lower than those for the $TcO_4^-$ anion. These complexes are still detectable at 9 M $H_2SO_4$ but they are absent at higher acidity. Thermodynamic data are not derived by the authors but a conditional constant can be obtained from the dependency of the published UV-visible spectra on $H_2O_2$ concentration:

$$TcO_4^- + H^+ + 2H_2O_2 \rightleftharpoons TcO(O_2)_2(H_2O)(OH) + H_2O(l)$$

$$\log_{10}K = \log_{10}[TcO(O_2)_2(H_2O)(OH)] - \log_{10}[TcO_4^-] - 2\log_{10}[H_2O_2] - \log_{10}[H^+]$$

A value of $\log_{10}K = (4.65 \pm 0.50)$ can be obtained in 6 M $H_2SO_4$. Remark: in the absence of $H_2O_2$, the pertechnetate ion is still the dominant Tc(VII) species, while at 7 M $H_2SO_4$ pertechnetic acid is formed [2010POI/WEC].

Both red (see [2013POI/BUR]) and blue solutions are unstable and transform in a few minutes by release of oxygen and transformation of the peroxo species of Tc(VII) in $TcO_3(OH)(H_2O)_2$, as identified by its UV-Visible spectrum (band at 275 nm). As shown in [2013POI/BUR], $TcO_3(OH)(H_2O)_2$ is predominant and thermodynamically stable at very high sulfuric acid concentrations.

**[2015YAL] and [2016YAL/GAO]**

The two references are almost identical, the first is a PhD-thesis, the second the publication based on this thesis. Important additional data included in the second reference concern in particular the determination of the hydration stage of aged $TcO_2$(am, hyd, aged). The authors studied the redox chemistry, solubility and hydrolysis of technetium in dilute solutions to concentrated NaCl, $CaCl_2$ and $MgCl_2$ solutions. All experiments were performed in glove boxes under Ar-atmosphere at room temperature.

The author derived thermodynamic data for solution complexes and solubility of $TcO_2 \cdot xH_2O$(am). Data were corrected for ion-interaction processes.

Using $E_h$/pH measurements, the effect of various redox systems ($Na_2S_2O_4$, Sn(II), Fe(II/III), Fe(0), hydroquinone), pH and ionic strength up to 4.5 M $MgCl_2$ on the redox state of Tc compared to the $TcO_4^-/TcO_2 \cdot 1.6H_2O$ redox boundary was studied and compared to calculations with thermodynamic data from [1999RAR/RAN]. As expected, the solubility of Tc(IV) in concentrated NaCl and $MgCl_2$ solutions is significantly enhanced at low and high pHs compared to dilute systems. Kinetics have been shown to play an important role when approaching the Tc reduction/solubility from oversaturation.

Solubility of $TcO_2$(am, hyd) was studied from undersaturated conditions using different reducing chemicals such as $Na_2S_2O_4$, $SnCl_2$ or Fe powder to maintain reducing conditions, depending upon target pH values used. The solid was characterised by XRD pattern as being amorphous. Tc(IV) concentrations were obtained after solvent extraction. The prepared solid was aged for two months before use. Establishment of equilibrium was followed for up to 600 days. In dilute solutions, 2-3 months are sufficient to reach equilibrium, but this was much longer in concentrated brines. For example, at 5 M NaCl at pH 2 equilibrium has not even been reached after 520 days. XAFS spectra were acquired in florescence mode. After long term equilibration, the number $x$ of water molecules in $TcO_2 \cdot xH_2O$(am) has been identified as $(0.6 \pm 0.3)$ [2016YAL/GAO] which is much lower than values reported in [1999RAR/RAN]. Despite the lower water content compared to previous studies, EXAFS analyses of the solid were rather similar to those given by [2002VIC/OUV] and [2004HES/XIA].

Within the pH range 1.5-4 in NaCl solutions, the logarithm of solubility increased with a slope of 2 with decreasing pH. Similar observations were made in $MgCl_2$ solutions. The slope would indicate dominance of $TcO^{2+}$ as solubility controlling aqueous complex, but XAFS data indicate polymer formation of Tc(IV) and formation of chloride complexes. In analogy to the work of [2003VIC/FAT] the author proposed a trimeric bi-charged complex $Tc_3O_5^{2+}$ limiting solubility in the acidic pH range. However, this is not in agreement with the present review. The experimental data of the present study were used in an overall fit of solubility data of various authors. The data of the authors are in very good agreement with the assumption of $TcO_2(OH)_2^{2+}$ as solubility limiting complex.

In the region between pH 4 and 9, a pH-independent solubility behaviour is observed in dilute to concentrated NaCl solutions, where the Tc(IV) concentration is not being affected by ionic strength, indicating solubility control by a dominant $TcO(OH)_2$(aq). In this study, $\log_{10} K^{\circ}_{s,\,TcO(OH)_2} = -(8.8 \pm 0.5)$ is determined, lower than, but consistent with the selection of $\log_{10} K^{\circ}_{s,\,TcO(OH)_2} = -(8.4 \pm 0.5)$ by [1999RAR/RAN]. The solubility decreases with decreasing hydration number.

Under more alkaline conditions, the logarithm of solubility of Tc(IV) increases with a well-defined slope of + 1. Using a SIT plot a value of $\log_{10} K^{\circ}_{s,\,TcO(OH)_3^-} = -(19.27 \pm 0.10)$ was obtained together with an ion interaction parameter $\Delta\varepsilon = (0.22 \pm 0.02)$ kg·mol$^{-1}$.

The authors compared their solubility data with the model of [2004HES/XIA] and noted a clear disagreement between the two. The ionic strength dependence of the solubility at high chloride concentrations could not be described adequately by the Pitzer model [1999NEC/FAN].

In high concentrated $CaCl_2$ and $MgCl_2$ solutions, solubility of $TcO_2$(am, hyd, aged) increased strongly indicating strong ion interaction in the whole pH range. The possible formation of Tc(IV) chloro-complexes of the type $Tc_3O_5Cl_m^{2-m}$ with $1 \leq m \leq 4$ was considered, based on EXAFS data showing Cl-Tc bonding at pH 2 in 4.5 M $MgCl_2$ solution. Application of the model of chloride complexation of the present review to the data of the authors indicates the potential formation of $TcCl_6^{2-}$ at pH 2 together with hydrolysis species, but since at this ionic strength of 13.5 the present model is not applicable, the modelling results are only used to provide an alternative explanation of the observed EXAFS data.

In solutions of up to 1 M $MgCl_2$ and $CaCl_2$, the solubility behaviour of $TcO_2$(am, hyd, aged) has been observed to be rather similar to that in NaCl solutions of corresponding ionic strength. However, a steep increase in the Tc(IV) solubility is observed in 4.5 M $MgCl_2$ and $CaCl_2$ solutions with $pH_m \approx 8$. Based on EXAFS data, DFT calculations and model calculations, the predominance of ternary Mg-Tc(IV)-OH and Ca-Tc(IV)-OH aqueous species has been proposed by the authors in concentrated alkaline solutions. Indeed, DFT calculations support the predominance of $Ca_3[TcO(OH)_5]^{3+}$ in concentrated $CaCl_2$ solutions. This species has been calculated to be stable both in the gas phase and enwrapped by one hundred water molecules in the liquid phase. Stability constants and ion interaction parameter have been derived for these ternary species by the authors:

$$\log_{10} K^{\circ}_{s,\,Ca_3TcO(OH)_5^{3+}} = -(41.53 \pm 0.30)$$

$$\varepsilon(Ca_3[TcO(OH)_5]^{3+}, Cl) = -(0.37 \pm 0.10) \text{ kg·mol}^{-1}$$

and

$$\log_{10} K^{\circ}_{s,\,Mg_3TcO(OH)_5^{3+}} = -(40.55 \pm 0.50)$$

$$\varepsilon(Mg_3[TcO(OH)_5]^{3+}, Cl) = \varepsilon(Ca_3[TcO(OH)_5]^{3+}, Cl) .$$

These data are consistent with an increase of solubility of $TcO_2$(am, hyd, aged) with the observed slope of + 3 with increasing pH in 4.5 M $MgCl_2$ or $CaCl_2$ solutions. However, due to the high ionic strength employed, inaccessible to SIT theory, these data were not selected in the present review.

**[2016GER/OBR]**

The authors studied the interaction of technetium and rhenium with sulfides in aqueous solutions, studied by small-angle X-ray scattering and ultramicrocentrifugation. This study is a follow up study based largely on [2015GER/SHI].

It was shown that, although the stoichiometry of technetium sulfide corresponds to the formula $Tc_2S_{7-x}$, the oxidation state of technetium in it is + 4 and the excess sulfur is present in a disulfide group so that its formula can correctly be written as $([Tc_3(\mu^3\text{-}S)(\mu^2S_2)_3(S_2)_{(3n-1)/n}]_n)$. The determination of the solubility of technetium sulfide is complicated by its tendency to form colloids. It was found that the size of the produced particles range from 0.02 to 12 μm. An increase in the particle size with time was observed with a growth rate exceeding the particle formation rate. Increasing temperature led to an increase in the size of the forming particles. Neither natural sedimentation nor centrifugation ensured that the measured Tc concentrations in solution have reached equilibrium with the solid phase, since small particles could not be separated from the solution. In consequence, no thermodynamic data can be obtained from this study. The authors state that the ultra-microcentrifugation with a molecular weight cut-off of 5 kDa separates both small and large colloids, thus allowing the determination of the true solubility. However a cutoff of 5 kDa would still correspond to $([Tc_3(\mu^3\text{-}S)(\mu^2S_2)_3(S_2)_{(3n-1)/n}]_n)$ nanoparticles with $n$ values of about 10. Hence the question of solution speciation (trimer or polymer) stays non-solved and no equilibrium constant or other thermodynamic data can be obtained.

# Discussion of selected references for Chapter 14's Auxiliary Data

## Data for vanadium compounds

### [1960KOE]

Koehler [1960KOE] measured at 303.2 K in 0.20 m NaOH enthalpies of the following formal reactions/processes:

$$0.5V_2O_5(cr) + 3OH^- \rightleftharpoons VO_4^{3-} + 1.5\ H_2O(l) \quad (A.626)$$
$$\Delta_r H_m(A.626) = -(66.27 \pm 0.08)\ kJ \cdot mol^{-1},$$

$$NaCl(cr) \rightleftharpoons Na^+ + Cl^- \quad (A.627)$$
$$\Delta_r H_m(A.627) = (3.64 \pm 0.04)\ kJ \cdot mol^{-1},$$

$$13.231H_2O(l) \rightleftharpoons 13.231H_2O(sol) \quad (A.628)$$
$$\Delta_r H_m(A.628) = (0.084 \pm 0.042)\ kJ \cdot mol^{-1},$$

$$NaVO_3(cr) + 2OH^- \rightleftharpoons Na^+ + VO_4^{3-} + H_2O(l) \quad (A.629)$$
$$\Delta_r H_m(A.629) = -(23.68 \pm 0.04)\ kJ \cdot mol^{-1},$$

$$(HCl \cdot 12.731H_2O)(l) + OH^-(sol) \rightleftharpoons 13.731H_2O(sol) + Cl^-(sol) \quad (A.630)$$
$$\Delta_r H_m(A.630) = -(59.45 \pm 0.17)\ kJ \cdot mol^{-1}.$$

Combining Reactions (A.626)-(A.630), Koehler [1960KOE] recommended for the reaction:

$$0.5V_2O_5(cr) + NaCl(cr) + 13.231H_2O(l) \rightleftharpoons NaVO_3(cr) + (HCl \cdot 12.731H_2O) \quad (A.631)$$

in 0.2 m NaOH $\Delta_r H_m(303.15\ K) = (20.59 \pm 0.21)\ kJ \cdot mol^{-1}$, and recalculated it to 298.15 K as $\Delta_r H_m(298.15\ K) = (21.21 \pm 0.21)\ kJ \cdot mol^{-1}$.

Combining this value with the CODATA-based [1989COX/WAG] enthalpy of formation of $H_2O(l)$ – (285.83 ± 0.04), HCl – (167.08 ± 0.10), the NEA based NaCl(cr) – (411.26 ± 0.12), the current selection of $V_2O_5(cr)$ – (1556.0 ± 3.0), the value of the relative apparent enthalpy of HCl in 4.36 m (for $(HCl \cdot 12.731\ H_2O)$, $\varphi_L = 4.76\ kJ \cdot mol^{-1}$, interpolated from [1965PAR]) we obtain for $NaVO_3(cr)$ $\Delta_f H_m^o(298.15\ K) = -(1148.65 \pm 1.53)\ kJ \cdot mol^{-1}$.

**[1962KIN/KOE]**

King *et al.* [1962KIN/KOE] obtained for reaction $2MgO(cr) + V_2O_5(cr) \rightleftharpoons Mg_2V_2O_7(cr)$ the value $\Delta_r H_m^o(298.15\ K) = \Delta_r H_m^o(303.15\ K) = -(81.80 \pm 0.92)$ kJ·mol$^{-1}$ $-(19.55 \pm 0.22)$ kcal·mol$^{-1}$ at 303.2 K and $\Delta_r C_{p,m}^o \approx 0$ J·K$^{-1}$·mol$^{-1}$) from enthalpies of solution of solid compounds in 4.36 m HCl at 303.2 K. Combining this value with the CODATA-based [1989COX/WAG] enthalpy of formation of MgO(cr) $-(601.6 \pm 0.3)$ and the current selection for $V_2O_5$(cr) $-(1556.0 \pm 3.0)$, this review calculates for $Mg_2V_2O_7$(cr), $\Delta_f H_m^o(298.15\ K) = -(2841.00 \pm 3.21)$ kJ·mol$^{-1}$.

The values of $S_m^o$ and $C_{p,m}^o$ are quoted from [1962WEL/KIN] (measured at 50-298 K, extrapolated below 50 K).

King *et al.* [1962KIN/KOE] obtained for the reaction $CaO(cr) + V_2O_5(cr) \rightleftharpoons Ca(VO_3)_2(cr)$ the value $\Delta_r H_m^o(298.15\ K) = \Delta_r H_m^o(303.15\ K) = -(143.43 \pm 0.63)$ kJ·mol$^{-1}$ at 303.2 K and $\Delta_r C_{p,m}^o \approx 0$ J·K$^{-1}$·mol$^{-1}$) from enthalpies of solution of solid compounds in 4.36 m HCl at 303.2 K. Combining this value with the CODATA-based [1989COX/WAG] enthalpy of formation of CaO(cr) $-(634.92 \pm 0.9)$ and the current selection for $V_2O_5$(cr) $-(1556.0 \pm 3.0)$, the present review calculates for $Ca(VO_3)_2$(cr), $\Delta_f H_m^o(298.15\ K) = -(2334.35 \pm 3.23)$ kJ·mol$^{-1}$.

The values of $S_m^o$ and $C_{p,m}^o$ are quoted from [1962KIN/WEL] (measured at 50-298 K, extrapolated below 50 K).

**[1967BER/HEP]**

Bertrand and Hepler [1967BER/HEP] measured at 298.2 K in ~ 0.61 m $HClO_4$ (0.595 M $HClO_4$) enthalpies of the following formal reactions/processes:

$$0.5V_2O_5(cr) + H^+ \rightleftharpoons VO_2^+ + 0.5H_2O(l) \quad \text{(A.632)}$$
$$\Delta_r H_m(\text{A.632}) = -(16.49 \pm 0.08)\ \text{kJ·mol}^{-1},$$

$$NaVO_3(cr) + 2H^+ \rightleftharpoons VO_2^+ + Na^+ + H_2O(l) \quad \text{(A.633)}$$
$$\Delta_r H_m(\text{A.633}) = -(27.99 \pm 1.05)\ \text{kJ·mol}^{-1},$$

$$NaCl(cr) \rightleftharpoons Na^+ + Cl^- \quad \text{(A.634)}$$
$$\Delta_r H_m(\text{A.634}) = (4.27 \pm 0.17)\ \text{kJ·mol}^{-1},$$

$$(HCl{\cdot}4.395H_2O)(l) \rightleftharpoons H^+(sol) + Cl^-(sol) + 4.395H_2O(sol) \quad \text{(A.635)}$$
$$\Delta_r H_m(\text{A.635}) = -(12.30 \pm 0.17)\ \text{kJ·mol}^{-1},$$

$$4.895H_2O(l) \rightleftharpoons 4.895H_2O(sol) \quad \text{(A.636)}$$
$$\Delta_r H_m(\text{A.636}) = (0.13 \pm 0.01)\ \text{kJ·mol}^{-1}.$$

Combining Reactions (A.632)-(A.636), the study [1967BER/HEP] recommended for the reaction:

$$0.5V_2O_5(cr) + NaCl(cr) + 4.895H_2O(l) \rightleftharpoons NaVO_3(cr) + (HCl{\cdot}4.395H_2O) \quad \text{(A.637)}$$

in 0.61 m $HClO_4$ $\Delta_r H_m$ (A.637) = (28.20 ± 1.08) kJ·mol$^{-1}$.

Combining this value with the CODATA-based [1989COX/WAG] enthalpy of formation of $H_2O$(l) – (285.83 ± 0.04), HCl – (167.08 ± 0.10), the NEA based NaCl(cr) – (411.26 ± 0.12), the current selection of $V_2O_5$(cr) – (1556.0 ± 3.0), the value of the relative apparent enthalpy of HCl in 12.63 m (for (HCl·4.395 $H_2O$), $\varphi_L$ = 12.96 kJ·mol$^{-1}$, interpolated from [1965PAR]), we obtain for $NaVO_3$(cr) $\Delta_f H^o_m$ (298.15 K) = – (1149.85 ± 1.83) kJ·mol$^{-1}$.

Final consideration of the experimental values of $\Delta_f H^o_m$ ($NaVO_3$, cr, 298.15 K):

The values for $\Delta_f H^o_m$ ($NaVO_3$, cr, 298.15 K): – (1148.65 ± 1.53) kJ·mol$^{-1}$ [1960KOE] and – (1149.85 ± 1.83) kJ·mol$^{-1}$ [1967BER/HEP], are consistent within the claimed uncertainties and the present review has selected weighted average value – (1149.14 ± 1.17), however, increased the uncertainty to 1.5 kJ·mol$^{-1}$.

Values of $S^o_m$ and $C^o_{p,m}$ are quoted from [1962KIN/WEL] (measured at 50-298 K, extrapolated below 50 K).

## Data for boron compounds

### [1948KEL/TOD]

Torgeson and Shomate have determined the enthalpy of formation of $CaB_2O_4$(cr) using dissolution calorimetry based on the following sequence of reactions:

$$B_2O_3(cr) + 3H_2O(1.00M\ HCl) \rightleftharpoons 2H_3BO_3(aq)\ ;$$
$$\Delta_r H = -(13.77 \pm 0.03)\ kJ\cdot mol^{-1};$$

$$CaB_2O_4(cr) + 2H_2O(aq) + 2H^+(aq) \rightleftharpoons Ca^{2+} + 2H_3BO_3(aq)\ ;$$
$$\Delta_r H = -(84.76 \pm 0.03)\ kJ\cdot mol^{-1};$$

$$CaO(cr) + 2H^+(aq) \rightleftharpoons Ca^{2+} + H_2O(aq)\ ;$$
$$\Delta_r H = -(194.05 \pm 0.05)\ kJ\cdot mol^{-1};$$

Torgeson and Shomate noted that the heat of dissolution of $B_2O_3$(cr) depends on the total amount of solid used and this review has selected the enthalpy of reaction based on the samples with less than 1.24 g dissolved oxide where this variation is small.

From the experimental heats of dissolution, Torgeson and Shomate report for the reaction:

$$CaO(cr) + B_2O_3(cr) \rightleftharpoons CaB_2O_4(cr)\ ;$$
$$\Delta_r H = -(123.09 \pm 0.08)\ kJ\cdot mol^{-1};$$

This review has used the slightly different value for the enthalpy of dissolution and have selected $\Delta_r H_m$ = – (123.08 ± 0.08) kJ·mol$^{-1}$. Kelley *et al.* also report the enthalpy of formation from the elements, $\Delta_f H^o_m$ ($CaB_2O_4$, cr) = – 2192.4 kJ·mol$^{-1}$, but without uncertainty estimate; this value is based on the following enthalpies of formation:

$\Delta_f H_m^o$ (CaO, cr) = – 635.1 kJ·mol$^{-1}$ and $\Delta_f H_m^o$ ($B_2O_3$, cr) = – 1434.1 kJ·mol$^{-1}$. These values differ from the NEA selected values: $\Delta_f H_m^o$ (CaO, cr) = – (634.92 ± 0.90) kJ·mol$^{-1}$ and $\Delta_f H_m^o$ ($B_2O_3$, cr) = – (1273.5 ± 1.4) kJ·mol$^{-1}$. The present review have used the NEA data to calculate recalculate the enthalpy of formation of $CaB_2O_4$(cr) and find $\Delta_f H_m^o$ ($CaB_2O_4$, cr) = – (2031.5 ± 1.7) kJ·mol$^{-1}$, which is identical with the value in the Glushko Tables.

Kelley *et al.* [1948KEL/TOD] determined the molar heat capacity and entropy of $CaB_2O_4$(cr) using low temperature calorimetry and report $C_{p,m}^o$ (298.15 K) = (104.0 ± 0.3) J·K$^{-1}$·mol$^{-1}$ and $S_m^o$ (298.15 K) = (105.02 ± 0.84) J·K$^{-1}$·mol$^{-1}$. The heat capacity was measured from 55 K to 298 K and the first part 0-55 K was estimated using a fitting of experimental data with a Debye-Einstein equation where the largest deviation between the model and the fit in the experimental data was one percent, the present review finds this procedure acceptable.

Using the selected entropies for Ca(cr), B(cr) and $O_2$(g), this review finds $\Delta_f S_m^o$ ($CaB_2O_4$, cr) = – (358.674 ± 0.944) J·K$^{-1}$·mol$^{-1}$, which is close to the value reported by Kelley *et al.* – (361.1 ± 2.1) J·K$^{-1}$·mol$^{-1}$; this review has selected the recalculated value. From the enthalpy and entropy of formation this review has selected $\Delta_f G_m^o$ ($CaB_2O_4$, cr) = – (1924.561 ± 1.723) kJ·mol$^{-1}$, which differs from the value in [1948KEL/TOD], $\Delta_f G_m^o$ ($CaB_2O_4$, cr) = – 2084.9 kJ·mol$^{-1}$, due to the different enthalpy of formation.

The enthalpy of formation of $NaBO_2$(cr) was recommended in the later Glushko handbook.

**[1982GLU/GUR]**

Glushko *et al.* report the enthalpy of formation, the entropy and heat capacity of $NaBO_2$, $\Delta_f H_m^o$ ($NaBO_2$, cr) = – (976.5 ± 2.5) kJ·mol$^{-1}$, $S_m^o$ ($NaBO_2$, cr) = (73.53 ± 0.1)J·K$^{-1}$·mol$^{-1}$ and $C_{p,m}^o$ = 65.94 J·K$^{-1}$·mol$^{-1}$. This selection was based on the following studies [1979SHU/BOR] and [1968ADA/JOE]. In the first study the authors measured heats of solution of $NaBO_2$(cr) and $B_2O_3$(glass) in 2 M $HNO_3$. Combining this with the enthalpy of solution of $Na_2O$(cr) in 2 M $HNO_3$ (calculated by the authors of the handbook) they obtain $\Delta_f H_m^o$ ($NaBO_2$, cr) = – (976.8 ± 2.4) kJ·mol$^{-1}$. An additional study of the enthalpy of formation of $NaBO_2$(cr) in 2N $HNO_3$ is reported in JANAF *Thermochemical tables* [1971STU/PRO], [1957GRE/WHI] and [1976YOS/TAK]. In [1968ADA/JOE] the authors measured heats of solution of $NaBO_2$(cr) and $B_2O_3$(cr) in a solution of hydrochloric acid with mol ratio 1HCl/12.731·$H_2O$; they obtained for the reaction $\frac{1}{2}Na_2O(cr) + \frac{1}{2}B_2O_3(cr) \rightleftharpoons NaBO_2(cr)$ an enthalpy of reaction, $\Delta_r H_m$ = – (131.8 ± 3.3) kJ·mol$^{-1}$, or $\Delta_f H_m^o$ ($NaBO_2$, cr) = – (975.8 ± 3.4) kJ·mol$^{-1}$, in a good agreement with the value from [1979SHU/BOR].

# Appendix B

# Ionic strength corrections[1]

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [1993MIL/CVI] is adopted in this review as outlined in Section 2.3.1. According to this definition, the standard state for a solute B in a solution is the (hypothetical) state of solute at the standard molality $m^\circ$, standard pressure $p^\circ$ or standard concentration $c^\circ$ and exhibiting infinitely dilute solution behaviour. However, for many reactions, measurements cannot be made accurately (or at all) in dilute solutions from which the necessary extrapolation to the standard state would be simple. This is invariably the case for reactions involving ions of high charge. Precise thermodynamic information for these systems can only be obtained in the presence of an inert electrolyte of sufficiently high concentration that ensures activity factors are reasonably constant throughout the measurements. This appendix describes and illustrates the method used in this review for the extrapolation of experimental equilibrium data to zero ionic strength.

The activity factors of all the species participating in reactions in high ionic strength media must be estimated in order to reduce the thermodynamic data obtained from the experiment to the state $I = 0$. Two alternative methods can be used to describe the ionic medium dependence of equilibrium constants:

- One method takes into account the individual characteristics of the ionic media by using a medium dependent expression for the activity coefficients of the species involved in the equilibrium reactions. The medium dependence is described by virial or ion interaction coefficients as used in the Pitzer equations [1973PIT] and in the specific ion interaction treatment.
- The other method uses an extended Debye-Hückel expression in which the activity coefficients of reactants and products depend only on the ionic charge and the ionic strength, but it accounts for the medium specific properties by

[1] This appendix contains much of the text of the TDB-2 Guideline written by Grenthe and Mompean [2013GRE/MOM], earlier versions of which have been printed in the previous NEA TDB reviews. The equations presented here are an essential part of the review procedure and are required to use the selected thermodynamic values. Parts of Section B.1.1 and the contents of Tables B-4, B-5, B-6 and B-7 have been revised by Rand *et al.* [2008RAN/FUG] and in the present review.

introducing ion pairing between the medium ions and the species involved in the equilibrium reactions. Earlier, this approach has been used extensively in marine chemistry, *cf.* Refs. [1979JOH/PYT], [1979MIL], [1979PYT], [1979WHI2].

The activity factor estimates are thus based on the use of Debye-Hückel type equations. The "extended" Debye-Hückel equations are either in the form of specific ion interaction methods or the Davies equation [1962DAV]. However, the Davies equation should in general not be used at ionic strengths larger than 0.1 mol·kg$^{-1}$. The method preferred in the NEA Thermochemical Database review is a medium-dependent expression for the activity coefficients, which is the specific ion interaction treatment in the form of the Brønsted-Guggenheim-Scatchard approach. Other forms of specific ion interaction methods (the Pitzer and Brewer "B-method" [1961LEW/RAN] and the Pitzer virial coefficient method [1979PIT]) are described in the NEA Guidelines for the extrapolation to zero ionic strength [2013GRE/MOM].

The specific ion interaction methods are reliable for intercomparison of experimental data in a given concentration range. In many cases this includes data at rather low ionic strengths, $I$ = 0.01 to 0.1 M, *cf.* Figure B-1, while in other cases, notably for cations of high charge ($\geq +4$ and $\leq -4$), the lowest available ionic strength is often 0.2 M or higher, see for example Figures V.12 and V.13 in [1992GRE/FUG]. It is reasonable to assume that the extrapolated equilibrium constants at $I = 0$ are more precise in the former than in the latter cases. The extrapolation error is composed of two parts, one due to experimental errors, and the other due to model errors. The model errors seem to be rather small for many systems, less than 0.1 in $\log_{10} K^{o}$. For reactions involving ions of high charge, which may be extensively hydrolysed, one cannot perform experiments at low ionic strengths. Hence, it is impossible to estimate the extrapolation error. This is true for all methods used to estimate activity corrections. Systematic model errors of this type are not included in the uncertainties assigned to the selected data in this review.

# B.1 The specific ion interaction equations

## B.1.1 Background

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solution, accounts for electrostatic, non-specific long-range interactions. At higher concentrations, short range, non-electrostatic interactions have to be taken into account. This is usually done by adding ionic strength dependent terms to the Debye-Hückel expression. This method was first outlined by Brønsted [1922BRO], [1922BRO2] and elaborated by Scatchard [1936SCA] and Guggenheim [1966GUG]. Biedermann [1975BIE] highlighted its practical value, especially for the

estimation of ionic medium effects on equilibrium constants. The two basic assumptions in the specific ion interaction treatment are described below.

- **Assumption 1:** The activity coefficient $\gamma_j$ of an ion $j$ of charge $z_j$ in the solution of ionic strength $I_m$ may be described by Eq. (B.1):

$$\log_{10} \gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k,I_m) m_k \tag{B.1}$$

$D$ is the Debye-Hückel term:

$$D = \frac{A\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \tag{B.2}$$

$A$ is a temperature and pressure dependent constant and $I_m$ is the molal ionic strength:

$$I_m = \frac{1}{2}\sum_i m_i z_i^2$$

The Debye-Hückel limiting slope, $A$, has a value of $(0.509 \pm 0.001)$ $\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$ at 298.15 K and 1 bar, (*cf.* Section B.1.2). The value 1.5 in the Debye-Hückel term was proposed by Scatchard [1976SCA] to minimise the ionic strength dependence of $\varepsilon(j,k)$ for a number of electrolytes, and it was found to be particularly appropriate between $I_m$ = 0.5 and 3.5 m. A constant value for all species simplifies modelling of both binary and multicomponent aqueous electrolyte systems, and makes it easier to give a consistent description of mean activity coefficient both in binary and multicomponent solutions ([1959ROB/STO], pp.435-441).

It should be mentioned that some authors have proposed different values ranging from 1.0 [1935GUG] to 1.6 [1962VAS]. However, the parameter is empirical and as such is correlated to the value of $\varepsilon(j,k,I_m)$. Hence, this variety of values does not represent an uncertainty range, but rather indicates that several different sets of values in the denominator of the Debye-Hückel term and $\varepsilon(j,k,I_m)$ may describe equally well the experimental mean activity coefficients of a given electrolyte. The ion interaction coefficients at 298.15 K listed in Table B-6, Table B-7, Table B-8 and Table B-9 have thus to be used with the value 1.5 $\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$.

The summation in Eq. (B.1) extends over all ions $k$ present in solution. Their molality is denoted by $m_k$, and the specific ion interaction parameters, $\varepsilon(j,k,I_m)$, in general depend only slightly on the ionic strength. The concentrations of the ions of the ionic medium are often very much larger than those of the reacting species. Hence, the ionic medium ions will make the main contribution to the value of $\log_{10}\gamma_j$ for the reacting ions. This fact often makes it possible to simplify the summation $\sum_k \varepsilon(j,k,I_m)m_k$, so that only ion interaction coefficients between the participating ionic species and the ionic medium ions are included, as shown in Eqs. (B.5) to (B.9).

- **Assumption 2:** The ion interaction coefficients, $\varepsilon(j,k,I_m)$ are zero for ions of the same charge sign and for uncharged species. The rationale behind this is that $\varepsilon$, which describes specific short-range interactions, must be small for ions of the

same charge since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species, but in some cases the experimental data allow determination of interaction coefficients for uncharged species with electroneutral combinations of ions, *cf.* Table B-8. Equation (B.1) will allow fairly accurate estimates of the activity coefficients in mixtures of electrolytes if the ion interaction coefficients are known. Ion interaction coefficients for simple ions can be obtained from tabulated data of mean activity coefficients of strong electrolytes or from the corresponding osmotic coefficients. Ion interaction coefficients for complexes can either be estimated from the charge and size of the ion or determined experimentally from the variation of the equilibrium constant with the ionic strength.

Ion interaction coefficients are not strictly constant but may vary slightly with the ionic strength. The extent of this variation depends on the charge type and is small for 1:1, 1:2 and 2:1 electrolytes for molalities less than 3.5 m. The concentration dependence of the ion interaction coefficients can thus often be neglected. This point was emphasised by Guggenheim [1966GUG], who has presented a considerable amount of experimental material supporting this approach. The concentration dependence is larger for electrolytes of higher charge. In order to reproduce accurately their activity coefficient data, concentration dependent ion interaction coefficients have to be used, *cf.* Lewis *et al.* [1961LEW/RAN], Baes and Mesmer [1976BAE/MES], or Ciavatta [1980CIA].

For cases where the uncertainties in the epsilon values collected in Table B-6 and Table B-7 are ± 0.03 kg·mol$^{-1}$ or greater, Ciavatta [1980CIA] proposed the use of Eq. (B.3)

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m \tag{B.3}$$

However, even if the value of $\varepsilon$ calculated in this way describes the variation with ionic strength slightly better than a constant value, this equation has no theoretical basis; $\varepsilon_2$ is a fitting parameter and the term $\varepsilon_2 \log_{10} I_m$ goes to minus infinity at the limiting value $I_m = 0$. This expression for the composition dependence of $\varepsilon$ should be avoided, even though the term $\varepsilon \cdot m = (\varepsilon_1 + \varepsilon_2 \log_{10} I_m) \cdot m$ (in the calculation of activity coefficients) is zero at $I_m = 0$. There may be cases where reviewers will still want to use Eq. (B.3) to describe the ionic strength variation of the interaction parameters, but the rationale behind this should then be described. However, as discussed by Rand *et al.* [2008RAN/FUG] (*cf.* Section IX.1.3.3) the one- and two-epsilon models usually will provide similar calculated results for values of $\log_{10} K^\circ$. As the two-epsilon model has been used in the current and previous volumes, the relevant parameters have been retained and augmented in Table B-8.

By using a more elaborate virial expansion, Pitzer and co-workers [1973PIT], [1973PIT/MAY], [1974PIT/KIM], [1974PIT/MAY], [1975PIT], [1976PIT/SIL], [1978PIT/PET], [1979PIT] have managed to describe measured activity coefficients of a large number of electrolytes with high precision over a large concentration range.

Pitzer's model generally contains three parameters as compared to one in the specific ion interaction treatment. The use of the treatment requires the knowledge of all these parameters. The derivation of Pitzer coefficients for many complexes, such as those of the actinides would require a very large amount of additional experimental work, since few data of this type are currently available.

The way in which the activity coefficient corrections are performed in this review according to the specific ion interaction treatment is illustrated below for a general case of a complex formation reaction. Charges on all species except the hydrogen ions are omitted for brevity.

$$m\,\mathrm{M} + q\,\mathrm{L} + n\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n + n\,\mathrm{H}^+$$

The formation constant of $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, ${}^*\beta_{q,n,m}$, determined in an ionic medium (1:1 salt NX) of the ionic strength $I_m$, is related to the corresponding value at zero ionic strength, ${}^*\beta^{\mathrm{o}}_{q,n,m}$ by Eq. (B.4).

$$\begin{aligned}\log_{10}{}^*\beta_{q,n,m} = \log_{10}{}^*\beta^{\mathrm{o}}_{q,n,m} + m\log_{10}\gamma_{\mathrm{M}} + q\log_{10}\gamma_{\mathrm{L}} + n\log_{10}a_{\mathrm{H_2O}} \\ -\log_{10}\gamma_{q,n,m} - n\log_{10}\gamma_{\mathrm{H}^+}\end{aligned} \tag{B.4}$$

The subscript $(q,n,m)$ denotes the complex ion, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$. If the concentrations of N and X are much greater than the concentrations of M, L, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$ and $\mathrm{H}^+$, only the molalities $m_{\mathrm{N}}$ and $m_{\mathrm{X}}$ have to be taken into account for the calculation of the term, $\sum_k \varepsilon(j,k,I_m)m_k$ in Eq. (B.1). For example, for the activity coefficient of the metal cation M, $\gamma_{\mathrm{M}}$, Eq. (B.5) is obtained at 298.15 K and 1 bar.

$$\log_{10}\gamma_{\mathrm{M}} = \frac{-z_{\mathrm{M}}^2\,0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} + \varepsilon(\mathrm{M},\mathrm{X},I_m)m_{\mathrm{X}} \tag{B.5}$$

Under these conditions and considering 1:1 electrolytes, $I_m \approx m_{\mathrm{X}} = m_{\mathrm{N}}$. Substituting the $\log_{10}\gamma$ values in Eq. (B.4) with the corresponding forms of Eq. (B.5) and rearranging leads to:

$$\log_{10}{}^*\beta_{q,n,m} - \Delta z^2 D - n\log_{10}a_{\mathrm{H_2O}} = \log_{10}{}^*\beta^{\mathrm{o}}_{q,n,m} - \Delta\varepsilon I_m \tag{B.6}$$

where, at 298.15 K and 1 bar:

$$\Delta z^2 = (m\,z_{\mathrm{M}} - q\,z_{\mathrm{L}} - n)^2 + n - mz_{\mathrm{M}}^2 - q\,z_{\mathrm{L}}^2 \tag{B.7}$$

$$D = \frac{0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} \tag{B.8}$$

$$\Delta\varepsilon = \varepsilon(q,n,m,\mathrm{N\ or\ X}) + n\varepsilon(\mathrm{H},\mathrm{X}) - q\varepsilon(\mathrm{N},\mathrm{L}) - m\varepsilon(\mathrm{M},\mathrm{X}) \tag{B.9}$$

Here $(m\,z_{\mathrm{M}} - q\,z_{\mathrm{L}} - n)$, $z_{\mathrm{M}}$ and $z_{\mathrm{L}}$ are the charges of the complex, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, the metal ion M and the ligand L, respectively.

Equilibria involving $H_2O(l)$ as a reactant or product require a correction for the activity of water, $a_{H_2O}$. The activity of water in an electrolyte mixture can be calculated as:

$$\log_{10} a_{H_2O} = \frac{-\phi_m \sum_k m_k}{\ln(10) M_{H_2O}^{-1}} \tag{B.10}$$

where $\phi_m$ is the osmotic coefficient of the mixture, $M_{H_2O}$ is the molar mass of $H_2O$ in kg, that is $M_{H_2O}$ = 0.0180153 kg·mol$^{-1}$, and the summation extends over all solute species $k$ with molality $m_k$ present in the solution. In the presence of an ionic medium NX as the dominant species, Eq. (B.10) can be simplified by neglecting the contributions of all minor species, *i.e.*, the reacting ions. Hence, for a 1:1 electrolyte of ionic strength $I_m \approx m_{NX}$, Eq. (B.10) becomes:

$$\log_{10} a_{H_2O} = \frac{-2 m_{NX} \phi_m}{\ln(10) M_{H_2O}^{-1}} \tag{B.11}$$

Alternatively, water activities can be taken from Table B-1. These have been calculated for the most common ionic media at various concentrations applying Pitzer's ion interaction model and the interaction parameters given in [1991PIT]. Data in *italics* have been calculated for concentrations beyond the validity of the parameter set applied. These data are therefore extrapolations and should be used with care.

Values of osmotic coefficients for single electrolytes have been compiled by various authors, *e.g.*, Robinson and Stokes [1959ROB/STO]. The activity of water can also be calculated from the known activity coefficients of the dissolved species. In the presence of an ionic medium, $N_{\nu_+}X_{\nu_-}$, of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to Eq. (B.12) (*cf.* Eqs. (23-39), (23-40) and (A4-2) in [1961LEW/RAN]).

$$\begin{aligned} 1-\phi_m = {} & \frac{A\ln(10)\left|z_+ z_-\right|}{I_m 1.5^3}\left[1+1.5\sqrt{I_m}-2\ln(1+1.5\sqrt{I_m})-\frac{1}{1+1.5\sqrt{I_m}}\right] \\ & -\ln(10)\ \varepsilon(\mathrm{N,X})\, m_{NX}\left(\frac{\nu_+\nu_-}{\nu_+ + \nu_-}\right) \end{aligned} \tag{B.12}$$

with the value 1.5 kg$^{½}$·mol$^{-½}$, which is mainly used in NEA reviews (*cf.*, Section B.1.2), rather than the implied 1.0 kg$^{½}$·mol$^{-½}$ in the expressions in Lewis and Randall, and $n_+$ and $n_-$ are the number of cations and anions in the salt formula ($\nu_+ z_+ = \left|\nu_- z_-\right|$) and in this case:

$$I_m = \frac{1}{2}\left|z_+ z_-\right| m_{NX}(\nu_+ + \nu_-).$$

Table B-1: Water activities $a_{H_2O}$ for the most common ionic media at various concentrations applying Pitzer's ion interaction approach and the interaction parameters given in [1991PIT] and using density conversions from Table 2-5. Data in *italics* have been calculated for concentrations beyond the validity of the parameter set applied. These data are therefore extrapolations and should be used with care.

| Water activities $a_{H_2O}$ at 298.15 K | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $c$ (M) | $HClO_4$ | $NaClO_4$ | $LiClO_4$ | $NH_4ClO_4$ | $Ba(ClO_4)_2$ | HCl | NaCl | LiCl |
| 0.100 | 0.9966 | 0.9966 | 0.9966 | 0.9967 | 0.9953 | 0.9966 | 0.9966 | 0.9966 |
| 0.250 | 0.9914 | 0.9917 | 0.9912 | 0.9920 | 0.9879 | 0.9914 | 0.9917 | 0.9915 |
| 0.500 | 0.9821 | 0.9833 | 0.9817 | 0.9844 | 0.9740 | 0.9823 | 0.9833 | 0.9826 |
| 0.750 | 0.9720 | 0.9747 | 0.9713 | 0.9769 | 0.9576 | 0.9726 | 0.9748 | 0.9731 |
| 1.000 | 0.9609 | 0.9660 | 0.9602 | 0.9694 | 0.9387 | 0.9620 | 0.9661 | 0.9631 |
| 1.500 | 0.9357 | 0.9476 | 0.9341 | 0.9542 | 0.8929 | 0.9386 | 0.9479 | 0.9412 |
| 2.000 | 0.9056 | 0.9279 | 0.9037 | | *0.8383* | 0.9115 | 0.9284 | 0.9167 |
| 3.000 | 0.8285 | 0.8840 | 0.8280 | | *0.7226* | 0.8459 | 0.8850 | 0.8589 |
| 4.000 | 0.7260 | 0.8331 | *0.7309* | | | 0.7643 | 0.8352 | 0.7991 |
| 5.000 | *0.5982* | *0.7744* | | | | 0.6677 | 0.7782 | 0.7079 |
| 6.000 | *0.4513* | *0.7075* | | | | *0.5592* | | *0.6169* |
| $c$ (M) | KCl | $NH_4Cl$ | $MgCl_2$ | $CaCl_2$ | NaBr | $HNO_3$ | $NaNO_3$ | $LiNO_3$ |
| 0.100 | 0.9966 | 0.9966 | 0.9953 | 0.9954 | 0.9966 | 0.9966 | 0.9967 | 0.9966 |
| 0.250 | 0.9918 | 0.9918 | 0.9880 | 0.9882 | 0.9916 | 0.9915 | 0.9919 | 0.9915 |
| 0.500 | 0.9836 | 0.9836 | 0.9744 | 0.9753 | 0.9830 | 0.9827 | 0.9841 | 0.9827 |
| 0.750 | 0.9754 | 0.9753 | 0.9585 | 0.9605 | 0.9742 | 0.9736 | 0.9764 | 0.9733 |
| 1.000 | 0.9671 | 0.9669 | 0.9399 | 0.9436 | 0.9650 | 0.9641 | 0.9688 | 0.9635 |
| 1.500 | 0.9500 | 0.9494 | 0.8939 | 0.9024 | 0.9455 | 0.9439 | 0.9536 | 0.9422 |
| 2.000 | 0.9320 | 0.9311 | 0.8358 | 0.8507 | 0.9241 | 0.9221 | 0.9385 | 0.9188 |
| 3.000 | 0.8933 | 0.8918 | 0.6866 | 0.7168 | 0.8753 | 0.8737 | 0.9079 | 0.8657 |
| 4.000 | 0.8503 | 0.8491 | 0.5083 | 0.5511 | *0.8174* | 0.8196 | 0.8766 | 0.8052 |
| 5.000 | | *0.8037* | | *0.3738* | *0.7499* | 0.7612 | 0.8446 | 0.7390 |
| 6.000 | | | | | *0.6728* | *0.7006* | *0.8120* | *0.6696* |

(Continued on next page)

Table B-1 (continued)

| Water activities $a_{H_2O}$ at 298.15 K | | | | | | |
|---|---|---|---|---|---|---|
| $c$ (M) | $NH_4NO_3$ | $Na_2SO_4$ | $(NH_4)_2SO_4$ | $Na_2CO_3$ | $K_2CO_3$ | NaSCN |
| 0.750 | 0.9768 | 0.9732 | 0.9728 | 0.9720 | 0.9683 | 0.9736 |
| 1.000 | 0.9694 | 0.9653 | 0.9640 | 0.9637 | 0.9570 | 0.9641 |
| 1.500 | 0.9548 | 0.9491 | 0.9455 | 0.9467 | 0.9316 | 0.9438 |
| 2.000 | 0.9403 | | 0.9247 | 0.9283 | 0.9014 | 0.9215 |
| 3.000 | 0.9115 | | 0.8735 | | 0.8235 | 0.8708 |
| 4.000 | 0.8829 | | 0.8050 | | 0.7195 | *0.8115* |
| 5.000 | *0.8545* | | | | *0.5887* | *0.7436* |
| 6.000 | *0.8266* | | | | | *0.6685* |

The activity of water is obtained by inserting Eq. (B.12) into Eq. (B.11). It should be mentioned that in mixed electrolytes with several components at high concentrations, it might be necessary to use Pitzer's equation to calculate the activity of water. On the other hand, $a_{H_2O}$ is nearly constant in most experimental studies of equilibria in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants. The medium electrolyte thus determines the osmotic coefficient of the solvent.

In natural waters the situation is similar; the ionic strength of most surface waters is so low that the activity of $H_2O(l)$ can be set equal to unity. A correction may be necessary in the case of seawater, where a sufficiently good approximation for the osmotic coefficient may be obtained by considering NaCl as the dominant electrolyte.

In more complex solutions of high ionic strengths with more than one electrolyte at significant concentrations, *e.g.*, ($Na^+$, $Mg^{2+}$, $Ca^{2+}$) ($Cl^-$, $SO_4^{2-}$), Pitzer's equation (*cf.* [2013GRE/MOM]) may be used to estimate the osmotic coefficient; the necessary interaction coefficients are known for most systems of geochemical interest.

Note that in all ion interaction approaches, the equation for the mean activity coefficients can be split up to give equations for conventional single ion activity coefficients in mixtures, *e.g.*, Eq. (B.1). The latter are strictly valid only when used in combinations which yield electroneutrality. Thus, while estimating medium effects on standard potentials, a combination of redox equilibria with, $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2(g)$, is necessary (*cf.* Example B.3).

### B.1.2 Ionic strength corrections at temperatures other than 25 °C (298.15 K)

Values of the Debye-Hückel parameter $A$ in Eqs. (B.2), (B.2a) and (B.12) are listed in Table B-2 for several temperatures at a pressure of 1 bar below 100 °C and at the steam saturated pressure for $t \geq 100$ °C. The values in Table B-2 can be calculated from the static dielectric constant and the density of water as a function of temperature and pressure, as discussed in various references [1974HEL/KIR], [1979BRA/PIT], [1981HEL/KIR], [1984ANA/ATK], [1990ARC/WAN], [2009PAT/HRU]. The values in Table B-2 are those from Helgeson *et al.* [1981HEL/KIR]. More recent expressions for the density and dielectric constant (*e.g.*, those of Archer and Wang [1990ARC/WAN] or Pátek *et al.* [2009PAT/HRU]) would generate very slightly different values, but the Table B-2 values should be used to provide consistent TDB activity coefficient expressions.

Table B-2: Values of the Debye-Hückel constant $A$ as a function of temperature at a pressure of 1 bar below 100 °C and at the steam saturated pressure for $t \geq 100$ °C. The uncertainty in the $A$ parameter is estimated by this review to be ± 0.001 $kg^{½}·mol^{-½}$ at 25 °C, and ± 0.006 $kg^{½}·mol^{-½}$ at 300 °C.

| $t$ / °C | $p$ / bar | $A$/ $kg^{½}·mol^{-½}$ |
|---|---|---|
| 0 | 1.00 | 0.491 |
| 5 | 1.00 | 0.494 |
| 10 | 1.00 | 0.498 |
| 15 | 1.00 | 0.501 |
| 20 | 1.00 | 0.505 |
| 25 | 1.00 | 0.509 |
| 30 | 1.00 | 0.514 |
| 35 | 1.00 | 0.518 |
| 40 | 1.00 | 0.523 |
| 50 | 1.00 | 0.534 |
| 75 | 1.00 | 0.564 |
| 100 | 1.013 | 0.600 |
| 125 | 2.32 | 0.642 |
| 150 | 4.76 | 0.690 |
| 175 | 8.92 | 0.745 |
| 200 | 15.5 | 0.810 |
| 250 | 39.7 | 0.979 |
| 300 | 85.8 | 1.256 |

In this review the term $Ba_j$, in the denominator of the Debye-Hückel term, $D$ of Eq. (B.2), has been assigned a value of 1.5 $kg^{1/2}\cdot mol^{-1/2}$ (Eq. (B.2a)), and is kept constant at all temperatures. Due to the variation of $B$ with temperature, this implies a temperature dependence for ion-size parameters. Assuming the ion size is in reality constant, it becomes obvious that this simplification introduces an error in $D$, which increases with temperature and ionic strength. However, this error is less than $\pm 0.01$ $kg^{1/2}\cdot mol^{-1/2}$ at $t \leq 100$ °C and $I < 6$ m, and less than $\pm 0.006$ $kg^{1/2}\cdot mol^{-1/2}$ at $t \leq 50$ °C and $I \leq 4$ m.

The values of $\varepsilon(j,k,I_m)$, obtained with the methods described in Section B.1.3 at temperatures other than 25 °C, will depend on the value adopted for $Ba_j$. Nevertheless, as long as a consistent approach is followed, values of $\varepsilon(j,k,I_m)$ absorb the choice of $Ba_j$, and for moderate temperature intervals (between 0 and 200 °C) the choice $Ba_j = 1.5$ $kg^{1/2}\cdot mol^{-1/2}$ is simple and is recommended by this review.

The variation of $\varepsilon(j,k,I_m)$ with temperature is discussed by Lewis *et al.* [1961LEW/RAN], Millero [1979MIL], Helgeson *et al.* [1981HEL/KIR], [1990OEL/HEL], Giffaut *et al.* [1993GIF/VIT2] and Grenthe and Plyasunov [1997GRE/PLY]. The absolute values for the reported ion interaction parameters differ in these studies due to the fact that the Debye-Hückel term used by these authors is not exactly the same. Nevertheless, common to all these studies is the fact that values of $(\partial\varepsilon/\partial T)_p$ are usually $\leq 0.005$ $kg\cdot K^{-1}\cdot mol^{-1}$ for temperatures below 200 °C. Therefore, if values of $\varepsilon(j,k,I_m)$ obtained at 25 °C are used in the temperature range 0 to 50 °C to perform ionic strength corrections, the error in $\log_{10}\gamma_j/I_m$ will be $\leq 0.13$ $kg\cdot mol^{-1}$. It is clear that in order to reduce the uncertainties in solubility calculations at $t \neq 25$ °C, studies on the variation of $\varepsilon(j,k,I_m)$ values with temperature should be undertaken.

## B.1.3 Evaluation of ion interaction coefficients

A scrutiny of the tables with conditional equilibrium constants listed in the NEA reviews show that most of them have been determined in mixed ionic media consisting of a ligand and perchlorate that make up the ionic strength, $I$. In addition the conditional constants at several ionic strengths are reported, which makes it straightforward to use SIT, both to extrapolate data to zero ionic strength and to determine $\log_{10}K^o$ and $\Delta\varepsilon$. However, the determination of the specific ion interaction parameters from the latter requires some care, as shown by the following examples, where the ionic strength is determined by the concentrations of free (not coordinated) ligand, $L^-$, and $ClO_4^-$:

$$M^{n+}(NaL, NaClO_4) + L^-(NaL, NaClO_4) \rightleftharpoons ML^{(n-1)+}(NaL, NaClO_4) \qquad (B.13)$$

**Example B.1**. When the complexes formed are very strong with $\log_{10}K > 4$, the change in the ionic medium composition is small, less than a few percent, when the perchlorate is replaced by a free ligand.

The value of $\Delta\varepsilon \cdot I$ for Reaction (B.13) is:

$$\Delta\varepsilon \cdot I = \varepsilon(\mathrm{ML}^{(n-1)+}, \mathrm{ClO_4^-}) \cdot [\mathrm{ClO_4^-}] + \varepsilon(\mathrm{ML}^{(n-1)+}, \mathrm{L^-}) \cdot [\mathrm{L^-}] - \varepsilon(\mathrm{M}^{n+}, \mathrm{ClO_4^-}) \cdot [\mathrm{ClO_4^-}] - \varepsilon(\mathrm{M}^{n+}, \mathrm{L^-}) \cdot [\mathrm{L^-}] - \varepsilon(\mathrm{L^-}, \mathrm{Na^+}) \cdot [\mathrm{Na^+}] - \varepsilon(\mathrm{L^-}, \mathrm{M}^{n+}) \cdot [\mathrm{M}^{n+}] \quad \text{(B.14)}$$

In this case we can make the approximation $\varepsilon(\mathrm{ML}^{(n-1)+}, \mathrm{L^-}) \cdot [\mathrm{L^-}]$, $\varepsilon(\mathrm{M}^{n+}, \mathrm{L^-}) \cdot [\mathrm{L^-}]$ and $\varepsilon(\mathrm{L^-}, \mathrm{M}^{n+}) \cdot [\mathrm{M}^{n+}]$ are all $\approx 0$, because the free ligand and the metal ion concentrations are very low and the individual ion-interaction parameters, $\varepsilon(\mathrm{ML}^{(n-1)+}, \mathrm{ClO_4^-})$ can accordingly be determined without problem, when $\varepsilon(\mathrm{M}^{n+}, \mathrm{ClO_4^-})$ and $\varepsilon(\mathrm{L^-}, \mathrm{Na^+})$ are known from mean-activity coefficients. The ionic strength is determined by the concentration of sodium perchlorate.

**Example B.2**. In systems where moderately strong complexes are formed, $\log_{10}K \approx$ 2-3, the change in the ionic medium composition is larger, but for changes up to 5-10 % one can still neglect the terms $\varepsilon(\mathrm{ML}^{(n-1)+}, \mathrm{L^-}) \cdot [\mathrm{L^-}]$ and $\varepsilon(\mathrm{M}^{n+}, \mathrm{L^-}) \cdot [\mathrm{L^-}]$, but this results in a larger uncertainty in the individual ion-interaction parameters.

**Example B.3**. In systems where weak complexes are formed, such as in chloride and nitrate systems, a significant amount of perchlorate has to be replaced with the ligand, L, in order to determine the conditional equilibrium constants. In this case, using $\mathrm{L^-} = \mathrm{Cl^-}$ as an example, the terms $\varepsilon(\mathrm{MCl}^{(n-1)+}, \mathrm{Cl^-}) \cdot [\mathrm{Cl^-}]$ and $\varepsilon(\mathrm{M}^{n+}, \mathrm{Cl^-}) \cdot [\mathrm{Cl^-}]$ can presumably be neglected, because only inner-sphere chloride complexes have been identified experimentally, which is not the case for perchlorates. The ionic strength is equal to $I = [\mathrm{ClO_4^-}] + [\mathrm{L^-}]$, where the first term is the total concentration of perchlorate and the second term approximately equal to the total concentration of L, because only a small amount of the ligand is coordinated. In this case, it is *only* possible to determine individual ion-interaction parameters if experiments at constant ionic strength but varying the ratio $[\mathrm{ClO_4^-}]$:$[\mathrm{L^-}]$ are performed (see Section B.2 in [2013LEM/BER], *Weak complexes within an ion-interaction approach: ion interaction coefficients versus equilibrium constants for ion pairs*).

Using the approximation that $\varepsilon(\mathrm{MCl}^{(n-1)+}, \mathrm{Cl^-}) \cdot [\mathrm{Cl^-}]$ and $\varepsilon(\mathrm{M}^{n+}, \mathrm{Cl^-}) \cdot [\mathrm{Cl^-}]$ and are both negligible because of small outer-sphere ion-interactions, we have for Reaction (B.15) studied in a $\mathrm{HCl/HClO_4}$ ionic medium using SIT, (Equation (B.16) from previous reviews):

$$\mathrm{UO_2^{2+}} + \mathrm{Cl^-} \rightleftharpoons \mathrm{UO_2Cl^+} \quad \text{(B.15)}$$

and

$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^{\circ} - \Delta\varepsilon I_m \quad \text{(B.16)}$$

$\log_{10} \beta_1^o = (0.170 \pm 0.021)$ and $\Delta\varepsilon(\text{B.16}) = \varepsilon(UO_2Cl^+, ClO_4^-) - \varepsilon(UO_2^{2+}, ClO_4^-) - \varepsilon(Cl^-, H^+) = -(0.248 \pm 0.022)$ kg·mol$^{-1}$, that is:

$$\varepsilon(UO_2Cl^+, ClO_4^-) = (0.33 \pm 0.04) \text{ kg·mol}^{-1}.$$

It should be noted that conditional equilibrium constants are better calculated directly from experimental values of Δε when these are available.

Table B- 3: The experimental equilibrium constants used for the extrapolation to $I = 0$ using SIT at 25 °C and 1 bar, according to Reaction (B.15). The linear regression of this set of data is shown in Figure B-1.

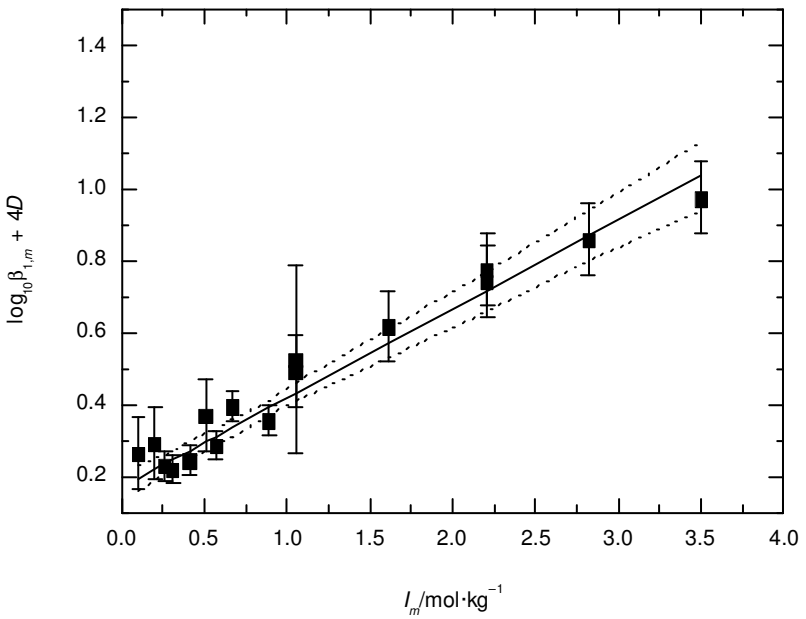
| $I_m$ | $\log_{10} \beta_1$ (exp) [(a)] | $\log_{10} \beta_{1,m}$ [(b)] | $\log_{10} \beta_{1,m} + 4\,D$ |
|---|---|---|---|
| 0.10 | – 0.17 ± 0.10 | – 0.174 | 0.264 ± 0.100 |
| 0.20 | – 0.25 ± 0.10 | – 0.254 | 0.292 ± 0.100 |
| 0.26 | – 0.35 ± 0.04 | – 0.357 | 0.230 ± 0.040 |
| 0.31 | – 0.39 ± 0.04 | – 0.397 | 0.220 ± 0.040 |
| 0.41 | – 0.41 ± 0.04 | – 0.420 | 0.246 ± 0.040 |
| 0.51 | – 0.32 ± 0.10 | – 0.331 | 0.371 ± 0.100 |
| 0.57 | – 0.42 ± 0.04 | – 0.432 | 0.288 ± 0.040 |
| 0.67 | – 0.34 ± 0.04 | – 0.354 | 0.395 ± 0.040 |
| 0.89 | – 0.42 ± 0.04 | – 0.438 | 0.357 ± 0.040 |
| 1.05 | – 0.31 ± 0.10 | – 0.331 | 0.491 ± 0.100 |
| 1.05 | – 0.277 ± 0.260 | – 0.298 | 0.525 ± 0.260 |
| 1.61 | – 0.24 ± 0.10 | – 0.272 | 0.618 ± 0.100 |
| 2.21 | – 0.15 ± 0.10 | – 0.193 | 0.744 ± 0.100 |
| 2.21 | – 0.12 ± 0.10 | – 0.163 | 0.774 ± 0.100 |
| 2.82 | – 0.06 ± 0.10 | – 0.112 | 0.860 ± 0.100 |
| 3.50 | 0.04 ± 0.10 | – 0.027 | 0.974 ± 0.100 |

(a) Equilibrium constants for Reaction (B.15) in aqueous HCl/$HClO_4$ ionic medium, with assigned uncertainties, corrected to 25 °C where necessary. For details of the data, see Section V.4.2.1.2 of [1992GRE/FUG].

(b) Equilibrium constants were converted from molarity to molality as described in Section 2.2.

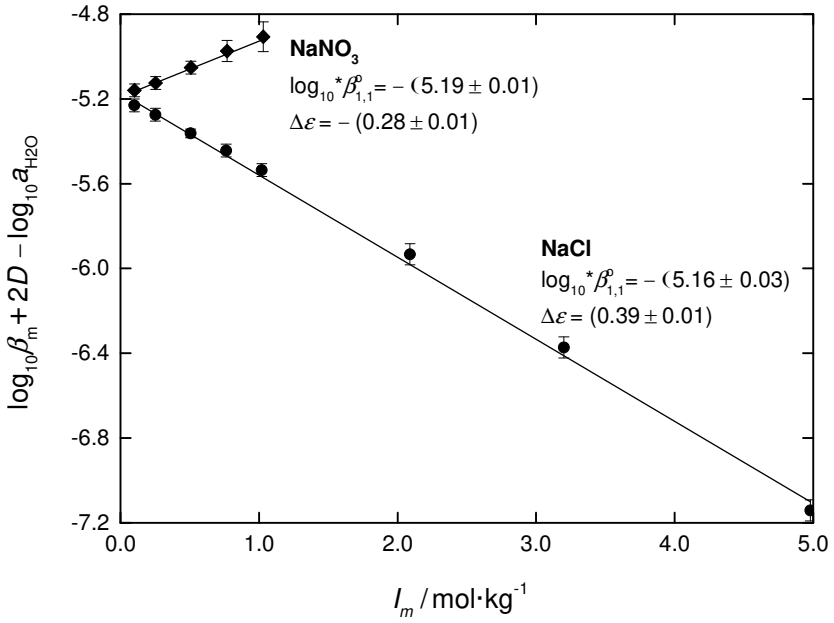
The experimental data are shown in Figure B-1, with the area enclosed by the dotted lines representing the uncertainty range obtained by using the results in $\log_{10} \beta_1^o$ and $\Delta\varepsilon$ and correcting back to $I \neq 0$.

Figure B-1: Plot of $\log_{10}\beta_1 + 4D$ *versus* $I_m$ for Reaction (B.15), at 25 °C and 1 bar. The straight line shows the result of the weighted linear regression, and the dotted lines represent the uncertainty range obtained from the estimated errors in the conditional equilibrium constants, $\log_{10}\beta$.




**Example B.4**. De Stefano *et al.* [2002DES/GIA] studied the hydrolysis of U(VI) in aqueous NaCl (0.1-4.5 M) and $NaNO_3$ (0.1-1 M) solutions with pH < 6 at $t$ = 25 °C. The model used to fit the data includes the (1,1) species, $UO_2OH^+$, and a number of polymeric species including $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, and $(UO_2)_3(OH)_7^-$. The SIT plot for reaction $UO_2^{2+} + H_2O(l) \rightleftharpoons UO_2OH^+ + H^+$, with the data from [2002DES/GIA] without correction for the complex formation of U(VI) with chloride or nitrate is given in Figure B-2 where the solid lines represent the best fits. In this case it is *not* possible to correct the conditional hydrolysis constants, $\log_{10}\beta_{1,1}$, for chloride complexes using the data in Example B.3, because these ion-interaction coefficients refer to a mixed chloride-perchlorate medium.

Figure B-2: SIT plot for reaction $UO_2^{2+} + H_2O(l) \rightleftharpoons UO_2OH^+ + H^+$, with the data from [2002DES/GIA] without correction for the complex formation of U(VI) with chloride or nitrate. Solid lines represent the best fits.




**Example B.5.** In some cases the experimental data refer to one ionic strength only and calculation of $\Delta\varepsilon$ from this conditional constant requires information on the individual ion-interaction constants of reactants and products. As some of these values are unknown they have to be estimated, examples are given in Table B-4 in [2003GUI/FAN], but when using these values one must ensure that they refer to the same ionic medium. The ionic-interactions reported in columns two and four in Table B-4 of [2003GUI/FAN] have not been obtained by taking account of chloride and nitrate complex formation and should not be used, however the corresponding values of $\log_{10}K^o$ are correct as seen in Example B.4.

**Example B.6.** The ion interaction coefficient $\varepsilon(H^+,Cl^-)$ can be obtained from published values of $\gamma_{\pm,\,HCl}$ *versus* $m_{HCl}$:

$$\begin{aligned} 2\log_{10}\gamma_{\pm,\,HCl} &= \log_{10}\gamma_{H^+} + \log_{10}\gamma_{Cl^-} \\ &= -D + \varepsilon(H^+,Cl^-)\,m_{Cl^-} \; -D \; + \; \varepsilon(H^+,Cl^-)\,m_{H^+} \\ \log_{10}\gamma_{\pm,\,HCl} &= -D + \varepsilon(H^+,Cl^-)\,m_{HCl} \end{aligned}$$

By plotting $(\log_{10}\gamma_{\pm,\mathrm{HCl}} + D)$ *versus* $m_{\mathrm{HCl}}$ a straight line with the slope $\varepsilon(\mathrm{H^+},\mathrm{Cl^-})$ is obtained. The degree of linearity should in itself indicate the range of validity of the specific ion interaction approach. Osmotic coefficient data can be treated in an analogous way.

**Example B.7.** When using the specific ion interaction treatment, the relationship between the redox potential of the couple, $\mathrm{UO_2^{2+}/U^{4+}}$, in a perchlorate medium of ionic strength, $I_m$, and the corresponding quantity at $I = 0$ should be calculated in the following way. The reaction in the galvanic cell:

$$\mathrm{Pt \mid H_2(g) \mid H^+ \vdots\vdots UO_2^{2+}, U^{4+} \mid Pt}$$

is:

$$\mathrm{UO_2^{2+} + H_2(g) + 2H^+ \rightleftharpoons U^{4+} + 2H_2O(l)}\,. \tag{B.17}$$

For this reaction

$$\log_{10} K^\circ = \log_{10}\left(\frac{a_{\mathrm{U^{4+}}}\cdot a_{\mathrm{H_2O}}^2}{a_{\mathrm{UO_2^{2+}}}\cdot a_{\mathrm{H^+}}^2\cdot f_{\mathrm{H_2}}}\right).$$

$$\log_{10}K^\circ = \log_{10}K + \log_{10}\gamma_{\mathrm{U^{4+}}} - \log_{10}\gamma_{\mathrm{UO^{2+}}} - 2\log_{10}\gamma_{\mathrm{H^+}} - \log_{10}f_{\mathrm{H_2}} + 2\log_{10}\alpha_{\mathrm{H_2O}}$$

$f_{\mathrm{H_2}} \approx p_{\mathrm{H_2}}$ at reasonably low partial pressure of $\mathrm{H_2(g)}$, $a_{\mathrm{H_2O}} \approx 1$ (which is a reasonable approximation for $I_m \leq 3$), and

$$\log_{10}\gamma_{\mathrm{U^{4+}}} = -16D + \varepsilon(\mathrm{U^{4+}},\mathrm{ClO_4^-})\,m_{\mathrm{ClO_4^-}}$$
$$\log_{10}\gamma_{\mathrm{UO_2^{2+}}} = -4D + \varepsilon(\mathrm{UO_2^{2+}},\mathrm{ClO_4^-})\,m_{\mathrm{ClO_4^-}}$$
$$\log_{10}\gamma_{\mathrm{H^+}} = -D + \varepsilon(\mathrm{H^+},\mathrm{ClO_4^-})\,m_{\mathrm{ClO_4^-}}$$

Hence,

$$\begin{aligned}\log_{10}K^\circ = {} & \log_{10}K - 10D \\ & + (\varepsilon(\mathrm{U^{4+}},\mathrm{ClO_4^-}) - \varepsilon(\mathrm{UO_2^{2+}},\mathrm{ClO_4^-}) - 2\varepsilon(\mathrm{H^+},\mathrm{ClO_4^-}))\,m_{\mathrm{ClO_4^-}}\end{aligned} \tag{B.18}$$

The relationship between the equilibrium constant and the redox potential is:

$$\ln K = \frac{nF}{RT}\,E \tag{B.19}$$

$$\ln K^\circ = \frac{nF}{RT}\,E^\circ. \tag{B.20}$$

$E$ is the redox potential in a medium of ionic strength $I$, $E^\circ$ is the corresponding standard potential at $I = 0$, and $n$ is the number of transferred electrons in the reaction considered. Combining Eqs. (B.18), (B.19) and (B.20) and rearranging them leads to Eq. (B.21):

$$E - 10D\left(\frac{RT\ln(10)}{nF}\right) = E^{\circ} - \Delta\varepsilon\, m_{ClO_4^-}\left(\frac{RT\ln(10)}{nF}\right) \qquad \text{(B.21)}$$

For $n = 2$ in the present example and $T = 298.15$ K, Eq. (B.21) becomes:

$$E/\text{mV} - 295.8\ D = E^{\circ}/\text{mV} - 29.58\,\Delta\varepsilon m_{ClO_4^-}$$

where

$$\Delta\varepsilon = \varepsilon(U^{4+}, ClO_4^-) - \varepsilon(UO_2^{2+}, ClO_4^-) - 2\varepsilon(H^+, ClO_4^-)\,.$$

### B.1.4 On the magnitude of ion interaction coefficients

Ciavatta [1980CIA] made a compilation of ion interaction coefficients for a large number of electrolytes. Similar data for complex formation reactions of various kinds were reported by Spahiu [1983SPA] and Ferri *et al.* [1983FER/GRE]. These and some other data for 25 °C and 1 bar have been collected and are listed in Section B.3.

It is obvious from the data in these tables that the charge of an ion is of great importance for determining the magnitude of the ion interaction coefficient. Ions of the same charge type have similar ion interaction coefficients with a given counter-ion. Based on the tabulated data, Grenthe *et al.* [1992GRE/FUG] proposed that it is possible to estimate, with an error of at most ± 0.1 kg·mol$^{-1}$ in $\varepsilon$, ion interaction coefficients for cases where there are insufficient experimental data for an extrapolation to $I = 0$. The error that is made by this approximation is estimated to be ± 0.1 kg·mol$^{-1}$ in $\Delta\varepsilon$ in most cases, based on comparison with $\Delta\varepsilon$ values of various reactions of the same charge type.

## B.2 Ionic strength dependence of enthalpies of reaction

Reaction enthalpies can be determined either from the temperature dependence of equilibrium constants, or better, directly using calorimetry. Correction of these data to ionic strength zero requires ion interaction coefficients at different temperature, information that in most cases is not available, see [1997GRE/PLY2], Ch. IX.9, p. 397. Calorimetric enthalpies of reaction obtained at different temperatures can be extrapolated to $I = 0$ data as described in [1997GRE/PLY2], Ch. IX. 10.2 and 10.3. Corrections using the Pitzer model require determination of at least three parameters, $\beta^{(o)L}$, $\beta^{(1)L}$ and $C^{L}$ for each reactant/product and the ones for the reaction product, typically a complex, must be obtained from experiments at different ionic strengths. As is the case for equilibrium constants, these data are rarely available. Extrapolation to zero ionic strength can also be made using the less parameterized SIT method by forming from experimentally measured $\Delta_r H_m^{\circ}$ values the function $Y$, which in the SIT depends linearly on $m$, the molality of the ionic medium electrolyte:

$$Y = \Delta_r H_m - rL_1 - \frac{3A_L \Delta(Z)^2 \sqrt{I_m}}{4(1+1.5\sqrt{I_m})} = \Delta_r H_m^o - RT^2 m \Delta\varepsilon_L \qquad \text{(B.22)}$$

where $A_L$ = 1.986 kJ·kg$^{1/2}$·mol$^{-3/2}$ is the Debye-Hückel limiting slope for the relative partial molar enthalpies at 298.15 K, 0.1 MPa; $r$ is the number of moles of water in the general equation for a chemical reaction $\sum_i \nu_i Q_i + r\mathrm{H_2O} = 0$; $\Delta\varepsilon_L = -RT^2 \ln 10 (\partial_T \Delta\varepsilon)$, see [1996PLY/GRE], [1997GRE/PLY2], Ch. IX.9 for detail; $L_1$ is the relative partial enthalpy of the water in the ionic medium, see $L_1$ values in solutions of some common electrolytes in Table B-4 below. Note that at ionic strengths up to ~ 1 $m$ the term $RT^2 m\Delta\varepsilon$ can often be neglected because the ion-interaction term, $\Delta\varepsilon_L$, is of the order of $10^{-3}$ kg·K$^{-1}$·mol$^{-1}$, *i.e.* relatively small and comparable with the uncertainty of experimental $\Delta_r H_m^o$ values, so the use of the Debye- Hückel term alone may be acceptable at small ionic strengths.

Table B-4: Values of relative partial molar enthalpy of water, $L_1$, in solutions of some common electrolytes from [1991PIT].

| $m$ / mol·kg$^{-1}$ | $L_1$ / kJ·mol$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | HCl | HBr | $HClO_4$ | LiCl | $LiClO_4$ | NaCl |
| 0.50 | – 0.005 | – 0.004 | 0.003 | – 0.004 | – 0.002 | 0.002 |
| 1.00 | – 0.017 | – 0.013 | 0.009 | – 0.012 | – 0.007 | 0.011 |
| 1.50 | – 0.037 | – 0.028 | 0.015 | – 0.025 | – 0.014 | 0.024 |
| 2.00 | – 0.064 | – 0.050 | 0.021 | – 0.043 | – 0.027 | 0.039 |
| 2.50 | – 0.101 | – 0.079 | 0.022 | – 0.067 | – 0.045 | 0.056 |
| 3.00 | – 0.148 | – 0.117 | 0.017 | – 0.099 | – 0.071 | 0.071 |
| 3.50 | – 0.206 | – 0.164 | 0.004 | – 0.139 | – 0.106 | 0.083 |
| 4.00 | – 0.278 | – 0.223 | – 0.019 | – 0.187 | – 0.152 | 0.089 |
| 4.50 | – 0.364 | – 0.293 | – 0.054 | – 0.245 | | 0.088 |
| 5.00 | | – 0.377 | – 0.105 | – 0.313 | | 0.077 |
| 5.50 | | – 0.474 | – 0.173 | – 0.393 | | 0.054 |
| 6.00 | | – 0.587 | – 0.260 | – 0.484 | | 0.018 |

| $m$ / mol·kg$^{-1}$ | NaBr | $NaNO_3$ | $NaClO_4$ | NaOH | KCl | $KNO_3$ |
|---|---|---|---|---|---|---|
| 0.50 | 0.003 | 0.008 | 0.008 | 0.001 | 0.002 | 0.010 |
| 1.00 | 0.014 | 0.027 | 0.030 | 0.006 | 0.010 | 0.031 |
| 1.50 | 0.030 | 0.052 | 0.062 | 0.012 | 0.022 | 0.068 |
| 2.00 | 0.050 | 0.080 | 0.099 | 0.016 | 0.039 | 0.128 |
| 2.50 | 0.073 | (0.010) | 0.140 | 0.014 | 0.058 | (0.22) |
| 3.00 | 0.095 | | 0.181 | 0.002 | 0.080 | |
| 3.50 | 0.117 | | 0.219 | – 0.023 | 0.103 | |
| 4.00 | 0.136 | | 0.251 | – 0.066 | 0.126 | |
| 4.50 | 0.149 | | 0.275 | (– 0.13) | 0.149 | |
| 5.00 | 0.156 | | 0.286 | | | |
| 5.50 | 0.155 | | 0.281 | | | |
| 6.00 | 0.143 | | 0.259 | | | |

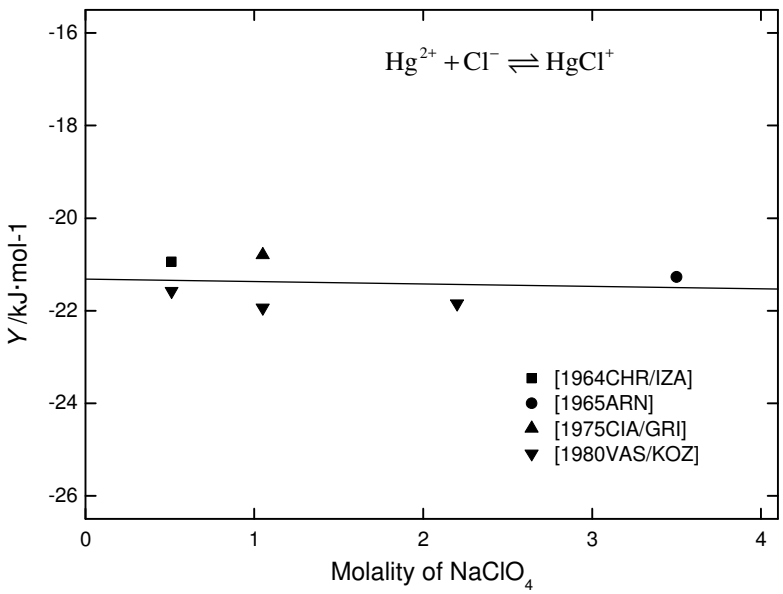
**Example B.8.** The enthalpy change for the reaction $Hg^{2+} + Cl^- \rightarrow HgCl^+$ has been studied in $NaClO_4$ ionic media of different ionic strength as shown in Table B-5.

Table B-5: Enthalpy change for the reaction $Hg^{2+} + Cl^- \rightarrow HgCl^+$ as reported in [1964CHR/IZA], [1965ARN], [1975CIA/GRI] and [1980VAS/KOZ].

| Ionic strength in molality | $\Delta_r H_m^\circ$ / $m$·kg$^{-1}$ | Reference |
|---|---|---|
| 0.51 | – (23.0 ± 1.0) | [1964CHR/IZA] |
| 3.50 | – (24.2 ± 1.0) | [1965ARN] |
| 1.05 | – (23.2 ± 0.5) | [1975CIA/GRI] |
| 0.51 | – (23.64 ± 0.5) | [1980VAS/KOZ] |
| 1.05 | – (24.35 ± 0.5) | |
| 2.20 | – (24.60 ± 0.5) | |

Figure B-3 shows a plot of *Y vs.* the molality based on the unweighted fit of the experimental data in Table B-4 from which $\Delta_r H_m^\circ$ = – (21.32 ± 1.02) kJ·mol$^{-1}$ and $\Delta\varepsilon_L$ = (0.07 ± 0.83)·10$^{-3}$ kg·K$^{-1}$·mol$^{-1}$ can be determined, the uncertainties are for the 0.95 confidence level.

Figure B-3: Plot of *Y vs.* the molality for the reaction $Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$ based on the unweighted fit of the experimental data in Table B-4.



The partial molar enthalpy of water, $L_1$, and of a solute, $L_2$, in different ionic media can be calculated from enthalpies of dilution, $\phi_L$, tabulated in [1965PAR], using the following definitions:

$$\overline{L_1} = \frac{n_2}{n_1}(\phi_L - \overline{L_2}) = -\frac{m_2}{n_w}\left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_m} \tag{B.23}$$

$$\overline{L_2} = \phi_L + m\left(\frac{\partial \phi_L}{\partial m}\right)_{T,P,n_m} \tag{B.24}$$

**Example B.9.** For the reactions:

$$UO_2CO_3(cr) + 2H^+ \rightarrow UO_2^{2+} + CO_2(g) + H_2O(l) \tag{B.25}$$

or

$$UO_2CO_3(cr) + 2HNO_3(aq) \rightarrow UO_2(NO_3)_2(aq) + CO_2(g) + H_2O(l) \tag{B.26}$$

the experimental value $\Delta_f H_m(H_2O)$ and $\Delta_f H_m(HNO_3)$ in the relevant ionic medium needs to be corrected and this can be done using the following data tabulated in [1965PAR]:

| $m$ | $\varphi_L$ / cal·mol$^{-1}$ |
|---|---|
| 12.33 | 1270 |
| 13.88 | 1495 |
| 13.5 | (1440) a short interpolation |

From these data we obtain:

$$\overline{L_1} = -1.99 \text{ kJ·mol}^{-1}$$

$$\overline{L_2} = 14.22 \text{ kJ·mol}^{-1}$$

One also needs the correction for $\overline{L_2}$ of $UO_2(NO_3)_2(aq)$, *i.e.* for the partial molar enthalpy of $UO_2(NO_3)_2(aq)$ at its trace concentrations in 13.5 m $HNO_3$, but there are no experimental data available.

Enthalpy corrections for dissolution reactions also need to be corrected for the relative molal enthalpy of the solvent as exemplified below.

**Example B.10.** Corrections for the enthalpy of water for a number of solid state reactions are straightforward as shown by the following example:

$$M[UO_2BO_3](cr) + nH_2O(l) \rightarrow M[UO_2(BO_3)]\cdot nH_2O(cr) \qquad (B.27)$$

The enthalpy of formation obtained by Chernorukov, Knyazev *et al.* [2003CHE/KNY3] and [2005KAR/CHE3] for the hydrated compound have been obtained by using the enthalpy of dissolution of the solid compounds in 11.6 M HCl. From the known value of the enthalpy of formation of $M[UO_2BO_3](cr)$ and $H_2O(l)$, they calculate the enthalpy of formation of the different hydrates. However, Chernorukov *et al.* used the enthalpy of formation of pure water $\Delta_f H^o(H_2O, l) = -(285.83 \pm 0.04)$ kJ·mol$^{-1}$, instead of its enthalpy in the solvent used (11.6 M HCl), which results in a significant error. The relative partial molar entropy of water, $L_1$(11.6 M HCl) = – 0.53 kJ·mol$^{-1}$, and the enthalpy of formation of water in the ionic medium used, $\Delta_f H^o(H_2O,$ 11.6 M HCl) = – 286.4 kJ·mol$^{-1}$.

## B.3 Tables of ion interaction coefficients

Table B-6, Table B-7, Table B-8 and Table B-9 contain the selected specific ion interaction coefficients used in this review, according to the specific ion interaction treatment described. Table B-6 contains cation interaction coefficients with $Cl^-$, $ClO_4^-$ and $NO_3^-$, Table B-7 anion interaction coefficients with $Li^+$, $Na^+$ (or $NH_4^+$) and $K^+$, and Table B-8 neutral species – electroneutral combination of ions. The coefficients have the units of kg·mol$^{-1}$ and are valid for 298.15 K and 1 bar. The species are ordered by charge and appear, within each charge class, in the standard order of arrangement, *cf.* Section 2.1.8.

It should be noted that ion interaction coefficients tabulated in Table B-6, Table B-7 and Table B-8 may also involve ion pairing effects, as described in Section B.1.3.1. In direct comparisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.

Table B-6: Ion interaction coefficients $\varepsilon(j,k)$ (kg·mol$^{-1}$) for cations $j$ with $k$ = $Cl^-$, $ClO_4^-$ and $NO_3^-$ at 298.15 K. The uncertainties represent the 95 % confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B-7. The coefficients $\varepsilon(M^{n+}, Cl^-)$ and $\varepsilon(M^{n+}, NO_3^-)$ reported by Ciavatta [1980CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section B.1.3.1.

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $H^+$ | $Cl^-$ | 0.12 ± 0.01 | |
| | $ClO_4^-$ | 0.14 ± 0.02 | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | 0.07 ± 0.01 | |
| $NH_4^+$ | $Cl^-$ | −0.01 ± 0.01 | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | −0.08 ± 0.04† | |
| | $NO_3^-$ | −0.06 ± 0.03† | |
| $H_2gly^+$ | $Cl^-$ | −0.06 ± 0.02 | Reported by Ciavatta [1988CIA]. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |
| $H_5edta^+$ | $Cl^-$ | −0.23 ± 0.15 | |
| | $ClO_4^-$ | −0.23 ± 0.15 | See Section VIII.3.7 of [2005HUM/AND]. |
| | $NO_3^-$ | −0.23 ± 0.15 | |
| $SnOH^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | −0.07 ± 0.13 | See Section VII.1.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $SnF^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.14 ± 0.10 | See Section VIII.3.1.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $SnCl^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.08 ± 0.07 | See Section VIII.3.2.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $SnBr^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.15 ± 0.07 | See Section VIII.3.3.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $SnNO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.17 ± 0.09 | See Section X.1.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $SnSCN^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.17 ± 0.29 | See Section XI.1.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $Tl^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | −0.21 ± 0.06† | |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $ZnHCO_3^+$ | $Cl^-$ | 0.2 | Taken from Ferri *et al.* [1985FER/GRE]. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |
| $CdCl^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.25 ± 0.02 | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | — | |
| $CdI^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.27 ± 0.02 | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | — | |
| $CdSCN^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.31 ± 0.02 | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | — | |
| $HgCl^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.19 ± 0.02 | Reported by Ciavatta [1988CIA]. |
| | $NO_3^-$ | — | |
| $Cu^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.11 ± 0.01 | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | — | |
| $Ag^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.00 ± 0.01 | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | − 0.12 ± 0.05† | |
| $NiOH^+$ | $Cl^-$ | − 0.01 ± 0.07 | Evaluated in [2005GAM/BUG] (Section V.3.1.1) for the reaction $Ni^{2+} + H_2O \rightleftharpoons NiOH^+ + H^+$ from $\Delta\varepsilon$ in chloride media / perchlorate media. |
| | $ClO_4^-$ | 0.14 ± 0.07 | |
| | $NO_3^-$ | — | |
| $NiF^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.34 ± 0.08 | Derived from $\Delta\varepsilon = \varepsilon(NiF^+,ClO_4^-) - \varepsilon(Ni^{2+},ClO_4^-) - \varepsilon(Na^+,F^-) = -(0.049 \pm 0.060)$ kg·mol$^{-1}$ (see Section V.4.2.3 of [2005GAM/BUG]). |
| | $NO_3^-$ | — | |
| $NiCl^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.47 ± 0.06 | See details in Section V.4.2.4 of [2005GAM/BUG]. |
| | $NO_3^-$ | — | |
| $NiNO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.44 ± 0.14 | See details in Section V.6.1.2 of [2005GAM/BUG], specially sub-section V.6.1.2.1 for an alternative treatment of this system. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Ni(H_2cit)^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.12 ± 0.50 | See Section VII.7 in [2005HUM/AND]. |
| | $NO_3^-$ | — | |
| $NiBr^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.59 ± 0.10 | See details in [2005GAM/BUG], *cf.* Section V.4.2.5, specially sub-section V.4.2.5.1 for an alternative treatment of this system. |
| | $NO_3^-$ | — | |
| $NiHS^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | − 0.85 ± 0.39 | See details in [2005GAM/BUG], Section V.5.1.1.2. |
| | $NO_3^-$ | — | |
| $NiSCN^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.31 ± 0.04 | Derived from $\Delta\varepsilon = \varepsilon(NiSCN^+,ClO_4^-) - \varepsilon(Na^+,SCN^-) - \varepsilon(Ni^{2+},ClO_4^-) = -(0.109\pm0.025)$ kg·mol$^{-1}$ (see [2005GAM/BUG], Section V.7.1.3.1). |
| | $NO_3^-$ | — | |
| $Fe(OH)_2^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.37 ± 0.18 | Determined in Section VII.1.3.2 of TDB-Iron Part 1. |
| | $NO_3^-$ | — | |
| $FeF^+$ | $Cl^-$ | | |
| | $ClO_4^-$ | 0.34 ± 0.07 | Determined in Section VIII.2.1.3 of TDB-Iron Part 1. |
| | $NO_3^-$ | | |
| $FeCl_2^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.52 ± 0.05 | Determined in Section VIII.2.3.2.2.1 of TDB-Iron Part 1. |
| | $NO_3^-$ | — | |
| $FeSO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.4 | Determined in Section IX.2.2.3 of TDB-Iron Part 2. |
| | $NO_3^-$ | — | |
| $FeSO_4^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.4 ± 0.1 | Determined in Section IX.1.2.1.4.1 of TDB-Iron Part 1. |
| | $NO_3^-$ | — | |
| $Zr_4(OH)_{15}^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.09 ± 0.92 | Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D. |
| | $NO_3^-$ | − 0.02 ± 1.46 | |
| $ZrF_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.20 ± 0.06 | Determined from SIT plot in [2005BRO/CUR]. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $YCO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.17 ± 0.04 | Taken from Spahiu [1983SPA]. |
| | $NO_3^-$ | — | |
| $Am(OH)_2^+$ | $Cl^-$ | −0.27 ± 0.20 | Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + nH_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + nH^+$ (An = Am, Cm). |
| | $ClO_4^-$ | 0.17 ± 0.04 | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmF_2^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.17 ± 0.04 | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmSO_4^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.22 ± 0.08 | Evaluated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmCO_3^+$ | $Cl^-$ | 0.01 ± 0.05 | Evaluated in [2003GUI/FAN] (Section 12.6.1.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (based on $\varepsilon(Am^{3+}, Cl^-) = (0.23 \pm 0.02)$ kg·mol$^{-1}$ and $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol$^{-1}$. |
| | $ClO_4^-$ | 0.17 ± 0.04 | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $Am(ox)^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.08 ± 0.10 | See Section VI.13 of [2005HUM/AND]. |
| | $NO_3^-$ | — | |
| $PuO_2^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.24 ± 0.05 | Derived from $\Delta\varepsilon = \varepsilon(PuO_2^{2+}, ClO_4^-) - \varepsilon(PuO_2^+, ClO_4^-) = (0.22 \pm 0.03)$ kg·mol$^{-1}$ [1995CAP/VIT]. In [1992GRE/FUG], $\varepsilon(PuO_2^+, ClO_4^-) = (0.17 \pm 0.05)$ kg·mol$^{-1}$ was tabulated based on [1989ROB], [1989RIG/ROB] and [1990RIG]. Capdevila and Vitorge's data [1992CAP], [1994CAP/VIT] and [1995CAP/VIT] were unavailable at that time. |
| | $NO_3^-$ | — | |
| $PuO_2F^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.29 ± 0.11 | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) reaction. |
| | $NO_3^-$ | — | |
| $PuO_2Cl^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.50 ± 0.09 | From $\Delta\varepsilon$ evaluated by Giffaut [1994GIF]. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $NpO_2^+$ | $Cl^-$ | $0.09 \pm 0.05$ | See Section 12.1 of [2001LEM/FUG]. |
| | $ClO_4^-$ | $0.25 \pm 0.05$ | Derived from $\Delta\varepsilon = \varepsilon(NpO_2^{2+}, ClO_4^-) - \varepsilon(NpO_2^+, ClO_4^-) = (0.21 \pm 0.03)$ kg·mol$^{-1}$ [1987RIG/VIT], [1989RIG/ROB] and [1990RIG]. |
| | $NO_3^-$ | — | |
| $NpO_2OH^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $-0.06 \pm 0.40$ | Estimated in [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $(NpO_2)_3(OH)_5^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.45 \pm 0.20$ | See Section 8.1.2 of [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $NpO_2F^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.29 \pm 0.12$ | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction. |
| | $NO_3^-$ | — | |
| $NpO_2Cl^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.50 \pm 0.14$ | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Pu(VI) reaction. |
| | $NO_3^-$ | — | |
| $NpO_2IO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.33 \pm 0.04$ | Estimated in [2001LEM/FUG] by assuming $\varepsilon(NpO_2IO_3^+, ClO_4^-) \approx \varepsilon(UO_2IO_3^+, ClO_4^-)$. |
| | $NO_3^-$ | — | |
| $Np(SCN)_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.17 \pm 0.04$ | Estimated in [2001LEM/FUG] by assuming $\varepsilon(Np(SCN)_3^+, ClO_4^-) \approx \varepsilon(AmF_2^+, ClO_4^-)$. |
| | $NO_3^-$ | — | |
| $Ca[NpO_2(OH)_2]^+$ | $Cl^-$ | $-0.07 \pm 0.08$ | This review |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |
| $UO_2^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.26 \pm 0.03$ | Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol$^{-1}$. |
| | $NO_3^-$ | — | |
| $UO_2OH^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $-0.06 \pm 0.40$ | Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ kg·mol$^{-1}$, where X = $Cl^-$, $ClO_4^-$ and $NO_3^-$. |
| | $NO_3^-$ | $0.51 \pm 1.4$ | |

(Continued on next page)

Table B-6 (continued)

| *j* | *k* | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $(UO_2)_3(OH)_5^+$ | $Cl^-$ | $0.81 \pm 0.17$ | Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X)$ = $(0.46 \pm 0.03)$ kg·mol$^{-1}$, where X = $Cl^-$, $ClO_4^-$ and $NO_3^-$. |
| | $ClO_4^-$ | $0.45 \pm 0.15$ | |
| | $NO_3^-$ | $0.41 \pm 0.22$ | |
| $UF_3^+$ | $Cl^-$ | $0.1 \pm 0.1$ | Estimated in [1992GRE/FUG]. |
| | $ClO_4^-$ | $0.1 \pm 0.1$ | |
| | $NO_3^-$ | — | |
| $UO_2F^+$ | $Cl^-$ | $0.04 \pm 0.07$ | Taken from Riglet *et al.* [1989RIG/ROB], where the following assumptions were made: $\varepsilon(Np^{3+}, ClO_4^-) \approx \varepsilon(Pu^{3+}, ClO_4^-)$ = 0.49 kg·mol$^{-1}$ as for other ($M^{3+}$, $ClO_4^-$) interactions, and $\varepsilon(NpO_2^{2+}, ClO_4^-) \approx \varepsilon(PuO_2^{2+}, ClO_4^-) \approx \varepsilon(UO_2^{2+}, ClO_4^-)$ = 0.46 kg·mol$^{-1}$. |
| | $ClO_4^-$ | $0.28 \pm 0.04$ | See Section 9.4.2.2.1 of [2003GUI/FAN]. |
| | $NO_3^-$ | — | |
| $UO_2Cl^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.33 \pm 0.04$ | Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X)$ = $(0.46 \pm 0.03)$ kg·mol$^{-1}$, where X = $Cl^-$, $ClO_4^-$ and $NO_3^-$. |
| | $NO_3^-$ | — | |
| $UO_2ClO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.33 \pm 0.04$ | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $UO_2Br^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.24 \pm 0.04$ | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $UO_2BrO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.33 \pm 0.04$ | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $UO_2IO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.33 \pm 0.04$ | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $UO_2N_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.3 \pm 0.1$ | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $UO_2NO_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.33 \pm 0.04$ | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $UO_2SCN^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.22 \pm 0.04$ | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $Th(OH)_3^+$ | $Cl^-$ | $0.06 \pm 0.05$ | See Table VII-16 in Section VII.3.6.1 of [2008RAN/FUG]. |
| | $ClO_4^-$ | $0.15 \pm 0.10$ | |
| | $NO_3^-$ | $0.05 \pm 0.15$ | |
| $ThF_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.1 \pm 0.1$ | See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG]. |
| | $NO_3^-$ | $0.0 \pm 0.2$ | |
| $Th(NO_3)_3^+$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.25 \pm 0.15$ | Evaluated in Section X.1.3.3 of [2008RAN/FUG], using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol$^{-1}$ where X = $ClO_4^-$ and $NO_3^-$. |
| | $NO_3^-$ | $0.25 \pm 0.15$ | |
| $H_6edta^{2+}$ | $Cl^-$ | $-0.20 \pm 0.16$ | Evaluated in [2005HUM/AND] (Section VIII.3.7). |
| | $ClO_4^-$ | $-0.20 \pm 0.16$ | |
| | $NO_3^-$ | $-0.20 \pm 0.16$ | |
| $Sn^{2+}$ | $Cl^-$ | $0.19 \pm 0.04$ | See Section VI.2.1 of [2012GAM/GAJ]. |
| | $ClO_4^-$ | $0.19 \pm 0.04$ | See Section VI.2.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $Sn_3(OH)_4^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $-0.02 \pm 0.16$ | See Section VII.1.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $Pb^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.15 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | $-0.20 \pm 0.12^\dagger$ | |
| $AlOH^{2+}$ | $Cl^-$ | 0.09 | Taken from Hedlund [1988HED]. |
| | $ClO_4^-$ | 0.31 | |
| | $NO_3^-$ | — | |
| $Al_2CO_3(OH)_2^{2+}$ | $Cl^-$ | 0.26 | Taken from Hedlund [1988HED]. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |
| $Zn^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.33 \pm 0.03$ | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | $0.16 \pm 0.02$ | |
| $ZnCO_3^{2+}$ | $Cl^-$ | $0.35 \pm 0.05$ | Taken from Ferri *et al.* [1985FER/GRE]. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Cd^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | $0.09 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| $Hg^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.34 \pm 0.03$ | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | $-0.1 \pm 0.1^\dagger$ | |
| $Hg_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.09 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | $-0.2 \pm 0.1^\dagger$ | |
| $Cu^{2+}$ | $Cl^-$ | $0.08 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | $0.32 \pm 0.02$ | |
| | $NO_3^-$ | $0.11 \pm 0.01$ | |
| $Ni^{2+}$ | $Cl^-$ | $0.17 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | $0.370 \pm 0.032$ | Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $Ni(ClO_4)_2$ solution ([2005GAM/BUG], Section V.4.3). |
| | $NO_3^-$ | $0.182 \pm 0.010$ | Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $Ni(NO_3)_2$ solution ([2005GAM/BUG], Section V.6.1.2.1). |
| $Co^{2+}$ | $Cl^-$ | $0.16 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | $0.34 \pm 0.03$ | |
| | $NO_3^-$ | $0.14 \pm 0.01$ | |
| $Fe^{2+}$ | $Cl^-$ | $0.17 \pm 0.01$ | Determined in Section VI.4.3 of TDB-Iron Part 1. |
| | $ClO_4^-$ | $0.37 \pm 0.04$ | Determined in Section VI.4.4 of TDB-Iron Part 1. |
| | $NO_3^-$ | — | |
| $FeOH^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.46 \pm 0.05$ | Section VII.1.3.1 of TDB-Iron Part 1 |
| | $NO_3^-$ | — | |
| $FeCl^{2+}$ | $Cl^-$ | $0.64 \pm 0.06$ | Determined in Section VIII.2.3.1.3 of TDB-Iron Part 1 |
| | $ClO_4^-$ | $0.63 \pm 0.05$ | Determined in Section VIII.2.3.2.2.1 of TDB-Iron Part 1 |
| | $NO_3^-$ | — | |
| $FeSCN^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.49 \pm 0.05$ | Determined in Section X.1.2.1 of TDB-Iron Part 2 (replacement). |
| | $NO_3^-$ | $0.13 \pm 0.04$ | Determined in Section X.1.2.1 of TDB-Iron Part 2 (estimate). |
| $Mn^{2+}$ | $Cl^-$ | $0.13 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Tc_2O_2(OH)_2^{2+}$ | $Cl^-$ | $-0.43 \pm 0.11$ | This review |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |
| $Zr(OH)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.62 \pm 0.39$ | Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D. |
| | $NO_3^-$ | — | |
| $ZrF_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.47 \pm 0.08$ | Determined from SIT plot in [2005BRO/CUR]. |
| | $NO_3^-$ | — | |
| $ZrCl_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.84 \pm 0.11$ | Determined from SIT plot in [2005BRO/CUR]. |
| | $NO_3^-$ | — | |
| $Zr(NO_3)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.84 \pm 0.11$ | Determined from SIT plot in [2005BRO/CUR]. |
| | $NO_3^-$ | — | |
| $YHCO_3^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.39 \pm 0.04$ | Taken from Spahiu [1983SPA]. |
| | $NO_3^-$ | — | |
| $AmOH^{2+}$ | $Cl^-$ | $-0.04 \pm 0.07$ | Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + n\,H_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + n\,H^+$. |
| | $ClO_4^-$ | $0.39 \pm 0.04$ | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmF^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.39 \pm 0.04$ | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmCl^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.39 \pm 0.04$ | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmN_3^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.39 \pm 0.04$ | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmNO_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.39 \pm 0.04$ | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmNO_3^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.39 \pm 0.04$ | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| *j* | *k* | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $AmH_2PO_4^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.39 ± 0.04 | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $AmSCN^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.39 ± 0.04 | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $PuO_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.46 ± 0.05 | By analogy with $\varepsilon(UO_2^{2+},ClO_4^-)$ as derived from isopiestic measurements in [1992GRE/FUG].The uncertainty is increased because the value is estimated by analogy. |
| | $NO_3^-$ | — | |
| $PuF_2^{2+}$ | $Cl^-$ | | |
| | $ClO_4^-$ | 0.36 ± 0.17 | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction. |
| | $NO_3^-$ | — | |
| $PuCl^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.39 ± 0.16 | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Am(III) reaction. |
| | $NO_3^-$ | — | |
| $PuI^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.39 ± 0.04 | Estimated in [2001LEM/FUG] by assuming $\varepsilon(PuI^{2+},ClO_4^-) \approx \varepsilon(AmSCN^{2+},ClO_4^-)$ and $\varepsilon(NH_4^+,I^-) \approx \varepsilon(Na^+,SCN^-)$. |
| | $NO_3^-$ | — | |
| $PuSCN^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.39 ± 0.04 | Estimated in [2001LEM/FUG] by assuming $\varepsilon(PuSCN^{2+},ClO_4^-) \approx \varepsilon(AmSCN^{2+},ClO_4^-)$. |
| | $NO_3^-$ | — | |
| $NpO_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.46 ± 0.05 | By analogy with $\varepsilon(UO_2^{2+},ClO_4^-)$ as derived from isopiestic measurements noted in [1992GRE/FUG]. The uncertainty is increased because the value is estimated by analogy. |
| | $NO_3^-$ | — | |
| $(NpO_2)_2(OH)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.57 ± 0.10 | See Section 8.1.2 in [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $NpF_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.38 ± 0.17 | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $NpSO_4^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.48 ± 0.11 | Estimated on Section 10.1.2.1 of [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $Np(SCN)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.38 ± 0.20 | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction. |
| | $NO_3^-$ | — | |
| $Ca_3[NpO_2(OH)_5]^{2+}$ | $Cl^-$ | – 0.20 ± 0.11 | This review |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |
| $UO_2^{2+}$ | $Cl^-$ | 0.21 ± 0.02 | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | 0.46 ± 0.03 | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | 0.24 ± 0.03 | Reported by Ciavatta [1980CIA]. These coefficients were not used in [1992GRE/FUG] because they were evaluated by Ciavatta [1980CIA] without taking chloride and nitrate complexation into account. Instead, Grenthe *et al.* used $\varepsilon(UO_2^{2+},X)$ = (0.46 ± 0.03) kg·mol$^{-1}$, for X = $Cl^-$, $ClO_4^-$ and $NO_3^-$. |
| $(UO_2)_2(OH)_2^{2+}$ | $Cl^-$ | 0.69 ± 0.07 | Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+},X)$ = (0.46 ± 0.03) kg·mol$^{-1}$, where X = $Cl^-$, $ClO_4^-$ and $NO_3^-$. |
| | $ClO_4^-$ | 0.57 ± 0.07 | |
| | $NO_3^-$ | 0.49 ± 0.09 | |
| $(UO_2)_3(OH)_4^{2+}$ | $Cl^-$ | 0.50 ± 0.18 | Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+},X)$ = (0.46 ± 0.03) kg·mol$^{-1}$, where X = $Cl^-$, $ClO_4^-$ and $NO_3^-$. |
| | $ClO_4^-$ | 0.89 ± 0.23 | |
| | $NO_3^-$ | 0.72 ± 1.0 | |
| $UF_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.3 ± 0.1 | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $USO_4^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.3 ± 0.1 | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $U(NO_3)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | 0.49 ± 0.14 | Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+},ClO_4^-)$ = (0.76 ± 0.06) kg·mol$^{-1}$. |
| | $NO_3^-$ | — | |
| $Th(OH)_2^{2+}$ | $Cl^-$ | 0.13 ± 0.05 | Calculated in Section VII.3.6.1 of [2008RAN/FUG]. |
| | $ClO_4^-$ | 0.33 ± 0.10 | |
| | $NO_3^-$ | 0.10 ± 0.15 | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $ThF_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.3 \pm 0.1$ | See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG]. |
| | $NO_3^-$ | $0.15 \pm 0.20$ | |
| $ThSO_4^{2+}$ | $Cl^-$ | $0.14 \pm 0.15$ | See Section IX.1.3.2 of [2008RAN/FUG]. |
| | $ClO_4^-$ | $0.3 \pm 0.1$ | |
| | $NO_3^-$ | — | |
| $Th(N_3)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.40 \pm 0.15$ | Estimated in Section X.1.2 of [2008RAN/FUG]. |
| | $NO_3^-$ | — | |
| $Th(NO_3)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.43 \pm 0.18$ | Estimated in Section X.1.3.3 of [2008RAN/FUG], using $\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol$^{-1}$ for X = $ClO_4^-$ and $NO_3^-$. |
| | $NO_3^-$ | $0.43 \pm 0.18$ | |
| $Th(H_2PO_4)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.4 \pm 0.1$ | Estimated in Section X.2.3.2 of [2008RAN/FUG]. |
| | $NO_3^-$ | — | |
| $Th(SCN)_2^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.38 \pm 0.20$ | See Section XI.1.3.6.1 of [2008RAN/FUG]. |
| | $NO_3^-$ | — | |
| $Be^{2+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.30 \pm 0.04$ | Taken from [1986BRU], where it appears to have been based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA]. |
| | $NO_3^-$ | — | |
| $Mg^{2+}$ | $Cl^-$ | $0.19 \pm 0.02$ | |
| | $ClO_4^-$ | $0.33 \pm 0.03$ | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | $0.17 \pm 0.01$ | |
| $Ca^{2+}$ | $Cl^-$ | $0.14 \pm 0.01$ | |
| | $ClO_4^-$ | $0.27 \pm 0.03$ | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | $0.02 \pm 0.01$ | |
| $Ba^{2+}$ | $Cl^-$ | $0.07 \pm 0.01$ | |
| | $ClO_4^-$ | $0.15 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $NO_3^-$ | $-0.28 \pm 0.03$ | |
| $Al^{3+}$ | $Cl^-$ | $0.33 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Ni_2OH^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.59 \pm 0.15$ | By assuming $\varepsilon(Ni_2OH^{3+}, ClO_4^-) \approx \varepsilon(Be_2OH^{3+}, ClO_4^-)$, see Section V.3.1.1 in [2005GAM/BUG]. |
| | $NO_3^-$ | — | |
| $Fe^{3+}$ | $Cl^-$ | $0.76 \pm 0.03$ | Determined in Section VI.4.2.2 of TDB-Iron Part 1. |
| | $ClO_4^-$ | $0.73 \pm 0.04$ | Determined in Sections VI.1.2.1.1.1 and VI.4.1 of TDB-Iron Part 1. |
| | $NO_3^-$ | $0.26 \pm 0.08$ | Determined in Section IX.4.1.3 of TDB-Iron Part 2 (analogy). |
| $Cr^{3+}$ | $Cl^-$ | $0.30 \pm 0.03$ | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | $0.27 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| $ZrOH^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.57 \pm 0.13$ | Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D. |
| | $NO_3^-$ | — | |
| $Zr_3(OH)_9^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.93 \pm 0.35$ | Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D. |
| | $NO_3^-$ | — | |
| $ZrF^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.63 \pm 0.10$ | Determined from SIT plot in [2005BRO/CUR]. |
| | $NO_3^-$ | — | |
| $ZrCl^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.87 \pm 0.10$ | Determined from SIT plot in [2005BRO/CUR]. |
| | $NO_3^-$ | — | |
| $Zr(NO_3)^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.88 \pm 0.11$ | Determined from SIT plot in [2005BRO/CUR]. |
| | $NO_3^-$ | — | |
| $La^{3+}$ | $Cl^-$ | $0.22 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | $0.47 \pm 0.03$ | |
| | $NO_3^-$ | — | |
| $La^{3+} \rightarrow Lu^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.47 \rightarrow 0.52$ | Taken from Spahiu [1983SPA]. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Am^{3+}$ | $Cl^-$ | $0.23 \pm 0.02$ | The $\varepsilon(An^{3+},Cl^-)$ for An = Am and Cm is assumed to be equal to $\varepsilon(Nd^{3+},Cl^-)$ which is calculated from trace activity coefficients of $Nd^{3+}$ ion in 0 – 4 m NaCl. These trace activity coefficients are based on the Pitzer ion interaction parameters evaluated in [1997KON/FAN] from osmotic coefficients in aqueous $NdCl_3$ – NaCl and $NdCl_3$ – $CaCl_2$. |
| | $ClO_4^-$ | $0.49 \pm 0.03$ | Estimated in [1995SIL/BID]. |
| | $NO_3^-$ | — | |
| $Pu^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.49 \pm 0.05$ | Estimated by analogy with $\varepsilon(Ho^{3+},ClO_4^-)$ [1983SPA] as in [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy. |
| | $NO_3^-$ | — | |
| $PuOH^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.50 \pm 0.05$ | Estimated in [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $PuF^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.56 \pm 0.11$ | Estimated in [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $PuCl^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.85 \pm 0.09$ | Derived from the $\Delta\varepsilon$ evaluated in [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $PuBr^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.58 \pm 0.16$ | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction, and by assuming $\varepsilon(H^+,Br^-) \approx \varepsilon(Na^+,Br^-)$ . |
| | $NO_3^-$ | — | |
| $Np^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.49 \pm 0.05$ | Estimated by analogy with $\varepsilon(Ho^{3+},ClO_4^-)$ [1983SPA] as in previous books in this series [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy. |
| | $NO_3^-$ | — | |
| $NpOH^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.50 \pm 0.05$ | Estimated in [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $NpF^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.58 \pm 0.07$ | Evaluated in [2001LEM/FUG]. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $NpCl^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.81 \pm 0.09$ | Derived from the $\Delta\varepsilon$ selected in [2001LEM/FUG]. |
| | $NO_3^-$ | — | |
| $NpI^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.77 \pm 0.26$ | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) chloride reaction, and by assuming $\varepsilon(H^+,I^-) \approx \varepsilon(Na^+,I^-)$ . |
| | $NO_3^-$ | — | |
| $NpSCN^{3+}$ | $Cl^-$ | $0.76 \pm 0.12$ | Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |
| $U^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.49 \pm 0.05$ | Evaluated in [2001LEM/FUG] by analogy with $\varepsilon(Am^{3+}, ClO_4^-)$. |
| | $NO_3^-$ | — | |
| $UOH^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.48 \pm 0.08$ | Evaluated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $UF^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.48 \pm 0.08$ | Estimated in [1992GRE/FUG]. |
| | $NO_3^-$ | — | |
| $UCl^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.50 \pm 0.10$ | Estimated in [2003GUI/FAN]. |
| | $NO_3^-$ | — | |
| $UBr^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.52 \pm 0.10$ | Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) =$ $(0.76 \pm 0.06)$ kg·mol$^{-1}$, for X = $Br^-$ and $ClO_4^-$. |
| | $NO_3^-$ | — | |
| $UI^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.55 \pm 0.10$ | Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) =$ $(0.76 \pm 0.06)$ kg·mol$^{-1}$, for X = $I^-$ and $ClO_4^-$. |
| | $NO_3^-$ | — | |
| $UNO_3^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.62 \pm 0.08$ | Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) =$ $(0.76 \pm 0.06)$ kg·mol$^{-1}$ for X = $NO_3^-$ and $ClO_4^-$. |
| | $NO_3^-$ | — | |
| $ThOH^{3+}$ | $Cl^-$ | $0.19 \pm 0.05$ | |
| | $ClO_4^-$ | $0.48 \pm 0.08$ | See Table VII-18 in Section VII.3.6.1 of [2008RAN/FUG]. |
| | $NO_3^-$ | $0.20 \pm 0.15$ | |

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Table B-6 (continued)

| *j* | *k* | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $ThF^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.48 \pm 0.08$ | Estimated in Section VIII.1.2.1 of [2008RAN/FUG] (Table VIII-8). |
| | $NO_3^-$ | $0.25 \pm 0.20$ | |
| $ThCl^{3+}$ | $Cl^-$ | $0.62 \pm 0.11$ | Calculated in Section VIII.2.2.1.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol$^{-1}$, for X = $Cl^-$ and $ClO_4^-$ |
| | $ClO_4^-$ | $0.62 \pm 0.11$ | |
| | $NO_3^-$ | — | |
| $ThClO_3^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.62 \pm 0.11$ | Calculated in Section VIII.2.2.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol$^{-1}$, for X = $ClO_3^-$ and $ClO_4^-$ |
| | $NO_3^-$ | — | |
| $ThBr^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.62 \pm 0.11$ | Calculated in Section VIII.3.2.1 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol$^{-1}$, for X = $Br^-$ and $ClO_4^-$ |
| | $NO_3^-$ | — | |
| $ThBrO_3^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.62 \pm 0.08$ | Calculated in Section VIII.3.2.2 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol$^{-1}$, for X = $BrO_3^-$ and $ClO_4^-$ |
| | $NO_3^-$ | — | |
| $ThN_3^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.55 \pm 0.15$ | See Section X.1.2 of [2008RAN/FUG]. |
| | $NO_3^-$ | — | |
| $ThNO_3^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.56 \pm 0.14$ | Calculated in Section X.1.3.3 of [2008RAN/FUG] using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol$^{-1}$, X = $ClO_4^-$ and $NO_3^-$. |
| | $NO_3^-$ | $0.56 \pm 0.14$ | |
| $Th(H_2PO_4)^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.5 \pm 0.1$ | Estimated in Section X.2.3.2 of [2008RAN/FUG]. |
| | $NO_3^-$ | — | |
| $Th(H_2PO_4)(H_3PO_4)^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.5 \pm 0.1$ | Estimated in Section X.2.3.2 of [2008RAN/FUG]. |
| | $NO_3^-$ | — | |
| $ThSCN^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.50 \pm 0.10$ | See Section XI.1.3.6.1 of [2008RAN/FUG]. |
| | $NO_3^-$ | — | |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Be_2OH^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.50 \pm 0.05$ | Taken from [1986BRU], where the assumption was made that $\varepsilon(Be^{2+}, ClO_4^-) = 0.30$ kg·mol$^{-1}$, apparently based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA]. |
| | $NO_3^-$ | — | |
| $Be_3(OH)_3^{3+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.51 \pm 0.05$ | Taken from [1986BRU], where the assumption was made that $\varepsilon(Be^{2+}, ClO_4^-) = 0.30$ kg·mol$^{-1}$, apparently based on the average of the values for $\varepsilon(Mg^{2+}, ClO_4^-)$ and $\varepsilon(Ca^{2+}, ClO_4^-)$ [1980CIA]. |
| | $NO_3^-$ | — | |
| $Sn^{4+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.7 \pm 0.2$ | See Section VI.3.1 of [2012GAM/GAJ]. |
| | $NO_3^-$ | — | |
| $Al_3HCO_3(OH)_4^{4+}$ | $Cl^-$ | 0.41 | Taken from Hedlund [1988HED]. |
| | $ClO_4^-$ | — | |
| | $NO_3^-$ | — | |
| $Ni_4(OH)_4^{4+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $1.08 \pm 0.08$ | Derived from $\Delta\varepsilon = 4\varepsilon(H^+, ClO_4^-) - \varepsilon(Ni_4OH_4^{4+}, ClO_4^-) - 4\varepsilon(Ni^{2+}, ClO_4^-)$ = $(0.16 \pm 0.05)$ kg·mol$^{-1}$ (see [2005GAM/BUG], Section V.3.1.1.1). |
| | $NO_3^-$ | — | |
| $Fe_2(OH)_2^{4+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $1.04 \pm 0.10$ | Determined in Section VII.1.3.3 of TDB-Iron Part 1. |
| | $NO_3^-$ | — | |
| $Zr^{4+}$ | $Cl^-$ | $0.33 \pm 0.09$ | |
| | $ClO_4^-$ | $0.89 \pm 0.10$ | Determined in [2005BRO/CUR] |
| | $NO_3^-$ | $0.33 \pm 0.35$ | |
| $Y_2CO_3^{4+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.80 \pm 0.04$ | Taken from Spahiu [1983SPA]. |
| | $NO_3^-$ | — | |
| $Pu^{4+}$ | $Cl^-$ | — | This review |
| | $ClO_4^-$ | $0.82 \pm 0.07$ | Derived from $\Delta\varepsilon = \varepsilon(Pu^{4+}, ClO_4^-) - \varepsilon(Pu^{3+}, ClO_4^-)$ = $(0.33 \pm 0.035)$ kg·mol$^{-1}$ [1995CAP/VIT]. Uncertainty estimated in [2001LEM/FUG]. In the [1992GRE/FUG], $\varepsilon(Pu^{3+}, ClO_4^-) = (1.03 \pm 0.05)$ kg·mol$^{-1}$ was tabulated based on references [1989ROB], [1989RIG/ROB], [1990RIG]. |

(Continued on next page)

Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| | | | Capdevila and Vitorge's data [1992CAP], [1994CAP/VIT] and [1995CAP/VIT] were unavailable at the time. |
| | $NO_3^-$ | — | |
| $Np^{4+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.84 \pm 0.06$ | Derived from $\Delta\varepsilon = \varepsilon(Np^{4+},ClO_4^-) - \varepsilon(Np^{3+},ClO_4^-) = (0.35 \pm 0.03)$ kg·mol$^{-1}$ [1989ROB], [1989RIG/ROB], [1990RIG]. |
| | $NO_3^-$ | — | |
| $U^{4+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.76 \pm 0.06$ | Estimated in [1992GRE/FUG]. Using the measured value of $\Delta\varepsilon = \varepsilon(U^{4+},ClO_4^-) - \varepsilon(U^{3+},ClO_4^-) = (0.35 \pm 0.06)$ kg·mol$^{-1}$ p.89 [1990RIG], where the uncertainty is recalculated in [2001LEM/FUG] from the data given in this thesis, and $\varepsilon(U^{3+},ClO_4^-) = (0.49 \pm 0.05)$ kg·mol$^{-1}$, a value for $\varepsilon(U^{4+},ClO_4^-)$ can be calculated in the same way as is done for $\varepsilon(Np^{4+},ClO_4^-)$ and $\varepsilon(Pu^{4+},ClO_4^-)$. This value, $\varepsilon(U^{4+},ClO_4^-) = (0.84 \pm 0.06)$ kg·mol$^{-1}$ is consistent with that tabulated $\varepsilon(U^{4+},ClO_4^-) = (0.76 \pm 0.06)$ kg·mol$^{-1}$, since the uncertainties overlap. The authors of [2001LEM/FUG] do not believe that a change in the previously selected value for $\varepsilon(U^{4+},ClO_4^-)$ is justified at present. |
| | $NO_3^-$ | — | |
| $Th^{4+}$ | $Cl^-$ | $0.25 \pm 0.03$ | Reported by Ciavatta [1980CIA]. |
| | $ClO_4^-$ | $0.70 \pm 0.10$ | Evaluated in Section VI.3.1 of [2008RAN/FUG]. |
| | $NO_3^-$ | $0.31 \pm 0.12$ | Evaluated in Section VI.3.1 of [2008RAN/FUG]. |
| $Th_4(OH)_{12}^{4+}$ | $Cl^-$ | $0.25 \pm 0.20$ | |
| | $ClO_4^-$ | $0.56 \pm 0.42$ | See Section VII.3.4.1.3 of [2008RAN/FUG]. |
| | $NO_3^-$ | $0.42 \pm 0.50$ | |
| $Th(H_3PO_4)^{4+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $0.7 \pm 0.1$ | Estimated in Section X.2.3.2 of [2008RAN/FUG]. |
| | $NO_3^-$ | — | |
| $Al_3(OH)_4^{5+}$ | $Cl^-$ | 0.66 | Taken from Hedlund [1988HED] |
| | $ClO_4^-$ | 1.30 | Taken from Hedlund [1988HED] |
| | $NO_3^-$ | — | |
| $Th_2(OH)_3^{5+}$ | $Cl^-$ | $0.29 \pm 0.09$ | |
| | $ClO_4^-$ | $0.91 \pm 0.21$ | Calculated in Section VII.3.4.1.1 of [2008RAN/FUG]. |
| | $NO_3^-$ | $0.69 \pm 0.25$ | |
| $Th_2(OH)_2^{6+}$ | $Cl^-$ | $0.40 \pm 0.16$ | |
| | $ClO_4^-$ | $1.22 \pm 0.24$ | Evaluated in Section VII.3.4.1.1 of [2008RAN/FUG]. |
| | $NO_3^-$ | $0.69 \pm 0.26$ | |

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Table B-6 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Zr_3(OH)_4^{8+}$ | $Cl^-$ | $0.33 \pm 0.28$ | Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D. |
| | $ClO_4^-$ | $1.89 \pm 0.31$ | |
| | $NO_3^-$ | $2.28 \pm 0.35$ | |
| $Zr_4(OH)_8^{8+}$ | $Cl^-$ | — | |
| | $ClO_4^-$ | $3.61 \pm 1.02$ | Determined in [2005BRO/CUR] from the overall fit of the hydrolysis data as described in Appendix D. |
| | $NO_3^-$ | — | |
| $Th_4(OH)_8^{8+}$ | $Cl^-$ | $0.70 \pm 0.20$ | Evaluated in Section VII.3.4.1.3 of [2008RAN/FUG]. |
| | $ClO_4^-$ | $1.69 \pm 0.42$ | |
| | $NO_3^-$ | $1.59 \pm 0.51$ | |
| $Th_6(OH)_{15}^{9+}$ | $Cl^-$ | $0.72 \pm 0.30$ | See details in Section VII.3.4.1.4 of [2008RAN/FUG]. |
| | $ClO_4^-$ | $1.85 \pm 0.74$ | |
| | $NO_3^-$ | $2.20 \pm 0.77$ | |
| $Th_6(OH)_{14}^{10+}$ | $Cl^-$ | $0.83 \pm 0.30$ | Estimated in Section VII.3.4.1.4 of [2008RAN/FUG]. |
| | $ClO_4^-$ | $2.2 \pm 0.3$ | |
| | $NO_3^-$ | $2.9 \pm 0.5$ | |

Table B-7: Ion interaction coefficients, $\varepsilon(j,k)$ (kg·mol$^{-1}$), for anions $j$ with $k$ = $Li^+$, $Na^+$ and $K^+$ at 298.15 K. The uncertainties represent the 95 % confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B-8.

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $OH^-$ | $Li^+$ | $-0.02 \pm 0.03$† | |
| | $Na^+$ | $0.04 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | $0.09 \pm 0.01$ | |
| $F^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.02 \pm 0.02$ | Evaluated in [1992GRE/FUG]. |
| | $K^+$ | $0.03 \pm 0.02$ | [1988CIA] |
| $HF_2^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.11 \pm 0.06$ | Evaluated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $Cl^-$ | $Li^+$ | $0.10 \pm 0.01$ | |
| | $Na^+$ | $0.03 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | $0.00 \pm 0.01$ | |
| $ClO_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.01 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | — | |
| $ClO_4^-$ | $Li^+$ | $0.15 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $Na^+$ | $0.01 \pm 0.01$ | |
| | $K^+$ | — | |
| $Br^-$ | $Li^+$ | $0.13 \pm 0.02$ | |
| | $Na^+$ | $0.05 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | $0.01 \pm 0.02$ | |
| $BrO_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.06 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | — | |
| $I^-$ | $Li^+$ | $0.16 \pm 0.01$ | |
| | $Na^+$ | $0.08 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | $0.02 \pm 0.01$ | |
| $IO_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.06 \pm 0.02$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $HSO_4^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.01 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $N_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.015 \pm 0.020$ | See Section X.1.2 of [2008RAN/FUG]. |
| | $K^+$ | — | |
| $NO_2^-$ | $Li^+$ | $0.06 \pm 0.04$† | |
| | $Na^+$ | $0.00 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | $-0.04 \pm 0.02$ | Reported by Ciavatta [1988CIA]. |
| $NO_3^-$ | $Li^+$ | $0.08 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $Na^+$ | $-0.04 \pm 0.03$† | |
| | $K^+$ | $-0.11 \pm 0.04$† | |
| $H_2PO_4^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.08 \pm 0.04$† | |
| | $K^+$ | $-0.14 \pm 0.04$† | |
| $H_2AsO_4^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.01 \pm 0.01$ | Evaluated in Appendix A of this review in the entry for [2002RAP/SAN] |
| | $K^+$ | — | |
| $HCO_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.00 \pm 0.02$ | These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $CO_3^{2-}$ and $HCO_3^-$ are based on [1980CIA]. |
| | $K^+$ | $-0.06 \pm 0.05$ | Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL]. |
| $Hox^-$ | $Li^+$ | $-0.28 \pm 0.09$ | Evaluated in Section VI.3.5 of [2005HUM/AND]. |
| | $Na^+$ | $-0.07 \pm 0.01$ | |
| | $K^+$ | $-0.01 \pm 0.08$ | |
| $H_2cit^-$ | $Li^+$ | $-0.11 \pm 0.03$ | Evaluated in Section VII.3.6 of [2005HUM/AND]. |
| | $Na^+$ | $-0.05 \pm 0.01$ | |
| | $K^+$ | $-0.04 \pm 0.01$ | |
| $CN^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.07 \pm 0.03$ | As reported in [1992BAN/BLI]. |
| | $K^+$ | — | |
| $SCN^-$ | $Li^+$ | — | Reported by Ciavatta [1980CIA]. |
| | $Na^+$ | $0.05 \pm 0.01$ | |
| | $K^+$ | $-0.01 \pm 0.01$ | |
| $HCOO^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.03 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $CH_3COO^-$ | $Li^+$ | $0.05 \pm 0.01$ | |
| | $Na^+$ | $0.08 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| | $K^+$ | $0.09 \pm 0.01$ | |
| $H_3edta^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.33 \pm 0.14$ | Evaluated in Section VIII.3.7 of [2005HUM/AND]. |
| | $K^+$ | $-0.14 \pm 0.17$ | |
| $SiO(OH)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.08 \pm 0.03$ | Evaluated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $Si_2O_2(OH)_5^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.08 \pm 0.04$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $Sn(OH)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.22 \pm 0.03$ | See Section VII.1.1 of [2012GAM/GAJ]. |
| | $K^+$ | — | |
| $SnCl_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.04 \pm 0.07$ | See Section VIII.3.2.1 of [2012GAM/GAJ]. |
| | $K^+$ | — | |
| $SnBr_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.16 \pm 0.08$ | See Section VIII.3.3.1 of [2012GAM/GAJ]. |
| | $K^+$ | — | |
| $B(OH)_4^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.07 \pm 0.05$† | |
| | $K^+$ | — | |
| $Ni(SCN)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.66 \pm 0.13$ | Evaluated in [2005GAM/BUG] (see Section V.7.1.3.1). |
| | $K^+$ | — | |
| $Ni(cit)^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.22 \pm 0.50$ | Evaluated in Section VII.7 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $Fe(SO_4)_2^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.24 \pm 0.14$ | Estimated in Section IX.1.2.1.4.3 of TDB-Iron Part 1. |
| | $K^+$ | — | |
| $TcO(OH)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.08 \pm 0.04$ | This review |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $ZrF_5^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.14 \pm 0.03$ | Determined from SIT plots in [2005BRO/CUR]. |
| | $K^+$ | — | |
| $Am(SO_4)_2^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.05 \pm 0.05$ | Estimated in [1995SIL/BID]. |
| | $K^+$ | — | |
| $Am(CO_3)_2^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.14 \pm 0.06$ | Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (An = Am, Cm) based on $\varepsilon(Am^{3+},Cl^-)$ = $(0.23 \pm 0.02)$ kg·mol$^{-1}$ and $\varepsilon(Na^+,CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol$^{-1}$. |
| | $K^+$ | — | |
| $Am(ox)_2^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.21 \pm 0.08$ | Evaluated in Section VI.13 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $Am(edta)^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.01 \pm 0.16$ | Evaluated in Section VIII.13.2.1 of [2005HUM/AND]. |
| | $K^+$ | $0.01 \pm 0.16$ | Estimated in [2005HUM/AND] Section VIII.13.2.1 by assuming $\varepsilon(K^+,Am(edta)^-) \approx \varepsilon(Na^+,Am(edta)^-)$. |
| $PuO_2CO_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.18 \pm 0.18$ | Estimated in [2001LEM/FUG] by analogy with $\varepsilon(Na^+,NpO_2CO_3^-)$. |
| | $K^+$ | — | |
| $Pu(edta)^-$ | $Li^+$ | — | |
| | $Na^+$ | — | |
| | $K^+$ | $0.01 \pm 0.16$ | Estimated in [2005HUM/AND], Section VIII.12.2.1 by assuming $\varepsilon(K^+,Pu(edta)^-) \approx \varepsilon(Na^+,Am(edta)^-)$. |
| $NpO_2(OH)_2^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.01 \pm 0.07$ | Estimated in [2001LEM/FUG] (Section 8.1.3). |
| | $K^+$ | — | |
| $NpO_2(OH)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.20 \pm 0.02$ | This review |
| | $K^+$ | — | |
| $NpO_2SO_4^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.07 \pm 0.13$ | This review |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| *j* | *k* | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $NpO_2HPO_4^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.05 \pm 0.11$ | This review |
| | $K^+$ | — | |
| $NpO_2CO_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.18 \pm 0.15$ | Calculated in [2001LEM/FUG] (Section 12.1.2.1.3). |
| | $K^+$ | — | |
| $NpO_2(ox)^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.4 \pm 0.1$ | Evaluated in Section VI.11.2.3 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $NpO_2(H_2edta)^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.18 \pm 0.16$ | Evaluated in Section VIII.11.2.3 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $(NpO_2)_2CO_3(OH)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.00 \pm 0.05$ | Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2). |
| | $K^+$ | — | |
| $UO_2(OH)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.24 \pm 0.09$ | This review. |
| | $K^+$ | — | |
| $UO_2F_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.14 \pm 0.05$ | Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1. |
| | $K^+$ | — | |
| $UO_2(N_3)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.0 \pm 0.1$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $(UO_2)_2CO_3(OH)_3^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.00 \pm 0.05$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $UO_2cit^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.11 \pm 0.09$ | Evaluated in [2005HUM/AND]. |
| | $K^+$ | — | |
| $Th(OH)_3(CO_3)^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.05 \pm 0.20$ | See Section XI.1.3.2 of [2008RAN/FUG]. |
| | $K^+$ | — | |
| $Mg(cit)^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.03 \pm 0.03$ | Evaluated in [2005HUM/AND]. |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $UO_2(Hedta)^-$ | $Li^+$ | — | |
| | $Na^+$ | $-0.18 \pm 0.16$ | Evaluated in Section VIII.10.2.4 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $Mg(Hedta)^-$ | $Li^+$ | — | |
| | $Na^+$ | $0.11 \pm 0.20$ | Estimated in Section VIII.5.1 of [2005HUM/AND] |
| | $K^+$ | — | |
| $SO_3^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.08 \pm 0.05$† | |
| | $K^+$ | — | |
| $SO_4^{2-}$ | $Li^+$ | $-0.03 \pm 0.04$† | |
| | $Na^+$ | $-0.12 \pm 0.06$† | |
| | $K^+$ | $-0.06 \pm 0.02$ | Reported by Ciavatta [1988CIA]. |
| $S_2O_3^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.08 \pm 0.05$† | |
| | $K^+$ | — | |
| $HPO_4^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.15 \pm 0.06$† | |
| | $K^+$ | $-0.10 \pm 0.06$† | |
| $CO_3^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.08 \pm 0.03$ | These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $CO_3^{2-}$ and $HCO_3^-$ are based on [1980CIA]. |
| | $K^+$ | $0.02 \pm 0.01$ | Reported by Ciavatta [1980CIA]. |
| $ox^{2-}$ | $Li^+$ | $-0.51 \pm 0.09$ | |
| | $Na^+$ | $-0.08 \pm 0.01$ | Evaluated in Section VI.3.5 of [2005HUM/AND]. |
| | $K^+$ | $0.07 \pm 0.08$ | |
| $Hcit^{2-}$ | $Li^+$ | $-0.17 \pm 0.04$ | |
| | $Na^+$ | $-0.04 \pm 0.02$ | Evaluated in Section VII.3.6 of [2005HUM/AND]. |
| | $K^+$ | $-0.01 \pm 0.02$ | |
| $H_2edta^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.37 \pm 0.14$ | Evaluated in Section VII.3.7 of [2005HUM/AND]. |
| | $K^+$ | $-0.17 \pm 0.18$ | |
| $SiO_2(OH)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.10 \pm 0.07$ | Evaluated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $Si_2O_3(OH)_4^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.15 \pm 0.06$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| *j* | *k* | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Ni(ox)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.26 \pm 0.03$ | Evaluated in Section VI.7.2 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $Ni(CN)_4^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.185 \pm 0.081$ | Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1). |
| | $K^+$ | — | |
| $Fe(CO_3)_2^{2-}$ | $Li^+$ | | |
| | $Na^+$ | $-0.05 \pm 0.05$ | By analogy. See Appendix A entry for [1992BRU/WER]. |
| | $K^+$ | | |
| $CrO_4^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.06 \pm 0.04$† | |
| | $K^+$ | $-0.08 \pm 0.04$† | |
| $Zr(OH)_6^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.10 \pm 0.10$ | Determined in [2005BRO/CUR] by analogy to known interaction coefficients of doubly charged anionic species with alkali ions (source: [2001LEM/FUG]). |
| | $K^+$ | — | |
| $ZrF_6^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.15 \pm 0.06$ | Determined from SIT plots in [2005BRO/CUR]. |
| | $K^+$ | — | |
| $NpO_2(OH)_4^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.12 \pm 0.04$ | This review |
| | $K^+$ | — | |
| $NpO_2(HPO_4)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.1 \pm 0.10$ | Estimated in [2001LEM/FUG]. |
| | $K^+$ | — | |
| $NpO_2(CO_3)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.02 \pm 0.14$ | Estimated by analogy in [2001LEM/FUG] Section 12.1.2.1.2 |
| | $K^+$ | — | |
| $NpO_2cit^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.06 \pm 0.03$ | Evaluated in Section VII.11 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $NpO_2(Hedta)^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.07 \pm 0.16$ | Estimated in Section VIII.11.2.3 of [2005HUM/AND]. |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $UO_2(OH)_4^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.01 \pm 0.04$ | This review |
| | $K^+$ | — | |
| $UO_2F_4^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.30 \pm 0.06$ | Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1. |
| | $K^+$ | — | |
| $UO_2(SO_4)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.12 \pm 0.06$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $UO_2(N_3)_4^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.1 \pm 0.1$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $UO_2(ox)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.18 \pm 0.07$ | Estimated in Section VI.1.2.4.1 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $UO_2edta^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.22 \pm 0.18$ | Estimated in Section VIII.10.2.4 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $UO_2(CO_3)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.02 \pm 0.09$ | These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $CO_3^{2-}$ and $HCO_3^-$ are based on [1980CIA]. |
| | $K^+$ | — | |
| $(UO_2)_2(OH)_2(SO_4)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.14 \pm 0.22$ | Evaluated in Section 9.5.1.1.2 of [2003GUI/FAN]. |
| | $K^+$ | — | |
| $ThF_6^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.30 \pm 0.06$ | See Table VIII-8 in Section VIII.1.2.1 of [2008RAN/FUG]. |
| | $K^+$ | — | |
| $Th(SO_4)_3^{2-}$ | $Li^+$ | $-0.068 \pm 0.003$ | In combination with $\varepsilon_2 = (0.093 \pm 0.007)$. |
| | $Na^+$ | $-0.091 \pm 0.038$ | See Section IX.1.3.2 of [2008RAN/FUG]. |
| | $K^+$ | $-0.091 \pm 0.038$ | |
| $Th(OH)_2(CO_3)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.1 \pm 0.2$ | See Section XI.1.3.2 of [2008RAN/FUG]. |
| | $K^+$ | — | |
| $Th(OH)_4(CO_3)^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.1 \pm 0.2$ | See Section XI.1.3.2 of [2008RAN/FUG]. |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| *j* | *k* | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Mg(ox)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.15 \pm 0.03$ | Estimated in Section VI.5.1 of [2005HUM/AND]. |
| | $K^+$ | $-0.15 \pm 0.10$ | Estimated in [2005HUM/AND], Section VI.5.1 by assuming $\varepsilon(K^+, Mg(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$. |
| $Mg(edta)^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.01 \pm 0.15$ | Evaluated in Section VIII.5.2 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $Ca(ox)_2^{2-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.15 \pm 0.10$ | Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(Na^+, Ca(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$. |
| | $K^+$ | $-0.15 \pm 0.10$ | Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(K^+, Ca(ox)_2^{2-}) \approx \varepsilon(Na^+, Mg(ox)_2^{2-})$. |
| $cit^{3-}$ | $Li^+$ | $-0.44 \pm 0.15$† | |
| | $Na^+$ | $-0.076 \pm 0.030$† | |
| | $K^+$ | $0.02 \pm 0.02$ | Evaluated in Section VI.3.6 of [2005HUM/AND]. |
| $Hedta^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.10 \pm 0.14$ | Evaluated in Section VIII.3.7 of [2005HUM/AND]. |
| | $K^+$ | $0.31 \pm 0.18$ | |
| $PO_4^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.25 \pm 0.03$† | |
| | $K^+$ | $-0.09 \pm 0.02$ | Reported by Ciavatta [1980CIA]. |
| $Si_3O_6(OH)_3^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.25 \pm 0.03$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $Si_3O_5(OH)_5^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.25 \pm 0.03$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $Si_4O_7(OH)_5^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.25 \pm 0.03$ | Estimated in [1992GRE/FUG]. |
| | $K^+$ | — | |
| $Ni(CN)_5^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.25 \pm 0.14$ | Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1). |
| | $K^+$ | — | |
| $Fe(CO_3)_3^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.23 \pm 0.07$ | By analogy. See Appendix A entry for [2005GRI]. |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Am(CO_3)_3^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.23 \pm 0.07$ | Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-2n)}$ (An = Am, Cm) based on $\varepsilon(Am^{3+},Cl^-) = (0.23 \pm 0.02)$ kg·mol$^{-1}$ and $\varepsilon(Na^+,CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol$^{-1}$. |
| | $K^+$ | — | |
| $Am(ox)_3^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.23 \pm 0.10$ | Estimated in [2005HUM/AND], Section VI.13.2.1 by assuming $\varepsilon(Na^+,Am(ox)_3^{3-}) \approx \varepsilon(Na^+,Am(CO_3)_3^{3-})$. |
| | $K^+$ | — | |
| $Np(CO_3)_3^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | — | |
| | $K^+$ | $-0.15 \pm 0.07$ | Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.5). |
| $NpO_2(CO_3)_2^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.33 \pm 0.17$ | Calculated in [2001LEM/FUG] (Section 12.1.2.1.3). |
| | $K^+$ | — | |
| $NpO_2(CO_3)_2OH^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.40 \pm 0.19$ | Estimated in [2001LEM/FUG] by analogy with $NpO_2(CO_3)_3^{4-}$. |
| | $K^+$ | — | |
| $NpO_2(ox)_2^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.3 \pm 0.2$ | Evaluated in Section VI.11.2.3 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $NpO_2edta^{3-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.20 \pm 0.16$ | Estimated in Section VIII.11.2.3 of [2005HUM/AND]. |
| | $K^+$ | — | |
| $edta^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.32 \pm 0.14$ | Evaluated in Section VIII.3.7 of [2005HUM/AND]. |
| | $K^+$ | $1.07 \pm 0.19$ | |
| $P_2O_7^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.26 \pm 0.05$ | Reported by Ciavatta [1988CIA]. |
| | $K^+$ | $-0.15 \pm 0.05$ | Reported by Ciavatta [1988CIA]. |
| $Fe(CN)_6^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | — | |
| | $K^+$ | $-0.17 \pm 0.03$ | |
| $Tc_2OCl_{10}^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.89 \pm 0.40$ | This review |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| *j* | *k* | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Zr(CO_3)_4^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.09 \pm 0.20$ | This value, referring to $\varepsilon(NH_4^+, Zr(CO_3)_4^{4-})$ has been estimated in [2005BRO/CUR] by analogy with the homovalent ion pair $(Na^+, U(CO_3)_4^{4-})$, see [1997GRE/PLY]. |
| | $K^+$ | — | |
| $NpO_2(CO_3)_3^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.40 \pm 0.19$ | Calculated in [2001LEM/FUG] (Section 12.1.2.1.2). |
| | $K^+$ | $-0.62 \pm 0.42$ | $\varepsilon(NH_4^+, NpO_2(CO_3)_3^{4-}) = -(0.78 \pm 0.25)$ kg·mol$^{-1}$ is calculated in [2001LEM/FUG] (Section 12.1.2.2.1). |
| $U(CO_3)_4^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.09 \pm 0.10$ | These values differ from those estimated in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $CO_3^{2-}$ and $HCO_3^-$ are based on [1980CIA]. |
| | $K^+$ | — | |
| $UO_2(CO_3)_3^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.01 \pm 0.11$ | These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $CO_3^{2-}$ and $HCO_3^-$ are based on [1980CIA]. |
| | $K^+$ | — | |
| $UO_2(ox)_3^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.01 \pm 0.11$ | Estimated in [2005HUM/AND], Section VI.10.2.4.1 by assuming $\varepsilon(Na^+, UO_2(ox)_3^{4-}) \approx \varepsilon(Na^+, UO_2(CO_3)_3^{4-})$. |
| | $K^+$ | — | |
| $(UO_2)_3(OH)_4(SO_4)_3^{4-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.6 \pm 0.6$ | Estimated in Section 9.5.1.1.2 of [2003GUI/FAN]. |
| | $K^+$ | — | |
| $NpO_2(CO_3)_3^{5-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.53 \pm 0.19$ | Calculated in [2001LEM/FUG] (Section 12.1.2.1.3). |
| | $K^+$ | $-0.22 \pm 0.03$ | Evaluated in [2003GUI/FAN] (discussion of [1998ALM/NOV] in Appendix A) from $\Delta\varepsilon$ for the reactions $KNpO_2CO_3(s) + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + K^+$ (in $K_2CO_3$–KCl solution) and $K_3NpO_2(CO_3)_2(s) + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + 3K^+$ (in $K_2CO_3$ solution) (based on $\varepsilon(K^+, CO_3^{2-}) = (0.02 \pm 0.01)$ kg·mol$^{-1}$). |
| $UO_2(CO_3)_3^{5-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.62 \pm 0.15$ | These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $CO_3^{2-}$ and $HCO_3^-$ are based on [1980CIA]. |
| | $K^+$ | — | |

(Continued on next page)

Table B-7 (continued)

| $j$ | $k$ | $\varepsilon(j,k)$ | Comments |
|---|---|---|---|
| $Th(OH)(CO_3)_4^{5-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.22 \pm 0.13$ | Evaluated in Section XI.1.3.2.1 of [2008RAN/FUG]. |
| | $K^+$ | — | |
| $Np(CO_3)_5^{6-}$ | $Li^+$ | — | |
| | $Na^+$ | — | |
| | $K^+$ | $-0.73 \pm 0.68$ | Calculated in [2001LEM/FUG] (Section 12.1.2.1.4). |
| $(NpO_2)_3(CO_3)_6^{6-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.46 \pm 0.73$ | Calculated in [2001LEM/FUG] (Section 12.1.2.1.2). |
| | $K^+$ | — | |
| $U(CO_3)_5^{6-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.30 \pm 0.15$ | These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $CO_3^{2-}$ and $HCO_3^-$ are based on [1980CIA]. |
| | $K^+$ | $-0.70 \pm 0.31$ | Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL]. |
| $(UO_2)_3(CO_3)_6^{6-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.37 \pm 0.11$ | These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $CO_3^{2-}$ and $HCO_3^-$ are based on [1980CIA]. |
| | $K^+$ | — | |
| $(UO_2)_2NpO_2(CO_3)_6^{6-}$ | $Li^+$ | — | |
| | $Na^+$ | $0.09 \pm 0.71$ | Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.2.1). |
| | $K^+$ | — | |
| $(UO_2)_5(OH)_8(SO_4)_4^{6-}$ | $Li^+$ | — | |
| | $Na^+$ | $1.10 \pm 0.5$ | Estimated in Section 9.5.1.1.2 of [2003GUI/FAN]. |
| | $K^+$ | — | |
| $Th(CO_3)_5^{6-}$ | $Li^+$ | — | |
| | $Na^+$ | $-0.30 \pm 0.15$ | Estimated in Section XI.1.3.2.1 of [2008RAN/FUG]. |
| | $K^+$ | — | |
| $(UO_2)_4(OH)_7(SO_4)_4^{7-}$ | $Li^+$ | — | |
| | $Na^+$ | $2.80 \pm 0.7$ | Estimated in Section 9.5.1.1.2 of [2003GUI/FAN]. |
| | $K^+$ | — | |

Table B-8: Ion interaction coefficients, $\varepsilon_1(j,k)$ and $\varepsilon_2(j,k)$, both in kg·mol$^{-1}$, for cations $j$ with $k$ = $Cl^-$, $ClO_4^-$ and $NO_3^-$ (first part), and for anions $j$ with $k$ = $Li^+$, $Na^+$ and $K^+$ (second part), according to the relationship $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$ at 298.15 K. The data are taken from Ciavatta [1980CIA], [1988CIA] unless indicated otherwise. The uncertainties represent the 95 % confidence level.

| $j\ k \rightarrow$ | $Cl^-$ | | $ClO_4^-$ | | $NO_3^-$ | |
|---|---|---|---|---|---|---|
| $\downarrow$ | $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_1$ | $\varepsilon_2$ |
| $NH_4^+$ | | | $-0.088 \pm 0.002$ | $0.095 \pm 0.012$ | $-0.075 \pm 0.001$ | $0.057 \pm 0.004$ |
| $Tl^+$ | | | $-0.18 \pm 0.02$ | $0.09 \pm 0.02$ | | |
| $Ag^+$ | | | | | $-0.1432 \pm 0.0002$ | $0.0971 \pm 0.000$ |
| $Pb^{2+}$ | | | | | $-0.329 \pm 0.007$ | $0.288 \pm 0.018$ |
| $Hg^{2+}$ | | | | | $-0.145 \pm 0.001$ | $0.194 \pm 0.002$ |
| $Hg_2^{2+}$ | | | | | $-0.2300 \pm 0.0004$ | $0.194 \pm 0.002$ |
| $j\ k \rightarrow$ | $Li^+$ | | $Na^+$ | | $K^+$ | |
| $\downarrow$ | $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_1$ | $\varepsilon_2$ |
| $OH^-$ | $-0.039 \pm 0.002$ | $0.072 \pm 0.006$ | | | | |
| $NO_2^-$ | $0.02 \pm 0.01$ | $0.11 \pm 0.01$ | | | | |
| $NO_3^-$ | | | $-0.049 \pm 0.001$ | $0.044 \pm 0.002$ | $-0.131 \pm 0.002$ | $0.082 \pm 0.006$ |
| $H_2PO_4^-$ | | | $-0.109 \pm 0.001$ | $0.095 \pm 0.003$ | $-0.1473 \pm 0.0008$ | $0.121 \pm 0.004$ |
| $B(OH)_4^-$ | | | $-0.092 \pm 0.002$ | $0.103 \pm 0.005$ | | |
| $SO_3^{2-}$ | | | $-0.125 \pm 0.008$ | $0.106 \pm 0.009$ | | |
| $SO_4^{2-}$ | $-0.068 \pm 0.003$ | $0.093 \pm 0.007$ | $-0.184 \pm 0.002$ | $0.139 \pm 0.006$ | | |
| $S_2O_3^{2-}$ | | | $-0.125 \pm 0.008$ | $0.106 \pm 0.009$ | | |
| $HPO_4^{2-}$ | | | $-0.19 \pm 0.01$ | $0.11 \pm 0.03$ | $-0.152 \pm 0.007$ | $0.123 \pm 0.016$ |
| $CrO_4^{2-}$ | | | $-0.090 \pm 0.005$ | $0.07 \pm 0.01$ | $-0.123 \pm 0.003$ | $0.106 \pm 0.007$ |
| $cit^{3-}$ | $-0.55 \pm 0.11$ [a] | $0.3 \pm 0.2$ [a] | $-0.15 \pm 0.03$ [a] | $0.13 \pm 0.03$ [a] | | |
| $PO_4^{3-}$ | | | $-0.29 \pm 0.02$ | $0.10 \pm 0.01$ | | |
| $TcO_4^-$ | | | | | $-0.24 \pm 0.05$ | $0.33 \pm 0.10$ |

a: See Section VII.3.6 of [2005HUM/AND].

Table B-9: SIT interaction coefficients $\varepsilon(j,k)$ (kg·mol$^{-1}$) for neutral species, *j*, with *k*, electroneutral combination of ions at 298.15 K.

| *j* *k* → ↓ | $Na^+ + ClO_4^-$ | $Na^+ + Cl^-$ | $K^+ + NO_3^-$ |
|---|---|---|---|
| H2ox(aq) | 0.00 ± 0.01 [b] | 0.00 ± 0.01 [b] | 0.00 ± 0.01 [b] |
| H3cit(aq) | 0.00 ± 0.01 [b] | 0.00 ± 0.01 [b] | 0.00 ± 0.01 [b] |
| H4edta(aq) | – 0.29 ± 0.14 | – 0.29 ± 0.14 | – 0.29 ± 0.14 |
| $SnBr_2$(aq) | 0.14 ± 0.07 | | |
| $SnSO_4$(aq) | 0.19 ± 0.35 | | |
| $Sn(NO_3)_2$(aq) | 0.130 ± 0.111 | | |
| Ni(ox)(aq) | – 0.07 ± 0.03 | – 0.07 ± 0.03 | |
| Ni(Hcit)(aq) | – 0.07 ± 0.5 | | |
| $Ni(SCN)_2$(aq) | 0.38 ± 0.06 [a] | | |
| Am(cit)(aq) | | 0.00 ± 0.05 | |
| Np(edta)(aq) | – 0.19 ± 0.19 [g] | | |
| $UO_2$ox(aq) | – 0.05 ± 0.06 | – 0.05 ± 0.06 | |
| Uedta(aq) | – 0.19 ± 0.19 | | |
| Mg(ox)(aq) | | 0.00 ± 0.03 | 0.0 ± 0.1[c] |
| Mg(Hcit)(aq) | 0.02 ± 0.05 | 0.02 ± 0.05 | |
| Ca(ox)(aq) | 0.0 ± 0.1 [d] | 0.0 ± 0.1 [e] | 0.0 ± 0.1 [f] |

(a): See Section V.7.1.3.1 in [2005GAM/BUG].

(b): Basic assumption made in [2005HUM/AND]. See Sections VI.3.5 and VII.3.6 of that review for discussions.

(c): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming $\varepsilon$(Mg(ox)(aq), $KNO_3$) ≈ $\varepsilon$(Mg(ox)(aq), NaCl).

(d): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming $\varepsilon$(Ca(ox)(aq), $NaClO_4$) ≈ $\varepsilon$(Mg(ox)(aq), NaCl).

(e): Estimated in Section VI.5.1 of [2005HUM/AND] by assuming $\varepsilon$(Ca(ox)(aq), NaCl) ≈ $\varepsilon$(Mg(ox)(aq), NaCl).

(f): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming $\varepsilon$(Ca(ox)(aq), $KNO_3$) ≈ $\varepsilon$(Mg(ox)(aq), NaCl).

(g): Estimated in Section VIII.11.2.2 of [2005HUM/AND] by assuming $\varepsilon$(Np(edta)(aq), $NaClO_4$) ≈ $\varepsilon$(Uedta(aq), $NaClO_4$).

Table B-10: Other ion interaction coefficients $\varepsilon(j,k)$ (kg·mol$^{-1}$) used in TDB-Iron Parts 1 and 2 for cations *j* and anions *k*.

| *j* | *k* | ε(*j*,*k*) | Comments |
|---|---|---|---|
| $H^+$ | $HSO_4^-$ | 0.14 ± 0.05 | Determined in TDB-Iron Part 1, p. 476, footnote |

# Appendix C

# Assigned uncertainties[1]

This appendix describes the origin of the uncertainty estimates that are given in the TDB tables of selected data. The original text in [1992GRE/FUG] has been retained in [1995SIL/BID], [1999RAR/RAN] and [2001LEM/FUG], except for some minor changes. Because of the importance of the uncertainty estimates, the present review offers a more comprehensive description of the procedures used. The primary experimental data on which the thermodynamic data and their uncertainties are based consist of equilibrium constants, reported as $\log_{10}K$ values, with an accuracy that in general is in the range 0.01 to 0.1 $\log_{10}$-units (corresponding to 0.06 and 0.57 kJ·.mol$^{-1}$, $\Delta G_r^o$) respectively. In calorimetric data of various types the accuracy is at best 0.1 kJ·mol$^{-1}$, but the composite uncertainty in the enthalpy of reaction in most thermodynamic cycles is often much larger, the uncertainty in molar entropies is typically around 1-3 %. The uncertainty in the reported Gibbs energies and enthalpies of formation is larger because they also include the uncertainties in the auxiliary data used. The thermodynamic data based on these experimental values are, however, reported with three decimals, in the present and previous reviews, where only one and in exceptional cases two decimals are justified. Nevertheless the reported values are given with three decimals because the current reviews are partly based on CODATA values, which for unknown reasons, are listed with three decimals. We have kept the current three decimals to avoid recalculation of the selected values. Users of the thermodynamic data should be aware that the three decimals do not correspond to the experimental uncertainty.

## C.1 The general problem

The focus of this section is on the uncertainty estimates of equilibria in solution, where the key problem is analytical, *i.e.*, the determination of the stoichiometric composition and equilibrium constants of complexes that are in rapid equilibrium with one another.

[1] This appendix essentially contains the text of the TDB-3 Guideline, [1999WAN/OST], earlier versions of which have been printed in all the previous NEA TDB reviews. Because of its importance in the selection of data and to guide the users of the values in Chapters 3, 4, 5, 6, 7 and 8, the text is reproduced here with minor revisions.

We can formulate analyses of the experimental data in the following way: From $N$ measurements, $y_i$, of the variable $y$ we would like to determine a set of $n$ equilibrium constants $k_r$, $r = 1, 2,\ldots, n$, assuming that we know the functional relationship:

$$y = f(k_1, k_2, \ldots k_r ... k_n; a_1, a_2, \ldots.) \quad \text{(C.1)}$$

where $a_1$, $a_2$ , *etc.* are quantities that can be varied but whose values ($a_{1i}$; $a_{2i}$; *etc.*) are assumed to be known accurately in each experiment from the data sets ($y_i$, $a_{1i}$, $a_{2i}$,…), $i = 1, 2, \ldots N$. The functional relationship (C.1) is obtained from the chemical model proposed and in general several different models have to be tested before the "best" one is selected. Details of the procedures are given in Rossotti and Rossotti [1961ROS/ROS].

When selecting the functional relationship (C.1) and determining the set of equilibrium constants that best describes the experiments one often uses a least-squares method. Within this method, the “best” description is the one that will minimise the residual sum of squares, $U$:

$$U = \sum_i w_i \left[ y_i - f(k_1 ... k_n;\ a_{1i},\ a_{2i} ...) \right]^2 \quad \text{(C.2)}$$

where $w_i$ is the weight of each experimental measurement $y_i$.

The minimum of the function (C.2) is obtained by solving a set of normal equations:

$$\frac{\partial U}{\partial k_r} = 0,\ r = 1, ..... n \quad \text{(C.3)}$$

A “true” minimum is only obtained if:

- the functional relationship (C.1) is correct, *i.e.*, if the chemical model is correct;
- all errors are random errors in the variable $y$, in particular there are no systematic errors;
- the random errors in $y$ follow a Gaussian (normal) distribution;
- the weight $w_i(y_i,\ a_{1i},\ a_{2i}, ....)$ of an experimental determination is an exact measure of its inherent accuracy.

To ascertain that the first condition is fulfilled requires chemical insight, such as information of the coordination geometry, relative affinity between metal ions and various donor atoms, *etc.* It is particularly important to test if the chemical equilibrium constants of complexes that occur in small amounts are chemically reasonable. Too many experimentalists seem to look upon the least-squares refinement of experimental data more as an exercise in applied mathematics than as a chemical venture. One of the tasks in the review of the literature is to check this point. An erroneous chemical model is one of the more serious types of systematic error.

The experimentalist usually selects the variable that he/she finds most appropriate to fulfill the second condition. If the estimated errors in $a_{1i}$, $a_{2i}$ … are smaller than the error in $y_i$, the second condition is reasonably well fulfilled. The choice of the error-carrying variable is a matter of choice based on experience, but one must be aware that it has implications, especially in the estimated uncertainty.

The presence of systematic errors is, potentially, the most important source of uncertainty. There is no possibility to handle systematic errors using statistics; statistical methods may indicate their presence, no more. Systematic errors in the chemical model have been mentioned. In addition there may be systematic errors in the methods used. By comparing experimental data obtained with different experimental methods one can obtain an indication of the presence and magnitude of such errors. The systematic errors of this type are accounted for both in the review of the literature and when taking the average of data obtained with different experimental methods. This type of systematic error does not seem to affect the selected data very much, as judged by the usually very good agreement between the equilibrium data obtained using spectroscopic, potentiometric and solubility methods.

The electrode calibration, especially the conversion between measured pH and $-\log_{10}[H^+]$ is an important source of systematic error. The reviewers have when possible corrected this error, as seen in many instances in Appendix A.

The assumption of a normal distribution of the random errors is a choice made in the absence of better alternatives.

Finally, a comment on the weights used in least-squares refinements; this is important because it influences the uncertainty estimate of the equilibrium constants. The weights of individual experimental points can be obtained by repeating the experiment several times and then calculating the average and standard deviation of these data. This procedure is rarely used, instead most experimentalists seem to use unit weight when making a least-squares analysis of their data. However, also in this case there is a weighting of the data by the number of experimental determinations in the parameter range where the different complexes are formed. In order to have comparable uncertainty estimates for the different complexes, one should try to have the same number of experimental data points in the concentration ranges where each of these complexes is predominant; a procedure very rarely used.

As indicated above, the assignment of uncertainties to equilibrium constants is not a straightforward procedure and it is complicated further when there is lack of primary experimental data. The uncertainty estimates given for the individual equilibrium constants reported by the authors and for some cases re-estimated by this review are given in the tables of this and previous reviews. The procedure used to obtain these estimates is given in the original publications and in the Appendix A discussions. However, this uncertainty is still a subjective estimate and to a large extent based on "expert judgment".

## C.2 Uncertainty estimates in the selected thermodynamic data

The uncertainty estimate in the selected thermodynamic data is based on the uncertainty of the individual equilibrium constants or other thermodynamic data, calculated as described in the following sections. A weighted average of the individual $\log_{10}K$ values is calculated using the estimated uncertainty of the individual experimental values to assign its weight. The uncertainty in this average is then calculated using the formulae given in the following text. This uncertainty depends on the number of experimental data points – for $N$ data points with the same estimated uncertainty, $\sigma$, the uncertainty in the average is $\sigma/\sqrt{N}$ . The average and the associated uncertainty reported in the tables of selected data are reported with many more digits than justified only in order to allow the users to back-track the calculations. The reported uncertainty is much smaller than the estimated experimental uncertainty and the users of the tables should look at the discussion of the selected constants in order to get a better estimate of the uncertainty in an experimental determination using a specific method.

One of the objectives of the NEA Thermochemical Database (TDB) project is to provide an idea of the uncertainties associated with the data selected in this review. As a rule, the uncertainties define the range within which the corresponding data can be reproduced with a probability of 95 % at any place and by any appropriate method. In many cases, the statistical treatment is limited or impossible due to the availability of only one or few data points. A particular problem has to be solved when significant discrepancies occur between different source data. This appendix outlines the statistical procedures, which were used for fundamentally different problems, and explains the philosophy used in this review when statistics were inapplicable. These rules are followed consistently throughout the series of reviews within the TDB Project. Four fundamentally different cases are considered:

1. One source datum available
2. Two or more independent source data available
3. Several data available at different ionic strengths
4. Data at non-standard conditions: Procedures for data correction and recalculation.

## C.3 One source datum

The assignment of an uncertainty to a selected value that is based on only one experimental source is a highly subjective procedure. In some cases, the number of data points, on which the selected value is based, allows the use of the "root mean square" [1982TAY] deviation of the data points, $X_i$, to describe the standard deviation, $s_X$, associated with the average, $\overline{X}$ :

$$s_X = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(X_i - \bar{X})^2} \quad . \tag{C.4}$$

The standard deviation, $s_X$, is thus calculated from the dispersion of the equally weighted data points, $X_i$, around the average $\bar{X}$, and the probability is 95 % that an $X_i$ is within $\bar{X} \pm 1.96\ s_X$, see Taylor [1982TAY] (pp. 244-245). The standard deviation, $s_X$, is a measure of the precision of the experiment and does not include any systematic errors.

Many authors report standard deviations, $s_X$, calculated with Eq. (C.4) (but often not multiplied by 1.96), but these do not represent the quality of the reported values in absolute terms. Therefore, it is thus important not to confuse the standard deviation, $s_X$, with the uncertainty, $\sigma$. The latter reflects the reliability and reproducibility of an experimental value and also includes all kinds of systematic errors, $s_j$, that may be involved. The uncertainty, $\sigma$, can be calculated with Eq. (C.5), assuming that the systematic errors are independent.

$$\sigma_X = \sqrt{s_X^2 + \sum_j (s_j^2)} \tag{C.5}$$

The estimation of the systematic errors $s_j$ (which, of course, have to relate to $\bar{X}$ and be expressed in the same units) can only be made by a person who is familiar with the experimental method. The uncertainty, $\sigma$, has to correspond to the 95 % confidence level preferred in this review. It should be noted that for all the corrections and recalculations made (*e.g.*, temperature or ionic strength corrections) the rules of the propagation of errors have to be followed, as outlined in Section C.6.2.

More often, the determination of $s_X$ is impossible because either only one or two data points are available, or the authors did not report the individual values. The uncertainty $\sigma$ in the resulting value can still be estimated using Eq. (C.5) assuming that $s_X^2$ is much smaller than $\sum_j (s_j^2)$, which is usually the case anyway.

## C.4 Two or more independent source data

Frequently, two or more experimental data sources are available, reporting experimental determinations of the desired thermodynamic data. In general, the quality of these determinations varies widely, and the data have to be weighted accordingly for the calculation of the mean. Instead of assigning weight factors, the individual source data, $X_i$, are provided with an uncertainty, $\sigma_i$, that also includes all systematic errors and represents the 95 % confidence level, as described in Section C.3. The weighted mean $\bar{X}$ and its uncertainty, $\sigma_{\bar{X}}$, are then calculated according to Eqs. (C.6) and (C.7).

$$\bar{X} \equiv \frac{\sum_{i=1}^{N}\left(\frac{X_i}{\sigma_i^2}\right)}{\sum_{i=1}^{N}\left(\frac{1}{\sigma_i^2}\right)} \tag{C.6}$$

$$\sigma_{\bar{X}} = \sqrt{\frac{1}{\sum_{i=1}^{N}\left(\frac{1}{\sigma_i^2}\right)}} \tag{C.7}$$

Equations (C.6) and (C.7) may only be used if all the $X_i$ belong to the same parent distribution. If there are serious discrepancies among the $X_i$, one proceeds as described below under Section C.4.1 . It can be seen from Eq. (C.7) that $\sigma_{\bar{X}}$ is directly dependent on the absolute magnitude of the $\sigma_i$ values, and not on the dispersion of the data points around the mean. This is reasonable because there are no discrepancies among the $X_i$, and because the $\sigma_i$ values already represent the 95 % confidence level. The selected uncertainty, $\sigma_{\bar{X}}$, will therefore also represent the 95 % confidence level.

In cases where all the uncertainties are equal, $\sigma_i = \sigma$, Eqs. (C.6) and (C.7) reduce to Eqs. (C.8) and (C.9).

$$\bar{X} = \frac{1}{N}\sum_{i=1}^{N} X_i \tag{C.8}$$

$$\sigma_{\bar{X}} = \frac{\sigma}{\sqrt{N}} \tag{C.9}$$

**Example C.1:**

Five data sources report values for the thermodynamic quantity, $X$. The reviewer has assigned uncertainties that represent the 95 % confidence level as described in Section C.3.

| $i$ | $X_i$ | $\sigma_i$ |
|---|---|---|
| 1 | 25.3 | 0.5 |
| 2 | 26.1 | 0.4 |
| 3 | 26.0 | 0.5 |
| 4 | 24.85 | 0.25 |
| 5 | 25.0 | 0.6 |

According to Eqs. (C.6) and (C.7), the following result is obtained:

$$\bar{X} = (25.3 \pm 0.2).$$

The calculated uncertainty, $\sigma_{\bar{X}}$ = 0.2, appears relatively small, but is statistically correct, as the values are assumed to follow a Gaussian distribution. As a consequence of Eq. (C.7), $\sigma_{\bar{X}}$ will always come out smaller than the smallest $\sigma_i$.

Assuming $\sigma_4 = 0.10$ instead of 0.25 would yield $\overline{X} = (25.0 \pm 0.1)$ and $\sigma_4 = 0.60$ would result in $\overline{X} = (25.6 \pm 0.2)$. In fact, the values $(X_i \pm \sigma_i)$ in this example are at the limit of consistency, *i.e.*, the range $(X_4 \pm \sigma_4)$ does not overlap with the ranges $(X_2 \pm \sigma_2)$ and $(X_3 \pm \sigma_3)$. There might be a better way to solve this problem. Three possible choices seem more reasonable:

i. The uncertainties, $\sigma_i$, are reassigned because they appear too optimistic after further consideration. Some assessments may have to be reconsidered and the uncertainties reassigned. For example, multiplying all the $\sigma_i$ by 2 would yield $\overline{X} = (25.3 \pm 0.3)$.

ii. If reconsideration of the previous assessments gives no evidence for reassigning the $X_i$ and $\sigma_i$ (95 % confidence level) values listed above, the statistical conclusion will be that all the $X_i$ do not belong to the same parent distribution and cannot therefore be treated in the same group (*cf.* item iii below for a non-statistical
explanation). The values for $i$ =1, 4 and 5 might be considered as belonging to Group A and the values for $i$ = 2 and 3 to Group B. The weighted average of the values in Group A is $X_A$ ($i$ = 1, 4, 5) = (24.95 ± 0.21) and of those in Group B, $X_B$ ($i$ = 2, 3) = (26.06 ± 0.31), the second digit after the decimal point being carried over to avoid loss of information. The selected value is now determined as described below under "Discrepancies" (Section C.4.1, Case I). $X_A$ and $X_B$ are averaged (straight average, there is no reason for giving $X_A$ a larger weight than $X_B$), and $\sigma_{\overline{X}}$ is chosen in such a way that it covers the complete ranges of expectancy of $X_A$ and $X_B$. The selected value is then $\overline{X} = (25.5 \pm 0.9)$.

iii. Another explanation could be that unidentified systematic errors are associated with some values. If this seems likely to be the case, there is no reason for splitting the values up into two groups. The correct way of proceeding would be to calculate the unweighted average of all the five points and assign an uncertainty that covers the whole range of expectancy of the five values. The resulting value is then $\overline{X} = (25.4 \pm 1.0)$, which is rounded according to the rules in Section C.6.3 to $\overline{X} = (25.4 \pm 1.1)$.

## C.4.1 Discrepancies

Two data are called discrepant if they differ significantly, *i.e.*, their uncertainty ranges do not overlap. In this context, two cases of discrepancies are considered. Case I: Two significantly different source data are available. Case II: Several, mostly consistent source data are available, one of them being significantly different, *i.e.*, an "outlier".

**Case I. Two discrepant data:** This is a particularly difficult case because the number of data points is obviously insufficient to allow the preference of one of the two values. If there is absolutely no way of discarding one of the two values and selecting the other, the only solution is to average the two source data in order to obtain the

selected value, because the underlying reason for the discrepancy must be unrecognised systematic errors. There is no point in calculating a weighted average, even if the two source data have been given different uncertainties, because there is obviously too little information to give even only limited preference to one of the values. The uncertainty, $\sigma_{\bar{X}}$, assigned to the selected mean, $\bar{X}$, has to cover the range of expectation of both source data, $X_1$, $X_2$, as shown in Eq. (C.10),

$$\sigma_{\bar{X}} = \left| X_i - \bar{X} \right| + \sigma_{\max} \tag{C.10}$$

where $i$ =1, 2, and $\sigma_{\max}$ is the larger of the two uncertainties $\sigma_i$, see Example C.1.ii and Example C.2.

**Example C.2:**

The following credible source data are given:

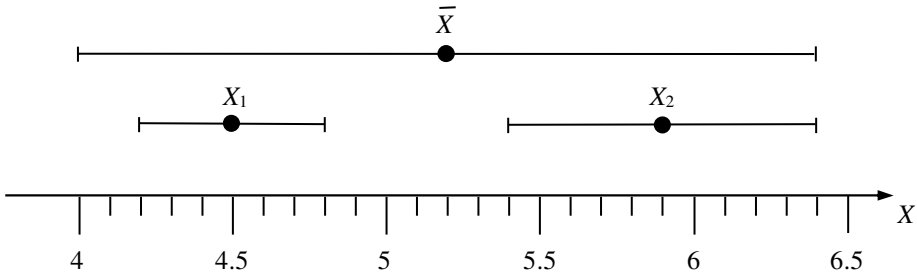
$$X_1 = (4.5 \pm 0.3)$$

$$X_2 = (5.9 \pm 0.5).$$

The uncertainties have been assigned by the reviewer. Both experimental methods are satisfactory and there is no justification to discard one of the data. The selected value is then:

$$\bar{X} = (5.2 \pm 1.2).$$

Figure C-1: Illustration for Example C.2.




**Case II. Outliers**: This problem can often be solved by either discarding the outlying data point, or by providing it with a large uncertainty to lower its weight. If, however, the outlying value is considered to be of high quality and there is no reason to discard all the other data, this case is treated in a way similar to Case I. Example C.3 illustrates the procedure.

**Example C.3:**

The following data points are available. The reviewer has assigned the uncertainties and sees no justification for any change.

| $i$ | $X_i$ | $\sigma_i$ |
|---|---|---|
| 1 | 4.45 | 0.35 |
| 2 | 5.9 | 0.5 |
| 3 | 5.7 | 0.4 |
| 4 | 6.0 | 0.6 |
| 5 | 5.2 | 0.4 |

There are two data sets that, statistically, belong to different parent distributions, A and B. According to Eqs. (C.6) and (C.7), the following average values are found for the two groups: $X_A(i = 1) = (4.45 \pm 0.35)$ and $X_B(i = 2, 3, 4, 5) = (5.62 \pm 0.23)$. The selected value will be the straight average of $X_A$ and $X_B$, analogous to Example C.1:

$$\overline{X} = (5.0 \pm 0.9).$$

## C.5 Several data at different ionic strengths

The extrapolation procedure for aqueous equilibria used in this review is the specific ion interaction model outlined in Appendix B. The objective of this review is to provide selected data sets at standard conditions, *i.e.,* among others, at infinite dilution for aqueous species. Equilibrium constants determined at different ionic strengths can, according to the specific ion interaction equations, be extrapolated to $I = 0$ with a linear regression model, yielding as the intercept the desired equilibrium constant at $I = 0$, and as the slope the stoichiometric sum of the ion interaction coefficients, $\Delta\varepsilon$. The ion interaction coefficient of the target species can usually be extracted from $\Delta\varepsilon$ and would be listed in the corresponding table of Appendix B.

The available source data may sometimes be sparse or may not cover a sufficient range of ionic strengths to allow a proper linear regression. In this case, the correction to $I = 0$ should be carried out according to the procedure described in Section C.6.1.

If sufficient data are available at different ionic strengths and in the same inert salt medium, a weighted linear regression will be the appropriate way to obtain both the constant at $I = 0$, $\overline{X}^{\circ}$, and $\Delta\varepsilon$. The first step is the conversion of the ionic strength from the frequently used molar (mol·dm$^{-3}$, M) to the molal (mol·kg$^{-1}$, $m$) scale, as described in Section 2.2. The second step is the assignment of an uncertainty, $\sigma_i$, to each data point $X_i$ at the molality, $m_{k,i}$, according to the rules described in Section C.3. A large number of commercial and public domain computer programs and routines exist

for weighted linear regressions. The subroutine published by Bevington [1969BEV] (pp.104 – 105) has been used for the calculations in the examples of this appendix. Eqs. (C.11) through (C.15) present the equations that are used for the calculation of the intercept $\overline{X}^{\,o}$ and the slope $-\Delta\varepsilon$ :

$$\overline{X}^{\,o} = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2}\right) \tag{C.11}$$

$$-\Delta\varepsilon = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2}\right) \tag{C.12}$$

$$\sigma_{\overline{X}^{\,o}} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}} \tag{C.13}$$

$$\sigma_{\Delta\varepsilon} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}} \tag{C.14}$$

where

$$\Delta = \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2} - \left(\sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\right)^2 . \tag{C.15}$$

In this way, the uncertainties, $\sigma_i$, are not only used for the weighting of the data in Eqs. (C.11) and (C.12), but also for the calculation of the uncertainties, $\sigma_{\overline{X}^{\,o}}$ and $\sigma_{\Delta\varepsilon}$, in Eqs. (C.13) and (C.14). If the $\sigma_i$ represents the 95 % confidence level, $\sigma_{\overline{X}^{\,o}}$ and $\sigma_{\Delta\varepsilon}$ will also do so. In other words, the uncertainties of the intercept and the slope do not depend on the dispersion of the data points around the straight line, but rather directly on their absolute uncertainties, $\sigma_i$.

**Example C.4:**

Ten independent determinations of the equilibrium constant, $\log_{10}{}^{*}\beta$, for the reaction:

$$UO_2^{2+} + HF(aq) \rightleftharpoons UO_2F^{+} + H^{+} \tag{C.16}$$

are available in $HClO_4/NaClO_4$ media at different ionic strengths. Uncertainties that represent the 95 % confidence level have been assigned by the reviewer. A weighted linear regression, ($\log_{10}{}^{*}\beta + 2D$) *vs.* $m_k$, according to the formula, $\log_{10}{}^{*}\beta$ (C.16) + $2D$ = $\log_{10}{}^{*}\beta^{o}$ (C.16) – $\Delta\varepsilon\, m_k$, will yield the correct values for the intercept, $\log_{10}{}^{*}\beta^{o}$ (C.16), and the slope, $\Delta\varepsilon$. In this case, $m_k$ corresponds to the molality of $ClO_4^-$. $D$ is the Debye-Hückel term, *cf.* Appendix B.

| $i$ | $m_{ClO_4^-,i}$ | $\log_{10}{}^{*}\beta + 2D$ | $\sigma_i$ |
|---|---|---|---|
| 1 | 0.05 | 1.88 | 0.10 |
| 2 | 0.25 | 1.86 | 0.10 |
| 3 | 0.51 | 1.73 | 0.10 |
| 4 | 1.05 | 1.84 | 0.10 |
| 5 | 2.21 | 1.88 | 0.10 |
| 6 | 0.52 | 1.89 | 0.11 |
| 7 | 1.09 | 1.93 | 0.11 |
| 8 | 2.32 | 1.78 | 0.11 |
| 9 | 2.21 | 2.03 | 0.10 |
| 10 | 4.95 | 2.00 | 0.32 |

The results of the linear regression are:

$$\text{intercept} = (1.837 \pm 0.054) = \log_{10}{}^{*}\beta^{o} \text{ (C.16)}$$

$$\text{slope} = (0.029 \pm 0.036) = -\Delta\varepsilon .$$

Calculation of the ion interaction coefficient $\varepsilon(UO_2F^+, ClO_4^-) = \Delta\varepsilon + \varepsilon(UO_2^{2+}, ClO_4^-) - \varepsilon(H^+, ClO_4^-)$: from $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol$^{-1}$, $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol$^{-1}$ (see Appendix B) and the slope of the linear regression, $\Delta\varepsilon = -(0.03 \pm 0.04)$ kg·mol$^{-1}$, it follows that $\varepsilon(UO_2F^+, ClO_4^-) = (0.29 \pm 0.05)$ kg·mol$^{-1}$. Note that the uncertainty ($\pm 0.05$) kg·mol$^{-1}$ is obtained based on the rules of error propagation as described in Section C.6.2:

$$\sigma = \sqrt{(0.04)^2 + (0.03)^2 + (0.02)^2} .$$

The resulting selected values are thus:

$$\log_{10}{}^{*}\beta^{o} \text{ (C.16)} = (1.84 \pm 0.05)$$

$$\varepsilon(UO_2F^+, ClO_4^-) = (0.29 \pm 0.05) \text{ kg·mol}^{-1}.$$

## C.5.1 Discrepancies or insufficient number of data points

Discrepancies are principally treated as described in Section C.4. Again, two cases can be defined. Case I: Only two data points are available. Case II: An "outlier" cannot be discarded. If only one data point is available, the procedure for correction to zero ionic strength outlined in Section C.6 should be followed.

**Case I. Too few molalities:** If only two source data are available, there will be no straightforward way to decide whether or not these two data points belong to the same parent distribution unless either the slope of the straight line is known or the two data refer to the same ionic strength. Drawing a straight line right through the two data points is an inappropriate procedure because all the errors associated with the two

source data would accumulate and may lead to highly erroneous values of $\log_{10} K^{\circ}$ and $\Delta\varepsilon$. In this case, an ion interaction coefficient for the key species in the reaction in question may be selected by analogy (charge is the most important parameter), and a straight line with the slope $\Delta\varepsilon$ as calculated may then be drawn through each data point. If there is no reason to discard one of the two data points based on the quality of the underlying experiment, the selected value will be the unweighted average of the two standard state data points obtained by this procedure, and its uncertainty must cover the entire range of expectancy of the two values, analogous to Case I in Section C.4. It should be mentioned that the ranges of expectancy of the corrected values at $I = 0$ are given by their uncertainties, which are based on the uncertainties of the source data at $I \neq 0$ and the uncertainty in the slope of the straight line. The latter uncertainty is not an estimate, but is calculated from the uncertainties in the ion interaction coefficients involved, according to the rules of error propagation outlined in Section C.6.2. The ion interaction coefficients estimated by analogy are listed in the table of selected ion interaction coefficients (Appendix B), but they are flagged as estimates.

**Case II. Outliers and inconsistent data sets:** This case includes situations where it is difficult to decide whether or not a large number of points belong to the same parent distribution. There is no general rule on how to solve this problem, and decisions are left to the judgment of the reviewer. For example, if eight data points follow a straight line reasonably well and two lie way out, it may be justified to discard the "outliers". If, however, the eight points are scattered considerably and two points are just a bit further out, one can probably not consider them as "outliers". It depends on the particular case and on the judgment of the reviewer whether it is reasonable to increase the uncertainties of the data to reach consistency, or whether the slope, $\Delta\varepsilon$, of the straight line should be estimated by analogy.

**Example C.5:**

Six reliable determinations of the equilibrium constant, $\log_{10}\beta$, of the reaction:

$$UO_2^{2+} + SCN^- \rightleftharpoons UO_2SCN^+ \qquad \text{(C.17)}$$

are available in different electrolyte media:

$I_c$ = 0.1 M ($KNO_3$) $\quad \log_{10}\beta$ (C.17) = (1.19 ± 0.03)

$I_c$ = 0.33 M ($KNO_3$) $\quad \log_{10}\beta$ (C.17) = (0.90 ± 0.10)

$I_c$ = 1.0 M ($NaClO_4$) $\quad \log_{10}\beta$ (C.17) = (0.75 ± 0.03)

$I_c$ = 1.0 M ($NaClO_4$) $\quad \log_{10}\beta$ (C.17) = (0.76 ± 0.03)

$I_c$ = 1.0 M ($NaClO_4$) $\quad \log_{10}\beta$ (C.17) = (0.93 ± 0.03)

$I_c$ = 2.5 M ($NaNO_3$) $\quad \log_{10}\beta$ (C.17) = (0.72 ± 0.03)

The uncertainties are assumed to represent the 95 % confidence level. From the values at $I_c$ = 1 M, it can be seen that there is a lack of consistency in the data, and that a linear regression similar to that shown in Example C.4 would be inappropriate. Instead, the use of $\Delta\varepsilon$ values from reactions of the same charge type is encouraged. Analogies with $\Delta\varepsilon$ are more reliable than analogies with single $\varepsilon$ values due to canceling effects. For the same reason, the dependency of $\Delta\varepsilon$ on the type of electrolyte is often smaller than for single $\varepsilon$ values.

A reaction of the same charge type as Reaction (C.17), and for which $\Delta\varepsilon$ is well known, is:

$$UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+ . \qquad (C.18)$$

The value of $\Delta\varepsilon$ (C.18) = – (0.25 ± 0.02) kg·mol$^{-1}$ was obtained from a linear regression using 16 experimental values between $I_c$ = 0.1 M and $I_c$ = 3 M Na(Cl,ClO$_4$) [1992GRE/FUG]. It is thus assumed that:

$$\Delta\varepsilon \text{ (C.17)} = \Delta\varepsilon \text{ (C.18)} = -(0.25 \pm 0.02) \text{ kg·mol}^{-1}.$$

The correction of $\log_{10}\beta$(C.17) to $I$ = 0 is done using the specific ion interaction equation, *cf.* TDB-2, which uses molal units:

$$\log_{10}\beta + 4D = \log_{10}\beta^\circ - \Delta\varepsilon\, I_m. \qquad (C.19)$$

$D$ is the Debye-Hückel term and $I_m$ the ionic strength converted to molal units by using the conversion factors listed in Table 2-5. The following list gives the details of this calculation. The resulting uncertainties in $\log_{10}\beta$ are obtained based on the rules of error propagation as described in Section C.6.2.

Table C-1: Details of the calculation of the equilibrium constant for Reaction (C.17) corrected to $I$ = 0, using (C.19).

| $I_m$ | electrolyte | $\log_{10}\beta$ | $4D$ | $\Delta\varepsilon\, I_m$. | $\log_{10}\beta^\circ$ |
|---|---|---|---|---|---|
| 0.101 | $KNO_3$ | (1.19 ± 0.03) | 0.438 | – 0.025 | (1.68 ± 0.03)[a] |
| 0.335 | $KNO_3$ | (0.90 ± 0.10) | 0.617 | – 0.084 | (1.65 ± 0.10)[a] |
| 1.050 | $NaClO_4$ | (0.75 ± 0.03) | 0.822 | – 0.263 | (1.31 ± 0.04) |
| 1.050 | $NaClO_4$ | (0.76 ± 0.03) | 0.822 | – 0.263 | (1.32 ± 0.04) |
| 1.050 | $NaClO_4$ | (0.93 ± 0.03) | 0.822 | – 0.263 | (1.49 ± 0.04) |
| 2.714 | $NaNO_3$ | (0.72 ± 0.03) | 0.968 | – 0.679 | (1.82 ± 0.13)[a] |

a: These values were corrected for the formation of the nitrate complex, $UO_2NO_3^+$, by using $\log_{10}\beta^\circ(UO_2NO_3^+)$ = (0.30 ± 0.15) [1992GRE/FUG].

As was expected, the resulting values, $\log_{10}\beta^\circ$, are inconsistent and have therefore to be treated as described in Case I of Section C.4. That is, the selected value will be the unweighted average of $\log_{10}\beta^\circ$, and its uncertainty will cover the entire range of expectancy of the six values. A weighted average would only be justified if the six values of $\log_{10}\beta^\circ$ were consistent. The result is:

$$\log_{10} \beta^{o} = (1.56 \pm 0.39).$$

# C.6 Procedures for data handling

## C.6.1 Correction to zero ionic strength

The correction of experimental data to zero ionic strength is necessary in all cases where a linear regression is impossible or appears inappropriate. The method used throughout the review involves application of the specific ion interaction equations described in detail in Appendix B. Two variables are needed for this correction, and both have to be provided with an uncertainty at the 95 % confidence level: the experimental source value, $\log_{10} K$ or $\log_{10} \beta$, and the stoichiometric sum of the ion interaction coefficients, $\Delta\varepsilon$. The ion interaction coefficients (see Tables B-4, B-5, B-6 and B-7 of Appendix B) required to calculate $\Delta\varepsilon$ may not all be known. Missing values therefore need to be estimated. It is recalled that the electric charge has the most significant influence on the magnitude of the ion interaction coefficients, and that it is in general more reliable to estimate $\Delta\varepsilon$ from known reactions of the same charge type, rather than to estimate single $\varepsilon$ values. The uncertainty of the corrected value at $I = 0$ is calculated by taking into account the propagation of errors, as described below. It should be noted that the ionic strength is frequently given in moles per $dm^3$ of solution (molar, M) and has to be converted to moles per kg $H_2O$ (molal, *m*), as the model requires. Conversion factors for the most common inert salts are given in Table 2.5.

**Example C.6:**

For the equilibrium constant of the reaction:

$$M^{3+} + 2H_2O(l) \rightleftharpoons M(OH)_2^+ + 2\,H^+, \qquad \text{(C.20)}$$

only one credible determination in 3 M $NaClO_4$ solution is known to be, $\log_{10}{}^{*}\beta\,(\text{C.20}) = -6.31$, to which an uncertainty of $\pm 0.12$ has been assigned. The ion interaction coefficients are as follows:

$$\varepsilon(M^{3+}, ClO_4^-) = (0.56 \pm 0.03)\ \text{kg·mol}^{-1},$$

$$\varepsilon(M(OH)_2^+, ClO_4^-) = (0.26 \pm 0.11)\ \text{kg·mol}^{-1},$$

$$\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ \text{kg·mol}^{-1}.$$

The values of $\Delta\varepsilon$ and $\sigma_{\Delta\varepsilon}$ can be obtained readily (*cf.* Eq. (C.22)):

$$\Delta\varepsilon = \varepsilon(M(OH)_2^+, ClO_4^-) + 2\varepsilon(H^+, ClO_4^-) - \varepsilon(M^{3+}, ClO_4^-) = -0.22\ \text{kg·mol}^{-1},$$

$$\sigma_{\Delta\varepsilon} = \sqrt{(0.11)^2 + (2\times 0.02)^2 + (0.03)^2} = 0.12\ \text{kg·mol}^{-1}.$$

The two variables are thus:

$$\log_{10}{}^{*}\beta\,(\text{C.20}) = -(6.31 \pm 0.12),$$

$$\Delta\varepsilon = -(0.02 \pm 0.12)\ \text{kg·mol}^{-1}.$$

According to the specific ion interaction model the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10}{}^{*}\beta\,(\text{C.20}) + 6D = \log_{10}{}^{*}\beta^{\circ}\,(\text{C.20}) - \Delta\varepsilon\, m_{\text{ClO}_4^-}$$

$D$ is the Debye-Hückel term:

$$D = \frac{0.509\sqrt{I_m}}{(1+1.5\sqrt{I_m})}.$$

The ionic strength, $I_m$, and the molality, $m_{\text{ClO}_4^-}$ ($I_m \approx m_{\text{ClO}_4^-}$), have to be expressed in molal units, 3 M $NaClO_4$ corresponding to 3.5 m $NaClO_4$ (see Section 2.2), giving $D = 0.25$. This results in:

$$\log_{10}{}^{*}\beta^{\circ}\,(\text{C.20}) = -4.88.$$

The uncertainty in $\log_{10}{}^{*}\beta^{\circ}$ is calculated from the uncertainties in $\log_{10}{}^{*}\beta$ and $\Delta\varepsilon$ (*cf.* Eq. (C.22)):

$$\sigma_{\log_{10}{}^{*}\beta^{o}} = \sqrt{\sigma^2_{\log_{10}{}^{*}\beta} + (m_{\text{ClO}_4^-}\sigma_{\Delta\varepsilon})^2} = \sqrt{(0.12)^2 + (3.5\times 0.12)^2} = 0.44$$

The selected, rounded value is:

$$\log_{10}{}^{*}\beta^{\circ}\,(\text{C.20}) = -(4.9 \pm 0.4).$$

## C.6.2 Propagation of errors

Whenever data are converted or recalculated, or other algebraic manipulations are performed that involve uncertainties, the propagation of these uncertainties has to be taken into account in a correct way. A clear outline of the propagation of errors is given by Bevington [1969BEV]. A simplified form of the general formula for error propagation is given by Eq. (C.21), supposing that $X$ is a function of $Y_1, Y_2, \ldots, Y_N$.

$$\sigma_X^2 = \sum_{i=1}^{N}\left(\frac{\partial X}{\partial Y_i}\sigma_{Y_i}\right)^2 \qquad \text{(C.21)}$$

Equation (C.21) can be used only if the variables, $Y_1, Y_2, \ldots, Y_N$, are independent or if their uncertainties are small, *i.e.*, the covariances can be disregarded. One of these two assumptions can almost always be made in chemical thermodynamics, and Eq. (C.21) can thus almost universally be used in this review. Eqs. (C.22) through (C.26) present explicit formulae for a number of frequently encountered algebraic expressions, where $c$, $c_1$, $c_2$ are constants.

$$X = c_1 Y_1 \pm c_2 Y_2 : \qquad \sigma_X^2 = (c_1 \sigma_{Y_1})^2 + (c_2 \sigma_{Y_2})^2 \tag{C.22}$$

$$X = \pm\, cY_1 Y_2 \text{ and } X = \pm \frac{cY_1}{Y_2} : \qquad \left(\frac{\sigma_X}{X}\right)^2 = \left(\frac{\sigma_{Y_1}}{Y_1}\right)^2 + \left(\frac{\sigma_{Y_2}}{Y_2}\right)^2 \tag{C.23}$$

$$X = c_1 Y^{\pm c_2} : \qquad \frac{\sigma_X}{X} = c_2 \frac{\sigma_Y}{Y} \tag{C.24}$$

$$X = c_1 e^{\pm c_2 Y} : \qquad \frac{\sigma_X}{X} = c_2 \sigma_Y \tag{C.25}$$

$$X = c_1 \ln\left(\left|c_2 Y\right|\right) : \qquad \sigma_X = c_1 \frac{\sigma_Y}{Y} \tag{C.26}$$

**Example C.7:**

A few simple calculations illustrate how these formulae are used. The values have not been rounded.

Eq. (C.22): $\Delta_r G_m = 2[-(277.4 \pm 4.9)]\ \text{kJ·mol}^{-1} - [-(467.3 \pm 6.2)]\ \text{kJ·mol}^{-1}$

$= -(87.5 \pm 11.6)\ \text{kJ·mol}^{-1}$.

Eq. (C.23): $K = \dfrac{(0.038 \pm 0.002)}{(0.0047 \pm 0.0005)} = (8.09 \pm 0.96)$

Eq. (C.24): $K = 4(3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$

Eq. (C.25): $K^\circ = e^{\frac{-\Delta_r G_m^\circ}{RT}}$; $\Delta_r G_m^\circ = -(2.7 \pm 0.3)\ \text{kJ·mol}^{-1}$

$R = 8.3145\ \text{J·K}^{-1}\text{·mol}^{-1}$

$T = 298.15\ \text{K}$

$K^\circ = (2.97 \pm 0.36)$.

Note that powers of 10 have to be reduced to powers of $e$, *i.e.*, the variable has to be multiplied by ln(10), *e.g.*,

$\log_{10} K = (2.45 \pm 0.10);\ K = 10^{\log_{10} K} = e^{(\ln(10)\cdot \log_{10} K)} = (282 \pm 65)$.

Eq. (C.26): $\Delta_r G_m^\circ = -RT \ln K^\circ$; $K^\circ = (8.2 \pm 1.2) \times 10^6$

$R = 8.3145\ \text{J·K}^{-1}\text{·mol}^{-1}$

$T = 298.15\ \text{K}$

$$\Delta_r G_m^o = -(39.46 \pm 0.36)\ \text{kJ·mol}^{-1}$$

$$\ln K^o = (15.92 \pm 0.15)$$

$$\log_{10} K^o = \ln K^o / \ln(10) = (6.91 \pm 0.06).$$

Again, it can be seen that the uncertainty in $\log_{10} K^o$ cannot be the same as in $\ln K^o$. The constant conversion factor of ln(10) = 2.303 is also to be applied to the uncertainty.

## C.6.3 Rounding

The standard rules to be used for rounding are:

1. When the digit following the last digit to be retained is less than 5, the last digit retained is kept unchanged.
2. When the digit following the last digit to be retained is greater than 5, the last digit retained is increased by 1.
3. When the digit following the last digit to be retained is 5 and
    a) there are no digits (or only zeroes) beyond the 5, an odd digit in the last place to be retained is increased by 1 while an even digit is kept unchanged;
    b) other non-zero digits follow, the last digit to be retained is increased by 1, whether odd or even.

This procedure avoids introducing a systematic error from always dropping or not dropping a 5 after the last digit retained.

When adding or subtracting, the result is rounded to the number of decimal places (not significant digits) in the term with the least number of places. In multiplication and division, the results are rounded to the number of significant digits in the term with the least number of significant digits.

In general, all operations are carried out in full, and only the final results are rounded, in order to avoid the loss of information from repeated rounding. For this reason, several additional digits are carried in all calculations until the final selected data set is developed, and only then are data rounded.

## C.6.4 Significant digits

The uncertainty of a value basically defines the number of significant digits a value should be given.

Example: (3.478 ± 0.008)

(3.48 ± 0.01)

$(2.8 \pm 0.4)$

$(10 \pm 1)$

$(105 \pm 20)$.

In the case of auxiliary data or values that are used for later calculations, it is often inconvenient to round to the last significant digit. In the value $(4.85 \pm 0.26)$, for example, the "5" is close to being significant and should be carried along a recalculation path in order to avoid loss of information. In particular cases, where the rounding to significant digits could lead to slight internal inconsistencies, digits with no significant meaning in absolute terms are nevertheless retained. The uncertainty of a selected value always contains the same number of digits after the decimal point as the value itself.

# Appendix D

# The estimation of entropies

The selected thermodynamic data in the NEA reviews are based on a combination of theory and experimental information; examples are the use of molecular partition functions for the estimate of entropies and heat capacities of gaseous compounds such as the gaseous uranyl(VI) halides. Theory is also used in the interpretation of EXAFS spectra of complexes in solution. The latter do not provide explicit thermodynamic information but are important because they provide information on the existence and structure of complexes in solution and often also on the range of existence of these, as exemplified by the studies of Hennig *et al.* [2005HEN/TUT], [2009IKE/HEN], [2010HEN/IKE] and Uehara *et al.* [2011UEH/FUJ]. As seen in the following, there is extensive information on the use of empirical methods for the estimate of entropies of solid compounds. Such information is not used by the NEA reviews for the selection of thermodynamic data, but can provide a check of the consistency of entropies obtained by low temperature calorimetry. Examples are offered by entropy determinations of $Na(UO_2)(SiO_3OH)\cdot H_2O$(cr) [2002KAR/CHE2] and $K(UO_2)(SiO_3OH)\cdot H_2O$(cr) [2002KAR/CHE] phases. The water content of these phases is not always well-known and can vary between the different alkali metal ions, resulting in unknown and often large uncertainties in the derived entropy values. Information on the expected variation in entropy between the different cations can, in this case, give indications of the presence of systematic errors in the data, allowing a better judgment on the quality of the reported data.

Appendix D of Grenthe *et al.* [1992GRE/FUG] presented an empirical method of estimating entropies of solid compounds. This method was expanded in the current version to involve more chemical elements. Latimer's method for entropy estimation [1951LAT] is based on the additivity principle, where cations give constant contributions to the entropy values, while the contributions of anions depend on the charge of the cation in the solid compounds under consideration.

Based on later experimental data, Naumov *et al.* [1971NAU/RYZ] prepared a revised table of parameters to be used with this method.

Langmuir [1978LAN] described an improved method of estimating entropy values for solid compounds containing the $UO_2^{2+}$ moiety. In his procedure, the contributions of "$UO_2^{2+}$" to the entropy of γ-$UO_3$, β-$UO_2(OH)_2$ and schoepite were used

to estimate the contribution of "$UO_2^{2+}$" to the entropy of other uranium compounds. Although Latimer [1951LAT] and Naumov *et al.* [1971NAU/RYZ] suggested a value of 39.3 $J \cdot K^{-1} \cdot mol^{-1}$ for each water of hydration in a crystalline solid hydrate, Langmuir [1978LAN] considered the value of 44.7 $J \cdot K^{-1} \cdot mol^{-1}$, the value for the entropy of ice-I from the compilation of Robie and Waldbaum [1968ROB/WAL], to be more appropriate.

Thus, the entropies in the literature, based on Latimer's method, may vary considerably, depending on the set of parameters used in the estimation. For some compounds, especially binary solids, more reliable entropy values may be estimated by comparison with values for closely related solids, rather than using Latimer's method. In the present review an attempt has been made to ensure that entropies estimated for solids have been calculated using consistent procedures.

Three methods are used. Most of the estimates of solids' entropies for which experimental data are unavailable, or unreliable, are calculated using Latimer's method with the parameters from Naumov *et al.* [1971NAU/RYZ]. The entropy contribution per water of hydration used is the one from Robie and Waldbaum, based on the value for ice-I [1968ROB/WAL]. Entropy values at 298.15 K, based on low-temperature heat capacity data have been selected in [1992GRE/FUG] for the following solid compounds of uranium(VI): $UO_2Cl_2$(cr), $UO_2CO_3$(cr), α-$UO_3$, β-$UO_3$, γ-$UO_3$, $UO_3 \cdot 2H_2O$(cr) (*i.e.*, $UO_2(OH)_2 \cdot H_2O$(cr)), $UO_2(NO_3)_2 \cdot 6H_2O$(cr), were used in the manner described by Langmuir, to calculate a contribution of 94.7 $J \cdot K^{-1} \cdot mol^{-1}$ for $UO_2^{2+}$ in uranium(VI) solids—as opposed to the value 93.3 $J \cdot K^{-1} \cdot mol^{-1}$ proposed by Langmuir [1978LAN].

Other parameters required, but not available from [1971NAU/RYZ] have been estimated in [1992GRE/FUG]. Values used are provided in Table D-1, for elements forming cations, whose contributions to the entropy are considered to be constant, and in Table D-2 for anions, whose contributions depend on the cation charge. Uncertainties are estimated as ± 4 $J \cdot K^{-1} \cdot mol^{-1}$ per contributing group other than water of hydration. For each water of hydration the uncertainty is estimated as ± 6 $J \cdot K^{-1} \cdot mol^{-1}$. This increased uncertainty reflects the fact that the parameters from Naumov *et al.* [1971NAU/RYZ] were derived by considering entropies from many compounds, some of which could have been hydrates. Thus there might be a problem for an internal inconsistency of these data.

In estimating entropies for solids containing U(III), U(IV) and U(V) no allowance has been made for contributions from the electronic degeneracy of the uranium ions. This is obviously incorrect, however, the sources (and weighting) of the data used to derive the Latimer parameters [1971NAU/RYZ] are not clear. Therefore, it is not certain if corrections should actually be applied, or if they are already included in the suggested parameters (or trends in parameters). In any future systematic attempt to improve the Latimer parameters only data for compounds containing ions without electronic contributions should be used.

A few examples of the use of the Latimer method can be given. This method predicts for $UO_2CO_3$(cr) (rutherfordine) $S_m^o \approx 94.7 + 49.7 = 144.1$ $J \cdot K^{-1} \cdot mol^{-1}$ as

compared with the experimental value of $S^o_m$ = (144.20 ± 0.30) $J \cdot K^{-1} \cdot mol^{-1}$ in [1987GUR/SER], but this good agreement may be fortuitous. Another examples is the estimation of the entropy for $La[(UO_2)(AsO_4)]_3 \cdot 15H_2O$(cr): $S^o_m \approx 57.7 + 3 \times 94.7 + 3 \times 79 + 15 \times 44.7 = 1249$ $J \cdot K^{-1} \cdot mol^{-1}$ as compared with the experimental value of $S^o_m = 1273$ $J \cdot K^{-1} \cdot mol^{-1}$ [2002KAR/CHE4].

For some solids, the entropy is known for one or more hydrates, but is not known for all. In such cases the unknown entropies are estimated using the known values and the recommended contribution of 44.7 $J \cdot K^{-1} \cdot mol^{-1}$ per water of hydration.

Finally, for some binary metal systems the contributions of some elements to the entropies of solids are taken from [1951LAT].

Table D-1: Contributions of some elements to entropies of solids ( $J \cdot K^{-1} \cdot mol^{-1}$), taken from [1951LAT].

| Element | Entropy | Element | Entropy | Element | Entropy | Element | Entropy |
|---|---|---|---|---|---|---|---|
| Ag | 53.6 | Dy | 60.2 | La | 57.7 | Sc | 40.6 |
| Al | 33.5 | Er | 60.7 | Li | 14.6 | Sm | 59.0 |
| Au | 64.0 | Eu | 59.0 | Lu | 61.9 | Sn | 54.8 |
| Ba | 57.3 | Fe | 43.5 | Mg | 31.8 | Sr | 50.2 |
| Be | 18.0 | Ga | 46.9 | Mo | 51.5 | Ta | 62.3 |
| Bi | 65.3 | Gd | 59.8 | Na | 31.4 | Tb | 59.8 |
| Ca | 38.9 | Ge | 47.3 | Nb | 51.0 | Ti | 41.0 |
| Cd | 54.0 | Hf | 61.9 | Nd | 58.2 | Tl | 64.4 |
| Ce | 57.7 | Hg | 64.4 | Ni | 43.9 | Tm | 61.1 |
| Co | 44.4 | Ho | 60.7 | Pb | 64.9 | Y | 50.2 |
| Cr | 42.7 | In | 54.4 | Pr | 57.7 | Yb | 61.5 |
| Cs | 56.9 | Ir | 63.6 | Rb | 49.8 | Zn | 45.6 |
| Cu | 45.2 | K | 38.5 | Re | 62.8 | Zr | 50.6 |

Table D-2: Contributions of some elements to solids' entropies ( $J \cdot K^{-1} \cdot mol^{-1}$) taken in most cases from [1951LAT]. The values in parentheses were not directly based on experimental values, but estimated by Naumov, Ryzhenko and Khodakovsky [1971NAU/RYZ].

| Anion | Average cation charge | | | |
|---|---|---|---|---|
| | +1 | +2 | +3 | +4 |
| $OH^-$ | 30.5 | 19.2 | 17.5 | (19.2) |
| $O^{2-}$ | 8.4 | 2.5 | 2.1 | 1.3 |
| $F^-$ | 23.0 | 17.6 | 16.1 | 20.1 |
| $Cl^-$ | 43.9 | 32.6 | 29.3 | 33.1 |
| $Br^-$ | 56.1 | 45.2 | 41.8 | 49.8 |
| $I^-$ | 63.2 | 54.4 | 55.2 | 51.0 |
| $IO_3^-$ | 104.6 | (92) | | |
| $CO_3^{2-}$ | 64.9 | 49.4 | | |
| $HCO_3^-$ | 70.7 | (54) | | |
| $NO_3^-$ | 90.8 | 73.2 | | |
| $SO_3^{2-}$ | 83.3 | 62.3 | 50.2 | (46)[(a)] |
| $SO_4^{2-}$ | 92.9 | 67.8 | 57.3 | (50) |
| $S^{2-}$ | 33.5 | 18.0 | 21.8 | 18.0 |
| $PO_4^{3-}$ | 79.5 | 62.8 | 57.3 | (50)[(a)] |
| $PO_3^-$ | 66.9 | 54.0 | (50.0) | (48)[(a)] |
| $HPO_4^{2-}$ | 87.9 | 72.4 | 66.9 | (63) |
| $H_2PO_4^-$ | 96.2 | (79) | (75) | |
| $Se^{2-}$ | 43.1 | 37.7 | 28.9 | |
| $ClO_4^-$ | 115 | (92) | | |
| $AsO_4^{3-}$ | (96) | (79) | (71) | |
| $H_2AsO_4^-$ | 116.7 | (100) | | |
| $VO_3^-$ | 82.4 | 67.4 | | |
| $VO_4^{3-}$ | 95.4 | 79.1 | | |
| $SiO_4^{4-}$ | 70.3 | 53.6 | (42) | 33.9 |
| $SiO_3^{2-}$ | 60.7 | 46.9 | (29) | |
| $CrO_2^-$ | (54) | 44.4 | | |
| $CrO_4^{2-}$ | 117.2 | (105) | | |
| $MoO_4^{2-}$ | 96.7 | 85.4 | | |
| $WO_4^{2-}$ | 98.3 | 87.0 | | |
| $TiO_3^{2-}$ | 60.7 | 54.0 | (38) | |
| $TiO_4^{4-}$ | (71) | 62.8 | (33) | |
| $ZrO_3^{2-}$ | (71) | 64.4 | | |
| $BO_2^-$ | 45.2 | 33.1 | | |
| $BO_3^{3-}$ | (50) | 33.5 | | |
| $AlO_2^-$ | 38.9 | 29.3 | | |
| $FeO_2^-$ | 58.6 | 48.5 | | |
| $H_2O$ | 44.7 | | | |
| $UO_2^{2+}$[(b)] | 94.7 | | | |
| U[(c)] | 66.9 | | | |

(a) Estimated in [1992GRE/FUG]

(b) Treated as a dipositive ion for the purpose of selecting anion contributions in [1992GRE/FUG]

(c) Proposed in [1992GRE/FUG] for uranium compounds not containing the uranyl(VI) group, $U^{VI}O_2$.

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This volume is the fourteenth of the series "Chemical Thermodynamics" published by the OECD Nuclear Energy Agency. It is the second update of the critical reviews published, successively, in 1992 as *Chemical Thermodynamics of Uranium*, in 1995 as *Chemical Thermodynamics of Americium*, in 1999 as *Chemical Thermodynamics of Technetium*, in 2001 as *Chemical Thermodynamics of Neptunium and Plutonium* and in 2003 as the first *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*. A team, composed of nine internationally recognised experts, has critically reviewed all the relevant scientific literature for the above mentioned systems that has appeared since the publication of the earlier volumes. The results of this assessment, carried out following the Guidelines of the Thermochemical Database Project, have been documented in the present volume, which contains new tables of selected values for formation and reaction data and an extensive bibliography. The database system developed at the NEA Data Bank ensures consistency within the recommended data sets. This volume will be of particular interest to scientists carrying out performance assessments of deep geological disposal sites for radioactive waste.

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