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EQ6, A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)

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Preface

This report is the first in a set of documenting version 7.0 (version 3245.1090 under the old numbering system) of the EQ3/6 software package. This set includes:

I. The EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

II. The EQPT User's Guide (Daveler and Wolery, 1992).

III. The EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b).

IV. The EQ6 Theoretical Manual and User's Guide (this report).

EQ3NR is the speciation-solubility code in the EQ3/6 package. EQ6 is a reaction path code and hence deals with the evolution of a water/rock system as reaction progress or time advances. EQPT is the EQ3/6 data file preprocessor.

The development of EQ3/6 has been supported by a number of programs concerned with geologic disposal of high level nuclear waste, including the Office of Nuclear Waste Isolation, the Salt Repository Project Office, the Waste Isolation Pilot Plant (through Sandia National Laboratory), the Nevada Nuclear Waste Storage Investigations, and the Yucca Mountain Site Characterization Project. Documentation for the package is aimed at satisfying the requirements of the U.S. Nuclear Regulatory Commission for software used for this purpose (Silling, 1983).

The Lawrence Livermore National Laboratory has not certified that EQ3/6 constitutes approved code for the conduct of quality affecting work for the Yucca Mountain Project.

No source codes or data files are reproduced in this report, nor are any computer media containing such items a part of this report or any of the other reports documenting this version of EQ3/6. The software itself must be obtained as described below.

The examples presented in this series of reports correspond to version 7.0 of the software and the R10 set of supporting thermodynamic data files. As of the date of publication of this report, the most recent version of the software is version 7.1 (containing bug fixes, but no enhancements), and the most recent set of data files is R16.

Agencies of the United States Government and their contractors may obtain copies of the software and its documentation from:

Energy Science and Technology Software Center
P. O. Box 1020
Oak Ridge, TN 37831-1020

Telephone: (615) 576-2606

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Requests to obtain the software under a licensing agreement should be addressed to:

Technology Transfer Initiatives Program, L-795
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Glossary of Symbols

a_i	Thermodynamic activity of the i-th aqueous solute species.
a_w	Thermodynamic activity of water.
$a_{\sigma\psi}$	Thermodynamic activity of the σ-th component of the ψ-th solid solution phase.
A_j	Thermodynamic affinity of the j-th reaction. The forward direction is implied, which in EQ3/6 is taken to be that in which the associated species is destroyed, for example by dissociation or dissolution.
$A_{+,j}$	Thermodynamic affinity of the j-th reaction (forward direction: dissociation, dissolution).
$A_{-,j}$	Thermodynamic affinity of the j-th reaction (reverse direction: formation, precipitation).
$A_{-,j,scaled}$	Scaled affinity of the j-th reaction (reverse direction); $A_{-,j,scaled} = \dfrac{A_{-,j}}{b_{j,scale}}$. Scaled affinities are used to chose which of several supersaturated phases to precipitate first.
Ah	Thermodynamic affinity (per electron) of a redox couple with respect to the standard hydrogen electrode; $Ah = F\,Eh$.
b_{sr}	Stoichiometric reaction coefficient, the number of moles of the s-th aqueous species appearing in the r-th aqueous reaction; it is negative for reactants and positive for products.
$b_{s\phi}$	Stoichiometric reaction coefficient, the number of moles of the s-th aqueous species appearing in the reaction for the dissolution of the ϕ-th pure mineral; it is negative for reactants and positive for products.
b_{sg}	Stoichiometric reaction coefficient, the number of moles of the s-th aqueous species appearing in the reaction for the dissolution of the g-th gas species; it is negative for reactants and positive for products.
$b_{j,scale}$	Affinity scaling factor for the j-th reaction; $b_{j,scale} = \sum_{s'=1}^{s_Q} \lvert b_{s'j} \rvert$.
$b_{T,r}$	The quantity $b_{s''r} + \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'r}$.
$b_{T,\phi}$	The quantity $\sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\phi}$.
$b_{T,\sigma\psi}$	The quantity $\sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\sigma\psi}$.
c	Stoichiometric mass coefficient; e.g., $c_{\varepsilon s}$ is the number of moles of the ε-th element per mole of the s-th aqueous species.

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$d\xi/dt$	The overall reaction rate; also symbolized by v.
$d\xi_j/d\xi$	Relative rate of the j-th irreversible reaction; also symbolized by v_j^{rel}.
$d\xi_j/dt$	Actual rate of the j-th irreversible reaction; also symbolized by v_j.
$dt/d\xi$	The inverse rate; also symbolized by $v_{1/t}$.
$\underline{d}$	An array of derivatives of increasing order.
D_{ij}	An element of the matrix $\underline{D}$.
$\underline{D}$	A matrix used to convert an array of finite differences of increasing order to an equivalent array of derivatives.
ε	Subscript indexing a chemical element.
ε_T	Total number of chemical elements in a chemical system.
e^-	The electron. In common thermodynamic formalism, this is usually a hypothetical species, not a real one.
Eh	Redox potential, volts.Theoretical equilibrium electrical potential of a redox couple; $Eh = \frac{2.303RT}{4F}(\log f_{O_2} - 4pH - 2\log a_w - \log K_{Eh})$, where f_{O_2} is understood to be the hypothetical equilibrium oxygen fugacity in aqueous solution.
f_g	Fugacity of the g-th gas.
f_j	Ratio of effective to total surface area of the i-th irreversibly reacting mineral.
f_{O_2}	Oxygen fugacity.
$\underline{f}$	An array of finite differences of increasing order.
F	The Faraday constant, 23062.3 cal/equiv-volt.
g	Subscript denoting a gas species.
$\bar{H}_{s'r}$	The factor $\frac{n_{s''}u_{s's''}}{b_{s''r}}$ or $\frac{n_{s''}c_{\varepsilon s''}}{b_{s''r}}$; the s''-th aqueous species is associated with the r-th aqueous reaction, and the ε-th chemical element is associated with the s'-th basis species.
$\tilde{H}_{zr}$	The factor $\frac{n_{s''}z_{s''}}{b_{s''r}}$.
$i_{T,+j}$	The number of terms appearing in the transition state theory or activity product term net forward rate law for the j-th irreversible reaction.
$i_{T,-j}$	The number of terms appearing in the transition state theory or activity product term net reverse rate law for the j-th irreversible reaction.
I	Ionic strength.
IAP	Ion activity product; see Q.
J_{ij}	An element of the Jacobian matrix $(\partial\alpha_i/\partial z_j)$.

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$\underline{J}$	The Jacobian matrix.
$k_{+,ij}$	Rate constant for the i-th term in the net forward rate law for the j-th irreversible reaction.
$k_{-,ij}$	Rate constant for the i-th term in the net reverse rate law for the j-th irreversible reaction.
$k_{T,i}$	The i-th coefficient in the polynomial for describing temperature as a function of reaction progress.
K	Thermodynamic equilibrium constant.
K_{Eh}	Thermodynamic equilibrium constant for the half-reaction $2H_2O_{(l)} = O_{2(g)} + 4H^+ + 4e^-$
K_w	Equilibrium constant for the reaction $H_2O_{(l)} = H^+ + OH^-$
m_i	Molal concentration of the i-th aqueous solute species.
m_s	Molal concentration of the s-th aqueous species.
n_i	Number of moles of the i-th aqueous solute species.
n_s	Number of moles of the s-th aqueous species.
n_w	Number of moles of water.
$n_{T,+,ij}$	The number of species whose thermodynamic activities appear in the i-th term of the net forward rate law for the j-th irreversible reaction.
$n_{T,-,ij}$	The number of species whose thermodynamic activities appear in the i-th term of the net reverse rate law for the j-th irreversible reaction.
n_ϕ	Number of moles of the ϕ-th pure mineral.
$n_{\sigma\psi}$	Number of moles of the σ-th end member of the ψ-th solid solution.
$n_{T,\varepsilon}$	Total number of moles of the ε-th chemical element.
$n_{T,s'}$	Total number of moles of the s'-th (basis) aqueous solute species.
$N_{+,nij}$	Exponent of the activity of the n-th species appearing in the i-th term of the net forward kinetic rate law for the j-th irreversible reaction.
$N_{-,nij}$	Exponent of the activity of the n-th species appearing in the i-th term of the net reverse kinetic rate law for the j-th irreversible reaction.
O_n	Final object function of the n-th algorithm for choosing a phase to delete from the equilibrium system.
O_{nj}	Object function of the n-th phase deletion algorithm for the j-th phase in the equilibrium system.
O_{1j}	Object function of the first phase deletion algorithm for the j-th phase in the equilibrium system.
$O_{2(g)}$	Oxygen gas; in aqueous solution, this refers to a fictive species; also symbolized as O_2.
P	Pressure, bars.
pH	The quantity - $\log a_{H+}$

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pe	Logarithm of the hypothetical electron activity; $pe = F\,Eh/(2.303\,RT) = Ah/(2.303\,RT)$.
$q_{+,ij}$	Kinetic activity product for the i-th term in the net forward rate law for the j-th irreversible reaction.
$q_{-,ij}$	Kinetic activity product for the i-th term in the net reverse rate law for the j-th irreversible reaction.
Q	Activity product of a reaction; IAP is used by many others (e.g., Parkhurst et al., 1980) to denote the same quantity.
r	Subscript denoting an aqueous reaction.
r_T	Total number of reactions for the dissociation/destruction of dependent aqueous species.
R	The gas constant, 1.98726 cal/mol-°K.
s	Subscript denoting an aqueous species ($s = w$ implies $H_2O_{(l)}$).
s'	Subscript denoting s in the range from 2 to s_Q, excluding s_B.
s''	Subscript implying the species formally associated with the aqueous reaction designated by r ($s'' = r + s_B$).
s_j	Surface area of the mineral destroyed/formed by the j-th irreversible reaction.
s_B	Subscript denoting the fictive redox species O_2.
s_Q	The total number of aqueous basis species; depending on the problem at hand, s_Q is equal to or greater than s_B.
s_T	Total number of aqueous species.
SI	Saturation index for a mineral; $SI = log\ (Q/K)$, where Q and K are the activity product and equilibrium constant, respectively, for the dissolution reaction.
t	Time.
T	Temperature, °K.
T_0	Temperature at $\xi = 0$ (or t =0 if in kinetic mode).
u	Stoichiometric mass balance coefficient calculated from reaction coefficients and certain model constraints; $u_{s's}$ is the stoichiometric factor for computing the contribution of the s-th aqueous species to the mass balance for the s'-th basis species.
v	Short for the overall reaction rate, $d\xi/dt$.
vj^{rel}	Short for the relative rate of the j-th irreversible reaction, $d\xi_j/d\xi$.
v_j	Short for the actual rate of the j-th irreversible reaction, $d\xi_j/dt$.
v_{Itt}	Short for the inverse rate of the overall reaction, $dt/d\xi$.
w	Subscript denoting water (e.g., a_w, the activity of water).
$\underline{w}$	Vector of increasing partial sums of preceding reaction progress steps.
$\underline{W}$	Array of partial derivatives of $log\,x_w$ with respect to $log\,m_{s'}$, where s' is a basis species. This derivative is zero for $s' = w$ or s_B.

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$\underline{\tilde{W}}$	Array of partial derivatives of $log\, x_w$ with respect to $log\, n_{s'}$, where s' is a basis species. This derivative is zero for $s' = s_B$.
x_i	Mole fraction of the i-th aqueous solute species.
x_w	Mole fraction of water in aqueous solution.
$x_{\sigma\psi}$	Mole fraction of the σ-th end member of the ψ-th solid solution.
x	A general algebraic variable.
z_s	Electrical charge of the s-th aqueous species.
z	Subscript implying a relation to the concept of charge balance (e.g., H_{zr}).
$\underline{z}$	Vector of algebraic master variables.
2.303	Symbol for and approximation to ln 10.
$\underline{\alpha}$	Newton-Raphson residual function vector.
α_z	Residual function for charge balance.
α_s	Residual function for mass balance of the s-th basis species.
α_ϕ	Residual function for equilibrium with a pure mineral.
$\alpha_{\sigma\psi}$	Residual function for equilibrium with the σ-th end member of the ψ-th solid solution.
$\underline{\beta}$	Newton-Raphson residual function vector, identical to $\underline{\alpha}$, except that mass balance residual elements are normalized by the corresponding values of total numbers of moles.
β_{max}	The largest absolute value of any element of $\underline{\beta}$.
$\underline{\delta}$	Newton-Raphson correction term vector.
δ_{max}	The largest absolute value of any element of $\underline{\delta}$.
δ_{conv}	Convergence function.
δ'	Under-relaxation parameter.
$\Delta\xi$	Increment of reaction progress.
$\Delta\xi_j$	Increment of reaction progress for an individual reaction.
Δt	Increment of time.
Δ_z	Calculated charge imbalance.
γ_i	Molal activity coefficient of the i-th aqueous solute species.
ξ	Overall reaction progress variable.
ξ_j	Reaction progress variable for the j-th irreversible reaction.
κ	Under-relaxation parameter in Newton-Raphson iteration.
$\lambda_{\sigma\psi}$	Rational (mole fraction) activity coefficient of the σ-th end member of the ψ-th solid solution.

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σ, σ'	Symbols denoting end member components of a solid solution.
$\sigma_{+,ij}$	Stoichiometric adjustment factor for the i-th mechanism in a transition state theory net forward rate law for the j-th irreversible reaction.
$\sigma_{-,ij}$	Stoichiometric adjustment factor for the i-th mechanism in a transition state theory net reverse rate law for the j-th irreversible reaction.
$\xi_{T,\psi}$	Total number of end members in the ψ-th solid solution.
ϕ	(a) Subscript denoting a pure mineral; (b) the osmotic coefficient of the aqueous solution.
ϕ_E	Total number of minerals of fixed composition in equilibrium with the aqueous phase.
ψ	Subscript denoting a solid solution.
ψ_E	Total number of solid solutions in equilibrium with the aqueous phase.
Ω	Water constant; 1000 divided by the molecular weight of water; about 55.51.
+	Subscript denoting a reaction proceeding in the forward sense; the convention in this report equates this with dissociation, dissolution, or destruction of the associated species.
-	Subscript denoting a reaction proceeding in the backward sense; the convention in this report equates this with association, precipitation, or formation of the associated species.

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EQ6, A Computer Program for Reaction Path Modeling of Aqueous Geochemical Systems: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0)

Abstract

EQ6 is a FORTRAN computer program in the EQ3/6 software package (Wolery, 1979). It calculates reaction paths (chemical evolution) in reacting water-rock and water-rock-waste systems. Speciation in aqueous solution is an integral part of these calculations. EQ6 computes models of titration processes (including fluid mixing), irreversible reaction in closed systems, irreversible reaction in some simple kinds of open systems, and heating or cooling processes, as well as solve "single-point" thermodynamic equilibrium problems. A reaction path calculation normally involves a sequence of thermodynamic equilibrium calculations. Chemical evolution is driven by a set of irreversible reactions (i.e., reactions out of equilibrium) and/or changes in temperature and/or pressure. These irreversible reactions usually represent the dissolution or precipitation of minerals or other solids. The code computes the appearance and disappearance of phases in solubility equilibrium with the water. It finds the identities of these phases automatically. The user may specify which potential phases are allowed to form and which are not. There is an option to fix the fugacities of specified gas species, simulating contact with a large external reservoir. Rate laws for irreversible reactions may be either relative rates or actual rates. If any actual rates are used, the calculation has a time frame. Several forms for actual rate laws are programmed into the code. EQ6 is presently able to model both mineral dissolution and growth kinetics. The user can specify modification or substitution of equilibrium constants at run time by using options on the **input** file. The output consists of an **output** file, a **tab** file (tables of output parameters), and a **pickup** file, which allows a restart capability. The chief numerical method employed for equilibrium calculations is a hybrid Newton-Raphson technique. This is supported by a set of algorithms which create and optimize starting values. When actual rate laws are used, EQ6 integrates them using a finite-difference based ordinary differential equation (ODE) solver. EQ6 reads a secondary unformatted data file (**data1**) that is created from a primary formatted data file (**data0**) by EQPT, the EQ3/6 data file preprocessor. There is currently a set of five data (**data0**) files. Three of these may be used with either the Davies equation or the B-dot equation to describe the activity coefficients, and their use is restricted to modeling dilute solutions. The other two of these use Pitzer's equations and are suitable for modeling solutions to high concentrations, though with fewer chemical components. The temperature range of the thermodynamic data on the data files varies from 25°C only to 0-300°C. The companion code EQ3NR must be used to initialize a a reaction path calculation by EQ6. EQ6 and the other codes in the EQ3/6 package are written in FORTRAN 77 and have been developed to run under the UNIX operating system on computers ranging from workstations to supercomputers.

1. Introduction

1.1. EQ6 and the EQ3/6 Package

EQ6 is a reaction path code for water-rock and water-rock-waste systems. It models the chemical evolution of such systems using thermodynamic and kinetic constraints. The kinds of reaction

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path calculations include simple titrations, fluid mixing, irreversible reaction in closed systems, irreversible reaction in fluid-centered flow-through systems, and systems in which the fugacities of certain gases are fixed by connection to a large external reservoir (such as the atmosphere). Reaction paths may also involve heating or cooling. EQ6 also makes "single point" thermodynamic calculations, in which for example the mineral supersaturations for an aqueous solution are eliminated by precipitation of an equilibrium suite of precipitated phases.

EQ6 is part of the EQ3/6 software package (see Wolery, 1992a). This report describes EQ6 in version 7.0 (version 3245.1090 in the old numbering system) of this package (see the EQ3/6 Package Overview and Installation Guide, Wolery, 1992a). Other codes in the package include EQPT (Daveler and Wolery, 1992), a data file preprocessor, and EQ6 (Wolery and Daveler, 1992), a reaction path code. The relationship of the EQ3NR code to EQ6, EQPT, and the set of supporting thermodynamic data files is shown in Figure 1. This figure depicts the flow of information involving these codes. At present, there are five distinct data files, denoted by the suffixes **com, sup, nea, hmw,** and **pit.** These are provided in formatted ASCII and are called **data0** files.EQPT processes these one at a time (looking for a file named simply **data0,** though these files are normally stored under names which include the relevant suffixes) and writes a corresponding unformatted data file, which is called simply **data1.** These are also normally stored under names including the relevant suffixes. To run EQ3NR or EQ6, the user must provide one of these files, which is known to each code simply as **data1.**

The user must select which of the five data files is most appropriate to a given problem. Each data file corresponds to a general formalism for treating the activity coefficients of the aqueous species and contains the relevant activity coefficient data as well as standard state thermodynamic data. The formalisms currently built into EQ3/6 are discussed in Chapter 3 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b). The **com**, **sup**, and **nea** data files are specific to a general extended Debye-Hückel formalism and can be used by EQ3NR and EQ6 with either the Davies (1962) equation or the B-dot equation (Helgeson, 1969). These equations are only valid in relatively dilute solutions. The **hmw** and **pit** data files are specific to the formalism proposed by Pitzer (1973, 1975) and can be used to model solutions extending to high concentrations. However, the scope of chemical components covered is smaller. The temperature limits on the data files also vary, from 25°C only to 0-300°C.

Some important data file characteristics are given in Table 1. The **com** (for "composite") data file is the largest of the three data files specific to the extended Debye-Hückel formalism. This is a product of Lawrence Livermore National Laboratory (LLNL) drawing on many data sources, including those on which the other four data files are based. The **sup** data file is based entirely on SUPCRT92 (Johnson, Oelkers, and Helgeson, 1992), a data base and program for dealing with thermodynamic data (see also Helgeson and Kirkham, 1974ab, 1976; Helgeson et al., 1978; Tanger and Helgeson, 1988; Shock and Helgeson, 1988, 1989, 1990; Shock, Helgeson, and Sverjensky, 1989; Johnson and Norton, 1991; and Shock et al., 1992). The **nea** data file is based entirely on Grenthe et al. (1989, draft report), a product of the Data Bank of the Nuclear Energy Agency of the European Community. This report has recently been published as Grenthe et al. (1992). The **hmw** data file is based on Harvie, Møller, and Weare (1984). The **pit** data file is based mostly on data summarized by Pitzer (1979). was expressly developed for this purpose. All five data files are maintained at LLNL in a relational data base described by Delany and Lundeen (1991). This relational data base is part of the Yucca Mountain Site Characterization Project's

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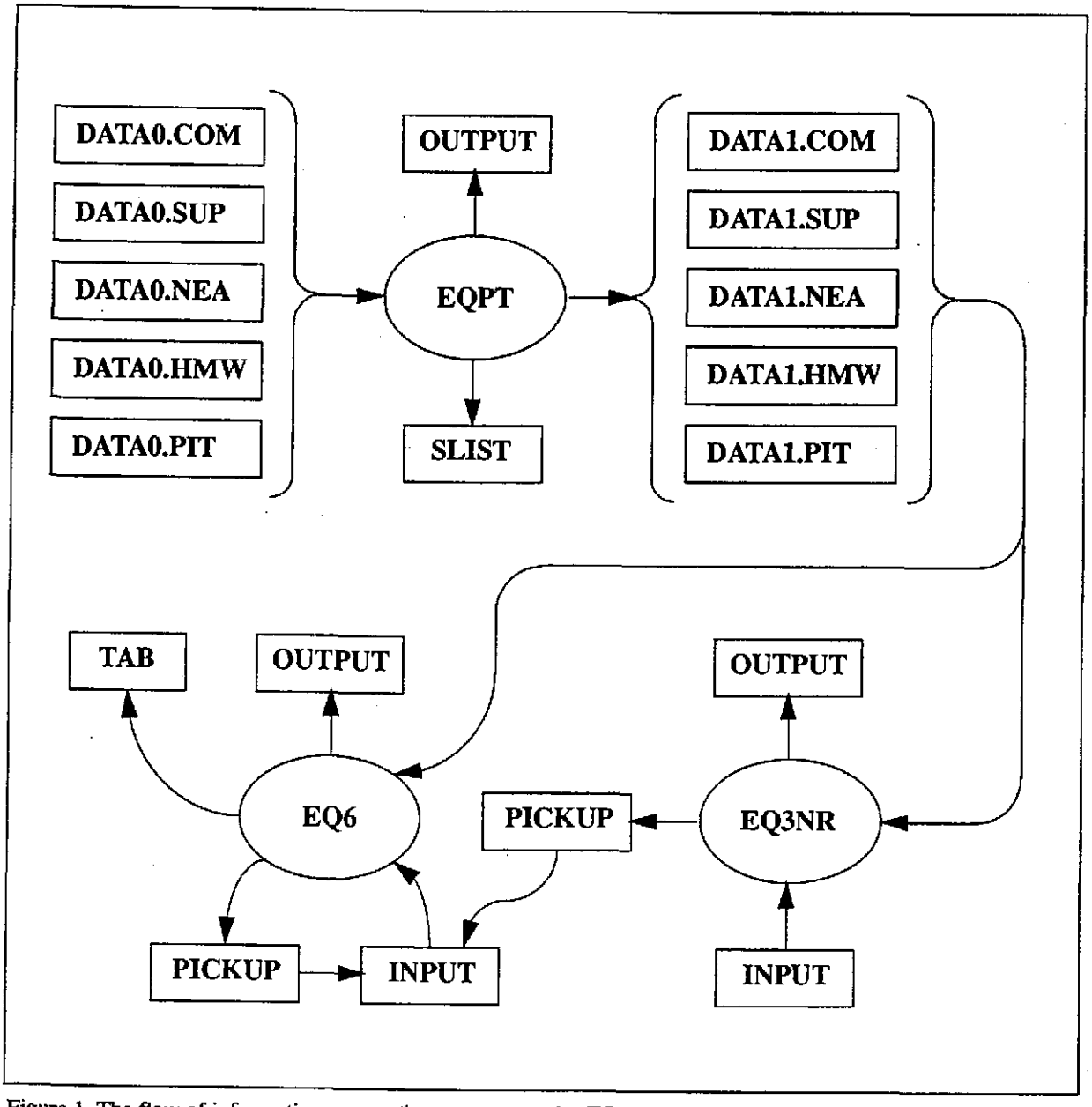

Figure 1. The flow of information among the computer codes EQPT, EQ3NR, and EQ6. Computer codes are represented by ovals, files by rectangles.

Technical Data Base.

The **sup** data file has a high level of internal consistency among the standard state thermodynamic data. In addition, the temperature-pressure dependence of these data are represented by a suite of equations of state for minerals, gases, and aqueous species that are well established in the geochemical literature (see references noted above). This data file covers a wide range of chemical elements and species of interest in the study of rock/water interactions (e.g., components which make up the major rock-forming and ore-forming minerals). It also includes a large num-

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Table 1. Major characteristics of the current five EQ3/6 data files ("R10" versions).

File Name (Suffix)	Source	Activity Coefficient Formalism	Temperature Limits	Number of Chemical Elements	Number of Basis Species	Number of Aqueous Species	Number of Pure Minerals	Number of Solid Solutions	Number of Gas Species
com	GEMBOCHS (LLNL)	Extended Debye-Hückel	0-300°C	78	147	852	886	12	76
sup	SUPCRT92	Extended Debye-Hückel	0-300°C	69	105	315	130	0	16
nea	NEA draft report	Extended Debye-Hückel	0-300°C	32	50	158	188	0	76
hmw	Harvie, Møller, and Weare (1984)	Pitzer's Equations	25°C only	9	13	17	51	0	3
pit	Pitzer (1979)	Pitzer's Equations	0-100°C	52	62	68	381	0	38

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ber of organic species, mostly of small carbon number (C_2-C_8). The **nea** data file is something of a specialty item. Its strongest point is a thorough representation of the thermodynamics of uranium species.

The **com** (composite) data file encompasses a much broader range of chemical elements and species. It includes the data found on the **sup** and **nea** data files, with preference given to data from the former in cases of overlap. It also includes some data found in the **hmw** data file, as well as other data which do not appear in any of the other data files. Some of these data are estimates based on correlations or extrapolations (as to higher temperature), and are not tied directly to experimental measurements. The **com** data file thus represents a melange of data, which by its nature offers less assurance of internal consistency. However, this offers the only means presently available for modeling aqueous solutions with a high degree of compositional complexity, such as the fluids expected to be found in and about a facility for the geologic disposal of industrial or nuclear waste (e.g., the potential repository for high-level nuclear waste at Yucca Mountain, Nevada).

The **hmw** data file has the highest degree of internal consistency of any of the five data files, including mutual consistency of activity coefficient data and standard state thermodynamic data. It can be applied to dilute waters or concentrated brines. However, it only treats the set of components present in the "sea-salt" system (the major cations and anions present in seawater, including carbonate and bicarbonate). The geochemically important components aluminum and silica are not included. Also, this data file is limited to a temperature of 25°C. The **pit** data file can also be applied to concentrated brines. It covers a larger set of components, but these mostly involve other cations and anions of strong electrolytes. Examples include lithium and bromide. This data file nominally covers the temperature range of 0-100°C. However, it represents a melange of data, not a carefully crafted internally consistent set.

The data file preprocessor EQPT (Daveler and Wolery, 1992) performs a number of functions. It checks the composition, charge, and reaction coefficient data on a **data0** file for internal consistency and fits interpolating polynomials to various temperature dependent data which are organized on the **data0** file on temperature grids. Such data include certain activity coefficient parameters, such as Debye-Hückel $A_{\gamma,10}$ and B_{γ}, and the equilibrium constants for the reactions represented on the data file. In addition, in the case of data files specific to the formalism of Pitzer's equations, observable interaction coefficients are mapped to a set of conventionally defined primitive interaction coefficients (see Chapter 3 of Wolery, 1992b). EQPT then writes the **data1** file corresponding to the input **data0** file. For details of the contents and structure of **data0** and **data1** files, see Daveler and Wolery (1992). Run-time alteration of the values of selected equilibrium constants can subsequently be selected by the user on the EQ3NR **input** file (see Chapter 6 of Wolery, 1992b). EQPT also writes to a screen file and an **output** file, both of which are generally significant only if an error condition is encountered. In addition, it writes an **slist** (species list) file. This is very useful to the user, as it lists the species that are represented on the data file and identifies which species are in the strict and auxiliary basis sets (See Chapter 5 of Wolery, 1992b).

A speciation-solubility problem to be run with EQ3NR is described on the EQ3NR **input** file. While this code is running, it writes to the screen file to keep the user apprised of what is going on. It writes an **output** file describing the results of the calculation. It also writes a **pickup** file,

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which contains a compact description of the aqueous solution (see Chapter 8 of Wolery, 1992b). The EQ3NR **pickup** file is important because it may be used as the bottom part of an EQ6 **input** file. It has no other real purpose. However, if one plans to define an aqueous solution as a special reactant for use in a fluid mixing calculation in EQ6, the corresponding composition may be extracted from an EQ3NR **pickup** file.

A reaction path problem to be run with EQ6 is described on the EQ6 **input** file (see Chapter 5 of the present report; see Chapter 6 for examples). This code also writes to the screen file to keep the user apprised of what is happening. EQ6 writes its own **output** file. It also writes its own **pickup** file, which may be used as an **input** file to restart a reaction path calculation where a previous one left off. In addition, EQ6 writes a **tab** file, which contains results in tabular form suitable for supporting local graphics postprocessing.

The EQ6 **output** file can be quite large. The user can effectively control its size by means of the print interval parameters (**dzprnt**, **dzprlg**, and **kstppr**) and print option switches (**iopr1** - **iopr20**). These parameters and switches appear on the **input** file (see Chapter 5).

The EQ6 **pickup** file is a complete EQ6 **input** file. This makes up the code's restart capability. It facilitates making a length calculation in segments, which is often more convenient than making a single long run. It can be modified if the user wishes to change the direction of the reaction path.

When EQ6 is running, it writes the data for the **tab** file onto a file called **tabx**, which is not shown in Figure 1. It contains the lines written for the **tab** file, but these are written to it in chronological order. This causes the data for the various tables on the **tab** file to appear in an interleaved mode. Each line is labeled as to which table it belongs to. Thus, **tabx** is known as the "scrambled" tab file. At the end of execution, EQ6 unscrambles the data on **tabx** onto **tab**. The **tabx** file is not normally used subsequently. However, there is an option (**iopt13** = 1) to append data to an existing **tabx** file, thus producing a **tab** file that summarizes more than just the results of the current run.

Because any EQ6 calculation depends on a previous EQ3NR or EQ6 calculation, one should use the same **data1** file throughout a given chain of runs. Substitution of a different kind of data file (e.g., **com** for **hmw**) may cause EQ6 to terminate upon encountering errors in processing the **input** file, as the sets of species present and exact names used vary among the data files. However, there is no mechanism built into the software to prevent such substitutions. If a data file of a given kind is modified, it may also be necessary to repeat a whole chain of calculations to assure consistency. If any **input** file directed modifications are to made to the thermodynamic data, these are best made at the start of a chain of calculations, on the EQ3NR **input** file. These modifications are then passed on to EQ6 on the **pickup** file.

This report describes the assumptions underlying the use of EQ6 and documents the mathematical derivations and the numerical techniques that are used by the code. The user should already be familiar with the assumptions underlying the EQ3NR code (Wolery, 1992b), and how to use that code. Several examples of the usage of EQ6, including the full **input** files and pertinent parts of the **output** and **tab** files, are presented and discussed. For a brief overview of the current status and recent development and future plans for the EQ3/6 package as a whole, see Wolery et al. (1990). For a more detailed plan of long-term development, see McKenzie et al. (1986).

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The remaining sections of this chapter describe the kinds of calculations made by EQ6. Chapter 2 reviews the history of EQ6 and discussions its current limitations and possible future development. Chapter 3 describes the governing equations and related concepts pertaining to EQ6 calculations. Chapter 4 discusses the various types of calculational models which can be addressed by EQ6. Chapter 5 describes the EQ6 **input** file. Sample problems are presented in Chapter 6. Chapter 7 presents the methods EQ6 uses to make thermodynamic equilibrium calculations. Chapter 8 describes the methods used to make reaction path calculations.

The code architecture is described in Chapter 9. Appendix A contains a glossary of the major code variables. The source code modules are listed and briefly described in Appendix B (for a similar treatment of EQLIB modules, see Appendix B of the EQ3/6 Package Overview and Installation Guide, Wolery, 1992a). Appendix C contains a list of error messages generated by EQ3NR modules, along with related notes (see Appendix C of Wolery, 1992a, for a similar list for EQLIB modules). Appendix D contains notes pertaining to known bugs and such. Appendix E presents two EQ6 **input** files which deal with more complex problems than those addressed in Chapter 6. Appendix F contains the EQ3NR **input** files that were used to initialize the EQ6 sample problems presented in Chapter 6 and a few more complex EQ6 **input** files are given in Appendix E.

EQ6 and the other codes in the EQ3/6 software package are written in FORTRAN 77 and have been developed to run under UNIX operating systems on computers ranging from workstations to supercomputers, including Sun SPARCstations, VAXes (ULTRIX operating system), Alliants (CONCENTRIX operating system), and Crays (UNICOS operating system). They are fairly readily portable to VAX computers running the non-UNIX VMS operating system. They may be portable as well to 386 and 486 PCs. Platforms used at LLNL include Sun SPARCstations and an Alliant FX/80. For details concerning platforms, see the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

1.2. Input to EQ6 from EQ3NR

To describe the function of EQ6, we first briefly review the output from EQ3NR (Wolery, 1992b). This comprises a model of the aqueous solution which provides a starting point for defining a problem for EQ6. EQ3NR calculates the aqueous species distribution (the concentrations and thermodynamic activities of individual species) and the total concentrations of aqueous basis species (in cases where these total concentrations are not input parameters). It also computes the saturation indices of minerals represented in the data base. These are expressed as $SI = log Q/K$, where Q is the ion activity product, K the equilibrium constant, and it is understand that these quantities pertain to the forward direction for a dissolution reaction. EQ3NR also calculates the thermodynamic state of each aqueous redox couple, expressing it as couple-specific values of Eh, pe, equilibrium oxygen fugacity, and Ah (redox affinity; Wolery, 1992b). Differences in the values of these corresponding functions define the degree of disequilibrium among any two aqueous redox couples (Wolery, 1992b).

After computing the speciation model, EQ3NR calculates a mass balance, in terms of the number of moles, for each chemical element present in the model. It also computes the charge balance, or more properly the imbalance, in terms of charge equivalents. The mass balances totals and the charge imbalance are calculated for a mass of aqueous solution containing one kilogram of sol-

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vent water. Each chemical element corresponds to a strict basis species (e.g., Na to Na^+). The charge balance corresponds to the basis species O_2, which is a fictive aqueous species. In its thermodynamic calculations, EQ6 uses these balance relations to find the number of moles of each of the strict basis species and the oxygen fugacity. Among other mass balances, EQ3NR computes one for oxygen and one for hydrogen, for which the associated strict basis species are the solvent (H_2O) and the hydrogen ion (H^+), respectively. The calculated charge imbalance in the EQ3NR model is passed on to EQ6, which maintains a this calculated imbalance. If there is no redox aspect to the computed model, the charge balance relation is not applicable and the oxygen fugacity is undefined.

EQ3NR makes use of auxiliary basis species, which can be used to split mass balances (defined in terms of basis species instead of chemical elements) so as to utilize corresponding analytical data (e.g., separate total concentrations for ferrous and ferric iron) and to deal with the possibility of disequilibria among species in aqueous solution. The auxiliary basis concept is not incorporated in the present version of EQ6. Therefore, if for example a model of a water is calculated by EQ3NR in which sulfate is not in equilibrium with sulfide, only one mass balance representing elemental sulfur is passed to EQ6. In its initial thermodynamic calculation, EQ6 will then "equilibrate" the solution. It is currently planned that the next version of EQ6 will define mass balances as in EQ3NR, and incorporate the option of using auxiliary basis species and hence reaction path calculations involving partial disequilibrium in the aqueous phase.

This set of mass balance totals, the charge imbalance, the logarithms of the number of moles of the strict basis species, and the logarithm of the oxygen fugacity are written by EQ3NR on its **pickup** file. This file is normally incorporated into the EQ6 **input** file (in which it comprises the bottom half of the file). The information transferred to EQ6 via the EQ3NR pickup file is sufficient for EQ6 to recalculate the speciation model, using the mass balance totals, the charge balance relation, the required equilibria, and the non-ideality constraints, for the specified initial temperature/pressure. If the latter is the temperature/pressure for which the EQ3NR calculation was made and if the EQ3NR model has no disequilibrium in the aqueous solution itself, the initial calculation represents only a confirmation of the values for the number of moles of the basis species and the oxygen fugacity that EQ3NR wrote on its **pickup** file. EQ6 may continue its thermodynamic calculations at the first point of reaction progress by precipitating minerals in order to eliminate supersaturations.

A useful change in constraints in going from EQ3NR to EQ6 is the *temperature jump*. This occurs when the temperature at the start of an EQ6 run differs from that pertaining to the results written onto the **pickup** file. This is handy when using the code to calculate high-temperature properties, such as pH or mineral saturation indices in an autoclave, when one has the pH, etc., for quenched fluid samples.

1.3. Thermodynamic Calculations

The thermodynamic equilibrium calculations made by EQ6 differ from those made by EQ3NR in important ways. EQ3NR computes the speciation of an aqueous solution according to specified temperature/pressure, total concentrations of dissolved components, pH, Eh, and/or many other possible constraints (See Wolery, 1992b). In EQ3NR, the number of moles of solvent water is fixed at a value corresponding to a mass of one kilogram. In EQ6,the number of moles of water

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is a variable to be calculated. To accommodate the additional unknown, EQ6 utilizes an additional mass balance relation (for the element oxygen). EQ3NR calculations do not involve precipitating minerals, although this code can compute the concentrations of components that are required to satisfy desired heterogeneous equilibria. In contrast, EQ6 does make calculations of precipitation from supersaturated solutions. In such calculations, the amount of solvent water, the *pH*, and the oxygen fugacity may all change.

An explicit electrical balance constraint is automatically included in the calculation if it is needed, as indicated by the presence of redox reactions in the model. This constraint includes the constant *imbalance* calculated by EQ3NR which was noted above. If the model contains no redox reactions, electrical balance (or a fixed imbalance) is implicit in the mass balance relations.

It is important to avoid the usage of an electrical balance constraint for a problem which has no significant redox aspects. Such systems tend to be highly ill-poised (lack much redox buffering capacity). EQ6 will then spend a lot of effort trying to accurately calculate the oxygen fugacity. Typically, this results in very small step sizes and long run times. Such calculations tend to exist on the edge of computational singularity. Thus, the code may also terminate abnormally or terminate normally but prematurely.

Two redox reactions appear on most of the supporting data files:

$$O_{2(aq)} = O_{2(g)} \tag{1}$$

$$H_{2(aq)} + \frac{1}{2} O_{2(g)} = H_2O_{(l)} \tag{2}$$

These reactions then normally form part of the calculated thermodynamic model. Thus, the explicit electrical balance constraint normally appears in the calculations. By default, EQ3NR computes the concentrations of $O_{2(aq)}$ and $H_{2(aq)}$ from the oxygen fugacity or *Eh*. Analytical values may also be entered, as these are auxiliary basis species. One of these species (most often $O_{2(aq)}$) is likely to be present in sufficient concentration to provide a reasonable amount of poising.

Problems may result if $O_{2(aq)}$ or $H_{2(aq)}$ are the only redox species in the model and neither is present in sufficient concentration to poise the system. In such cases, one should either increase the concentration of one of these to obtain some poising. Alternatively, both species should be deleted from the model so that the charge balance constraint and the oxygen fugacity are not employed in the calculation. This can not be is done by merely entering zero concentrations for these species on the EQ3NR **input** file. One must specifically suppress these species and the associated reactions. This can be done most safely by using the **nxmod** suppress option on the EQ3NR **input** file (see Chapter 6 of Wolery, 1992b) It can also be done using the **iopt11** option on the EQ6 **input** file (see Chapter 5 of the present report).

All minerals and other solids read into memory from the data base are potential precipitates. The user may disallow the precipitation of some or all such phases by means of appropriate options on the **input** file (see Chapter 5). If precipitation of a phase is suppressed, the aqueous solution is permitted to be supersaturated with it. In many cases, this often corresponds better to reality than assuming solubility equilibrium is a controlling factor. The **input** file options for choosing

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suppression of solid phases are highly flexible: it is easy to suppress specific individual phases (**nxmod** suppress options), groups of pure minerals composed of specified chemical elements (**nxopt** subset-selection suppression options), all pure minerals phases (an **nxopt** subset-selection suppression option), and all solid solutions (**iopt4** = 0). In general, all solid phases should be suppressed when using the code to calculate high temperature solution properties (such as *pH* in an autoclave) from measurements on quenched samples.

A thermodynamic calculation is made in stages, each of which assumes a given phase assemblage. This assemblage begins with the aqueous phase described on an EQ3NR **pickup** file. After making the calculation for a given assemblage, EQ6 checks to see if there are any non-suppressed phases for which the aqueous solution is supersaturated. If there are, the code picks one to add to the phase assemblage and makes a new calculation. If the phase is a pure mineral, the new calculation includes one new equation (the mass action expression for the corresponding solubility equilibrium) and one new unknown (the number of moles of the new mineral). If the phase is a solid solution, the new calculation includes a new equation for each end member component (the corresponding mass action equation) and the set of unknowns is expanded to include the number of moles of each such component. If the new calculation is successful, the code repeats the process as necessary to remove all cases of "unexcused" supersaturation.

Mineral species present in the equilibrium phase assemblage are not formally considered to be basis species, the special set of building blocks used in writing chemical reactions. However, the number of moles of each such mineral species is used as an algebraic master variable in making equilibrium calculations. In this restricted sense, one may say that such mineral species are added to the basis set.

EQ6 uses the logarithms of the number of moles of the active basis species and the mineral species in the equilibrium phase assemblage as algebraic master iteration variables. This forces the values calculated during iteration to remain in physically realistic space; that is, it prevents the generation of zero or negative values for the number of moles of any of the species corresponding to the algebraic master iteration variables (Wolery, 1979). If a mineral phase does not belong in the equilibrium phase assemblage, the iteration diverges in a typical fashion which allows the offending phase to be identified: the number of moles of one or more of the mineral species comprising the phase diverges toward zero (Wolery, 1979). When the code is precipitating mineral phases from an aqueous solution which is initially supersaturated with many phases, it is not unusual for the code to add a mineral which does not belong in the final, completely equilibrated assemblage. A subsequent attempt to add another mineral to the assemblage results in such divergence, which allows identification of the phase which needs to be removed from the assemblage.

The present versions of EQ6 and EQ3NR use a hybrid Newton-Raphson algorithm to make thermodynamic calculations. This differs from the modified Newton-Raphson method used in older versions of EQ6 (Wolery, 1979) and EQ3NR (Wolery, 1983). In the old method, the ionic strength and the equivalent stoichiometric ionic strength were included as matrix variables. The expressions for the activity coefficients of the aqueous species then depended only on the two ionic strength functions, and these expressions were substituted into the balance equations in formulating the Jacobian matrix. Thus the two ionic strength functions, and indirectly the activity coefficients of the aqueous species, were corrected by Newton-Raphson steps. To accommodate

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expressions such as Pitzer's equations, which depend on the specific composition of the solution, not just the ionic strength, a hybrid approach is now utilized. The ionic strength functions have been deleted as matrix variables. The activity coefficients of aqueous species are now treated as constants within a Newton-Raphson step, and are modified by simple recalculation between such steps. This process is described in more detail in Chapter 7.

The activity coefficients of solid solution end member components (see Chapter 4 of Wolery, 1992b) are handled as before, by substitution of the expressions for these quantities into the mass action equations used to define solubility equilibria. These activity coefficients are therefore directly corrected in a Newton-Raphson step. In future versions, this treatment is likely to be modified so that all activity coefficients are treated by simple recalculation between Newton-Raphson steps.

EQ6 follows any basis switching that was made in the initializing EQ3NR calculation. Basis switching redefines the identifies of the basis species used in the calculations. As a general rule, the calculations tend to proceed somewhat more smoothly if a species that dominates a mass balance (or at least makes a significant contribution to it) is employed in the basis. For most calculations, basis switching is not necessary. EQ6 has an automatic basis switching feature, which can be engaged by setting **iopt7** to 1 on the **input** file.

Pre-Newton-Raphson-iteration optimization is employed if starting values produce unfavorable residuals. The algorithm employed in the present version of EQ6 is patterned after one employed more successfully in EQ3NR. Its major weakness is that it can not optimize the algebraic master variables for H^+ and O_2. It also is incapable of optimizing the algebraic master variables for any mineral species in the equilibrium phase assemblage. This optimization algorithm is discussed in more detail in Chapter 7.

Newton-Raphson iteration is automatically assisted as needed by under-relaxation techniques. If necessary, the code will scan the range of oxygen fugacity corresponding to the stability field of liquid water to find a starting value that will lead to convergence.

In practical usage, most "equilibrium" calculations the user is likely to make using EQ6 really represent cases of what is called *partial equilibrium*. The code describes a chemical system by an array of simple reactions, each written in terms of a few species. The reaction coefficients are either integers or simple rational numbers. The concept of partial equilibrium is that some (usually most) such reactions are in a state of equilibrium, while others, usually few in number and representing heterogeneous processes such as mineral dissolution/precipitation, are not. Thus, partial equilibrium could be equally well referred to as partial disequilibrium. Stating that a reaction is in partial equilibrium means that it is in a state of equilibrium, but other reactions in the same system may not be in equilibrium.

"Equilibrium" calculations can be modified in simple ways to deal with partial equilibrium. One type of partial equilibrium has already been discussed above, that which results when an aqueous solution is supersaturated with respect to some solid phase, but there is no precipitation of that phase. Another example would be the case of aqueous redox disequilibrium, where the behavior of a dissolved element must be described by separate mass balances for two different oxidation states, instead of a single mass balance for both forms and a mass action equation describing

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equilibrium between the two forms. As noted earlier, the present version of EQ6 does not have the capability to model disequilibrium in the aqueous phase.

1.4. Reaction Paths

A reaction path represents the process by which a set of irreversible (not at equilibrium) reactions proceed to a state of thermodynamic equilibrium. These reactions drive the chemical evolution of a system as they each proceed toward a state of equilibrium. Consider the interaction of K-feldspar ($KAlSi_3O_{8(c)}$) placed in contact with distilled water. The aqueous solution is undersaturated with respect to this mineral, so there is a thermodynamic driving force for the K-feldspar to dissolve.

The process can be divided into steps in which small increments of this mineral are added to the aqueous solution in the manner of a titration. The reaction path calculation can be conceptualized as a sequence of thermodynamic equilibrium calculations for systems of increasing mass balance totals (number of moles) of potassium, aluminum, silicon, and oxygen. The unreacted mass of the K-feldspar is not considered part of the *equilibrium system* for which these calculations are made. This reaction path terminates when there is no remaining mass of the reactant or when the solution becomes saturated. If there is sufficient reactant present to saturate the solution, then part of the problem is to determine how much of the mineral must be dissolved to achieve this condition. Along the path, various secondary minerals, such as gibbsite ($Al(OH)_{3(c)}$) and kaolinite ($Al_2S_2iO_5(OH)_4$) may precipitate when their solubilities are reached. Some, such as gibbsite, may be transient products, redissolving before the end of the reaction path. Determining which such minerals precipitate, when they precipitate, and if and when they redissolve, is also part of the problem.

Consider another simple scenario, which begins with an aqueous solution that is slightly undersaturated with respect to anhydrite ($CaSO_{4(c)}$). The temperature is then increased in a sequence of steps from the initial value to some value sufficiently high to precipitate this mineral, which becomes less soluble with increasing temperature. At some intermediate temperature, the solution will become saturated and the mineral will appear and grow as the temperature continues to be raised. This process can also be conceptualized as a series of thermodynamic calculations. Here, however, the total masses of the components remain constant, but the change in temperature changes the thermodynamic properties of the system. Part of the problem here is to find the temperature at which precipitation begins, and to quantify the extent of precipitation as a function of temperature.

Reaction path problems can be defined with more than one irreversible reaction proceeding simultaneously. It is also possible to define such paths which include both irreversible reactions and changing temperature/pressure. The extent of such processes can be described by reaction progress variables (Helgeson, 1968). They are usually denoted by the Greek letter ξ (xi). Some physical feel for them can be introduced by pointing out that irreversible reaction is much like a titration. The reaction progress variable is either equivalent or proportional to the quantity of titrant, or reactant, that has been consumed in the titration (along the reaction path). More rigorous definition of reaction progress variables will be deferred to Chapter 3. When there is more than one irreversible reaction, each is described by its corresponding reaction progress variable (ξ_j).

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The evolution of the system as a whole can also be described by an overall reaction progress variable (ξ).

Reaction path calculations take place without reference to a time frame if the rate functions specified by the user for the irreversible processes include only *relative rates* that describe the extent of progress with respect to an overall reaction progress variable. Time is completely arbitrary and the most that one can say is that time should increase as reaction progress increases. Such a calculation is said to be in *reaction progress mode*. If the rate for one or more irreversible processes is defined in terms of its progress with respect to time, then the calculation has a definite time frame and is said to be in *time mode*. It is then possible to calculate both a relative rate and an actual rate for each irreversible reaction.

The major obstacle to reaction path modeling in a time mode is the lack of availability of realistic rate laws for all of the relevant irreversible reactions (cf. Delany, Puigdomenech, and Wolery, 1986). For such reaction, the user must provide EQ6 with both a rate law and the appropriate constants. The study of the kinetics of reactions occurring in aqueous geochemical systems is still in the pioneering stage. There is not general agreement with regard to the functional form of the rate laws, let alone the values of the corresponding constants (rate constants, activation energies, etc.). The user must be prepared to justify whatever kinetic rate laws he chooses to employ. EQ6 is set up to offer a choice of rate law options. In the present version of EQ6, the constants required by rate laws are entered on the **input** file.

There is a two-fold advantage of using real kinetics in reaction path calculations. The first is that the results of the calculations are placed in a time frame. The second is that the ratio of the rates of any two irreversible reactions is realistically evaluated as the ratio of the two corresponding actual rates. In calculations in reaction progress mode, this ratio is evaluated as the ratio of the corresponding relative rates, which must be arbitrarily chosen by the user and are usually fixed throughout the reaction path calculation.

The extra price that must be paid in making calculations in time mode is that the code is faced with integrating ordinary differential equations (the rate laws). The number of steps along the reaction path, hence the number of thermodynamic calculations that must be made, must be sufficiently large to solve these equations with acceptable accuracy. In calculations in reaction progress mode, the step size can be made fairly large. This may reduce the resolution, but it also may also greatly reduce the run time of the calculation.

To define a reaction path problem to run on EQ6, the user supplies a thermodynamic model of an aqueous solution, obtained by running EQ3NR, chooses a set of irreversible reactions ("reactants") and/or changes in temperature/pressure, provides parameters to define the rates of these processes, and chooses from among the various model options that are available. The code does the rest. It may be necessary to repeat a run several times, changing various options, before a satisfactory model is obtained. For example, one might choose to let the aqueous solution supersaturate with various phases rather than have them precipitate according to solubility equilibrium. Or, one might vary the values of certain thermodynamic data, particularly in cases where the data are not well known. Repeated runs may also be required to determine the sensitivity of the results to the assumptions that go into the calculations (e.g., speciation, thermodynamic data, kinetic data).

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The reaction paths calculated by EQ6 usually pertain to well-mixed closed systems or well-mixed systems into which reactants are titrated. There is an option for computing the evolution of the first packet of water flowing through a reactant medium and/or a temperature/pressure gradient. In this model, the water moves on and loses contact with product minerals that form according to partial equilibrium. EQ6 also does calculations in which specified gas fugacities are fixed, presuming that the system is connected to a large external gas reservoir, such as the atmosphere (Delany and Wolery, 1984).

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2. More About EQ6

2.1. Historical Development

H.C. Helgeson introduced the first computer program for making reaction path calculations in geochemical systems (Helgeson, 1968; Helgeson et al., 1970). It computed reaction path models along the lines of "arbitrary" kinetics, in which mineral reactants are titrated into an aqueous solution with which they are not in equilibrium. This code, called PATHI (pronounced "path-one"), performed its own initializing aqueous speciation-solubility calculation. Unlike EQ6, however, that was the only type of "single point" thermodynamic calculation the code made. It had no capability to precipitate supersaturated phases at the start of a run, and consequently would terminate execution when supersaturations were encountered at this point.

The major difference between PATHI and EQ6 was that PATHI, once past the initializing calculation, treated all the equations governing the reaction path as ordinary differential equations (ODEs). This was made possible by differentiating all the algebraic equations such as mass balance, mass action, etc., with respect to ξ, the overall progress variable, to put them in the same class with the relative rate expressions. Numerical integration of these equations gives results that, ignoring errors in the integration, would be equivalent to results obtained using EQ6.

The ODE integration method in PATHI was fairly simple. The first and second derivatives of the mass/concentration variables used to describe the model were evaluated after each step by solving a matrix equation similar to the Jacobian matrix used by EQ6 in Newton-Raphson iteration. In fact, for the same choice of master variables, these matrices would be identical. They are solved, however, for different right-hand-side vectors. In the case of PATHI, solution with one right-hand-side gave an array of first-order derivatives, and solution with another gave the second derivatives. Making a step to another point of reaction progress was done by evaluating the second-order Taylor's series in which these derivatives appeared.

The method described above is not an efficient way to integrate ODEs. Execution times of PATHI were extremely long. Nevertheless, the code was sufficiently capable to demonstrate the usefulness and significance of such calculations.It operated in one of two modes. The first simulated reaction in a closed system, in which the undissolved portions of mineral reactants were considered to be physically present in the system, but not in equilibrium with the aqueous solution. Perturbation of the aqueous solution chemistry by the incremental dissolution of these reactants led to saturation with respect to other, "product" minerals, which would then form and grow and sometimes later redissolve under the condition of partial (individual) equilibrium. The second mode was a spin-off from the first, simulating reaction in a flow-through open system that focused on the evolution of a packet of aqueous solution flowing through a medium containing reactant minerals. The chief difference was that any product minerals formed were considered to be physically separated from the moving fluid and thus could not alter its subsequent evolution by redissolving.

PATHI's calculational capabilities were demonstrated in some early modeling studies. Helgeson, Garrels, and Mackenzie (1969) applied it to a theoretical study of the weathering of feldspar and feldspathic rock and the evolution of the participating aqueous solutions. Helgeson (1970) also presented several examples of calculations pertaining to hydrothermal ore deposition.

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The integration scheme used in PATHI was inefficient because as it moved to a new point of reaction progress, it made no use of the information at immediately preceding points. Essentially, doing so involves constructing finite difference functions up to some order, commonly four to eight. Only the first derivatives then need be solved by the matrix equation noted above. The second and higher derivatives could be approximated using finite differences. This is essentially what happens when one utilizes a method such as the predictor-corrector methods of variable order described by Gear (1971ab). At least four known modifications of PATHI (all unpublished) incorporated Gear's methodology. One was the FASTPATH code developed at the Kennecott Copper Company (see Schlitt and Jackson, 1981). Other versions were created at Los Alamos National Laboratory (C. Herrick), the University of Arizona (J. Knight; see Capuano and Cole, 1982), and the University of British Columbia (T. H. Brown, E. H. Perkins). The latter two were complete rewrites of the original code.

These versions of PATHI were much more efficient, but they still had three major drawbacks. One was the inability to deal with an initial aqueous solution with supersaturations. The second drawback was "drift," or manifestation of error in the integration along the reaction path. Of principal concern was a calculated charge imbalance that tended to grow as the calculation progressed. This was periodically eliminated by executing an aqueous speciation-solubility calculation (just like the initializing calculation) that readjusted the total concentration of one of the ionic components. This correction was thus only cosmetic. The third drawback was that the matrix required to calculate the necessary derivative functions would occasionally become computationally singular, causing the run to terminate. This usually happened during a sharp change in the oxygen fugacity (though this is not the only possible cause).

EQ6 (Wolery, 1978, 1979) is a successor to PATHI, in that it was originally written to perform the same modeling functions. However, it was a completely new code. Separation of the solution of algebraic equations and ODEs made it possible to precipitate initially supersaturated solutions, avoid the drift problem, and step over small intervals of reaction progress in which the matrix was computationally singular. The use of the Newton-Raphson method to solve the algebraic equations appearing in thermodynamic calculations was influenced in part by Morel and Morgan (1972), who used it in the equilibrium code REDEQL. EQ6 employs a finite-difference based method to generate predictor functions for the algebraic master variables (number of moles of basis species). These functions are closely analogous to the predictor functions used in the Gear (1971ab) ODE integration method. They are used to calculate starting values for the Newton-Raphson calculations at new points of reaction progress, and in search algorithms which find the points of reaction progress at which occur certain events of interest, such as the appearance and disappearance of product minerals. The use of algebraic solution methods in essence replaces the corrector part of Gear's ODE integration method. Thus, EQ6 corrects to satisfy the governing algebraic equations instead of their differential counterparts. Originally, EQ6 had no capability to deal with real kinetics, the introduction of which required the introduction of ODE methods to integrate the corresponding rate laws. These methods are now coupled with algebraic methods.

Wolery (1978) initially used EQ6 to model the interactions between sea water and basalt in hydrothermal systems at mid-ocean ridges. It has since been applied in studies of the following:

- Rock/water interactions in the East Mesa geothermal system, Imperial Valley, California (Taylor et al., 1980).
- Dissolution of UO_2 in ground water at low and elevated temperatures (Wolery, 1980).

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- The origin of the copper ore body at Butte, Montana (Brimhall, 1980).
- Hydrothermal interactions of oceanic peridotite with sea water (Janecky, 1982, 1989).
- The role of ground water flow on the genesis of stratabound ore deposits (Garven, 1982).
- The evolution of ground water and formation of secondary minerals at Rainier Mesa, Nevada (Kerrisk, 1983).
- Seawater-basalt interaction at mid-ocean ridges, at both high and low temperature (Bowers and Taylor, 1985, 1987; Bowers, von Damm, and Edmond, 1985;, Gitlin, 1985; Berger, Schott, and Loubet, 1987; and Janecky and Shanks, 1988).
- Sulfide deposition at mid-ocean ridges resulting from mixing between hydrothermal solutions and seawater (Janecky and Seyfried, 1984).
- Hydrothermal alteration of the Columbia River basalt of Washington state (Arthur, 1989).
- Hydrothermal alteration of volcanic rocks at Valles Caldera, New Mexico (White and Chuma, 1989).
- Geochemistry of the Archean hydrosphere and the formation of banded iron formations (Glassley, Jackson, and Bourcier, 1989).
- Calculation of synthetic mineral sequences in burial diagenesis (Bruton, 1989).
- Exploration of the role of chemical kinetics in geochemical processes (Helgeson and Murphy, 1983); Murphy, 1989).
- Modeling tuff-water hydrothermal experiments in a time frame (Delany, 1985)
- Karst development in coastal plain sands (Isphording and Flowers, 1988).
- The dissolution of spent fuel nuclear waste form (Bruton and Shaw, 1987)
- The kinetics of leaching of borosilicate glass nuclear waste form (Bourcier, Knauss, and Merzbacher, 1989).
- Alteration of cement-based grouts for nuclear waste repositories (Gardiner et al., 1989)
- Aqueous alteration of hydrous meteorites (Zolensky, Bourcier, and Gooding, 1989).

This is not a complete list of every use of EQ6 to date. However, it does give a good picture of the kinds of problems to which the code may be applied. The works cited here may also be helpful as resources to users contemplating similar usage.

Chapter 1 of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a) contains a review of other codes, including some with reaction path capabilities (notably PHREEQE; Plummer, Parkhurst, and Thorstenson, 1980). Some of the usages of these other codes provide excellent examples of how to use any reaction path code. Plummer, Parkhurst, and Thorstenson (1983) present an excellent study of modeling groundwater evolution in a carbonate terrain. Reed (1983) gives a nice example of modeling pertaining to seawater-basalt reaction and ore deposition.

Neither version 7.0 nor any preceding versions of EQ6 released by Lawrence Livermore National Laboratory have any capability for predicting isotopic mass transfer. Bowers and Taylor (1985) produced the first known modified version with such a capability and used it in their study. Janecky and Shanks (1988) also modified a version to include isotopic modeling. Bowers (1989) gives a review of the development and application of isotopic mass transfer models. Such a capability may be added to the "mainstream" EQ6 in the future (McKenzie et al., 1986).

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The addition of kinetics to EQ6 was started in 1982 and originally dealt only with mineral dissolution kinetics. Helgeson and Murphy (1983) had independently added such a capability to a version of EQ6 at about the same time. A capability to model precipitation growth kinetics was added later to the "mainstream" EQ6 (Delany, Puigdomenech, and Wolery, 1986).

The development of kinetic reaction path modeling follows the recent growth of interest in geochemical kinetics beginning in the late 1970s. Much information has recently come to light pertaining to the nature of mechanisms and rate laws (See for example Aagaard and Helgeson, 1982; Berner, 1978, 1980, 1981; Berner and Holdren, 1979; Blum and Lasaga, 1991; Carroll-Webb and Walther, 1988; Chou and Wollast, 1984, 1985; Holdren and Berner, 1979; Furrer and Stumm, 1986; Grandstaff, 1976, 1977, 1978; Helgeson, Murphy, and Aagaard., 1984; Knauss and Wolery, 1986, 1988; Lasaga, 1981ab; Murphy and Helgeson, 1987, 1989; Petrovich, 1976, 1981ab; Petrovich, Berner, and Goldhaber., 1976; Rimstidt and Barnes, 1980; Schott, Berner, and Sjöberg, 1981; Talman and Nesbitt, 1988; Wollast and Chou, 1985; Wood and Walther, 1983; Zinder, Furrer, and Stumm, 1986). Kinetic reaction path modeling has only become a possibility due to the recent availability of quantitative descriptions of the rates of some geochemically important reactions.

Much work remains to be done to establish a solid and widely applicable data base of rate laws and rate parameters for mineral dissolution and growth. The more recent work (e.g., Furrer and Stumm, 1986; Zinder, Furrer and Stumm, 1986; Carroll-Webb and Walther, 1988; Blum and Lasaga, 1991) has focused on developing models which directly couple the dissolution or growth rate of a mineral to the chemical species present on its surface. Thus, models accounting for surface chemistry are becoming increasingly important, because they are needed to deal with dissolution and growth kinetics as well as the mass balance of certain components. Version 7.0 of EQ3/6 has no capability for dealing with surface chemistry models, however. Consequently, it still needs development to deal with the most recently proposed models of mineral dissolution and growth kinetics.

The inclusion of actual kinetics requires EQ6 to integrate ODEs, because actual rate laws are by nature ODEs. At the present time, EQ6 calculates predictor functions for the rate functions, just as it does for the algebraic master variables. However, the usage is somewhat different in that the calculation is dependent on the predictor functions for the rates being accurate. The code uses these functions to integrate the rates to compute the increments of irreversible reaction (i.e., changes in the total masses of the components). In contrast, the predictor functions for the algebraic master variables do not have to be very accurate, because the corresponding equations are algebraic instead of differential and can be corrected by Newton-Raphson iteration. Therefore, in a kinetic reaction path run the step sizes will generally be kept smaller than if there were no actual kinetics in the model, and the run will take longer to execute.

EQ6 was modified in 1984 to allow calculations for a model system presumed to be in equilibrium with an external gas reservoir (Delany and Wolery, 1984). This is the "fixed fugacity" capability. For example, the dissolution of a mineral in an open beaker on a time scale of as little as a few hours is best modeled accounting for exchange of CO_2 between the aqueous solution and the atmosphere. This would essentially fix the CO_2 fugacity of the fluid in the beaker. The reaction path in such a system can be significantly different from one in which the system is closed (Delany and Wolery, 1984).

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Another development in the evolution of both EQ3NR and EQ6, which began in 1983, was the addition of the option to use Pitzer's (1973, 1975, 1979, 1987) equations to calculate the activity coefficients of aqueous species (See Chapter 3 of the EQ3NR Theoretical Manual and User's Guide, Wolery, 1992b). This gave EQ3/6 6 a limited capability to treat concentrated aqueous solutions. EQ3/6 6 formerly offered only an equation due to Helgeson et al. (1970) for the activity of water and the B-dot equation of Helgeson (1969) for solute activity coefficients. This option has been preserved, but should not be used when the ionic strength exceeds about one molal. An option to use the Davies (1962) equation was added at the same time as were Pitzer's equations. However, it is not much if any better than the B-dot set of equations and is generally subject to the same restrictions.

There have, of course, been more recent developments pertaining to EQ6 and the EQ3/6 software package. For a description of these, the reader is referred to Chapter 1 of the EQ3/6 Package Overview and Installation Guide, Wolery, 1992a).

2.2. Limitations and Future Development

The user of EQ6 should be aware of its limitations, both those that are inherent in any code of this type, and also those that pertain to the current state of development of the code. EQ6 is currently under development, and this process will probably continue along the lines discussed by McKenzie et al. (1986). Active users should follow both this code development and also the continuing development of the science that affects how the code can be used. A list of capabilities that have been planned for EQ6 (McKenzie et al., 1986) but which do not exist in the present version are listed and briefly discussed in Chapter 1 of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a). Known bugs and such pertaining to the present version of EQ6 are discussed in Appendix D of the present report.

What goes into a computer code is a strong determinant of what comes out of it. One such factor affecting EQ6 is the scope and quality of the thermodynamic data base. It is particularly important that all the species that should be significant contributors to the mass balances in the thermodynamic calculations be represented in the supporting thermodynamic data base, even if the corresponding data are not of high quality. It is not legitimate to leave an important species out of the model just because high quality data for it are lacking. If necessary, perturbation calculations on the data in question should be done (for example, by using the **nxmod** option feature) to get some handle on the sensitivity.

Similar comments pertain to other supporting data. If the user is modeling the behavior of brines, loosely defined here as any aqueous solutions with ionic strengths greater than one molal, then an appropriate activity coefficient option should be selected (in version 7.0 of EQ6, the only such choice is Pitzer's equations). The user should be aware of the limitations imposed by both the option itself and also those related to the scope and quality of the data base that supports the option.

It is important to recognize that the user is called upon to make important decisions at the start of the run. The code can at best provide workable defaults, meaning choices that allow the code to run. However, such choices may not be always suitable for the situation of interest. For example, unless the user specifies otherwise, the code will precipitate any mineral in the data base that supersaturates the aqueous solution. It may be more realistic in many cases to allow precipitation

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of only appropriately selected phases (using the **nxmod** suppression option or the **nxopt** subset-selection suppression options, using the **nxopex** exceptions feature). For example, when the aqueous solution becomes saturated with a potential secondary mineral, the user must choose whether it will be (a) precipitated as required by solubility equilibrium, (b) not precipitated even if the fluid is supersaturated, or (c) precipitated, but according to a rate law instead of a solubility constraint.

The area of kinetics (real kinetics) poses some special problems. Here, growth of knowledge is now progressing at a fast pace. There are still a number of questions regarding the rate laws themselves, let alone such supporting data as rate coefficients and activation energies. The user must bear the burden of assuring that he is using the correct rate laws and supporting parameters. The EQ6 code is set up to treat rate laws in modular fashion. The currently programmed rate laws can be modified and new ones can be added (though there is at present no capability for dealing with surface chemistries with which to link some of the more recent rate equations). The user selects from among the programmed rate laws and provides the necessary supporting data on the input file. There are no kinetic data files to parallel any of the thermodynamic data files.

Redox disequilibrium is a factor that appears in many natural and artificial environments, and is important to recognize in geochemical modeling (See Chapter 2 of the EQ3NR Theoretical Manual and User's Guide, Wolery, 1992b). It would be helpful to be able to model even simple redox disequilibrium, in which there is no interconversion of the forms of an element in more than one oxidation state. For example, Janecky (1982) found it necessary to modify a version of the EQ3/6 data base to "fool" EQ6 into treating sulfate and sulfide as separate components so that sulfate reduction was entirely suppressed. However, although this method (modifying the data base) does permit redox disequilibrium calculations to be made, it is not a satisfactory long-term solution to the problem.

Mineral surfaces form important sinks in aqueous systems for some (especially trace) components. The surface chemistry models necessary to describe this (as well as to link with rate laws for mineral dissolution and growth) have not been incorporated into the present version of EQ3/6. Surface chemistry models have been incorporated into some other codes, some of which are noted in Chapter 1 of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).The present version of EQ6 does have some capability to deal with solid solutions (see Chapter 4 of Wolery, 1992b), which may also act as major sinks for trace components. Although surface speciation and solid solution are very different phenomena, they are often lumped together in a crude concept of "sorption."

These are some of the major capability limitations concerning the present version of EQ3/6. For a complete list of capability limitations, see Chapter 1 of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

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3. Governing Equations

3.1. General Discussion

As noted earlier, in EQ6 there is a separation in the methodology of treating equations that are intrinsically algebraic from those that are intrinsically differential. The former govern thermodynamic calculations, and the latter comprise rate laws for irreversible processes. This numerical decoupling makes it possible to perform thermodynamic calculations, given the necessary inputs of total number of moles of components, the temperature, and the pressure, independently of the integration of rate equations. This contrasts to the treatment used in the PATHI code (Helgeson, 1968, Helgeson, et al., 1970), in which the algebraic relations were differentiated with respect to ξ and the resulting ODEs were integrated numerically. This decoupling permits making "single point" thermodynamic calculations, such as the temperature jump, problems in which rate equations do not even appear.

In EQ6 reaction path models, the two types of equations are coupled in the mathematically formal sense, but the solution of each is performed semi-independently. Each type of calculation is performed alternately, the output of one becoming the input to the next execution of the other. For example, in moving a step forward in reaction progress (ξ), the rate equations are integrated. This defines new values for the temperature, the pressure, and the total number of moles of the components, which are inputs to the following thermodynamic calculation. This in turn gives a new distribution of species, from which may be calculated values for the rates of the irreversible processes at the new point. If accuracy tests on the ODE integration are satisfied, these rate values are then used in making the next integration step. Otherwise, the step size may be cut until those tests are satisfied.

When the rate chosen to constrain an irreversible process is a relative rate ($d\xi_j/d\xi$), the rate function is either a constant or a simple function of the overall reaction progress variable (ξ). When EQ6 operates in the mode of arbitrary kinetics (all irreversible processes constrained by relative rate expressions, no time variable in the model), these rates can be integrated by simple closed-form expressions. It is therefore possible to take arbitrarily large step sizes, subject only to the following conditions.

In the case of closed and open system calculations, the rate of an irreversible reaction is set to zero when the corresponding thermodynamic driving force, the affinity, is no longer positive. Affinities are outputs of the thermodynamic calculations. EQ6 locates the point of reaction progress where the affinity goes to zero. If the corresponding reactant is a mineral, then this means that the aqueous solution has reached saturation. The code then changes the status of the reactant to inactive (meaning it is effectively removed from the set of reactants). Any remaining mass of the reactant is then moved into the *equilibrium system*. Titration calculations are very similar to closed system calculations, but the rate of an irreversible reaction is not set to zero when saturation is reached, and the remaining reactant mass continues to be added to the equilibrium system according to the rate law.

The rate of an irreversible reaction rate also becomes zero when the associated "reactant" becomes exhausted, no matter what kind of system model the code is dealing with. The user spec-

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ifies how much of a reactant is available at the start of the run. The code then finds the point of reaction progress at which exhaustion occurs.

The purpose of this chapter is to review the governing equations pertaining to calculations in EQ6. The following section reviews the algebraic equations that govern thermodynamic equilibrium calculations. All of these equations have been discussed in the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b), although some of the equations have some slight differences in the way they pertain to EQ6. The final section of this chapter discusses the equations dealing with reaction progress, reaction rates, temperature, and pressure.

3.2. Constraints on Thermodynamic Calculations

3.2.1. Mass Balance

Mass balance in EQ6 takes on a slightly different form than in EQ3NR. All species appearing in the equilibrium system contribute to mass balance. In EQ3NR, this system consisted only of the aqueous phase. However, in EQ6 it also includes minerals and other substances in equilibrium with the aqueous solution. A second difference is that in EQ3NR, mass balance was treated in terms of molal concentrations. In EQ6, it is treated in terms of numbers of moles. The molal concentration of the s-th aqueous species (m_s) is related to the corresponding number of moles (n_s) by the equation:

$$m_s = \frac{\Omega n_s}{n_w} \tag{3}$$

where Ω is the number of moles of water (≈ 55.51) comprising a mass of one kilogram and n_w is the number of moles of water.

A general expression of mass balance for the s'-th basis species in an equilibrium system composed of aqueous solution, pure minerals, and solid solutions, is:

$$\sum_{s=1}^{s_T} u_{s's} n_s + \sum_{\phi=1}^{\phi_T} u_{s'\phi} n_\phi + \sum_{\psi=1}^{\psi_T} \sum_{\sigma=1}^{\sigma_{T,\psi}} u_{s'\sigma\psi} n_{\sigma\psi} = n_{T,s'} \tag{4}$$

This is an extension of the mass balance equation used in EQ3NR (Wolery, 1992b), in addition to the conversion from molalities to numbers of moles. Here s_T is the number of aqueous species in the system, ϕ_T is the number of minerals of fixed composition present and in equilibrium with the water, ψ_T is the number of such solid solution phases, and $\sigma_{T,\psi}$ is the number of components in the ψ-th solid solution. Also, n_ϕ is the mass of the ϕ-th pure mineral present, $n_{\sigma\psi}$ is the mass of the σ-th component of the ψ-th solid solution, and $n_{s'}$ is the total number of moles of the s'-th basis species. The stoichiometric factors ($u_{s's}$, $u_{s'\phi}$, and $u_{s'\sigma\psi}$) relate the contributions of the aqueous, pure mineral, and solid solution species to the mass balance. For non-basis species, these factors are computed from reaction coefficients; the factor for a basis species in its own

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mass balance is unity. There is such a mass balance equation for each of the basis species present in the model except the s_B-th, the fictive aqueous species O_2.

The present version of EQ6 actually uses mass balances defined in terms of chemical elements. Thus, for the ε-th element, the appropriate expression is:

$$\sum_{s=1}^{s_T} c_{\varepsilon s} n_s + \sum_{\phi=1}^{\phi_T} c_{\varepsilon\phi} n_\phi + \sum_{\psi=1}^{\psi_T} \sum_{\sigma=1}^{\sigma_{T,\psi}} c_{\varepsilon\sigma\psi} n_{\sigma\psi} = n_{T,\varepsilon} \tag{5}$$

The factors $c_{\varepsilon s}$, $c_{\varepsilon\phi}$, and $c_{\varepsilon\sigma\psi}$ are the coefficients of this element in the chemical formulas for the s-th aqueous species, the ϕ-th pure mineral, and the σ-th component of the ψ-th solid solution, respectively. This equation is equivalent to eq (4) if the set of active basis species contains no auxiliary basis species.

If an auxiliary basis is present, the number of basis species minus one is greater than the number of chemical elements. Hence, there is then a greater number of corresponding mass balance equations in the model constraints.

3.2.2. Charge Balance

The charge balance equation comes into the calculations if a redox parameter is needed to complete the model, which is generally the case. The fictive aqueous species is the corresponding basis species, and the primary redox parameter is the oxygen fugacity. From this, other redox parameters can be calculated, such as *Eh*, *pe*, or *Ah* (see Wolery, 1992b). The charge balance equation can be written as:

$$\sum_{s}^{s_T} z_s n_s = 0 \tag{6}$$

where z_s is the electrical charge. This is analogous to eq (5), except that the weighting factors are different and there are no terms for non-aqueous species.

In practice, the initial model computed by EQ3NR may be either charge balanced or out of charge balance. EQ6 can handle either case. EQ3NR calculates the charge imbalance (Δ_z) at the end of it speciation calculation and writes this on its **pickup** file as the variable **electr.** EQ6 then adds this term into the electrical balance, so that the initial charge imbalance is maintained throughout the run. In other words, eq (6) is replaced by:

$$-\Delta_z + \sum_{s}^{s_T} z_s n_s = 0 \tag{7}$$

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3.2.3. Mass Action

A mass action equation describes thermodynamic equilibrium for a given chemical reaction. The reactions on the EQ3/6 data file are always written so as to destroy the associated non-basis species (e.g., the dissociation reaction of an aqueous complex, the dissolution reaction of a mineral). All other species appearing in the reaction are basis species. The mass action expression for j-th reaction for the destruction of the associated species, denoted here as the i-th, takes the following form when the associated species is not a gas:

$$b_{ij} log a_i + b_{s_B j} log f_{O_2} + \sum_{\substack{s' = 1 \\ s' \neq s_B}}^{s_Q} b_{s'j} log a_{s'} = log K_j \tag{8}$$

Here the reaction coefficients b are negative for reactants and positive for products, following the usual EQ3/6 convention. The symbol a represents thermodynamic activity of the species denoted by the subscript. K_j is the equilibrium constant. The fictive aqueous species O_2 is the s_B-th species. The symbol s' implies a basis species. If the associated species is a gas, the corresponding mass action equation is:

$$b_{ij} log f_i + b_{s_B j} log f_{O_2} + \sum_{\substack{s' = 1 \\ s' \neq s_B}}^{s_Q} b_{s'j} log a_{s'} = log K_j \tag{9}$$

Here the fugacity (f) appears in place of the activity of the i-th species. Currently EQ6 does not treat the possible existence of a gas phase in the equilibrium system. Hence, eq (9) is used only to compute equilibrium fugacities.

Thermodynamic activities are treated by the following familiar relations. In the case of solvent water, the activity is given by:

$$log a_w = log x_w + log \lambda_w \tag{10}$$

where x_w is the mole fraction of water in the aqueous solution and λ_w is the corresponding mole fraction activity coefficient. The mole fraction of water is given by:

$$x_w = \frac{\Omega}{\Omega + \Sigma m} \tag{11}$$

where Σm is the sum of the molalities of the solute species. For the i-th aqueous solute species, the activity is given by:

$$log a_i = log m_i + log \gamma_i \tag{12}$$

where γ_i is the corresponding the molal activity coefficient. For the ϕ-th pure mineral, the activity is a constant:

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$$log a_{\phi} = 0 \tag{13}$$

For the σ-th component of the ψ-th solid solution, the activity is defined analogously to that of solvent water:

$$log a_{\sigma\psi} = log x_{\sigma\psi} + log \lambda_{\sigma\psi} \tag{14}$$

Here $x_{\sigma\psi}$ is the mole fraction of the component and $\lambda_{\sigma\psi}$ is the corresponding mole fraction activity coefficient. The mole fraction of the σ-th component of the ψ-th phase is given by:

$$x_{\sigma\psi} = \frac{n_{\sigma\psi}}{\sum_{\sigma' = 1}^{\sigma_{T,\psi}} n_{\sigma'\psi}} \tag{15}$$

where $\sigma_{T,\psi}$ is the number of components in the components in the ψ-th phase.

3.2.4. Activity Coefficients of Aqueous Species

Activity coefficients are functions of solution composition, temperature, and pressure. However, there is no recognized single universal set of equations for calculating them in aqueous solutions. Instead, there are various equations that each have their own strengths and weaknesses. Each must provide not only the molal activity coefficients of the solute species, but also the mole fraction activity coefficient of water (or equivalently, its activity). Several different models have been programmed into EQ3/6. These are discussed in detail in Chapter 3 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b).

The activity coefficient option is specified on the **input** file by the option switch **iopg1**. The existing options are:

-1 The Davies (1962) equation.

0 The B-dot equation (Helgeson, 1969).

1 Pitzer's (1973, 1975, 1979, 1987) equations.

The Davies equation and the B-dot equation are simple extended Debye-Hückel models. The activity coefficients are treated as functions of the ionic strength:

$$I = \sum_{s=1}^{s_T} m_s z_s^2 \tag{16}$$

These models ignore any dependence on the specific composition of the aqueous solution. This is realistic only in dilute solutions, and these options should not be used in calculations involving solutions in which the ionic strength exceeds 1.0 molal. In comparison with the best physical chemistry measurements, inaccuracy is apparent at values less than 0.1 molal. The **com**, **sup**, and

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nea data files may be used with the Davies and B-dot equations. A large number of chemical components may be treated using these models.

Pitzer's (1973, 1975, 1979, 1987) equations treat the activity coefficients as functions of both the ionic strength and the specific composition of the aqueous solution. strength. These equations may be applied to concentrated brines (e.g., Harvie, Møller, and Weare, 1984). The **hmw** and **pit** data files may be used with Pitzer's equations. A more restricted set of chemical components may be treating using Pitzer's equations.

The mole fraction activity coefficient of water and the molal activity coefficients of aqueous solute species are evaluated by the EQLIB module **gcoeff.f**. The coding of new models is relatively easy. The most troublesome aspect of adding new models with any applicability to concentrated solutions is the input of the necessary supporting data.

3.2.5. Activity Coefficients of Solid Solution Components

The activities and activity coefficients of solid solution components are defined on the usual mole fraction scale. The treatment of solid solutions in EQ3/6 is currently limited to simple molecular mixing models. These are models in which the components are end members, equivalent to pure minerals. The existing capabilities are described elsewhere (Chapter 4 of the EQ3NR Theoretical Manual and User's Guide, Wolery, 1992b; Wolery, 1979, Table 3, p. 12-13; Bourcier, 1985. 1989) and require coding not only for evaluating the activity coefficient (λ), but also the derivative function $\Lambda_{ij} = (d \log \lambda_i / d \log x_j)$, where i and j both denote components.

3.2.6. Saturation Indices and Affinities

Saturation indices and affinities are important because they are measures of the thermodynamic driving forces behind the progress of irreversible reactions. These quantities form an important bridge between calculations that are purely thermodynamic and those that pertain to dynamic evolution. If there is no positive driving force for a reaction, it will not proceed in the forward direction. Unless the user has specified titration mode (**nmodl1** = 1), EQ6 sets a calculated rate to zero when the corresponding driving force is zero or opposed to further progress. The affinity function also appears directly as a parameter in some important kinetic rate laws, as will be noted later in this chapter.

The saturation index (*SI*) is a commonly used measure of the state of an aqueous solution with respect to the progress of some reaction, usually the dissolution of a mineral. It is defined by:

$$SI = \log \frac{Q_+}{K_+} \tag{17}$$

where Q is the ion activity product (*IAP*), K is the equilibrium constant, and the subscript "+" denotes that these quantities pertain to the reaction as written for the dissolution/dissociation/destruction of the associated species (the forward direction in EQ3/6). Saturation indices are zero for the case of exact saturation, negative for undersaturation, and positive for supersaturation.

In expanded EQ3/6 nomenclature, Q is evaluated for the j-th reaction according to:

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$$\log Q_{+,j} = b_{ij}\log a_i + b_{s_B j}\log f_{O_2} + \sum_{\substack{s'=1 \\ s' \neq s_B}}^{s_Q} b_{s'j}\log a_{s'} \tag{18}$$

Here must f_i be substituted for a_i if the i-th species is a gas. Because the present version of EQ6 does not treat the possible presence of a gas phase in the equilibrium system, ion activity products and saturation indices for reactions for destruction of gas species are not currently evaluated.

The saturation index of the ψ-th solid solution phase can be constructed from the saturation indices of its components according to:

$$SI_\psi = \sum_{\sigma=1}^{\sigma_{T,\psi}} x_\sigma SI_{\sigma\psi} \tag{19}$$

This can be easily derived by creating a reaction for the dissolution of the phase by making a linear combination of the reactions for the individual components.

If a solid solution is present in the equilibrium system, the thermodynamic activity of each of its components that is also present is defined and eq (18) and hence eq (19) can be evaluated. Of course, the saturation index of each of the components, hence that of the phase, will of necessity have a value of zero, so this is not very interesting. However, if a solid solution is not present, the thermodynamic activity of each of its components is not directly available, and eqs (18) and (19) by themselves are inadequate to determine a saturation index. The scheme presently used in EQ3/6 is to define a hypothetical saturation index as that corresponding to the composition which maximizes the value of this index (Bourcier, 1985, 1989).

The affinity is closely related to the saturation index. Affinities may be defined for both the forward ("+") and reverse ("-") directions of a reaction. In EQ3/6, "forward" means in the direction of dissolution/ dissociation/destruction of the associated species. Hence, "-" signifies precipitation/association/production of the associated species.

Following these conventions, the affinity to dissolve/dissociate/disappear is related to the saturation index by:

$$A_+ = -2.303RT\,SI \tag{20}$$

The affinity to precipitate/associate/form is related to the SI by:

$$A_- = 2.303RT\,SI = -A_+ \tag{21}$$

When the affinity is positive, it means that the reaction is thermodynamically favored to move in the corresponding direction. Note that affinity has the dimensions of energy per mole (of reaction progress). Also, the affinity to precipitate/associate/form follows the same sign conventions with respect to supersaturation/undersaturation as the saturation index.

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3.3. Constraints Related to Reaction Progress

3.3.1. The Reaction Progress Variable

The reaction progress variable (ξ) is a measure of the extent to which a reaction has proceeded. Any chemical reaction can be written in the following format:

$$aA + bB + \ldots = cC + dD + \ldots \tag{22}$$

Here A, B, etc. are reactants, C, D, etc., are products, and a, b, c, d, etc., are the reaction coefficients (all positive when written in this form). There are two equivalent ways to describe a complex chemical process, such as rock/water interaction. The first is to consider it as an array of simple reactions. Here the reaction coefficients are constants and are usually chosen to be small integers or common rational numbers such as 1/2, 1/4, etc. The second is to view the whole process as a single reaction, whose reaction coefficients are generally neither "nice" numbers nor constants along a reaction path.

In EQ6, reaction progress variables are used to describe only the reactions that are irreversible (not at equilibrium). The irreversible process is defined by an array of simple irreversible reactions, corresponding to the first case described above. Each of these reactions has its own associated progress variable (ξ_j). There is in addition an overall reaction progress variable (ξ) for the process as a whole, which corresponds to the second case described above.

It is possible to define progress variables for reversible reactions as well. This is done in some methods for making thermodynamic calculations (See Van Zeggeren and Storey, 1970), in which case these parameters are used as iteration variables in place of masses or concentrations of component species (in this usage, reaction progress variables are generally symbolized by λ instead of ξ.) This type of treatment is not used in EQ6, however.

Reaction progress variables are commonly defined in the following differential form (e.g., Helgeson, 1968; Lasaga, 1981a):

$$d\xi_j = -\frac{dn_{A,j}}{a_j} = \ldots = +\frac{dn_{C,j}}{c_j} = \ldots \tag{23}$$

$$d\xi = -\frac{dn_A}{a} = \ldots = +\frac{dn_C}{c} = \ldots \tag{24}$$

Here j denotes an irreversible reaction. The total change in the mass of a component must be the sum of the changes due to the individual reactions. Hence,

$$dn_A = \sum_{j=1}^{j_T} dn_{A,j} \tag{25}$$

and so forth for B, C, D, where j_T is the total number of individual irreversible reactions. Then coefficients of the overall reaction are related to those of the individual reactions by

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$$a = \sum_{j=1}^{j_T} a_j \left(\frac{d\xi_j}{d\xi} \right) \tag{26}$$

and so forth for b, c, and d. The quantity $d\xi_j / d\xi$ (also symbolized as v_j^{rel}) is called the relative rate of the j-th irreversible reaction.

The motivation behind the reaction progress variable is to normalize the effect of the reaction coefficients that appear in a given reaction. Recasting eqs (23) and (24) in terms of derivatives leads to the following results.

$$-\frac{dn_A}{d\xi_j} = a_j \tag{27}$$

$$+\frac{dn_C}{d\xi_j} = c_j \tag{28}$$

$$-\frac{dn_A}{d\xi} = a \tag{29}$$

$$+\frac{dn_C}{d\xi} = c \tag{30}$$

These equations lead to the derivative equivalent of eq (25):

$$\frac{dn_A}{d\xi} = \sum_{j=1}^{j_T} \frac{dn_A}{d\xi_j} \tag{31}$$

and so forth for B, C, and D.

Following the usual EQ3/6 convention for writing reactions on the data file, the reaction coefficients (b) are intrinsically negative for reactants. Switching to this notation, eqs (27) and (28) can be written for the i-th component without regard to whether it is a reactant or a product:

$$\frac{dn_i}{d\xi_j} = b_{ij} \tag{32}$$

Similarly, eqs (29) and (30) can be written as:

$$\frac{dn_i}{d\xi} = b_i \tag{33}$$

where b_i is the coefficient of this component in the overall reaction. Eq (26) can be written as:

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$$b_i = \sum_{j=1}^{j_T} b_{ij} \left(\frac{d\xi_j}{d\xi} \right) \tag{34}$$

It should be clear that changes in the quantities of the components A, B, C, D, etc., can be obtained by integrating with respect to the appropriate progress variable. For the case of an individual reaction, this gives:

$$\Delta n_{i,j} = \int_{\xi_{j,0}}^{\xi_{j,1}} b_{ij} d\xi_j \tag{35}$$

where the subscripts 0 and 1 signify two successive points along the reaction path. Because the coefficients in this equation are constants, integration of this equation yields the following result:

$$\Delta n_{i,j} = b_{ij} \Delta \xi_j \tag{36}$$

where $\Delta \xi_j = \xi_{j,1} - \xi_{j,0}$. This result leads to a more immediate understanding of the reaction progress variable. Basically, it says that the change in the number of moles of component i due to reaction j is proportional to the change in ξ_j. Thus, when $\Delta \xi_j = 1$, $\Delta n_{i,j} = b_{ij}$

The overall reaction equivalent of eq (35) is:

$$\Delta n_i = \int_{\xi_0}^{\xi_1} b_i d\xi \tag{37}$$

However, the overall reaction coefficient b_i is not in general a constant. Substituting eq (34) into eq (37) and integrating gives:

$$\Delta n_i = \sum_{j=1}^{j_T} b_{ij} \Delta \xi_j \tag{38}$$

This is the central equation used to calculate irreversible mass transfer in EQ6. Note that it depends on integrating the relative rates ($d\xi_j / d\xi$) with respect to the overall reaction progress variable.

3.3.2. Reaction Rates and Time

The user of EQ6 specifies for each irreversible reaction a function for either the relative rate or the absolute rate ($d\xi_j / dt$, also symbolized as v_j). If a relative rate function is specified, then the evaluation of eq (38) is straightforward. If an actual rate is specified, then a relative rate function is derived from this as shown below. Time is not defined unless at least one actual rate specification is included in the model to be calculated. The scheme used here to handle relative rates and

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time when calculating a kinetic reaction path is very similar to that described by Helgeson and Aagaard (1979) and Helgeson and Murphy (1983). It differs in two ways (Delany, Puigdomenech, and Wolery, 1986). First, the approach is extended to allow mixing of relative rates with absolute rates in defining a problem. Second, it allows consideration of the kinetics of reactions proceeding in the backward direction.

In reaction progress mode (no time frame), ξ is simply the integration variable and no further definition is required. In time mode, this is not the case. A convenient definition is then given by:

$$\xi = \sum_{j=1}^{j_K} |\xi_j| \tag{39}$$

where j_K is the number of irreversible reactions constrained by actual rate laws (j_K is usually equal to j_T, but may be lesser if relative rates are directly specified for some of the irreversible reactions). In the treatment of Helgeson and Aagaard (1979) and Helgeson and Murphy (1983), the overall reaction progress variable is defined as the sum of the individual reaction progress variables instead of as the sum of their absolute values. The motivation behind the definition given in eq (39) becomes clearer by differentiating it with respect to time. Letting ν represent the overall rate ($d\xi/dt$), the result can be written as

$$\nu = \sum_{j=1}^{j_K} |\nu_j| \tag{40}$$

Having defined ν, one can now calculate relative rates for the irreversible reactions constrained by absolute rates:

$$\nu_j^{rel} = \frac{\nu_j}{\nu} \tag{41}$$

The inverse rate ($dt/d\xi$ or $\nu_{1/t}$) can be similarly calculated:

$$\nu_{1/t} = \frac{1}{\nu} \tag{42}$$

It is then possible to calculate absolute rates for irreversible reactions which are constrained by relative rates:

$$\nu_j = \nu_j^{rel}\nu \tag{43}$$

The progress increment for the j-th irreversible reaction can be calculated for a reaction progress step by integrating the relative rate (Helgeson and Aagaard, 1979; Helgeson and Murphy, 1983; Delany, Puigdomenech, and Wolery, 1986):

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$$\Delta\xi_j = \int_{\xi_0}^{\xi_1} v_j d\xi \tag{44}$$

Similarly, a time increment can be calculated for a reaction progress step by integrating the inverse rate:

$$\Delta t = \int_{\xi_1}^{\xi_2} v_{1/t} d\xi \tag{45}$$

This has the advantage of allowing one to use ξ as the independent variable in calculations either reaction progress mode or time mode. Furthermore, in the latter mode, it allows the calculations to extend to the case in which time reaches infinity (Delany, Puigdomenech, and Wolery, 1986). This would not be possible if time were used as the independent variable. Chapter 8 discusses the evaluation of eqs (44) and (45) when the relative rates and the inverse rate are represented as truncated Taylor's series.

3.3.3. Rate Laws Programmed into EQ6

Rate laws are coded into the EQ6 module **rtcalc.f**. The rate laws must be written in terms of parameters that currently appear in the code. For example, Lasaga (1981a) proposed a rate law for feldspar dissolution that is explicitly linked to the sorption of hydrogen ion on the feldspar surface. Such a rate law can not be dealt with in the present version of EQ6, because there is no provision for treatment of sorption (surface chemistry) phenomenon (development of such a capability is planned; McKenzie et al., 1986). Also, at the present time, the use of kinetic rate laws is restricted to the dissolution and precipitation growth kinetics of solids.

A more detailed discussion of rate law modeling in EQ6, including a discussion of the underlying scientific foundation and the presentation of several examples, is given by Delany, Puigdomenech, and Wolery (1986). The discussion here will be somewhat abbreviated. All rate laws evaluated by EQ6 describe net rates. However, the code permits the user to apply to each irreversible reaction one rate law for the net forward (e.g., dissolution) reaction and another for the net backward (e.g., precipitation) reaction. For some types of rate laws, one of these forms can be specified to apply to both net forward and backward rates, the actual net direction being determined by the sign of the calculated rate.

The forward rate law for the **nrc**-th irreversible reactant is determined by **nrk(nrc)**, which is read from the input file (See Chapter 5). Currently available choices are:

nrk	Rate Law
-1	Use specified backward rate law form (**nrpk** must be 1, 2, or 4).
0	Illegal value.
1	Relative rate.

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2 Transition-state theory.

3 Constant rate (proportional to surface area).

4 Activity term rate law.

The backward rate law is specified by **nrpk(nrc)**. Currently available choices are:

nrpk	Rate Law
-1	Use specified forward rate law form (**nrk** must be 1, 2, or 4).
0	Instantaneous equilibration.
1	Relative rate.
2	Transition-state theory.
3	Constant rate (proportional to surface area).
4	Activity term rate law.

If both forward and backward forms are given for an irreversible reaction, the sign of the affinity determines which form is evaluated. Some rate laws yield rates that are always consistent with the reaction affinities; that is, the sign of the rate always matches that of the thermodynamic driving force, and the rate is zero when that driving force is zero. The transition state theory and activity term rate laws have this property. For such rate laws, one form (forward or backward) can be used to describe the net reaction rate regardless of the sign of the affinity (the user, however, must decide whether or not this is really appropriate). For other rate laws, it is important to remember that EQ6 truncates the calculated rate (sets it to zero) in the absence of a favoring thermodynamic driving force.

The following discussion is patterned after Delany, Puigdomenech, and Wolery (1986). In general, net rate expressions can be written for both the forward (+) and backward (-) directions, thus separately defining v_j and $-v_j$ (or v_j^{rel} and $-v_j^{rel}$), in terms of forward and backward rate constants, respectively. In the code, which form is evaluated depends on the sign of the affinity. If $A_{+,j}$ is positive or zero, the forward form is evaluated; otherwise, the backward form is used.

There is no justification for the use of elaborate expressions for relative rates. Only one expression for relative rates is programmed into EQ6, a truncated second-order Taylor's series in overall reaction progress. The two forms are:

$$v_j^{rel} = k_{+,1j} + k_{+,2j}\xi + \frac{1}{2}k_{+,3j}\xi^2 \tag{46}$$

$$-v_j^{rel} = k_{-,1j} + k_{-,2j}\xi + \frac{1}{2}k_{-,3j}\xi^2 \tag{47}$$

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Here $k_{+,ij}$ and $k_{-,ij}$ are forward and backward rate constants. Values for these are entered on the **input** file when this rate law is selected. Normally, relative rates are specified as constants; i.e., only the first term on the right hand side is used. Picking reasonable values for relative rates is not easy even then. One useful rule of thumb when modeling the interaction of a rock with a water is to pick the relative rates of dissolution of the minerals in the rock such that they are proportional to their abundances.

The transition-state theory (TST) rate law takes the forms:

$$v_j = f_j s_j \sum_{i=1}^{i_{T,+,j}} k_{+,ij} \left(\prod_{n=1}^{n_{T,+,ij}} a_n^{-N_{+,nij}} \right) \left(1 - e^{-\frac{A_{+,j}}{\sigma_{+,ij} RT}} \right) \tag{48}$$

$$v_j = f_j s_j \sum_{i=1}^{i_{T,-,j}} k_{-,ij} \left(\prod_{n=1}^{n_{T,-,ij}} a_n^{-N_{-,nij}} \right) \left(1 - e^{-\frac{A_{-,j}}{\sigma_{-,ij} RT}} \right) \tag{49}$$

Here s_j is the total surface area of the phase dissolving in the j-th irreversible reaction. The factor f_j is a fudge factor representing the proportion of effective to total surface area; normally, it is taken as unity. The net forward form provides for treating $i_{T,+,j}$ parallel mechanisms. For each, there is a rate constant ($k_{+,ij}$) a *kinetic activity product*, and a term that depends on the affinity ($A_{+,j}$). The kinetic activity product (which can be symbolized as $q_{+,ij}$; Delany, Puigdomenech, and Wolery, 1986) depends on the thermodynamic activities of $n_{T,+,ij}$ species, each raised to a non-zero power characteristic of the mechanism ($-N_{+,nij}$). The kinetic activity product has a value of unity if $n_{T,+,ij} = 0$. The kinetic activity product most often reflects the dependence of the reaction mechanism on pH, and usually consists of just the activity of the hydrogen ion raised to some power (See Delany, Puigdomenech, and Wolery, 1986). The affinity factor goes to zero when the affinity goes to zero, forcing the reaction rate to do likewise. This factor also depends on the gas constant (R), the absolute temperature (T), and a stoichiometric factor ($\sigma_{+,ij}$) that relates the affinity of a macroscopic reaction ($A_{+,j}$) to that of the corresponding microscopic or elementary reaction ($A_{+,j}/\sigma_{+,ij}$). The stoichiometric factor is usually taken as having a value of unity. The net reverse form parallels the net forward form. If one desires to use TST to describe the kinetics of both the net forward and reverse directions, one ought ordinarily input to the code only one of the above forms and direct the code to use it regardless of the sign of the affinity (set **nrk** or **nrpk**, as appropriate, to -1).

The transition state theory rate law is probably the most important of the kinetic rate laws used in EQ6. For an introduction to the theory suitable for geochemists, see Aagaard and Helgeson (1982) or Lasaga (1981b). Note that the TST rate law is a function of the chemistry of the aqueous solution, but is not an explicit function of time.The rate law for quartz dissolution and growth proposed by Rimstidt and Barnes (1980), though written in a slightly different form, is equivalent to a one-term form of the above equation (See Delany, Puigdomenech, and Wolery, 1986). More recent work on quartz dissolution by Knauss and Wolery (1988) suggests a two-term form, re-

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flecting a region of *pH* in which the rate is independent of *pH* and essentially follows the behavior observed by Rimstidt and Barnes (1980), and a region of higher *pH* in which the rate increases with increasing *pH*. The transition state theory rate law form has also been applied to the dissolution kinetics of many other minerals, especially feldspars and other silicates (e.g., Helgeson, Murphy, and Aagaard, 1984; Wollast and Chou, 1985; Knauss and Wolery, 1986, 1988; Murphy and Helgeson, 1987, 1989). This is currently a very active field, and it is not possible here to summarize all the progress to date or even to name all of the investigators who have made important contributions to the field. A number of significant works were cited previously in Chapter 2.

Transition state theory has the strongest theoretical foundation among the various rate laws which have been applied to the kinetics of mineral dissolution and growth (see for example Lasaga, 1981b; Aagaard and Helgeson, 1982; Delany, Puigdomenech, and Wolery, 1986). Nevertheless, the reader should be aware that in aqueous geochemistry it has been used primarily merely to provide a mathematical form which can be used to explain some measurements. Such explanations may not be unique, even within the scope of the theory itself. The actual mechanisms, and even the number of mechanisms required to explain available data, may be open to debate.

As eqs (48) and (49) used in the present version of EQ6, the species whose activities may appear in the kinetic activity product must all be aqueous species. Several investigators (e.g., Lasaga, 1981a; Wollast and Chou, 1985; Murphy and Helgeson, 1987; Carroll-Webb and Walther, 1988) have developed transition state theory models for mineral dissolution in which speciation on the surface of the mineral is treated in the rate model. Two approaches to incorporating such models into a code such as EQ6 are possible. One is to try to treat the surface speciation implicitly in the rate expression, so that the rate expression is still evaluated in terms of the activities of aqueous species instead of those of surface species with which they are in equilibrium (see Lasaga, 1981a, for an example). The other approach is to treat surface speciation in an explicit manner, just as aqueous species are normally treated. The number of moles of surface species would then be included, for example, in calculating mass balances. Kinetic activity products could then include contributions from surface species in the usual manner. This is a more rigorous and general approach, and may be implemented in future versions of EQ6.

Another problem concerns the issue of rate dependence on particle size when ultrafine particles are present (e.g., Holdren and Berner, 1979; Petrovich, 1981ab). Attempts have been made to quantify this (e.g., Helgeson, Murphy, and Aagaard, 1984; Talman and Nesbitt, 1988). No explicit treatment of this is provided in the present version of EQ6. It is possible, however, to use the *special reactant* feature to create a second form of a reactant mineral, with a higher dissolution rate, in order to make a first-order simulation of the presence of a component of ultrafines.

The constant rate "rate law" forms are:

$$v_j = f_j s_j k_{+,1j} \tag{50}$$

$$-v_j = f_j s_j k_{-,1j} \tag{51}$$

The rate is not actually constant unless the surface area is constant. There is no dependence of this rate law on chemistry, which is unrealistic. However, this rate law is still of some usefulness.

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The activity product term rate law forms are:

$$v_j = f_j s_j \sum_{i=1}^{i_{T,+,j}} k_{+,ij} \left(\prod_{n=1}^{n_{T,+,ij}} a_n^{-N_{+,nij}} \right) \tag{52}$$

$$v_j = f_j s_j \sum_{i=1}^{i_{T,-,j}} k_{-,ij} \left(\prod_{n=1}^{n_{T,-,ij}} a_n^{-N_{-,nij}} \right) \tag{53}$$

The parameters have essentially the same practical meaning as in the TST equations. The activity product term rate law is the next most useful form after transition state theory. Whereas a one-term transition state theory form is not unusual and has the property of giving a result that is always consistent with the affinity, the activity product term rate law usually has four terms, and the terms and the rate constants are normally adjusted so that result is consistent with the affinity, which does not appear explicitly in the equation. If so, and if this rate is to govern both dissolution and growth kinetics, only one form should be input to EQ6. The archetype of the activity product term rate law is the rate law of Plummer, Wigley, and Parkhurst (1978), which has been applied mainly to the dissolution and growth kinetics of carbonate minerals. The theoretical basis of this rate law does not appear to be as firm as that of transition state theory. Also, the experimental data to which this rate law has been fit can be explained equally well by a one-term transition state theory form (Delany, Puigdomenech, and Wolery, 1986).

3.3.4. Temperature and Pressure

In most EQ6 runs, the temperature and pressure are constants. However, for many processes, the temperature and/or pressure change along the reaction path. EQ6 is set up to deal such changes, provided that the user defines these changes as functions of the overall reaction progress variable or of time.

The present version of EQ6 does not make corrections for pressures off the pressure-temperature curve established on the data base. The standard curve is 1.013 bar (1 atm) up to 100°C, and the steam/water equilibrium curve at higher temperatures. Thus, pressure is currently parameterized as a function of temperature. Plans call for removing this limitation in the future (McKenzie et al., 1986); pressure will then be treated in the same fashion as temperature.

Temperature is specified as a function of the overall reaction progress (ξ) if the code is operating in reaction progress mode (no time frame; the **input** file variable **iopt1** is set to 0). It is specified as a function of time (t) if the code is operating in time mode (**iopt1** set to 1). As discussed previously, the code uses reaction progress as the primary independent variable in reaction path calculations, even in time mode. Nevertheless, one can still specify the temperature as a function of time, which is itself calculated as a function of reaction progress using eq (45). Two functional forms for specifying the temperature are presently available in EQ6.

If the **input** file variable **jtemp** is set to 0, the code treats temperature as a third-order polynomial:

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$$T = T_0 + k_{T1}x + k_{T2}x^2 + k_{T3}x^3 \tag{54}$$

Here T_0 is the temperature at x = 0 and x is either ξ or t, depending on the value of the **input** file variable **iopt1**. If this variable is set to 0, the code is in reaction progress mode and $x = \xi$. Otherwise, $x = t$.

If **jtemp** is set to 1, the temperature changes according to a fluid-mixing scenario. A second aqueous solution is assumed to be present as a special reactant. The temperature is then given by:

$$T = \frac{T_0 k_{T1} + \xi k_{T2}}{\xi + k_{T1}} \tag{55}$$

This equation assumes that the two fluids have equal heat capacities. Here T_0 is the temperature of the first fluid and k_{T2} that of the second.(The parameter k_{T1} is the ratio of the mass of the first fluid to the mass of the second fluid at $\xi = 1$. Normally the starting mass of the first fluid is very close to 1 kg, and 1 "mole" of the second fluid is also defined to be very close to 1 kg. If the relative rate of addition of the second fluid to the first is fixed at 1.0 (a logical choice, as this corresponds to a 50:50 mix), then k_{T1} can be taken as unity. Because k_{T1} must be defined as a constant, the relative rate of the reactant fluid must also be constant (i.e., $k_{+,2j}$ and $k_{+,3j}$ must each be set to 0).

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4. Types Of EQ6 Calculational Models

4.1. Introduction

EQ6 calculational models can first be broken down into "single-point" thermodynamic equilibrium calculations and reaction path calculations. A single point thermodynamic calculation is essentially just the special case of a reaction path with no steps. Reaction paths may be calculated for titrations, irreversible reaction in closed systems, and irreversible reaction in certain well defined types of open systems. Such calculations may be in reaction progress mode or time mode, depending on the absence or presence of actual rate laws.

The purpose of this chapter is to discuss the various kinds of calculations EQ6 is capable of making, to note the assumptions peculiar to the different kinds of calculational scenarios, and to introduce some of the corresponding key **input** file parameters. A comprehensive discussion of the **input** file is presented in Chapter 5.

4.2. "Single-Point" Thermodynamic Calculations

4.2.1. General Discussion

Single point thermodynamic calculations are useful for several purposes. For example, suppose an EQ3NR calculation shows that an aqueous solution is supersaturated with several minerals. An single point calculation can find which of possibly many such minerals would actually be present if the system were to reach thermodynamic equilibrium. A single point calculation with a temperature jump can be used to calculate the high temperature, *in situ pH* and other properties of an aqueous fluid in an autoclave experiment from measurements made on quenched fluid samples. A single point calculation is specified on the EQ6 **input** file by setting **kstpmx** = 0. This variable is the maximum number of steps of reaction progress that will be taken before the program terminates execution of the current problem.

4.2.2. Precipitating Supersaturated Phases

An aqueous solution may be supersaturated with respect to a large number of minerals. EQ6 can be used to calculate the assemblage of aqueous solution plus minerals that would result if the aqueous system reached thermodynamic equilibrium. In general, only a few of the phases that supersaturate the solution prior to precipitation appear in the final assemblage. This is a result of the common ion effect. For example, if the water is supersaturated with respect to more than one aluminum-bearing mineral, precipitation of any one of these minerals reduces the concentration and thermodynamic activity of Al^{3+}, thereby lowering the saturation index of all aluminum-bearing minerals. EQ6 finds the correct phase assemblage through a trial and error process discussed in Chapter 7. As part of the calculation, EQ6 determines any changes in the amount of solvent, the *pH*, the *Eh*, etc., that result from the precipitation of the mineral phases. An example of such a calculation is presented in Chapter 6.

This type of calculation typically occurs at the beginning of every EQ6 calculation, whether or not it is to be made for just one point. Precipitation of supersaturated phases (so that no solubility is exceeded) is a default condition. Any mineral loaded into memory is eligible to be precipitated unless the user suppresses it. This may be done using either the **nxopt** subset selection suppres-

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sion options or the **nxmod** suppression option (see Chapter 5 for discussion of these options). Exceptions to the subset selection suppression options may be specified (**nxopex**; see Chapter 5). By using the subset selection suppression option **all** in conjunction with the exceptions option, the user may specify just those minerals which are not to be suppressed.

4.2.3. The Temperature Jump

A temperature jump occurs when the temperature at the start of an EQ6 calculation does not match that of the initializing calculation done by EQ3NR or a previous run of EQ6. Temperature jumps may occur at the start of a reaction path calculation, as well as in a single point calculation. At the present time, pressure is constrained to be a function of temperature (a limitation of the current thermodynamic data files), so a corresponding *pressure jump* may occur as well. When generalized pressure corrections are available in EQ6, independent pressure jumps may also be possible.

EQ6 detects a temperature jump by calculating the starting temperature from the relevant parameters specified in the top part of the **input** file (**tempc0**, **jtemp**, **tk1**, **tk2**, and **tk3**; see Chapter 5) and comparing it with the temperature of the previous calculation (**tempci**) which appears on the bottom part of the **input** file.

The temperature jump is useful for calculating the thermodynamic properties of an aqueous solution when the measurements (as of *pH*, *Eh*, etc.) pertain to samples of the fluid that have been heated or cooled from the temperature of interest (such as the *in situ* temperature of an autoclave). Such sampling and measurement are normally carried out so as to avoid mineral precipitation. Thus, all mineral precipitation should be suppressed in the calculations. The **nxopt** subset selection suppression **all** (see chapter 5) is convenient for this purpose. Thus, one can use EQ6 to estimate the *in situ* or *at temperature pH* in an autoclave experiment from measurements including the quench (room temperature) *pH*. Other properties, such as the *in situ* oxygen fugacity, *Eh*, *pe*, saturation indices, reaction affinities, and equilibrium gas fugacities, are also calculated. An example of such a calculation is given in Chapter 6.

It is also possible to use a single point temperature jump calculation to find the quench properties that correspond to a fluid generated in an elevated temperature reaction path simulation. For purposes of comparing experimental results with theoretical simulations, it is better to estimate the *in situ* properties from the measured quench properties than to calculate the quench properties corresponding to the simulations. One may have to conduct a series of simulations in order to arrive at a satisfactory model for a single experiment. One might therefore have to perform a larger number of calculations to obtain the quench properties from the simulations than would be required to obtain the *in situ* properties from the experiment.

4.3. Reaction Path Calculations

There are three major system models for of reaction path calculation in EQ6:

- Titration (**nmodl1** = 1).
- Closed system (**nmodl1** = 2).

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- Fluid-centered flow-through open system (**nmodl1** = 3).

Here **nmodl1** is a parameter which appears on the **input** file. Another possible system model, not currently implemented in EQ6, would be a solid-centered flow-through open system. Any of the above system models can be modified so that the system behaves as though open to a large external reservoir of gas. This results in models with fixed fugacities for the relevant gas species. The "closed" system model is therefore partially open under this option.

Reaction path calculations may be long and complex. The step size control mechanism is a major factor in determining the run time. In its normal calculational mode, EQ6 generates finite-difference approximations of the iteration variables used in the thermodynamic calculations, using data from the most recent points of reaction progress. It uses these to generate starting estimates at a new point. The step size is normally constrained to a range in which these approximations are accurate. Furthermore, EQ6 also normally constrains the step size in the process of locating phase boundaries (where a phase either appears or disappears). A consequence of these step size control factors is that the state of the reacting system is usually calculated at numerous points of reaction progress between those for which printed or plotted output is generated.

When operating in time mode, the finite-difference predictor functions (here generated for both algebraic master variables and rate functions) must be kept accurate in order to get an accurate integration. The normal phase boundary location constraints must also be operative. Full accuracy constraints are also required for any type of flow-through model, in time mode or not. All of these conditions require the use of normal calculation mode. However, in reaction progress mode with **nmodl1** = 1 or 2, significant reduction in run time may be achievable by modes employing more relaxed constraints on the step size.

EQ6 therefore offers two special calculational modes for obtaining shorter run times. *Economy mode* is selected by setting **nmodl2** = 1 (see Chapter 5). This loosens the general step size constraints associated with maintaining accuracy in the finite-difference predictor functions. It causes EQ6 to operate in a calculational mode more like that of PHREEQE (Parkhurst, Plummer, and Thorstenson, 1980). Economy mode does not compromise the code's abilities to locate phase boundaries. *Super economy mode* may be selected by setting **nmodl2** = 2. In this mode, the step size is typically larger, usually matching the desired print interval. In super economy mode, the code does not locate phase boundaries. Selection of economy mode or super economy mode is disallowed when other model constraints (such as **nmodl1** = 3) require normal calculational mode.

The pre-Newton-Raphson optimization algorithm in the present version of EQ6 has limited capabilities (see Chapter 7). This often causes the subsequent hybrid Newton-Raphson iteration to fail to converge when the code is run in economy mode or super economy mode. The code then recovers by cutting the step size so as to obtain convergence. Thus, usage of these calculational modes often fails to produce any real economy. The use of these modes in the present version of EQ6 is therefore not recommended.

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4.3.1. Simulating a Titration Process

4.3.1.1. General Discussion

A titration process involves the addition of reactants to a system. This option is selected in EQ6 by setting **nmodl1** = 1 on the **input** file. The titration mode of EQ6 is strictly non-kinetic, so only relative rates may be specified. The concept of relative rates was explained in Chapter 3. In the titration model, if there is only one reactant, its relative rate is usually set to 1.0. The number of moles of reactant reacted is then normally numerically equivalent to the reaction progress variable ξ.

The titration concept is illustrated in Figure 2. At each step of reaction progress, a small quantity of reactant (represented by the small cubes) is added to the contents of the flask, which is a system comprised of the aqueous solution and any product phases. After each addition, the increment of reactant dissolves and any product phases re-equilibrate with the aqueous solution. Usually some secondary phases are transients- that is, phases that disappear later on in the process. The growth and dissolution of such phases proceeds at whatever rate is required to maintain solubility equilibrium.

If the aqueous solution becomes saturated with a reactant (in equilibrium with it), then the substance continues to be titrated into the aqueous system according to the governing relative rate law. In the titration model, the calculated rate functions are not truncated by the absence of a thermodynamic driving force, as they are under the closed system (**nmodl1** = 2) and fluid-centered flow-through open system (**nmodl1** = 3) options. However, the mass increments under the condition of saturation effectively do not dissolve, but merely accumulate as secondary mass of the same substance. It is as though the small cube in Figure 2 simply fell to the bottom of the flask without dissolving.

A reactant that is titrated into the system can be any kind of substance: a mineral, non-mineral crystalline solid, a glass phase, a "whole" rock, a gas, or another aqueous solution. The key point is that each reactant must have some stoichiometry. It may or may not have any defined thermodynamic stability (if not, then it is always unstable, and there is no possible saturation condition). A more detailed discussion about reactants and how the user of EQ6 deals with them is presented in Chapter 5.

4.3.1.2. Fluid Mixing

A good example of a titration model is fluid mixing. The reactant in this case is a second aqueous solution. It is entered on the **input** file as a *special reactant* (**jcode** = 2). The composition of one mole of this substance is given that file. See Chapter 5 for details. For aqueous solution reactants, the recommended procedure is to equate one "mole" with the mass of solution containing 1 kg of solvent water. The composition of such a solution must be determined by a separate EQ3NR calculation. The special reactant composition of this solution can be conveniently extracted from the EQ3NR **pickup** file.

One aspect of fluid mixing calculations in EQ6 is that the mass of the system being titrated, and the contained mass of solvent water, increases dramatically. At $\xi = 0$, the mass of solution is around 1 kg and the solvent mass = 1 kg (barring any equilibration at this point). At $\xi = 1$, using

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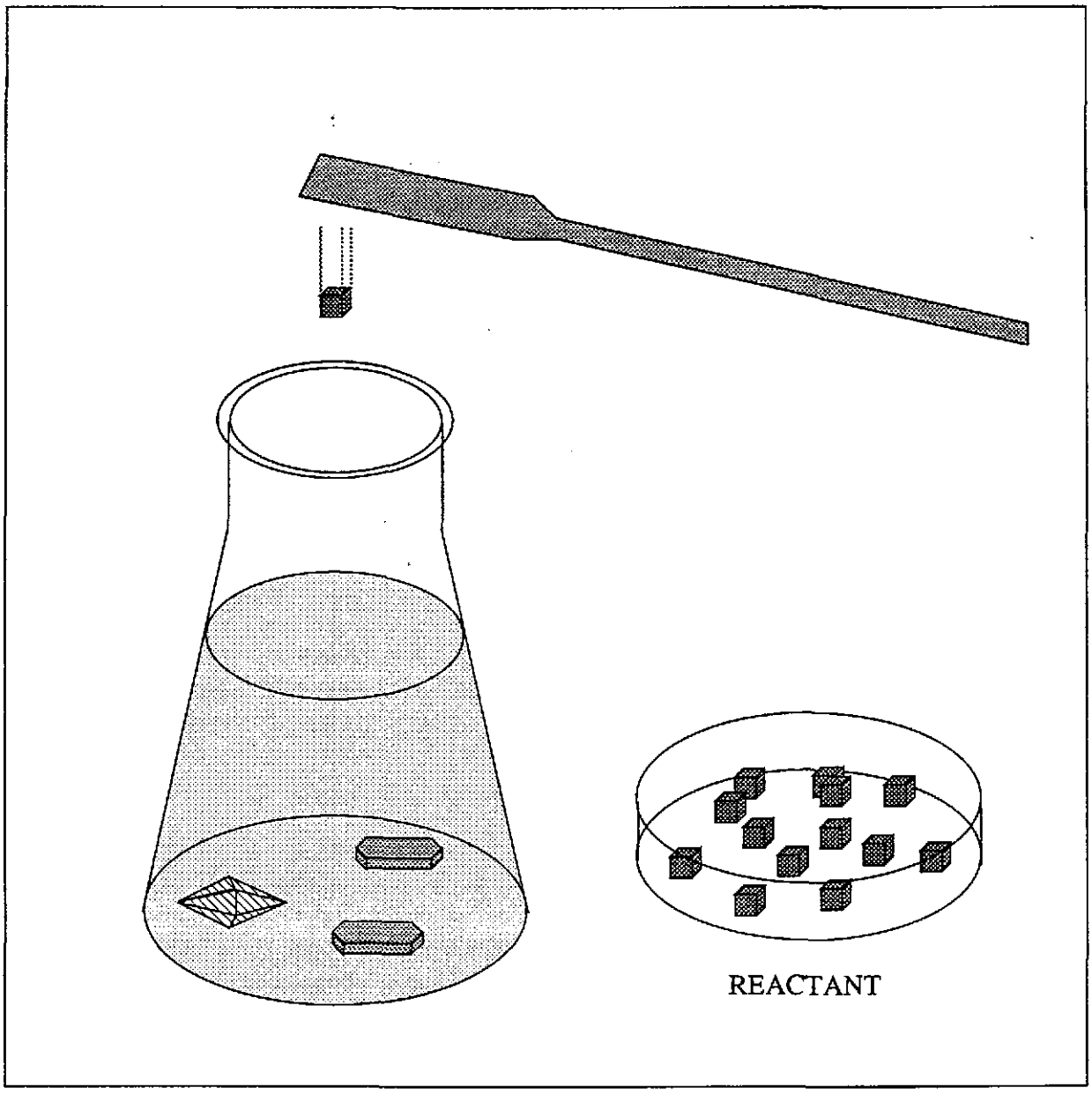

Figure 2. Conceptual model of a titration process. A reactant is added in small increments (depicted as small cubes) to a system consisting of an aqueous solution and various product minerals. Dissolution of each increment of reactant changes the fluid chemistry, driving the formation of product phase (depicted by the diamond-shaped and tabular crystals on the bottom of the flask).

the above recommended definition of one "mole" for an aqueous solution, the mass of solution is around 2 kg and the mass of solvent water is also around 2 kg.

It is possible to run such a calculation in which the two waters being mixed have different temperatures (See Chapter 5). Here, the user specifies **jtemp** = 1 on the **input** file. The temperature of the first aqueous solution (the one the second is being titrated into) is specified as **tempc0.** The temperature of the second water is given as **tk2.** The ratio of the mass of the first water to that contained in one "mole" of the second is specified as **tk1**. With the above definition of one

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"mole" of aqueous solution, **tk1** = 1. This temperature calculation currently assumes that the heat capacity of the two initial waters and all mixtures of the two is the same.

4.3.1.3. Evaporation

Evaporation can be thought of as a sort of negative titration, in which the titrating substance, solvent water, is removed from the system rather than added to it. An evaporation run is easily set up by declaring $H_2O_{(l)}$ a reactant and specifying a negative relative rate. If v_j^{rel} is set to -1, then each unit advancement of ξ corresponds to the removal of 1 mole of solvent. Recall that the number of moles of water in 1 kg is about 55.51. Assuming the usual case in which there is an amount of aqueous solution containing 1 kg of solvent, the upper practical limit on ξ (specified by the parameter **zimax**, see Chapter 5) would be about 55.51. If the extent of evaporation would increase the ionic strength above about one molal, the user should specify an activity coefficient option that is valid for the case of highly concentrated salt solutions. In the present version of EQ3/6, the only option suitable for this is Pitzer's equations (**iopg1** = 1).

4.3.2. Calculating the Reaction Path in a Closed System

Calculating the reaction path in a closed system is conceptually and calculationally very similar to the case of computing a simulation of a titration process. This option is specified on the **input** file by **nmodl1** = 2 (**nmodl1** = 0 defaults to **nmodl1** = 2). The conceptual process is illustrated in Figure 3. The chief difference between the closed system model is that the unreacted masses of reactants are considered to be *in the system*, instead of outside it. A small increment of the remaining mass of each reactant dissolves at each step of reaction progress. The effect is the same as in the titration model, with one exception.

In the closed system, a reactant that saturates may be treated in one of two ways. If a precipitation kinetics rate law is specified for such a reactant, then the unreacted mass is treated according to the rate law specifications, as is the case under the titration option. However, if no such rate law is specified, then all of the unreacted mass is immediately transferred to secondary mineral status. The governing rate function is then set to zero. This is primarily a consequence of there being no material left to react, although it is also true that some rate laws (see Chapter 3) evaluate to zero when the driving affinity is zero. In this case, the rate description of the formation/dissolution of the phase shifts from the specified rate law to the rate that is consistent with keeping the reaction at equilibrium.

4.3.3. A Fluid-Centered Flow-Through Open System

The fluid-centered flow-through system is a special type of open system which follows the evolution of a particular packet of water as it flows through a medium. This option is specified on the **input** file by **nmodl1** = 3. The medium could be a fracture, a pipe, or a porous medium. The concept is illustrated in Figure 4. Reactants are presumed to line the medium in homogeneous fashion and interact with the fluid packet as it passes by. Alternatively, there may be no reactants, only a change in temperature or pressure. Either way, secondary phases form as a result. As the packet moves on, it physically separates from the masses of secondary phases produced. The result is that transiently formed product phases do not have the opportunity to redissolve in that particular packet of fluid. A consequence is that overall equilibrium can be achieved sooner in terms of reaction progress than is the case in the closed system.

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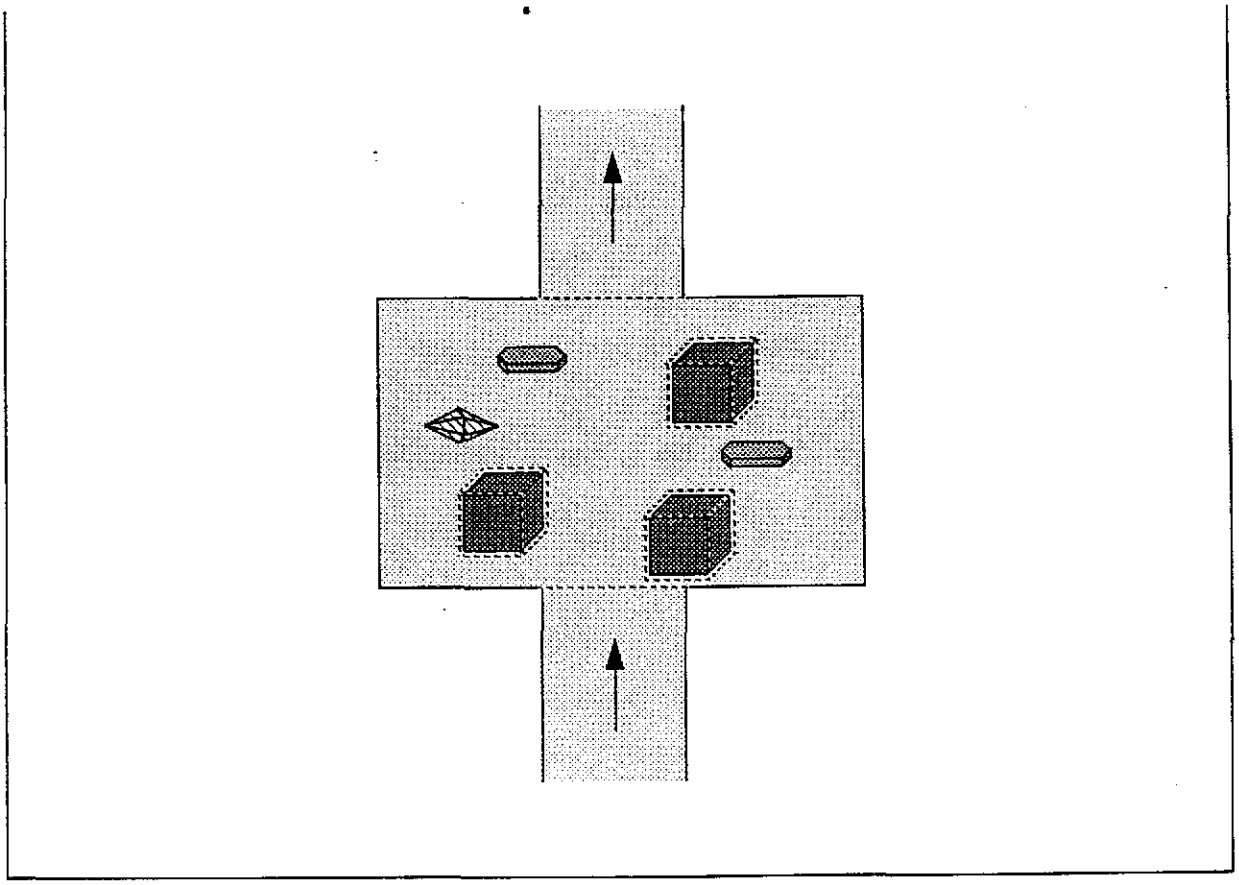

Figure 5. Conceptual model of irreversible reaction in a solid-centered flow-through open system. Water flows in at a constant composition and flows out at another, variable composition. The direction of flow is shown by the arrows. The reactant is represented by the cubes. The product minerals are depicted by diamond-shaped and tabular crystals. All solids are constrained to remain physically in the system.

This option is invoked by specifying each gas to be so treated, the desired fugacity, and an optional mass of the gas to be added to the system at the start of the run. Calculationally, the "external reservoir" is treated as part of the reacting system, and the desired fugacity is maintained by the solubility equilibrium for a fictive mineral whose composition is identical to that of the gas. Without the presence of such a phase, the desired fugacity is really only an upper limit. That is the reason for the option to add mass of the gas component to the system. This permits the user to saturate the system. The mass of such a fictive mineral is finite and may be exhausted. The user may wish to choose the initial addition of mass of gas to the system in order define a point at which the external reservoir of the gas is exhausted.

The idea behind using a fictive mineral is as follows. Reactions for the dissolution of gas species are maintained on the data file in order to permit the calculation of equilibrium fugacities. Such a reaction is illustrated by the case for $CO_{2(g)}$:

$$CO_{2(g)} + H_2O_{(l)} = H^+ + HCO_3^- \tag{56}$$

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The corresponding mass action equation is:

$$log a_{H^+} + log a_{HCO_3^-} - log f_{CO_2} - log a_w = log K_{CO_{2(g)}} \tag{57}$$

Now consider the parallel reaction for the dissolution of the corresponding fictive mineral ($CO_{2(s)}$):

$$CO_{2(s)} + H_2O_{(l)} = H^+ + HCO_3^- \tag{58}$$

The corresponding mass action equation is:

$$log a_{H^+} + log a_{HCO_3^-} - log a_w = log K_{CO_{2(s)}} \tag{59}$$

(the thermodynamic activity of a pure solid is unity). Subtracting eq (56) from eq (58) and eq (57) from eq (59) respectively yields:

$$CO_{2(s)} = CO_{2(g)} \tag{60}$$

and

$$log f_{CO_2} = log K_{CO_{2(s)}} - log K_{CO_{2(g)}} \tag{61}$$

This shows how a fixed fugacity model can be imposed by equilibrium with a fictive solid. A slight rearrangement of eq (57) shows how to choose the equilibrium constant for the fictive mineral:

$$log K_{CO_{2(s)}} = log K_{CO_{2(g)}} + log f_{CO_2} \tag{62}$$

Invocation of this option causes the corresponding gas reaction and its thermodynamic $^{\delta\alpha\tau\alpha}$ to be copied into the corresponding mineral data arrays. The *log K* function is then modified according to eq (57).

4.3.6. Changing Temperature and Pressure

The temperature and pressure of most reaction path runs are both constant. However, it is possible to make calculations in which they vary as a function of reaction progress or time. In the present version of EQ6, the pressure is parameterized as a function of temperature. It is not yet possible to use EQ6 to calculate models in which the pressure varies independently. The means of executing this type of option are described in Chapter 5. This is a particularly useful option to use in conjunction with the fluid-centered flow-through system mode of calculation (**nmodl1** = 3). This combination permits calculation of consequences of heating and cooling as a packet of water moves through a pipe, fracture, or other medium.

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5. The EQ6 Input File: Setting Up The Problem

5.1. Input File Characteristics

We examine in this chapter the EQ6 **input** file. This file is the means by which the user specifies a problem to be solved by the code. The user must supply a compatible **data1** file, and the results obtained may differ if the problem is run with more than one such data file. Some examples of EQ6 **input** files are presented in this chapter, and the reader will find more examples, along with the corresponding **output** files, in Chapter 6 and Appendix E.

The reader is already presumed to be familiar with the companion code EQ3NR and its **input** file structure and contents as described in the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b). Water compositions intended for use in reaction path calculations can not be directly input to EQ6. Instead, they must first be processed through EQ3NR. The necessary data is then written on the EQ3NR **pickup** file, which is then used in constructing input for EQ6.

The EQ6 **input** file is physically analogous to the EQ3NR **input** file and is processed during code execution in like manner. Like the EQ3NR **input** file, it presently exists in one of two formats. "W" format, the original format, is a compact form more suitable for use by experienced users. "D" format is a menu-style format that is much less compact, but which may be easier to use for less experienced users. The present manual will focus more on the "W" format, as this naturally leads into a discussion of the relevant code variables. Some examples will be given of problems presented in both formats.

An EQ6 **input** file of either format contains a title field to provide space for internal documentation. In addition, an **input** file may contain remarks in comment lines. These are marked by an asterisk in column one and are analogous to comment lines in FORTRAN source code. They may appear anywhere in the **input** file.

Like EQ3NR, EQ6 writes an "instant echo" of the **input** file on the **output** file. This is particularly helpful in identifying the causes of read format errors, which most commonly occur when a line is missing or out of the proper sequence. This feature also provides a record of the **input** file used for a given run. However, it does not include comment lines. If necessary, a lost **input** file may be recovered (less comment lines) by extracting the echo from the **output** file.

The number of lines in an EQ6 **input** file in either format is variable. Whether or not some potential lines appear in a given file depends upon the contents of other lines. Some items, such as blocks of data for the set of reactants, appear in succession until a terminator appears. Certain options, if invoked, require corresponding additional lines of input.

Users deal with species in terms of their names, which are 24-byte character variables. There are no species index numbers for users to bother with. Internally, EQ6 sets up its own internal indexing schemes at run time. The species names given on the **input** file must match perfectly with those on the data file used or the code will not recognize them. In such a case, the code will write an error message and terminate activity on the current problem input.

The recommended way of creating a new **input** file is to use an old one as a template. This works best if the old one is as close as possible to the desired new one. To this end, a representative se-

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lection of sample input files is included in the distribution package for EQ3/6 (Wolery and Daveler, 1992a). The distribution package also includes some software which converts input files in "W" format to "D" format. Using this template approach reduces the necessary knowledge a user must have concerning **input** file formats, and minimizes the need to consult the related documentation.

Structurally, the EQ6 **input** file consists of two parts. The first or top part contains: text documenting the problem; various model options (e.g., closed vs. open system, time frame vs. no time frame; solid solutions or no solid solutions); various print and debugging options; specification of irreversible reactions ("reactants") and corresponding rate law parameters; and tolerance and setscrew parameters which affect the numerical behavior of the code.

The second or bottom part corresponds to the EQ3NR **pickup** file. When EQ3NR writes this part, it contains: text documenting the EQ3NR problem; some model options which carry over from EQ3NR to EQ6; and a compact description of the aqueous solution. EQ6 writes its own **pickup** file, which is a complete **input** file that can be used to continue a reaction path calculation from the point reached at the end of the current run. In such a case, the bottom part of the file, the text documenting the EQ3NR problem is replaced by text describing the EQ6 problem, and the compact description of the aqueous solution is replaced by a compact description of the equilibrium system (aqueous solution plus phases in equilibrium with it). There is an option to read the "bottom" part of the input for a problem directly from the EQ3NR **pickup** file. This is rarely used and its use is currently not recommended.

In normal usage, users should not alter the contents of the bottom part of the **input** file as written by a previous EQ3NR or EQ6 run, except for the alter/suppress options (see **nxmod**, below). These options permit suppressing the formation of individually selected species, or changing the equilibrium constants that determine their formation. Pure mineral species may also be suppressed using subset-selection options (See **nxopt**, below) that appear on the top part of the **input** file.

Technically, multiple problems may be specified on an EQ6 **input** file, in which case there is a top and bottom part for each problem. However, such stacking is almost never done, owing largely to the complexity of a reaction path problem and the execution time required to solve it. In fact, it is sometimes convenient to break a given problem up into run segments, each of which corresponds to a single code execution. Each new segment is started using as the **input** file the **pickup** file generated for the previous run segment. The advantage of this approach is that a code user can check the results of a short run segment, especially a the start of the problem, to confirm that the calculation is really proceeding as intended.

The problem input for a given code execution must be entirely in one format. That is, it is not possible to mix "W" and "D" formats in any way, such as "W" format for one problem and "D" for a second, or "D" for the top part and "W" for the bottom part. Because EQ3NR writes its **pickup** files in the same format as the corresponding **input** files, the user should run EQ3NR in the same format that he intends to use with EQ6.

Any EQ6 **input** file depends on the results of a previous EQ3NR or EQ6 run. Those results depend in turn on the **data1** file used. Thus, the contents of any EQ6 **input** file also depend on that

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data1 file. Running this **input** file with a different **data1** file is a dangerous practice. Running with a different kind of **data1** file, such as substituting the **com** file for the **hmw** file, should never be done. The problem may not run at all. If it does, the results may be markedly different than if the **data1** file now employed had been used consistently through the entire calculational chain of previous EQ3NR and EQ6 runs. Even substituting a more recent version of the same kind of data file may cause such problems. Use of the alter/suppress (**nxmod**) options have the potential to cause similar problems. It is safest to invoke these options in the EQ3NR run which initiates a given calculational chain.

The "W" format **input** file is read by module **readz.f**, which in turn calls module **readrt.f** to read blocks of rate law input. The source code for these modules is extensively documented internally by of comment lines. On-line access to the source code of this module may helpful to users, serving as a kind of on-line documentation. The "D" format **input** file is read by the module **rd6-new.f**, which calls a number of other modules in carrying out this function (the EQ6 modules **rd6sup.f**, **rd6ff.f**, **rd6rea.f**, **rd6tol,f**, **rdmole.f**, **rd6log.f**, and **rd6prs.f**, and the EQLIB modules **rdtyp0.f**, **rdastr.f**, **rdtyp6.f**, **rdtyp7.f**, and **rdtyp8.f**). The source codes of these modules may also be helpful to users as on-line documentation.

5.2. Using the Input File: General Discussion

The purpose of this section is to address the major functional concerns regarding the use of the EQ6 **input** file, discussing for each the relevant features and variables. Because the discussion will involve the relevant **input** file variables, it is somewhat slanted in terms of illustration toward the "W" format. An understanding of the concerns discussed here are critical, however, toward the proper use of both the "W" and "D" **input** file formats. This section does not address every variable that appears on the **input** file. Technical details regarding each such variable, and how it is handled on the **input** file in either format, will be given in the following sections of this chapter.

EQ6 will stop if a reaction path has reached a point of overall thermodynamic equilibrium. This occurs in the closed or fluid-centered flow-through open system models when all reactants are either exhausted or have saturated the aqueous solution. The code also stops if, in time frame mode, the time has extended to infinity. The **input** file also provides several arbitrary controls on the length of a run segment. The parameter **zimax** is an upper limit on the value of the overall reaction progress parameter, **zi1** (ξ). This limit will be located exactly if **zi1** would otherwise exceed it. The parameter **timemx** is an upper limit on time (in seconds). It is not located exactly, but the code (when operating in the time frame mode) will stop after the first step which exceeds this limit (recall that the code always uses reaction progress as the independent variable). The parameter **kstpmx** is the maximum allowed number of steps in the run segment and perhaps offers the easiest way for the user to control the length of a run. A "single point" thermodynamic calculation (e.g., precipitate minerals until no supersaturations remain and then stop) is carried out by setting **kstpmx** = 0.

The parameter **cplim** is a limit on the number of computing units used. A computing unit is an administrative measure of the usage of a computer, and is installation dependent. The **cplim** feature is not active in the LLNL version of EQ6. If desired, it should be enabled locally at installations at which the consequence of exceeding the predetermined limit on computing units is catastrophic termination resulting in no **pickup** file being generated. A call to a local system rou-

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tine must be provided to return the number of computing units used. Several commented-out examples are given in the EQ6 source code. The value of **cplim** should be sufficiently less than the actual administrative limit for EQ6 to write a pickup file and terminate before catastrophic termination occurs.

EQ6 does not print the state of the geochemical system being modeled at every step of reaction progress. It does give such a print when a significant event occurs, such as the precipitation of a new secondary phase or the point of exhaustion of a reactant phase. Apart from these kinds of print points, the user may specify three kinds of print intervals, one linear in reaction progress (**dzipr**), the second logarithmic in reaction progress (**dzprlg**), and the third defined in terms of the number of steps since the last print point (**ksppmx**). The print points generated by the first two of these variables are independent of the occurrence of the other kinds of print points mentioned above. The logarithmic print interval usually provides the best spacing of detailed information. A too-small value of the linear print interval could produce a lot of not very useful printout. Consequently, the default value for the linear print interval is pseudo-infinite, which turns off this print control mechanism. Reasonable values for the logarithmic print interval range from 0.25 to 1.0. The default is 0.5. The default for **ksppmx** is 25.

There are three general option switch arrays, which are analogous to those in EQ3NR. The **iopt** switches are model option switches. The **iopr** switches are print option switches, and the **iodb** switches are debugging print options. In general, these switches do not correspond specifically to their EQ3NR counterparts. For example, **iopt1** in EQ6 determines whether the code runs in ordinary reaction progress mode (no time frame) or kinetic reaction progress mode (time frame). In contrast, **iopt1** in EQ3NR determines the choice of redox variable used in the problem input. This function has no meaning for EQ6. Conversely, the function of **iopt1** in EQ6 has no meaning for EQ3NR. Some of these option switches, however, are the same for both codes. However, there are also some cases in which the same specific function exists for both codes but is not assigned to the same option switch. As was the case for EQ3NR, the **iodb** switches should all be set to zero, except in debugging runs.

The activity coefficient options are specified on the bottom part of the input by the **iopg1** and **iopg2** option switches. The **iopg** option switches, which deal with activity coefficients, have the same meanings as in EQ3NR. The user should make the desired selections in the initializing EQ3NR run. It is not advisable under most circumstances to later change these options without going back to EQ3NR and repeating the initializing calculation.

Much of the work in intelligent reaction-path modeling involves deciding which secondary phases will be allowed to precipitate. The EQ6 code itself can decide if a given phase must precipitate in order to avoid supersaturating the aqueous solution. The code does not know, however, whether it would make more sense, geochemically speaking, to precipitate the phase or to allow the supersaturation. The default condition is that EQ6 will precipitate the phase. Every mineral read from those on the data file is a potential candidate. The user, however, can specify that precipitation of certain phases is to be suppressed. There are two methods of doing this on the **input** file.

The first method is to use the subset-selection suppression options for pure minerals. The parameter nxopt is the number of such options given on the file. The two options, entered as **uxopt(n)**, **n = 1**, **nxopt**, are **all** and **alwith**. If **all** is used, **nxopt** should be 1 and no **alwith** options should

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appear. Each **alwith** option requires a separate entry, and must be followed by an argument (**uxcat(n)**) that is the symbol of a chemical element on the data file. Under the **all** option, all pure minerals are suppressed. Under an **alwith** option, those minerals containing the specified elements are suppressed. Note that the sub-set-selection suppression options do not apply to solid solutions. They may be extended to do this in the future. At the present time, however, solid solutions must be either all suppressed by setting **iopt4** = 0 or by suppressing each individual solid solution via **nxmod** alter/suppress options (see below).

Exceptions to the **all** and **alwith** options may also be specified. The parameter **nxopex** is the number of exceptions. The names of the exceptions are entered as **uxopex(j,n)**, j = 1, 2, **n** = 1, **nxopex**. Thus, to allow only amorphous silica, kaolinite, and ferric hydroxide as potential precipitates, one would specify on the **input** file:

nxopt	= 1
uxopt(1)	= all
nxopex	= 3
uxopex(1)	= sio2(am)
uxopex(2)	= kaolinite
uxopex(3)	= fe(oh)3

Note that this situation is the complement of the normal one where every mineral read from the data base is allowed to precipitate. To suppress precipitation of all potassium and magnesium minerals, except K-feldspar, illite, and sepiolite, one would specify:

nxopt	= 2
uxopt(1)	= alwith k
uxopt(2)	= alwith mg
nxopex	= 3
uxopex(1)	= k-feldspar
uxopex(2)	= muscovite
uxopex(3)	= sepiolite

The "**nxmod**" alter/suppress functions (using the parameters **nxmod**, **uxmod**, **jxmod**, **kxmod**, and **xlkmod**), described sufficient detail earlier in this section, permit suppression of individually named minerals. More generally, they permit either suppression of a given species (aqueous species, pure mineral, gas, or solid solution) or, for aqueous species, pure minerals, and gases, changes in the associated equilibrium constants. They are also in the EQ3NR code (where they are relevant only in the case of aqueous species), and are passed on to EQ6 through the pickup file. The **nxmod** alter/suppress options are the only part of the lower half of the EQ6 **input** file that the user should modify in normal use.

The other major block of input the user must provide on the **input** file defines the reactant phases and how they react irreversibly in an aqueous geochemical system. The parameter **nrct** is the number of reactants so defined. This number may be zero, for example, if the user wants to cal-

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culate just the consequences of heating or cooling an aqueous solution. If it is not zero, a sequence of input blocks follows, one per reactant.

A reactant input block begins with the name of a reactant (**ureac(j,nrc)**), where **nrc** denotes the **nrc**-th reactant on the input file). This is followed by a species type code, **jcode(nrc)**, which has the following meanings:

0	Pure mineral.
1	Solid solution.
2	Special reactant.
3	Aqueous species.
4	Gas species.

A special reactant is a species that is not on the supporting thermodynamic data base. A special reactant could be a pure mineral, a whole rock (oceanic basalt was treated this way by Wolery, 1978) or a second aqueous solution in a fluid-mixing scenario. Special reactants are specified in the EQ6 **input** file by listing the number of moles of each component element with respect to some reference unit, usually moles. The parameter **jreac(nrc)** is a status code that should be left blank when preparing an EQ6 **input** file. The parameter **morr(nrc)** is the number of reference units of reactant. If the reactant is a whole rock or second aqueous solution, it is convenient to use 1 kg mass as the reference unit instead of moles. The parameter **modr(nrc)** is the number of reference units of reactant that have been destroyed. The user should leave this parameter blank when creating a new **input** file, and normally should not change the EQ6-written **morr** and **modr** values on a **pickup** file.

If the reactant is a solid solution, the names of the pure mineral end- members (**uendb(j,nxr)**, **j** = 1, 2, for the **nxr**-th reactant that is a solid solution) must follow, along with the corresponding mole fractions. These will be normalized if they do not sum to unity. If the reactant is a special reactant, a value for the volume (cm^3) of one mole of substance under the conditions of the run (**vreac(nrc)**) may be entered, followed by the symbol for each chemical element (**uesrb(ncb,nsr)**, where the reactant is the **nsr**-th special reactant) and the corresponding number of moles of the element per mole of special reactant. For special reactants that are whole rocks or aqueous solutions, it is recommended that one arbitrarily equate one mole with a mass of 1 kg.

The surface area of a reactant is read in as **sk(nrc)**. This is given in units of square centimeters. It is the absolute surface area, not the specific surface area, which might have units of cm^3/mol or cm^3/g. The surface area may or may not actually be used in the calculations, depending on the rate options selected. There are currently two possible treatments, determined by the reactant surface area code **nsk(nrc)**:

0	Constant surface area.
1	Surface area changes in proportion to the reactant mass.

Information Only

The default for **sk(nrc)** is 100 cm^3. The parameter **fk(nrc)** is a fudge factor equal to the ratio of effective surface area to total surface area. It is used in the calculations only when **sk(nrc)** is used. Its default value is unity.

The parameters **nrk(nrc)** and **nrpk(nrc)** are the net forward (dissolution) and net reverse (precipitation) rate law codes. The various models were discussed in Chapter 3. The options for **nrk** are:

-1	Use the net reverse form (**nrpk** must be 1, 2, or 4).
0	Illegal value.
1	Relative rate law (arbitrary kinetics).
2	Transition-state theory rate law (**jcode** must be 0 or 1).
3	Linea rate law.
4	Activity product term rate law (**jcode** must be 0 or 1).

The options for **nrpk** are:

-1	Use the net forward form (**nrk** must be 1, 2, or 4).
0	Instantaneous adjustment to partial equilibrium.
1	Relative rate law (arbitrary kinetics).
2	Transition-state theory rate law (**jcode** must be 0 or 1).
3	Linear rate law.
4	Activity product term rate law (**jcode** must be 0 or 1).

In addition, **nrk** and **nrpk** can not both be 1 or 3 for the same reactant.

Kinetic rate laws in addition to the ones listed above can be added by defining new **nrk** options in the module **reacts.f** and making necessary additions to module **readrt.f**, which reads the **input** file, and module **scribe.f**, which writes the **pickup** file.

5.3. "W" Format

A short summary of the contents of the EQ6 **input** file in "W" format is given in Tables 1 and 2. Table 1 is a summary of the complete file, but it refers to Table 2 for the case of rate law input. Parameters for which it is recommended that the user simply take the default value are marked by a superscript "^{D}." To take the default value for a given parameter, leave the corresponding input field blank. Parameters whose input values are subjected to a range test are marked by a superscript "^{R}." Following Tables 1 and 2 is Table 3, which lists and describes each of the **input** file parameters. This is followed by an example of an EQ6 **input** file in "W" format. More examples are presented in Chapter 6. A discussion of the EQ6 **input** file in "D" format is given in the following section of this chapter.

The EQ6 **input** file is fairly lengthy, and it requires some work to learn how to use it. However, in compensation, EQ6 offers a lot of flexibility by combining many capabilities in a single code.

Information Only

Table 1. Short Summary of the EQ6 **input** file ("W" format, read by module **readz.f**).

TOP PART

Parameters	Format
Do **n** from 1, ending with the string 'endit.' in column 1:	
ntitl1(n)	(a80)
End do	
nmodl1, nmodl2	(12x,i2,22x,i2)
tempc0, jtemp	(12x,e12.5,12x,i2)
tk1, tk2, tk3	(3(12x,e12.5))
zistrt, zimax	(2(12x,e12.5))
tstrt, timemx	(12x,e12.5,12x,e12.5)
kstpmx, cplim	(12x,i12,12x,e12.5)
dzprnt, dzprlg, ksppmx	(2(12x,e12.5),12x,i5)
dzplot, dzpllg, ksplmx	(2(12x,e12.5),12x,i5)
ifile	(12x,i2)
iopt1 - iopt10	(12x,10i5)
iopt11 - iopt20	(12x,10i5)
iopr1 - iopr10	(12x,10i5)
iopr11 - iopr20	(12x,10i5)
iodb1 - iodb10	(12x,10i5)
iodb11 - iodb20	(12x,10i5)
nxopt (^{R})	(12x,i2)
If **nxopt** > 0 (have pure mineral subset-selection suppression options):	
Do **n** = 1, **nxopt**	
uxopt(n), uxcat(n)	(12x,a6,1x,a12)
nxopex (^{R})	(12x,i2)
If **nxopex** > 0:	
Do **i** = 1, **nxopex**	

Information Only

```
        uxopex(i)                                   (12x,a12)
      End do
    End if
  End do
End if

nffg (R)                                            (12x,i2)
If nffg > 0 (have fixed fugacity options):
  Do n = 1, nffg
    uffg(n)(1:12),moffg(n),xlkffg(n)                (12x,a12,2(12x,e12.5)
  End do
End if

nrct (R)                                            (12x,i2)
If nrct > 0 (have reactants)
  Do n = 1, nrct:
    ureac(n)                                        (12x,a18)
    jcode(n), jreac(n)                              (12x,i2,22x,i2)
    morr(n), modr(n)                                (12x,e12.5,12x,e12.5)
    If jcode(n) = 0 (pure mineral reactant):
      Specify rate data- see Table 2.
    Else if jcode(n) = 1 (solid solution reactant):
      nxr = nxr + 1
      Do i from 1, ending with the string 'endit.' in the
      uendb field:
        uendb(i,nxr), rxbarb(i,nxr)                 (3x,a18,3x,e12.5)
      End do
      Specify rate data- see Table 2.
    Else if jcode(n) = 2 (special reactant):
      nsr = nsr + 1
      vreac(n)                                      (12x,e12.5)
      Do i from 1, ending with the string 'endit.' in the
      uesrb field:
        uesrb(i,nsrt), cesrb(i,nsr)                 (3x,a6,3x,e12.5)
```

Information Only

End do

Specify rate data- see Table 2.

Else if **jcode(n)** = 3:

Specify rate data- see Table 2.

Else if **jcode(n)** = 4:

Specify rate data- see Table 2.

End do

End if

dlzidp (^{D})	(12x,e12.5)
tolbt (^{D}), **toldl** (^{D}), tolx (^{D})	(3(12x,e12.5))
tolsat (^{D}), **tolsst** (^{D})	(2(12x,e12.5))
screw1 (^{D}), **screw2** (^{D}), **screw3** (^{D})	(3(12x,e12.5))
screw4 (^{D}), **screw5** (^{D}), **screw6** (^{D})	(3(12x,e12.5))
zklogu (^{D}), **zklog1** (^{D}), **zkfac** (^{D})	(3(12x,e12.5))
dlzmx1 (^{D}), **dlzmx2** (^{D}), **nordlm**	(2(12x,e12.5),12x,i2)
itermx (^{D}), **ntrymx** (^{D})	(12x,i2,22x,i2)
npslmx (^{D}), **nsslmx** (^{D}), **ioscan** (^{D})	(12x,i2,2(22x,i2))

LOWER PART

Parameters	Format
Do **n** from 1, ending with the string 'endit.' in column 1:	
utitl2(n)	(a80)
End do	
tempci	(12x,e12.5)
nxmod	(12x,i2)
If **nxmod** > 0 (have alter/suppress options):	
Do **i** = 1, **nxmod**	
uxmod(i)	(12x,a18)
jxmod(i), **kxmod(i)**, **xlkmod(i)**	(12x,i2,22x,i2,22x,e12.5)

Information Only

```
  End do
End if

iopg1, iopg2, iopg3                                  (12x,2,2(22x,i2))
iopg4, iopg5, iopg6                                  (12x,i2,2(22x,i2))
iopg7, iopg8, iopg9                                  (12x,i2,2(22x,i2))
iopg10                                               (12x,i2)
kct, ksq, kmt                                        (12x,i2,2(22x,i2))
kxt, kdim, kprs                                      (12x,i2,2(22x,i2))

Do i = 1, kct:
  uelemb(i), mteb(i), mteaqb(i)                      (3x,a6,9x,e25.15,3x,e25.15)
End do

electr                                               (18x,e25.15)

Do i = 1, kdim:
  unrms(i), undms(i), zvclgi(i)                      (3x,a16,3x,a16,3x,e25.15)
End do

If kprs > 0: (have phases in the physically removed system)*:
  Do i from 1, ending with the string 'endit.' in the uprs
  field:
    uprs(i), mprmn(i)                                (3x,a16,3x,e25.15)
  End do

  k = i + 1
  Do i from 1, ending with the string 'endit.' in the
  uprs(1:8) field:
    uprs(i + k)(1:12)                                (3x,a16)
    Do j from 0, ending with the string 'endit.' in the
    uprs(13:20) field:
      uprs(k + j + i)(13:24), mprmx(j + i)           (3x,a16,3x,e25.15)
    End do
    i = i + j
  End do
```

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End if

(^{D}) Default values are recommended (i.e., leave these blank on the **input** file).
(^{R}) The range of this variable is checked.
* The input for describing the contents of the physically removed system is conceptually much simpler than it appears here, owing the manner in which the data are stored.

Table 2. Summary of Rate Law Input ("W" format; read by module **readrt.f**).

nsk(n), sk(n), fk(n)	(12x,i2,22x,e12.5,12x,e12.5))
nrk(n), nrpk(n)	(12x,i2,22x,i2)

Net Dissolution Rate Law (**nrk(n)** > 0)

If **nrk(n)** = 1 (relative rate law):	
rk(j,n), j = 1,3	(3(12x,e12.5))
Else if **nrk(n)** = 2 (TST rate law):	
imech(n)	(12x,i2)
Do **i** = 1 to **imech(n)**:	
rk(i,n), ndact(i,n), csigma(i,n)	(12x,e12.5,12x,i2,22x,e12.5))
If **ndact(i,n)** > 0 (have species appearing in the activity product):	
Do **j** = 1 to **ndact(i,n)**:	
udac(j,i,n), cdac(j,i,n)	(12x,a8,16x,e12.5)
End do	
End if	
End do	
Else if **nrk(n)** = 3 (linear rate):	
rk(1,n)	(12x,e12.5)
Else if **nrk(n)** = 4 (activity term rate law):	
imech(n)	(12x,i2)
Do **i** = 1 to **imech(n)**:	
rk(i,n), ndact(i,n), csigma(i,n)	(12x,e12.5,12x,i2,22x,e12.5))

Information Only

If **ndact(i,n)** > 0 (have species appearing in the activity product):

Do **j** = 1 to **ndact(i,n)**:

udac(j,i,n), cdac(j,i,n) (12x,a8,16x,e12.5)

End do

End if

End do

End if

Net Precipitation Rate Law (**nrpk(n)** > 0)

If **nrpk(n)** = 1 (relative rate law):

rpk(j,n), **j** = 1,3 (3(12x,e12.5))

Else if **nrpk(n)** = 2 (TST rate law):

ipmech(n) (12x,i2)

Do **i** = 1 to **ipmech(n)**:

rpk(i,n), npdact(i,n), cpsigma(i,n) (12x,e12.5,12x,i2,22x,e12.5))

If **npdact(i,n)** > 0 (have species appearing in the activity product):

Do **j** = 1 to **npdact(i,n)**:

upda c(j,i,n), cpdac(j,i,n) (12x,a8,16x,e12.5)

End do

End if

End do

Else if **nrpk(n)** = 3 (linear rate):

rpk(1,n) (12x,e12.5)

Else if **nrpk(n)** = 4 (activity term rate law):

ipmech(n) (12x,i2)

Do **i** = 1 to **ipmech(n)**:

rpk(i,n), npdact(i,n), cpsigma(i,n) (12x,e12.5,12x,i2,22x,e12.5))

If **npdact(i,n)** > 0 (have species appearing in the activity product):

Do **j** = 1 to **npdact(i,n)**:

updac(j,i,n), cpdac(j,i,n) (12x,a8,16x,e12.5)

Information Only

```
        End do
      End if
    End do
  End if
```

Table 3. EQ6 input file parameters.

utitl1	Up to 100 lines of text that describe the input problem, terminated by an 'endit.' beginning in column 1.
nmodl1	Type of physical model: 1 = Titration model. 2 = Closed system. 3 = Fluid-centered flow-through open system.
nmodl2	Economy mode permission switch: 0 = Normal reaction path tracing mode. 1 = Allow selection of economy mode (not currently recommended). 2 = All selection of super economy mode (not currently recommended).
tempc0	Initial temperature (°C)
jtemp	Temperature tracking option: 0 = Power series tracking (**tempc = tempc0 + tk1*zi1 + tk2*zi1**2 + tk3*zi1**3**) 1 = Fluid mixing tracking (tempc = (**tempc0*tk1 + zi1*tk2**) / (**zi1 + tk1**))
tk1, tk2, tk3	Temperature tracking coefficients (see above)
zistrt	Starting value of the reaction progress variable.
zimax	Maximum value of the reaction progress variable.
tstrt	The model time, seconds, at the initial value of reaction progress.
timemx	The maximum model time, seconds.
kstpmx	Maximum number of steps of reaction progress.
cplim	Maximum number of computing units (not curreutly used).
dzprnt	Linear print interval, specified in terms of reaction progress.
dzprlg	Logarithmic print interval, specified in terms of reaction progress.

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ksppmx The maximum number of steps between print points.

dzplot Linear plot increment specified in terms of reaction progress (not currently used).

dzpllg Logarithmic plot interval, specified in terms of reaction progress (not currently used).

ksplmx The maximum number of steps between plot points (not currently used).

ifile Specifies from which file read the lower part of the current problem input:

60 = Read from the file **input**.

9 = Read from the file **pickup**. This refers to the EQ3NR **pickup** file.

iopt1 Kinetic mode switch:

0 = Reaction progress (arbitrary kinetics) mode.

1 = Reaction progress/time mode (kinetics).

iopt2 Phase boundary search flag:

0 = The step size is constrained by the locations of the predicted phase boundaries.

1 = The location of the phase boundaries are estimated from the Taylor's series and printed. The step size is not constrained, however.

2 = The locations of the phase boundaries are ignored.

iopt3 Control flag for the pickup file:

-1 = Do not write a pickup file.

0 = Write a complete pickup fie at the end of the reaction path calculation.

1 = Write a complete pickup file at each print point.

iopt4 Solid solution flag:

0 = Ignore solid solutions.

1 = Solid solutions are allowed.

iopt5 Specifies whether mineral masses are transferred to the physically removed system after the initial equilibrium calculation:

0 = No transfer.

1 = Starting minerals remain but with trivial masses.

2 = Starting minerals are removed.

iopt6 Specifies whether the physically removed system should be cleared before the first step of reaction progress:

0 = No.

1 = Yes.

iopt7 Specifies automatic basis switching mode:

0 = Off.

1 = On.

Information Only

iopt8 Specifies the type of Taylor's series representation used for the master variables:

-1 = Linear for kcol = all master variables:

0 = Linear for all master variables, unless the machine exponent range is too small; in that case, logarithmic for **kcol** = 1, **ksq**.

1 = Logarithmic for all.

iopt9, iopt10

Not currently used.

iopt11 Specifies whether redox reactions should be suppressed:

0 = No.

1 = Suppresses all redox reactions. This can be a dangerous option. It should be specified only when the aqueous system being modeled is indifferent to redox parameters throughout the run.

iopt12 Not currently used.

iopt13 Determines how the **tab** file will be handled:

-1 = Do not write a **tab** file.

0 = Write a **tab** file.

1 = Append to the **tabx** file of a previous run. If the **input** file contains multiple problems, this option applies only to the first. It is reset to 0 for any succeeding problems.

iopt14 - iopt20

Not currently used.

iopr1 Specifies whether to print the loading and non-loading of species from the **data1** file into memory:

0 = No print.

1 = Print.

iopr2 Specifies whether to print the derivatives of the basis elements at each print point:

0 = No print.

1 = Print.

iopr3 Specifies whether to print all species loaded into memory, and their associated *log K* values:

0 = No print.

1 = Print.

iopr4 Specifies

-1 = No print.

0 = Print species which have a molal concentration of at least 1.e-12.

1 = Print all aqueous species.

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iopr5 Specifies whether to print the cation/H^+ ion activity ratios at each print point:

0 = No print.

1 = Print.

iopr6 Specifies whether to print the bulk element and oxide composition of the theoretical mineral assemblage as each print point:

0 = No print.

1 = Print.

iopr7 Specifies whether to print the mineral saturation states at each print point:

-1 = No print.
0 = Prints for all minerals not undersaturated by more than 10 kcal.

1 = Prints for all minerals.

iopr8 Specifies whether to print a gas species summary at each print point:

0 = No print.

1 = Print.

iopr9 Specifies whether to print a table of mean molal activity coefficients:

0 = No print.

1 = Print.

iopr10 Specifies whether to print a tabulation of Pitzer coefficients:

0 = Only print warnings for species without coefficients.

1 = Print species name, and number of Pitzer coefficients.

2 = Print species name and names of the coefficients.

iopr11 Specifies whether to print the tabulation of major species for each element:

0 = No print.

1 = Print.

iopr12 - iopr20

Not currently used.

iodb1 Specifies whether general diagnostic messages are printed:

0 = No Print.

1 = Print level 1 diagnostics.

2 = Print level 1 and level 2 diagnostics.

iodb2 Specifies whether to print information describing optimization done before Newton-Raphson calculations:

0 = No print.

1 = Print summary information.

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2 = Print detailed information.

iodb3 Specifies whether to print step size and order selection information:

0 = No print.

1 = Print chosen scaling factor.

2 = Print the orders under consideration and their step size scaling factors.

iodb4 Specifies whether to print details of Newton-Raphson iterations:

0 = No print.

1 = Print summary of Newton-Raphson iterations.

2 = Also print residual functions and correction terms for Newton-Raphson iteration.

4 = Also print the Jacobian matrix.

iodb5 Specifies whether to print search.f iterations:

0 = No print.

1 = Print.

iodb6 Specifies whether to print iterations made to compute hypothetical saturation indices of solid solution phases:

0 = No print.

1 = Print.

iodb7 Specifies whether to print details of finite difference and derivative calculations:

0 = No print.

1 = Print for calculations for actual rates only.

2 = Print for all such calculations

iodb8 Specifies whether EQ6 changes the value of the variable **iodb3**:

0 = Do not change **iodb3**.

1 = Set **iodb3** to 1 whenever **delzi** is less than or equal to **dlzmx1**. Set **iodb3** to 0 whenever **delzi** is greater than **dlzmx1**.

iodb9 Specifies whether to print kinetics diagnostic messages:

0 = No print.

1 = Print level 1 diagnostics.

2 = Print level 1 and level 2 diagnostics.

iodb10 Specifies whether to check basis variable finite difference and Taylor's series expressions:

0 = No check.

k = Test finite difference and Taylor's series by calculating values at the fit points of the **k**-th algebraic master variable.

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iodb11 Specifies whether to check reaction rate finite difference and Taylor's series expressions:

0 = No check.

n = Test finite difference and Taylor's series by calculating values at the fit points of the **n**-th reaction rate variable.

iodb12 Specifies whether the killer option is used. This allows the user to interactively remove species from an attempted species assemblage:

0 = No kill option.

1 = Kill option.

iodb13 - iodb15

Not currently used.

iodb16 Specifies whether **akmatr.f** diagnostic prints should be made:

0 = No print.

1 = Print. This routine writes the matrix that is used to estimate derivatives from finite differences.

iodb17 - iodb20

Not currently used.

nxopt Specifies the number of mineral subset-selection suppression values that will follow.

uxopt This variable is used along with **uxcat** to specify mineral subset-selection suppression:

'all' = Suppress precipitation of all pure minerals.

'alwith' = Suppress all solids composed of a specified chemical element (e.g. 'alwith mg').

uxcat The name of a chemical element. Used in conjunction with **uxopt**.

nxopex Specifies the number of exceptions to the mineral subset-selection suppression option.

uxopex The names of minerals that are exceptions to the mineral subset-selection suppress option.

nffg Specifies the number of fixed fugacity gases.

uffg The name of fixed fugacity gas species.

moffg The number of added moles of a fixed fugacity gas.

xlkffg The logarithm of the desired fugacity for fixed fugacity gases.

nrct The number of reactants.

ureac The names of the reactants.

jcode The reactant type:

0 = pure mineral.

1 = solid solution.

2 = special reactant.

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3 = aqueous species.

4 = gas.

jreac The reactant status flag:

0 = React.

-1 = Saturated, but the remaining reactant mass continues to react irreversibly. There is usually a secondary product mass of the same species, so the net rate of reaction is zero and the solution does not saturate.

1 = Exhausted.

2 = Saturated. If **nmodl1** = 2, the status of any remaining reactant mass is changed to that of a product phase.

morr The number of moles of reactant remaining.

modr The number of mole of reactant destroyed.

uendb The names of end members for each solid solution reactant.

rxbarb The mole fraction of each end member of a solid solution reactant.

vreac The molar volume of each special reactant, cm^3/mol.

uesrb The names of the chemical elements composing special reactants.

cesrb The number of moles of chemical element per mole of special reactant.

nsk Surface area flag for reactants:

0 = Fixed surface area.

1 = Fixed specific surface area.

sk Surface area of a reactant, cm^3.

fk Ratio of effective surface area to total surface area of a reactant.

nrk Dissolution rate law code for a reactant:

-1 = Use the specified precipitation rate law (**nrpk(nrc)** must be 1, 2, or 4).

0 = Illegal value.

1 = Relative rate law.

2 = Transition state theory (TST) net rate law; **jcode(nrc)** must be 0 or 1.

3 = Linear rate law.

4 = Activity product term rate law (i.e. the Plummer et al., 1978, rate law for carbonates); **jcode(nrc)** must be 0 or 1.

nrpk The precipitation rate law code (Note: you cannot have both **nrk** and **nrpk** equal to 1, or both equal to 3):

1 = Use the dissolution rate law (**nrk(nrc)** must be 2 or 4).

0 = Precipitation governed by instantaneous equilibrium, if mineral formation is not suppressed.

1 = Relative rate law.

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2 = Transition state theory (TST) rate law; **jcode(nrc)** must be 0 or 1.

3 = Linear rate law.

4 = Activity product term rate law (e.g. Plummer et al., 1978, rate law for carbonates); **jcode(nrc)** must be 0 or 1.

rk Rate constants for dissolution rate laws.

imech The number of terms in a TST or activity product term rate law for dissolution.

ndact The number of species whose activities appear in either a TST kinetic activity product or a term of the activity product term rate law for dissolution.

csigma The TST sigma factor for a dissolution rate law.

udac The name of aqueous species whose activities appear in a TST kinetic activity product or a term of the activity product term rate law for dissolution.

cdac The exponent of the activity of species in a TST kinetic activity product or a term of the activity product term rate law for dissolution.

rpk Rate constants for precipitation rate laws.

ipmech The number of terms in a TST or activity product term rate law for precipitation.

npdact The number of species whose activities appear in either a TST kinetic activity product or a term of the activity product term rate law for precipitation.

cpsigm The TST sigma factor for a precipitation rate law.

updac The name of aqueous species whose activities appear in a TST kinetic activity product or a term of the activity product term rate law for precipitation.

cpdac The exponent of the activity of species in a TST kinetic activity product or a term of the activity product term rate law for precipitation.

dlzidp Transfer interval for the removal of mineral phases from the equilibrium system to the physically removed system.

tolbt The convergence tolerance for residual magnitude during Newton-Raphson iteration.

toldl The convergence tolerance for correction magnitude during Newton-Raphson iteration.

tolx The convergence tolerance for search/find algorithms.

tolsat The supersaturation tolerance, kcal. EQ6 will not attempt to precipitate a phase if its affinity to precipitate is below this tolerance. A good value for this variable is 0.0001 kcal.

tolsst The supersaturation tolerance above which the program may cut the step size to accurately locate a phase appearance boundary. This variable must exceed **tolsat**.

screw1 Setscrew for step-size control. It bounds the absolute value of the highest order term in any Taylor's series, for a basis variable. It is used to choose the order and step size in normal computational mode, and only the order in economy mode.

screw2 Not currently used.

screw3 Setscrew for step-size control. It bounds the absolute value of the highest order term in any Taylor's series for rate functions (kinetic mode only). It also serves a function similar to that of **screw4** in testing the estimate error in the absolute time or the reaction progress of any individual irrevers-

Information Only

ible reaction. If either the **screw3** or **screw4** tests are satisfied, for corrector iteration or step size cuts, no action is taken.

screw4 The tolerance of corrector iteration or step size cut, for differences between actual and predicted rate function values (kinetic mode only).

screw5 The maximum magnitude of Newton-Raphson correction term per iteration.

screw6 The step size parameter for economy mode. This bounds the change in a basis variable.

zklogu Threshold or target value for the logarithm of the number of moles of mineral phases. It is used in several related ways:

(1) When the logarithm of the number of moles of a mineral phase does not exceed this value, EQ6 does not limit the step size to try to keep the corresponding Taylor's series accurate according to the **screw1** criterion.

(2) This parameter is the target logarithm of the number of moles for trying to use Taylor's series to locate in advance a phase disappearance boundary.

(3) In the flow-through system mode, it also defines the maximum number of moles ($(10^{zklogu}$) a mineral phase the user is willing to let redissolve. This parameter also limits the number of moles that can be shifted to the physically removed system. Recommended values are -6. to -10.

zklogl Control parameter for the transfer of mass of mineral phases in the equilibrium system to the physically removed system. The number of moles in the former is reduced by a factor of 10^{-zklog}l.

zkfac Determines the minimum number of moles of a mineral that will be left in the equilibrium system, after a partial shift to the physically removed system. The minimum number of moles is calculated as 10^{zklgmn} (where **zklgmn** = log (**zkfac** + **zklogu**). If the number of moles is less than this to start with, no mass is transferred from the equilibrium system.

dlzmx1 The step size for order zero.

dlzmx2 Upper limit on step size for order greater than zero.

nordlm The maximum allowable order in finite difference calculations.

itermx The Newton-Raphson iteration limit.

ntrymx The maximum number of attempted phase assemblages at any given point of reaction progress.

npslmx The maximum number of steps sliding forward to try to get over a critical region around a phase bonndary.

nsslmx The maximum number of steps sliding forward to try to get over a critical region of redox instability.

ioscan Oxygen fugacity scanning switch:

1 = No scanning is permitted.

0 = Scanning is permitted.

utitl2 Up to thirty lines of text that describe the previous EQ6, or EQ3NR run.

tempci The temperature (°C) at the end of the previous EQ3NR or EQ6 run.

nxmod The number of **nxmod** alter/suppress options.

uxmod The name of each species affected by an **nxmod** alter/suppress option.

jxmod The type of species affected by an alter/suppress option:

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0 = pure mineral.

1 = solid solution.

2 = special reactant.

3 = aqueous species.

4 = gas.

kxmod The nxmod alter/suppress option (see **jxmod** and **uxmod**):

-1 = Suppress.

0 = Replace the *log K* by **xlkmod**.

1 = Augment the *log K* by **xlkmod** units.

2 = The *log K* changed as if the corresponding Gibbs energy of reaction were decremented by **xlkmod** kcal/mole.

xlkmod The *log K* increment for an **nxmod** alter option.

iopg1 Choice of aqueous species activity coefficient equations:

-1 Davies (1962) equation.:

0 B-dot set of equations.

1 Pitzer's equations.

iopg2 Choice of *pH* scale:

-1 Internal scale of equations used for aqueous species activity coefficients.

0 NBS *pH* scale.

1 The *pH* scale on which ($log\gamma_{H^+} = 0$).

iopg3 - iopg10

Not currently used.

kct The number of chemical elements in the Jacobian matrix.

ksq The number of aqueous basis species.

kmt The position of the last pure mineral in the Jacobian matrix.

kxt The position of the last solid solution in the matrix.

kdim The dimension of the Jacobian matrix.

kprs Flag indicating that values of the number of moles of mineral phases in the physically removed system are appended to the input file:

0 = Not appended.

1 = Appended.

uelemb The names of chemical elements in the Jacobian matrix.

mteb The total number of moles of the elements in the equilibrium system.

mteaqb The total number of moles of the elements in the aqueous solution.

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electr	The fixed electrical imbalance carried in the calculations.
unrms	The names of run master species.
undms	Names of data file master species. If an entry in this array does not match the same entry in the unrms array, a basis switch is to be made.
zvclgi	The logarithm of the number of moles of each master species in the equilibrium system.
uprs	The names of mineral phases/components in the physically removed system.
mprmu	The number of moles of pure minerals in the physically removed system.
mprmx	The number of moles of components of solid solutions in the physically removed system.

Example of an EQ6 input file in "W" format.

```
EQ6 input file name= pptminssw.6i
Description= "Precipitate minerals from sea water"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Precipitate minerals from sea water, so as to eliminate any
supersaturations.

  Purpose: to demonstrate the ability of the code to find an
equilibrium assemblage of minerals and aqueous solution, starting
with a solution which is supersaturated with respect to a great
many minerals.

  The sea water composition is taken from the sea water test
case of Nordstrom et al. (1979), as represented by the EQ3NR
test case input file swpar.3i.

  The option switch iopt4 is set to 1 to direct the code to
allow the precipitation of solid solutions.

  Note that no reaction path is calculated, and no reactants are
defined.

                          References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical
  models for equilibrium calculations in aqueous systems: In Jenne,
  E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium
  Series, v. 93, American Chemical Society, Washington, D.C.,
  p. 857-892.

endit.
    nmodl1=  2                nmodl2=  0
    tempc0=  2.50000E+01       jtemp=  0
       tk1=  0.00000E+00         tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.00000E+00      zimax=  0.00000E+00
     tstrt=  0.00000E+00     timemx=  1.00000E+38
    kstpmx=           000     cplim=  0.00000E+00
    dzprnt=  1.00000E+38    dzprlg=  1.00000E+38    ksppmx=   100
    dzplot=  1.00000E+38    dzpllg=  1.00000E+38    ksplmx= 10000
     ifile= 60
*               1    2    3    4    5    6    7    8    9   10
  iopt1-10=     0    0    0    1    0    0    0    0    0    0
     11-20=     0    0    0    0    0    0    0    0    0    0
  iopr1-10=     0    0    0    0    0    0    0    0    0    0
 iopr11-20=     0    0    0    0    0    0    0    0    0    0
  iodb1-10=     0    0    0    0    0    0    0    0    0    0
     11-20=     0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
     nxopt=  0
* nffg = number of gas species with fixed fugacities
     nffg =  0
* nrct = number of reactants
      nrct=  0
*-----------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00      toldl=  0.00000E+00       tolx=  0.00000E+00
    tolsat=  0.00000E+00     tolsst=  0.00000E+00
    screw1=  0.00000E+00     screw2=  0.00000E+00     screw3=  0.00000E+00
    screw4=  0.00000E+00     screw5=  0.00000E+00     screw6=  0.00000E+00
```

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```
    zklogu=        0.000    zklogl=        0.000     zkfac=        0.000
    dlzmx1=  0.00000E+00    dlzmx2=  0.00000E+00    nordlm=  0
    itermx=  0              ntrymx=  0
    npslmx=  0              nsslmx=  0              ioscan=  0
*-----------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= swpar.3i
Description= "Sea water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery
```

Sea water, including all solute components present above 1 mg/kg, plus phosphate, iodide, iron, and aluminum. This is a moderately pared-down version of swtst.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III). An even more pared-down version of that benchmark sea water test case is in swmaj.3i.

Purpose: to test the code on an intermediate-sized problem involving a moderately concentrated solution and to initialize the EQ6 test case input files swtitr.6i and pptminssw.6i. The first of these two test cases simulates an alkalinity titration. The second is calculation of the precipitation of an equilibrium mineral assemblage so as to eliminate any remaining supersaturations. The activity coefficients of the aqueous species are calculated from the B-dot equation and related equations.

The original test problem permits specification of the total alkalinity instead of total HCO3-. This was expressed in the following equivalent units:

141.682 mg/L HCO3- (total alkalinity expressed as HCO3-; not the conventional HCO3 alkalinity)
0.00240659 eq/kg
0.00237625 eq/L

This is equivalent to:

116.208 mg/L CaCO3 (total alkalinity)

This is the more standard way of reporting alkalinity (see Standard Methods, 1976).

References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.


```
endit.
    tempci=  0.25000E+02
     nxmod=  0
     iopg1=  0              iopg2=  0              iopg3=  0
     iopg4=  0              iopg5=  0              iopg6=  0
     iopg7=  0              iopg8=  0              iopg9=  0
    iopg10=  0
       kct= 18                ksq= 19                kmt= 19
       kxt= 19               kdim= 19               kpre=  0
   o                 0.556292934873695E+02
   al                0.741247535207941E-07
   b                 0.426650000017602E-03
   br                0.842260712858255E-03
   ca                0.102874394948167E-01
   cl                0.545882260036914E+00
   f                 0.731640559293086E-04
   fe                0.358121295978775E-07
   h                 0.111019979193190E+03
   c                 0.202200000033000E-02
   p                 0.655000000923346E-06
   i                 0.488556470864836E-06
   k                 0.102076049345140E-01
   mg                0.531495577213419E-01
   na                0.468382241336329E+00
   si                0.712332506197997E-04
   s                 0.282312967909961E-01
   sr                0.929011641419945E-04
   electr            0.941548303390327E-04
   h2o               h2o                    0.174435898352698E+01
   al+++             al+++                 -0.168757468067617E+02
   b(oh)3(aq)        b(oh)3(aq)            -0.349803404354275E+01
   br-               br-                   -0.307840824476432E+01
   ca++              ca++                  -0.203330616490948E+01
   cl-               cl-                   -0.280369740425874E+00
```

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```
f-                f-                -0.425669422361815E+01
fe++              fe++              -0.147603987676824E+02
h+                h+                -0.810795449990283E+01
hco3-             hco3-             -0.289236023955907E+01
hpo4--            hpo4--            -0.686418890155608E+01
i-                i-                -0.631347718189878E+01
k+                k+                -0.200082008283642E+01
mg++              mg++              -0.139064657758565E+01
na+               na+               -0.351799312045118E+00
sio2(aq)          sio2(aq)          -0.428419738323244E+01
so4--             so4--             -0.187869018306158E+01
sr++              sr++              -0.409423802648238E+01
o2(g)             o2(g)             -0.164317951929624E+02
```

5.4. "D" Format

The EQ6 **input** file in "D" format is illustrated by the following example, which is of the same problem that was just presented in "W" format. The mapping between the two is largely self-evident. The "D" format EQ6 **input** file is many ways analogous to its EQ3NR counterpart. The most immediately obvious characteristic is the use of the "|" character to delimit fields in which data are entered. The principal option switches are set in blocks in which an asterisk ("*") is used to mark the desired choice. If more than one choice is marked for the same option, the code writes an error message and execution stops. When EQ6 reads an **input** file in "D" format, it immediately checks the range limits and notes discrepancies in the instant echo on the **output** file. When the code reads an **input** file in "W" format, such checks are made after the **input** file has been read.

In "D" format, one does not enter a **jcode** number to define the type of a reactant. Instead, one uses one of the following strings:

jcode	"D" format string	Meaning
0	'MINERAL'	Pure mineral.
1	'SOLID SOLUTION'	Solid solution.
2	'SPECIAL'	Special reactant.
3	'AQUEOUS'	Aqueous species.
4	'GAS'	Gas species.

Although these strings are shown in upper case, the code is actually indifferent to their case. Similar strings are treated in the same manner.

Instead of entering a **kxmod** number to define the type of an "**nxmod**" alter/suppress option, one uses one of the following strings:

kxmod	"D" format string	Meaning
-1	'SUPPRESS'	Suppress the phase/reaction.
0	'REPLACE'	Replace the *log K*.
1	'AUGMENTK'	Augment the *log K*.

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2	'AUGMENTG'	The *log K* changed as if the corresponding Gibbs energy of reaction were decremented by **xlkmod** kcal/mole.

Example of an EQ6 input file in "D" format.

```
EQ6 input file name= pptminssw.6i
Description= "Precipitate minerals from sea water"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Precipitate minerals from sea water, so as to eliminate any
supersaturations.

  Purpose: to demonstrate the ability of the code to find an
equilibrium assemblage of minerals and aqueous solution, starting
with a solution which is supersaturated with respect to a great
many minerals.

  The sea water composition is taken from the sea water test
case of Nordstrom et al. (1979), as represented by the EQ3NR
test case input file swpar.3i.

  The option switch iopt4 is set to 1 to direct the code to
allow the precipitation of solid solutions.

  Note that no reaction path is calculated, and no reactants are
defined.

                          References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical
  models for equilibrium calculations in aqueous systems: In Jenne,
  E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium
  Series, v. 93, American Chemical Society, Washington, D.C.,
  p. 857-892.

 calculational mode   |*normal     | economy          | super economy
 model type           | titration  |*closed           | open
 temperature model    |*power      | fluid mixing
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c
 tstart(c)|  25.00    |tk1|     0.    |tk2|     0.    |tk3|     0.
 starting value of zi |      0.    |max. value of zi    |      0.
 starting time (sec)  |      0.    |max. time (sec)     | 1.00000E+38
 max. steps           |         0  |max. steps w/o print|       100
 linear print interval| 1.00000E+38|log print interval  | 1.00000E+38
 suppress mineral phases
 phases w/ elements|                        |                        n
 phases except     |                        |                        n
 fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
 none                                |                |                n
c                 R A T E     L A W S
c 1 = relative                  rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory   rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate        rate = CHECK DOCUMENTATION

c                 R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                 S U R F A C E    T Y P E
c 0 = fixed surface area     1 = fixed specific surface area
c
c                 N O T E S
c status and jreac are normally not set by the user
 reactants   (ss) solid solution only     (sp) special reactant only
 REACTANT          | none                    |status    |
```

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```
-----------------------------------------------------------------------
options
-----------------------------------------------------------------------
 - SOLID SOLUTIONS -
     ignore solid solutions
   * process solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * don't print
     lists species loaded into memory
 - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
   * don't print
     print
 - LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
   * don't print
     print
 - LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
   * only species > 10**-12 molal
     all species
     don't print
 - LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
   * don't print
     print
 - LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
   * don't print
     print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
   * don't print
     print
 - PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
   * don't print
     print
 - TAB FILES -
   * write
     append to previous tabx file
     don't write
 - WRITE PICKUP FILE -
   * write pickup file at end of run
     don't write pickup file
     write pickup file for each print point
 - PHYSICALLY REMOVED SUBSYSTEM -
   * does nothing
     transfer minerals but leave trivial mass in the system
     transfer minerals
 - CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
   * does nothing
     clear p.r.s. before first reaction progress advance
 - PHASE BOUNDARY SEARCH -
   * step size constrained by predicted phase boundaries
     phase boundaries estimated from Taylor's series and printed
     locations of phase boundaries ignored
 - AUTO BASIS SWITCHING -
   * off
     on
 - SUPPRESS REDOX REACTIONS -
   * does nothing
     suppress all redox reactions
 - LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
   * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
     logarithmic for kcol = 1,kbt
     linear for kcol = 1,kdim
 - AZERO AND HYDRATION NUMBERS -
   * no change
     read in new azero and hydration numbers
 - PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
   * does nothing
     print
 - PITZER DATABASE INFORMATION -
   * print only warnings
     print species in model and number of Pitzer coefficients
     print species in model and names of Pitzer coefficients
 - PRINT DIAGNOSTIC MESSAGES -
   * don't print
     print level 1 messages
     print level 2 messages
 - PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
   * don't print
     print summary information
     print detailed information
 - PRINT STEP SIZE AND ORDER -
   * don't print
     print scale factor
     print orders and step size scaling factors
 - CONTROL STEP SIZE AND ORDER PRINT -
   * does nothing
     print step size and order when delzi .le. dlzmxl
 - NEWTON ITERATIONS -
   * don't print
     print summary of newton iterations
     print summary, residual functions and correction terms
```

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```
    print summary, residual functions, correction terms and matrix
 - PRINT SEARCH ITERATIONS -
   * don't print
     print
 - PRINT HPSAT ITERATIONS -
   * don't print
     print
 - PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
   * don't print
     print computations from RDERIV, and RTAYLR
     print computations from RDERIV, RTAYLR, DERIV and TAYLOR
 - PRINT KINETICS DIAGNOSTIC MESSAGES -
   * don't print
     print level 1 diagnostics
     print level 1 and level 2 diagnostics
 - PRINT AKMATR -
   * don't print
     print level 1 diagnostics
 - KILL ITERATION VARIABLES -
   * does nothing
     allow selection of variables to remove
-------------------------------------------------------------------------
 development options  (used for code development)
-------------------------------------------------------------------------
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
-------------------------------------------------------------------------
 tolerances                          desired values - defaults info-only
-------------------------------------------------------------------------
 number of N-R iterations                          40       itermx
 p.r.s. transfer interval                          varies   dlzidp
 residual magnitude                                1.0e-06  tolbt
 correction magnitude                              1.0e-06  toldl
 search/find tolerance                             varies   tolx
 supersaturation                                   varies   tolsat
 supersaturation set size                          varies   tolsst
 max. size Taylor's series term                    1.0e-04  screw1
 max. initial value betamx                         n/a      screw2
 max. Taylor's series term (kin.)                  1.0e-04  screw3
 corrector iteration                               1.0e-04  screw4
 max. size of N-R correction term                  4.0      screw5
 step size (economy mode)                          4.0      screw6
 log mass of phases                                varies   zklogu
 decrement mass (p.r.s.)                           2.0      zklogl
 min. left after p.r.s.                            .98      zkfac
 initial step size                                 varies   dlzmxl
 upper limit step size                             varies   dlzmx2
 maximum order                                     6        nordlm
 num. attempted assemblages                        25       ntrymx
 slide -> over phase bound.                        8        npslmx
 slide -> over redox insta.                        3        nsslmx
 fo2 scan control                                  none     ioscan
-------------------------------------------------------------------------
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= swpar.3i
Description= "Sea water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  Sea water, including all solute components present above 1 mg/kg,
plus phosphate, iodide, iron, and aluminum. This is a moderately
pared-down version of swtst.3i, which contains the full benchmark
sea water test case of Nordstrom et al. (1979, Table III). An even
more pared-down version of that benchmark sea water test case is
in swmaj.3i.

  Purpose: to test the code on an intermediate-sized problem
involving a moderately concentrated solution and to initialize the
EQ6 test case input files swtitr.6i and pptminssw.6i. The first of
these two test cases simulates an alkalinity titration. The second
is calculation of the precipitation of an equilibrium mineral
assemblage so as to eliminate any remaining supersaturations. The
activity coefficients of the aqueous species are calculated from
the B-dot equation and related equations.

  The original test problem permits specification of the total
alkalinity instead of total HCO3-. This was expressed in the
following equivalent units:

    141.682 mg/L HCO3- (total alkalinity expressed as HCO3-;
                        not the conventional HCO3 alkalinity)
    0.00240659 eq/kg
    0.00237625 eq/L

This is equivalent to:

    116.208 mg/L CaCO3 (total alkalinity)

This is the more standard way of reporting alkalinity (see Standard
Methods, 1976).
```

Information Only

References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.

temperature (C)	25.000
electrical imbalance	9.415483033903270E-05
number of aqueous master species	19
position of last pure mineral	19
position of last solid solution	19

suppressed species	(suppress,replace,augmentk,augmentg)	value
none		

iopg options

- pH SCALE CONVENTION -
  - * modified NBS
  - internal
  - rational
- ACTIVITY COEFFICIENT OPTIONS -
  - * use B-dot equation
  - Davies' equation
  - Pitzer's equations

elements, moles and moles aqueous

o	5.562929348736950E+01	0.000000000000000E+00
al	7.412475352079411E-08	0.000000000000000E+00
b	4.266500000176020E-04	0.000000000000000E+00
br	8.422607128582550E-04	0.000000000000000E+00
ca	1.028743949481670E-02	0.000000000000000E+00
cl	5.458822600369140E-01	0.000000000000000E+00
f	7.316405592930859E-05	0.000000000000000E+00
fe	3.581212959787750E-08	0.000000000000000E+00
h	1.110199791931900E+02	0.000000000000000E+00
c	2.022000000330000E-03	0.000000000000000E+00
p	6.550000009233460E-07	0.000000000000000E+00
i	4.885564708648360E-07	0.000000000000000E+00
k	1.020760493451400E-02	0.000000000000000E+00
mg	5.314955772134190E-02	0.000000000000000E+00
na	4.683822413363290E-01	0.000000000000000E+00
si	7.123325061979969E-05	0.000000000000000E+00
s	2.823129679099610E-02	0.000000000000000E+00
sr	9.290116414199449E-05	0.000000000000000E+00

master species and logarithmic basis variables

h2o	h2o	1.744358983526980E+00
al+++	al+++	-1.687574680676170E+01
b(oh)3(aq)	b(oh)3(aq)	-3.498034043542750E+00
br-	br-	-3.078408244764320E+00
ca++	ca++	-2.033306164909480E+00
cl-	cl-	-2.803697404258740E-01
f-	f-	-4.256694223618150E+00
fe++	fe++	-1.476039876768240E+01
h+	h+	-8.107954499902830E+00
hco3-	hco3-	-2.892360239559070E+00
hpo4--	hpo4--	-6.864188901556080E+00
i-	i-	-6.313477181898780E+00
k+	k+	-2.000820082836420E+00
mg++	mg++	-1.390646577585650E+00
na+	na+	-3.517993120451180E-01
sio2(aq)	sio2(aq)	-4.284197383232440E+00
so4--	so4--	-1.878690183061580E+00
sr++	sr++	-4.094238026482380E+00
o2(g)	o2(g)	-1.643179519296240E+01

physically removed subsystem (solid solution, mineral, moles)

none		

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6. Sample Problems: Inputs And Outputs

6.1. Introduction

This chapter presents several examples of the usage of EQ6. Each example includes the corresponding EQ6 **input** files in both "W" and "D" formats. The initializing EQ3NR **input** files are presented in Appendix F. Users should compare the sample EQ6 **input** files with the **input** file descriptions given Chapter 5. The code output presented for each example will vary, usually consisting of some combination of parts of the **output** and **tab** files. The size of the **output** file is comparable to that of EQ3NR for single point thermodynamic equilibrium calculations, but much greater in the case of reaction path (multi-point) runs (usually several thousand lines, sometimes several ten thousands of lines). A complete **output** file is provided for the first example given in this chapter. The **tab** file is not very useful for the single point calculations, but provides a compact description of the most pertinent data for reaction path runs. For other detailed examples of the usage of EQ6, the reader is directed to Delany and Wolery (1984), Delany (1985), Delany, Puigdomenech, and Wolery (1986), and Jackson (1988). The examples presented here were run on a Sun SPARCstation IPC using optimized code, using the "W" format input files and the "R10" **com** and **hmw** data files.

The examples presented here are relatively simple. A few **input** files addressing more complex problems are presented without external comments or computed results in Appendix E.

On the **output** and **tab** files one will frequently see "+999" and "-999". These are respectively treated in EQ3/6 as the logarithms of plus infinity and zero, respectively. In the context of their appearance in these files, they generally signify a condition of "no data." On EQ6 **output** and **tab** files, for example, the *Eh* is listed as "-999" for problems in which oxidation-reduction is not part of the computed model. In some cases one may also see on these files "1.e+38." This is used as a proxy for infinity. The time variable is likely to show this value in problems run in time mode.

6.2. Finding Precipitates from Multiply-Supersaturated Sea Water

The first example is a single point calculation. Surface sea water at 25°C is supersaturated with respect to a large number of minerals. The objective here is to precipitate an equilibrium assemblage of minerals. The code must choose which of many supersaturated minerals belong in the relatively small final assemblage. The code finds this assemblage by adding one new mineral at a time (see Chapter 7). At the end of the process, no supersaturations remain. The mineral precipitation causes changes in many of the solution properties, including the *pH* (initially 8.22). The activity coefficients of the aqueous species are computed from the B-dot equation (**iopg1** = 0). The supporting data file is the **com** file.

The initializing EQ3NR **input** file is **swpar.3i** (see Appendix F). This is a slightly more extended sea water model than that in the **swmaj.3i** file presented in Chapter 7 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b). Both are based on the sea water test case of Nordstrom et al. (1979). The model used here includes several trace elements, the most significant of which for the present example are iron, aluminum, and silica. The composition of this solution in terms of total concentrations of the strict basis species is as follows (taken from the EQ3NR **output** file **swpar.3o**):

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species	mg/l	mg/kg	moles/kg
h2o	0.10256E+07	0.10022E+07	0.5562929349E+02
al+++	0.20467E-02	0.20000E-02	0.7412475352E-07
b(oh)3(aq)	26.997	26.381	0.4266500000E-03
br-	68.872	67.300	0.8422607129E-03
ca++	421.93	412.30	0.1028743949E-01
cl-	19805.	19353.	0.5458822600E+00
f-	1.4225	1.3900	0.7316405593E-04
fe++	0.20467E-02	0.20000E-02	0.3581212960E-07
h+	0.11452E+06	0.11190E+06	0.1110199792E+03
hco3-	126.26	123.38	0.2022000000E-02
hpo4--	0.64335E-01	0.62866E-01	0.6550000009E-06
i-	0.63448E-01	0.62000E-01	0.4885564709E-06
k+	408.42	399.10	0.1020760493E-01
mg++	1322.0	1291.8	0.5314955772E-01
na+	11020.	10768.	0.4683822413E+00
sio2(aq)	4.3800	4.2800	0.7123325062E-04
so4--	2775.4	2712.0	0.2823129679E-01
sr++	8.3302	8.1400	0.9290116414E-04

There is a an example of redox disequilibrium in this model, as shown by the following results:

couple	eh, volts	pe-	log fo2	ah, kcal
default	0.500	0.8452E+01	-16.432	11.531
acetic a/hco3-	0.500	0.8452E+01	-16.432	11.531
acetone(/hco3-	0.500	0.8452E+01	-16.432	11.531
clo4- /cl-	0.500	0.8452E+01	-16.432	11.531
ethane(a/hco3-	0.500	0.8452E+01	-16.432	11.531
fe+++ /fe++	0.500	0.8452E+01	-16.432	11.531
h2(aq) /h2o	0.500	0.8452E+01	-16.432	11.531
hs- /so4--	0.500	0.8452E+01	-16.432	11.531
io3- /i-	0.500	0.8452E+01	-16.432	11.531
methane(/hco3-	0.500	0.8452E+01	-16.432	11.531
methanol/hco3-	0.500	0.8452E+01	-16.432	11.531
o2(aq) /h2o	0.732	0.1237E+02	-0.746	16.881
so3-- /so4--	0.500	0.8452E+01	-16.432	11.531

The disequilibrium is evidenced by the different values for the parameters associated with the $O_{2(aq)}/H_2O$ couple. It is a consequence of having entered an *Eh* of 500 mV and an independent concentration for $O_{2(aq)}$. Note that EQ6 will "equilibrate" all redox couples when it makes the first equilibrium calculation, when the phase assemblage consists of just the aqueous solution.

EQ3NR calculated the following table of saturation indices for pure minerals:

----- summary of stoichiometric mineral saturation states -----

(minerals with affinities .lt. -10 kcal are not listed)

mineral	log q/k	aff, kcal	state	mineral	log q/k	aff, kcal	state
albite	-0.428	-0.584		albite high	-1.747	-2.383	
albite low	-0.428	-0.584		amesite-14a	4.036	5.506	ssatd
analcime	-0.305	-0.417	satd	analcime-dehy	-6.660	-9.087	
andalusite	-5.201	-7.095		andradite	4.472	6.101	ssatd
anhydrite	-0.978	-1.335		anorthite	-6.359	-8.675	
anthophyllite	0.486	0.663	ssatd	aragonite	0.506	0.691	ssatd
arcanite	-5.249	-7.161		artinite	-1.929	-2.632	
bassanite	-1.627	-2.220		beidellite-ca	-1.544	-2.107	
beidellite-h	-2.858	-3.899		beidellite-k	-1.553	-2.119	
beidellite-mg	-1.383	-1.887		beidellite-na	-1.338	-1.825	
bischofite	-7.292	-9.949		bloedite	-5.783	-7.889	
boehmite	-1.776	-2.423		boric acid	-3.339	-4.555	
brucite	-1.797	-2.451		calcite	0.651	0.888	ssatd
caso4:0.5h2o(beta)	-1.795	-2.449		celadonite	3.418	4.664	ssatd
celestite	-1.740	-2.374		chalcedony	-0.556	-0.759	
chrysotile	3.818	5.209	ssatd	clinochlore-14a	7.451	10.165	ssatd
clinochlore-7a	4.077	5.563	ssatd	clinoptilolite-ca	-5.482	-7.479	
clinoptilolite-k	-4.603	-6.280		clinoptilolite-na	-2.598	-3.544	
clinozoisite	-6.052	-8.256		coesite	-1.095	-1.494	
corundum	-5.735	-7.824		cristobalite	-0.835	-1.140	
cristobalite-a	-0.835	-1.140		cristobalite-b	-1.279	-1.745	
dawsonite	-0.425	-0.580		diaspore	-0.931	-1.271	
diopside	-1.264	-1.724		dolomite	3.234	4.413	ssatd
dolomite-dis	1.690	2.306	ssatd	dolomite-ord	3.234	4.413	ssatd
enstatite	-1.102	-1.503		epidote	1.452	1.981	ssatd
epidote-ord	1.452	1.981	ssatd	epsomite	-2.627	-3.585	

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fe(oh)3	-0.977	-1.333		ferrite-ca	1.619	2.208	ssatd
ferrite-mg	2.834	3.867	ssatd	fluorapatite	9.086	12.396	ssatd
fluorite	-1.461	-1.993		forsterite	-3.129	-4.268	
gaylussite	-4.614	-6.294		gibbsite	-0.149	-0.203	satd
gismondine	-1.348	-1.839		glauberite	-3.510	-4.788	
goethite	4.152	5.664	ssatd	gypsum	-0.818	-1.116	
halite	-2.592	-3.536		hematite	9.272	12.649	ssatd
hexahydrite	-2.855	-3.895		huntite	1.944	2.652	ssatd
hydromagnesite	-3.389	-4.624		hydroxylapatite	-0.208	-0.284	satd
ice	-0.146	-0.200	satd	illite	0.479	0.654	ssatd
jadeite	-1.768	-2.412		k-feldspar	0.934	1.274	ssatd
kainite	-6.931	-9.456		kalicinite	-5.551	-7.573	
kalsilite	-1.672	-2.281		kaolinite	-0.366	-0.499	satd
kbr	-6.522	-8.898		kieserite	-4.276	-5.834	
kyanite	-4.930	-6.726		lansfordite	-1.631	-2.225	
laumontite	-2.047	-2.792		lawsonite	-2.009	-2.741	
magnesite	0.955	1.303	ssatd	magnetite	-0.059	-0.081	satd
margarite	-5.826	-7.949		maximum microcline	0.934	1.274	ssatd
mesolite	2.646	3.610	ssatd	mgl.25so4(oh)0.5:0	-6.025	-8.220	
mgl.5so4(oh)	-6.222	-8.489		mirabilite	-2.632	-3.591	
monohydrocalcite	-0.191	-0.260	satd	monticellite	-5.600	-7.641	
montmor-ca	-0.033	-0.045	satd	montmor-k	0.029	0.039	satd
montmor-mg	0.198	0.270	satd	montmor-na	0.240	0.328	satd
mordenite	-2.691	-3.671		muscovite	2.093	2.856	ssatd
na2co3	-7.091	-9.674		na2co3:7h2o	-5.910	-8.063	
na4ca(so4)3:2h2o	-6.794	-9.270		nabr	-6.749	-9.208	
nabr:2h2o	-5.895	-8.042		nahcolite	-3.476	-4.743	
natrolite	-1.010	-1.378		natron	-5.598	-7.637	
nepheline	-2.896	-3.951		nesquehonite	-1.770	-2.415	
nontronite-ca	9.982	13.618	ssatd	nontronite-h	8.668	11.826	ssatd
nontronite-k	9.973	13.606	ssatd	nontronite-mg	10.143	13.838	ssatd
nontronite-na	10.188	13.900	ssatd	okenite	-5.206	-7.102	
oxychloride-mg	-5.538	-7.555		paragonite	-0.165	-0.225	satd
pentahydrite	-3.187	-4.348		periclase	-6.826	-9.313	
phlogopite	6.738	9.193	ssatd	picromerite	-7.192	-9.812	
pirssonite	-4.749	-6.479		prehnite	-3.243	-4.425	
pseudowollastonite	-4.523	-6.171		pyrophyllite	-2.556	-3.487	
quartz	-0.285	-0.389	satd	sanidine high	-0.265	-0.362	satd
saponite-ca	6.256	8.536	ssatd	saponite-h	4.943	6.743	ssatd
saponite-k	6.248	8.524	ssatd	saponite-mg	6.418	8.756	ssatd
saponite-na	6.463	8.817	ssatd	scolecite	0.035	0.048	satd
sellaite	-1.358	-1.853		sepiolite	1.833	2.501	ssatd
sillimanite	-5.564	-7.591		sio2(am)	-1.571	-2.143	
smectite-high-fe-m	-2.579	-3.519		smectite-low-fe-mg	-0.988	-1.347	
srcl2:6h2o	-7.285	-9.939		srf2	-5.090	-6.944	
srhpo4	-6.161	-8.405		starkeyite	-3.567	-4.866	
stilbite	1.152	1.572	ssatd	strontianite	0.681	0.929	ssatd
sylvite	-3.530	-4.816		syngenite	-4.742	-6.470	
talc	5.244	7.155	ssatd	thenardite	-3.385	-4.618	
thermonatrite	-6.880	-9.386		tremolite	4.547	6.204	ssatd
tridymite	-0.456	-0.623		wairakite	-6.441	-8.787	
whitlockite	-2.548	-3.476		wollastonite	-4.285	-5.846	
zoisite	-6.096	-8.317					

```
 15 approx. saturated pure minerals
  0 approx. saturated end-members of specified solid solutions
  0 saturated end-members of hypothetical solid solutions


 42 supersaturated pure minerals
  0 supersatd. end-members of specified solid solutions
  0 supersatd. hypothetical solid solution phases
```

Note that the solution is supersaturated with respect to 42 pure minerals, most of them aluminosilicates. Saturation indices for solid solutions were not computed, because **iopt4** was set to 0 on the **input** file.

The EQ6 **input** file for this example is **pptminssw.6i**. This was presented in Chapter 5 in both "W" and "D" formats and will not be repeated here. Note that the bottom half of the file is the **pickup** file from the initializing EQ3NR run just discussed. This part begins with a line containing, "`pickup file written by eq3nr.7.0R124`." Note also that **iopt4** is set to 1, enabling the use of solid solutions (**iopt4** has the same usage in both EQ3NR and EQ6).

The EQ6 **output** file for this run, **pptminssw.6o**, is given below. Note the general resemblance to an EQ3NR **input** file. It contains time and date statistics, copyright notice and disclaimers, instant echo of the **input** file, problem description (including values of assigned default values), and detailed description of the state of the system as computed by the code. The problem descrip-

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tion part is written by module **echoz.f**, which is analogous to the EQ3NR module **echox.f.** The detailed description of the results, which here corresponds to a zero value of reaction progress, is produced by module **scripz.f**, which is analogous to the EQ3NR module **scripx.f.** In a multi-point run, **scripz.f** is called to write such a description of the state of the system at various points of reaction progress along the reaction path.

EQ6 first makes an equilibrium calculation for just the aqueous phase. This is the "phase assemblage no. 1" on the **output** file. Hybrid Newton-Raphson iteration converges in 15 iterations ("iter = 15"). The code then finds the solution to be supersaturated with 27 pure minerals and 7 solid solutions. The 15 iterations are taken primarily because of the need to obtain internal redox equilibrium. This equilibration may have a small effect on the mineral saturation indices. In the present case, however, this effect is not qualitatively significant. The reason the code now reports supersaturation with 27 pure minerals instead of the 42 reported by EQ3NR is because the solid solutions feature has been enabled. A pure mineral which is a solid solution end member is technically suppressed as a pure phase when the solid solution option is turned on. Thus, supersaturation of such a mineral is not reported.

The code then begins precipitating minerals one at a time, choosing them according to the algorithm described in Chapter 7. It first chooses ordered dolomite ($MgCa(CO_3)_2$;"dolomite-ord") as the first mineral to precipitate. Convergence is achieved in 11 iterations. The code then reports supersaturation for 19 pure minerals and 3 solid solutions. The number of supersaturations is significantly reduced because of the common ion effect (in this case, changes in the activities of the calcium, magnesium, hydrogen, and bicarbonate ions due to precipitation of dolomite).

Hematite (Fe_2O_3) is the next mineral to be added to the phase assemblage. The code converges in 12 iterations. It then reports supersaturations for 17 pure minerals and 3 solid solutions. The next phase to be precipitated is fluorapatite ($Ca_5F(PO_4)_3$). The code converges in 12 iterations and then reports supersaturations for 16 pure minerals and 3 solid solutions.

The code then adds muscovite ($KAl_3Si_3O_{10}(OH)_2$)to the phase assemblage and converges in 12 iterations. The code now reports supersaturation for only one phase, the solid solution dioctahedral smectite (a complex aluminosilicate, here treated as an ideal solution of 12 end member components; "smectite-di").

The code then adds dioctahedral smectite to the phase assemblage. The code runs 14 iterations and crashes. The code determines that hematite should be dropped from the phase assemblage. Upon removing this phase, the code converges in 12 iterations. Thus, the final phase assemblage consists of the aqueous solution, ordered dolomite, fluorapatite, muscovite, and dioctahedral smectite. The hematite and the dioctahedral smectite are both sinks for iron. When the smectite was added to the phase assemblage, it in effect took the available iron away from the hematite, forcing it to disappear from the system.

The aqueous solution in the equilibrated system differs in some interesting ways from the initial solution. The *pH* changed to 6.76 from 8.22. The *Eh* changed to 818 mV from 500 mV, primarily as a result of the redox equilibration involving $O_{2(aq)}$.

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The EQ6 output file (pptminssw.6o), sea water mineral precipitation test case:

```
EQ6, version 3245R119x

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"quality affecting work" for the Yucca Mountain Project.

Run  18:52      5Dec91


--- reading the input file ---
EQ6 input file name= pptminssw.6i
Description= "Precipitate minerals from sea water"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Precipitate minerals from sea water, so as to eliminate any
supersaturations.

  Purpose: to demonstrate the ability of the code to find an
equilibrium assemblage of minerals and aqueous solution, starting
with a solution which is supersaturated with respect to a great
many minerals.

  The sea water composition is taken from the sea water test
case of Nordstrom et al. (1979), as represented by the EQ3NR
test case input file swpar.3i.

  The option switch iopt4 is set to 1 to direct the code to
allow the precipitation of solid solutions.

  Note that no reaction path is calculated, and no reactants are
defined.

                          References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical
  models for equilibrium calculations in aqueous systems: In Jenne,
  E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium
  Series, v. 93, American Chemical Society, Washington, D.C.,
  p. 857-892.

endit.
```

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```
    nmodl1=  2                 nmodl2=  0
    tempc0=  2.50000E+01        jtemp=  0
       tk1=  0.00000E+00          tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.00000E+00        zimax=  0.00000E+00
     tstrt=  0.00000E+00       timemx=  1.00000E+38
    kstpmx=            0        cplim=  0.00000E+00
    dzprnt=  1.00000E+38       dzprlg=  1.00000E+38     ksppmx=   100
    dzplot=  1.00000E+38       dzpllg=  1.00000E+38     ksplmx= 10000
     ifile= 16
*                1    2    3    4    5    6    7    8    9   10
  iopt1-10=      0    0    0    1    0    0    0    0    0    0
     11-20=      0    0    0    0    0    0    0    0    0    0
  iopr1-10=      0    0    0    0    0    0    0    0    0    0
 iopr11-20=      0    0    0    0    0    0    0    0    0    0
  iodb1-10=      0    0    0    0    0    0    0    0    0    0
     11-20=      0    0    0    0    0    0    0    0    0    0
     nxopt=  0
     nffg =  0
      nrct=  0
*-----------------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00        toldl=  0.00000E+00       tolx=  0.00000E+00
    tolsat=  0.00000E+00       tolsst=  0.00000E+00
    screw1=  0.00000E+00       screw2=  0.00000E+00     screw3=  0.00000E+00
    screw4=  0.00000E+00       screw5=  0.00000E+00     screw6=  0.00000E+00
    zklogu=        0.000       zklogl=        0.000      zkfac=        0.000
    dlzmx1=  0.00000E+00       dlzmx2=  0.00000E+00     nordlm=  0
    itermx=  0                 ntrymx=  0
    npslmx=  0                 nsslmx=  0               ioscan=  0
*-----------------------------------------------------------------------------
EQ3NR input file name= swpar.3i
Description= "Sea water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery
```

Sea water, including all solute components present above 1 mg/kg, plus phosphate, iodide, iron, and aluminum. This is a moderately pared-down version of swtst.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III). An even more pared-down version of that benchmark sea water test case is in swmaj.3i.

Purpose: to test the code on an intermediate-sized problem involving a moderately concentrated solution and to initialize the EQ6 test case input files swtitr.6i and pptminssw.6i. The first of these two test cases simulates an alkalinity titration. The second is calculation of the precipitation of an equilibrium mineral assemblage so as to eliminate any remaining supersaturations. The activity coefficients of the aqueous species are calculated from the B-dot equation and related equations.

The original test problem permits specification of the total alkalinity instead of total HCO3-. This was expressed in the following equivalent units:

```
141.682 mg/L HCO3- (total alkalinity expressed as HCO3-;
                    not the conventional HCO3 alkalinity)
0.00240659 eq/kg
0.00237625 eq/L
```

This is equivalent to:

```
116.208 mg/L CaCO3 (total alkalinity)
```

This is the more standard way of reporting alkalinity (see Standard Methods, 1976).

References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.


```
endit.
    tempci=  2.50000E+01
     nxmod=  0
     iopg1=  0                 iopg2=  0                 iopg3=  0
     iopg4=  0                 iopg5=  0                 iopg6=  0
     iopg7=  0                 iopg8=  0                 iopg9=  0
    iopg10=  0
       kct= 18                   ksq= 19                   kmt= 19
       kxt= 19                  kdim= 19                  kprs=  0
*   component              moles total              moles aqueous
   o                    5.562929348736950E+01        0.000000000000000E+00
```

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```
al                  7.412475352079411E-08        0.000000000000000E+00
b                   4.266500000176020E-04        0.000000000000000E+00
br                  8.422607128582550E-04        0.000000000000000E+00
ca                  1.028743949481670E-02        0.000000000000000E+00
cl                  5.458822600369140E-01        0.000000000000000E+00
f                   7.316405592930859E-05        0.000000000000000E+00
fe                  3.581212959787750E-08        0.000000000000000E+00
h                   1.110199791931900E+02        0.000000000000000E+00
c                   2.022000000330000E-03        0.000000000000000E+00
p                   6.550000009233460E-07        0.000000000000000E+00
i                   4.885564708648360E-07        0.000000000000000E+00
k                   1.020760493451400E-02        0.000000000000000E+00
mg                  5.314955772134190E-02        0.000000000000000E+00
na                  4.683822413363290E-01        0.000000000000000E+00
si                  7.123325061979969E-05        0.000000000000000E+00
s                   2.823129679099610E-02        0.000000000000000E+00
sr                  9.290116414199449E-05        0.000000000000000E+00
electr              9.415483033903270E-05
h2o                 h2o                           1.744358983526980E+00
al+++               al+++                        -1.687574680676170E+01
b(oh)3(aq)          b(oh)3(aq)                   -3.498034043542750E+00
br-                 br-                          -3.078408244764320E+00
ca++                ca++                         -2.033306164909480E+00
cl-                 cl-                          -2.803697404258740E-01
f-                  f-                           -4.256694223618150E+00
fe++                fe++                         -1.476039876768240E+01
h+                  h+                           -8.107954499902830E+00
hco3-               hco3-                        -2.892360239559070E+00
hpo4--              hpo4--                       -6.864188901556080E+00
i-                  i-                           -6.313477181898780E+00
k+                  k+                           -2.000820082836420E+00
mg++                mg++                         -1.390646577585650E+00
na+                 na+                          -3.517993120451180E-01
sio2(aq)            sio2(aq)                     -4.284197383232440E+00
so4--               so4--                        -1.878690183061580E+00
sr++                sr++                         -4.094238026482380E+00
o2(g)               o2(g)                        -1.643179519296240E+01

--- the input file has been successfully read ---

--- reading the data1 file ---


                    --- list of solid solutions ---

 1  biotite                  no.components=   2
        model type=   1  (ideal solution                )
 2  carbonate-calcite        no.components=   6
        model type=   1  (ideal solution                )
 3  chlorite-ss              no.components=   2
        model type=   1  (ideal solution                )
 4  clinoptilolite-ss        no.components=   6
        model type=   1  (ideal solution                )
 5  epidote-ss               no.components=   2
        model type=   1  (ideal solution                )
 6  garnet-ss                no.components=   2
        model type=   1  (ideal solution                )
 7  olivine                  no.components=   2
        model type=   3  (binary, parabolic maclaurin   )
 8  orthopyroxene            no.components=   2
        model type=   1  (ideal solution                )
 9  plagioclase              no.components=   3
        model type=   1  (ideal solution                )
10  sanidine-ss              no.components=   3
        model type=   1  (ideal solution                )
11  saponite-tri             no.components=   5
        model type=   1  (ideal solution                )
12  smectite-di              no.components=  12
        model type=   1  (ideal solution                )

--- the data1 file has been successfully read ---

* note - (eq6/flgstz) This run involves at least
      one redox reaction.  The code will therefore use a
      redox parameter and the charge balance constraint.

* note - (eqlib/inbdot) The following aqueous species
      have been assigned a default hard core diameter of
        4.000 Angstroms-
        cacl2(aq)
        caco3(aq)
        caso4(aq)
        fe(ch3coo)2(aq)
        fecl2(aq)
        kbr(aq)
        kcl(aq)
        khso4(aq)
        ki(aq)
        koh(aq)
        mgco3(aq)
        nabr(aq)
        nach3coo(aq)
        naf(aq)
```

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```
nahsio3(aq)
nai(aq)
srco3(aq)
```

```
eeeee  qqq   666
e     q   q 6
eeee  q   q 6666
e     q q q 6   6
eeeee  qqq   666
          q
```

```
eq6.3245R119x
 supported by eqlib.3245R153
```

```
EQ6 input file name= pptminssw.6i
Description= "Precipitate minerals from sea water"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery
```

Precipitate minerals from sea water, so as to eliminate any supersaturations.

Purpose: to demonstrate the ability of the code to find an equilibrium assemblage of minerals and aqueous solution, starting with a solution which is supersaturated with respect to a great many minerals.

The sea water composition is taken from the sea water test case of Nordstrom et al. (1979), as represented by the EQ3NR test case input file swpar.3i.

The option switch iopt4 is set to 1 to direct the code to allow the precipitation of solid solutions.

Note that no reaction path is calculated, and no reactants are defined.

References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems: In Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

```
EQ3NR input file name= swpar.3i
Description= "Sea water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery
```

Sea water, including all solute components present above 1 mg/kg, plus phosphate, iodide, iron, and aluminum. This is a moderately pared-down version of swtst.3i, which contains the full benchmark sea water test case of Nordstrom et al. (1979, Table III). An even more pared-down version of that benchmark sea water test case is in swmaj.3i.

Purpose: to test the code on an intermediate-sized problem involving a moderately concentrated solution and to initialize the EQ6 test case input files swtitr.6i and pptminssw.6i. The first of these two test cases simulates an alkalinity titration. The second is calculation of the precipitation of an equilibrium mineral assemblage so as to eliminate any remaining supersaturations. The activity coefficients of the aqueous species are calculated from the B-dot equation and related equations.

The original test problem permits specification of the total alkalinity instead of total HCO_3^-. This was expressed in the following equivalent units:

```
141.682 mg/L HCO3- (total alkalinity expressed as HCO3-;
                    not the conventional HCO3 alkalinity)
0.00240659 eq/kg
0.00237625 eq/L
```

This is equivalent to:

```
116.208 mg/L CaCO3 (total alkalinity)
```

This is the more standard way of reporting alkalinity (see Standard Methods, 1976).

Information Only

References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.


```
data0.com.R10
THERMODYNAMIC DATABASE
generated by gembochs/INGRES  15-apr-91
+-------------------------------------------------------------------

  The activity coefficients of aqueous solute species
and the activity of water are calculated according to the
b-dot equation plus others


   no. of elements in the data base =  78
   no. of elements dimensioned for = 100
   no. of active elements =  18

      no. of aqueous species dimensioned for = 800
      no. of aqueous species loaded = 388
      no. of active aqueous species = 234

         no. of aqueous reactions dimensioned for = 699
         no. of aqueous reactions loaded = 309
         no. of active aqueous reactions = 216


            no. of pure minerals dimensioned for = 850
            no. of pure minerals loaded = 303
            no. of active pure minerals = 260

            no. of gases dimensioned for =  80
            no. of gases loaded =  27
            no. of active gases =  27

               no. of solid solutions in the data base =  12
               no. of solid solutions dimensioned for =  50
               no. of active solid solutions =  12

   zistrt =  0.000000E+00 (initial value of zi)
   zimax  =  1.000000E+38 (maximum value of zi)
   timemx =  1.000000E+38 (maximum value of time, sec)
   kstpmx =             0 (maximum number of steps this run)


      dzprnt =  1.000000E+38 (linear print interval)
      dzprlg =  1.000000E+38 (logarithmic print interval)
      dlzidp =  1.000000E+38 (p.r.s. transfer interval)

      maximum permitted step sizes.....
         dlzmx1 =  1.000000E-02 (nord=0)
         dlzmx2 =  1.000000E+38 (nord.ge.1)
      nordlm =  6 (maximum permitted order)


   temperature =     25.000 c


   nmodl1 =  2 (physical system switch)
     1 = titration, 2 = closed, 3 = flow-through)
   nmodl2 =  0 (economy mode permission switch)
     0 = normal, 1 = economy, 3 = super economy)

      iopt1  =  0 (kinetic mode switch)
      iopt2  =  0 (suppress phase boundary location)
      iopt3  =  0 (interfacing output switch)
      iopt4  =  1 (permit solid solutions switch)
      iopt5  =  0 (remove initial solids switch)
      iopt6  =  0 (clear p.r.s. at start switch)
      iopt7  =  0 (auto basis switch mode switch)
      iopt8  =  0 (linear vs. log taylors series)
      iopt9  =  0 (not used)
      iopt10 =  0 (not used)
      iopt11 =  0 (suppress all redox reactions switch)
      iopt12 =  0 (not used)
      iopt13 =  0 (tab file output switch)
      iopt14 =  0 (not used)
      iopt15 =  0 (not used)
      iopt16-20    (not used)
      ifile  = 16 (supplementary input file)

         iopg1  =  0 (choice of act. coeff. equations)
```

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```
        iopg2  =  0 (choice of ph scale)
        iopg3  =  0 (not used)
        iopg4  =  0 (not used)
        iopg5  =  0 (not used)
        iopg6  =  0 (not used)
        iopg7  =  0 (not used)
        iopg8  =  0 (not used)
        iopg9  =  0 (not used)
        iopg10 =  0 (not used)

     iopr1  =  0 (print loading of species from data1)
     iopr2  =  0 (print derivatives of basis elements)
     iopr3  =  0 (print loaded species and log k values)
     iopr4  =  0 (print aqueous species distribution)
     iopr5  =  0 (print cation/h+ activity ratios)
     iopr6  =  0 (print element/oxide comp. of mineral assemblage)
     iopr7  =  0 (print mineral affinity summary)
     iopr8  =  0 (print gas fugacity summary)
     iopr9  =  0 (print mean molal activity coefficient)
     iopr10 =  0 (print tabulation of pitzer coefficients)
     iopr11 =  0 (print major species for each element)
     iopr12-20   (not used)

        iodb1  =  0 (enable comp. messages)
        iodb2  =  0 (print pre-newton-raphson optimization)
        iodb3  =  0 (print order/scaling info.)
        iodb4  =  0 (print newton iteration info.)
        iodb5  =  0 (print search iterations)
        iodb6  =  0 (print hpsatz iterations)
        iodb7  =  0 (print f.d. and t.s. calculations)
        iodb8  =  0 (turns iodb3 on and off)
        iodb9  =  0 (print kinetics info.)
        iodb10 =  0 (check basis var. f.d. and t.s.)
        iodb11 =  0 (check reac. rate f.d. and t.s.)
        iodb12 =  0 (iteration variable killer option)
        iodb13 =  0 (not used)
        iodb14 =  0 (not used)
        iodb15 =  0 (not used)
        iodb16 =  0 (turn on akmatr prints)
        iodb17-20   (not used)

    tolbt  =  1.000000E-06 (residual function convergence tolerance)
    toldl  =  1.000000E-06 (correction term convergence tolerance)
    tolx   =  1.000000E-06 (sol-sol reactant/product identity tolerance)
    tolsat =  5.000000E-03 (lower supersaturation tolerance)
    tolsst =  1.000000E-02 (upper supersaturation tolerance)


screw1 =  1.000E-04 (primary step-size parameter for basis variables)
screw2 =    0.00000 (not used)
screw3 =  1.000E-04 (step size parameter for rate functions)
screw4 =  1.000E-04 (corrector parameter for rate functions)
screw5 =    4.00000 (under-relaxation control for n-r iteration)
screw6 =    4.00000 (step size parameter for economy mode)

    zklogu =     -6.000 (threshhold log mass for solids)
    zklogl =      2.000 (log mass decrement for p.r.s shift)
     zkfac =      0.800 (shift adjustment factor)
    zklgmn =     -6.097 (minimum log mass after a shift)


        itermx= 40 (newton-raphson iteration limit)
        ntrymx= 25 (phase assemblage try limit)
        npslmx= 12 (critical phase instability slide limit)
        nsslmx=  8 (critical redox instability slide limit)


--- inactive loaded aqueous species ---


  ag+                    am+++                  ar(aq)
  au+                    ba++                   be++
  cd++                   ce+++                  co++
  cro4--                 cs+                    cu++
  dy+++                  er+++                  eu+++
  ga+++                  gd+++                  h2aso4-
  he(aq)                 hg++                   ho+++
  in+++                  kr(aq)                 la+++
  li+                    lu+++                  mn++
  moo4--                 nd+++                  ne(aq)
  ni++                   no3-                   np++++
  pb++                   pd++                   pr+++
  pu++++                 ra++                   rb+
  reo4-                  rn(aq)                 ruo4--
  sc+++                  seo3--                 sm+++
  sn++                   tb+++                  tco4-
  th++++                 ti(oh)4(aq)            tl+
  tm+++                  uo2++                  vo++
  wo4--                  xe(aq)                 y+++
  yb+++                  zn++                   zr(oh)2++
  (o-phth)--             ag++                   am++++
  amo2+                  amo2++                 au+++
```

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```
benzene(aq)            co+++                  cr++
cr+++                  cro4---                cu+
eu++                   glycine(aq)            h2aso3-
hg2++                  methanamine(aq)        mn+++
mno4--                 n2(aq)                 n3-
nh4+                   no2-                   np+++
npo2+                  npo2++                 pb++++
pu+++                  puo2+                  puo2++
ru(oh)2++              ru++                   ru+++
ruo4(aq)               ruo4-                  se--
seo4--                 sm++                   sn++++
tc+++                  tco++                  tco4--
tco4---                u+++                   u++++
uo2+                   v+++                   vo2+
vo4---                 yb++                   zr++++
1-heptanol(aq)         1-heptene(aq)          1-heptyne(aq)
1-hexanol(aq)          1-hexene(aq)           1-hexyne(aq)
1-octanol(aq)          1-octene(aq)           1-octyne(aq)
1-pentanol(aq)         1-pentene(aq)          1-pentyne(aq)
2-butanone(aq)         2-heptanone(aq)        2-hexanone(aq)
2-octanone(aq)         2-pentanone(aq)        al(o-phth)+
ca(o-phth)(aq)         ethylbenzene(aq)       h(o-phth)-
h2(o-phth)(aq)         heptanoate             heptanoic acid(aq)
hexanoate              hexanoic acid(aq)      n-butylbenzene(aq)
n-heptane(aq)          n-heptylbenzene(aq     n-hexane(aq)
n-hexylbenzene(aq)     n-octane(aq)           n-octylbenzene(aq)
n-pentane(aq)          n-pentylbenzene(aq     n-propylbenzene(aq
na(o-phth)-            octanoate              octanoic acid(aq)
phenol(aq)             s5--                   toluene(aq)

--- inactive loaded minerals ---

albite high            andradite              annite
anorthite              antigorite             beidellite-ca
beidellite-k           beidellite-mg          beidellite-na
calcite                clinochlore-14a        clinoptilolite-ca
clinoptilolite-k       clinoptilolite-na      clinoptilolite-sr
clinozoisite           daphnite-14a           enstatite
epidote                fayalite               ferrosilite
forsterite             grossular              magnesite
mayenite               montmor-ca             montmor-k
montmor-mg             montmor-na             nontronite-ca
nontronite-k           nontronite-mg          nontronite-na
o-phthalic acid        phlogopite             sanidine high
saponite-ca            saponite-h             saponite-k
saponite-mg            saponite-na            siderite
strontianite

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

stepping to zi=  0.0000E+00, delzi=  0.0000E+00, nord= 0

  attempted species assemblage no.   1

          1      1  h2o
          2      3  al+++
          3      7  b(oh)3(aq)
          4     10  br-
          5     11  ca++
          6     14  cl-
          7     22  f-
          8     23  fe++
          9     26  h+
         10     28  hco3-
         11     32  hpo4--
         12     33  i-
         13     35  k+
         14     40  mg++
         15     43  na+
         16     60  sio2(aq)
         17     63  so4--
         18     64  sr++
         19     79  o2(g)

iter =   15
     27 supersaturated pure minerals
      7 supersaturated solid solutions

                        the most supersaturated phases     affinity, kcal

                          1      94   dolomite-ord            4.41261006
                          2      92   dolomite                4.41261006
                          3   50200   carbonate-calcite       1.72178172
                          4     287   talc                    7.15485933
                          5      93   dolomite-dis            2.30560787
                          6      65   chrysotile              5.20875841
                          7      24   aragonite               0.69064457
                          8     134   huntite                 2.65211752
```

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attempted species assemblage no. 2

1	1	h2o
2	3	al+++
3	7	b(oh)3(aq)
4	10	br-
5	11	ca++
6	14	cl-
7	22	f-
8	23	fe++
9	26	h+
10	28	hco3-
11	32	hpo4--
12	33	i-
13	35	k+
14	40	mg++
15	43	na+
16	60	sio2(aq)
17	63	so4--
18	64	sr++
19	79	o2(g)
20	94	dolomite-ord

iter = 11
19 supersaturated pure minerals
3 supersaturated solid solutions

the most supersaturated phases			affinity, kcal
1	130	hematite	12.03480169
2	122	goethite	5.35698269
3	51200	smectite-di	14.04521531
4	221	nontronite-h	12.47633063
5	113	fluorapatite	6.31636224
6	201	muscovite	6.91972996
7	155	kaolinite	3.53968133
8	119	gibbsite	1.63721830

attempted species assemblage no. 3

1	1	h2o
2	3	al+++
3	7	b(oh)3(aq)
4	10	br-
5	11	ca++
6	14	cl-
7	22	f-
8	23	fe++
9	26	h+
10	28	hco3-
11	32	hpo4--
12	33	i-
13	35	k+
14	40	mg++
15	43	na+
16	60	sio2(aq)
17	63	so4--
18	64	sr++
19	79	o2(g)
20	94	dolomite-ord
21	130	hematite

iter = 12
17 supersaturated pure minerals
3 supersaturated solid solutions

the most supersaturated phases			affinity, kcal
1	113	fluorapatite	6.31634693
2	201	muscovite	6.91973121
3	155	kaolinite	3.53968525
4	119	gibbsite	1.63722021
5	178	mesolite	3.83582000
6	141	illite	3.31987394
7	229	paragonite	3.83882640
8	51200	smectite-di	2.65675260

attempted species assemblage no. 4

1	1	h2o
2	3	al+++
3	7	b(oh)3(aq)
4	10	br-
5	11	ca++
6	14	cl-
7	22	f-
8	23	fe++
9	26	h+
10	28	hco3-
11	32	hpo4--

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```
          12      33  i-
          13      35  k+
          14      40  mg++
          15      43  na+
          16      60  sio2(aq)
          17      63  so4--
          18      64  sr++
          19      79  o2(g)
          20      94  dolomite-ord
          21     113  fluorapatite
          22     130  hematite

iter =   12
     16 supersaturated pure minerals
      3 supersaturated solid solutions

                        the most supersaturated phases     affinity, kcal

                          1     201   muscovite                6.92093688
                          2     155   kaolinite                3.54062111
                          3     119   gibbsite                 1.63768564
                          4     178   mesolite                 3.83633158
                          5     141   illite                   3.32073692
                          6     229   paragonite               3.84003196
                          7   51200   smectite-di              2.65767980
                          8     173   maximum microcline       1.65806777

  attempted species assemblage no.   5

           1       1  h2o
           2       3  al+++
           3       7  b(oh)3(aq)
           4      10  br-
           5      11  ca++
           6      14  cl-
           7      22  f-
           8      23  fe++
           9      26  h+
          10      28  hco3-
          11      32  hpo4--
          12      33  i-
          13      35  k+
          14      40  mg++
          15      43  na+
          16      60  sio2(aq)
          17      63  so4--
          18      64  sr++
          19      79  o2(g)
          20      94  dolomite-ord
          21     113  fluorapatite
          22     130  hematite
          23     201  muscovite

iter =   12
      0 supersaturated pure minerals
      1 supersaturated solid solutions

                        the most supersaturated phases     affinity, kcal

                          1   51200   smectite-di              1.24718907

  attempted species assemblage no.   6

           1       1  h2o
           2       3  al+++
           3       7  b(oh)3(aq)
           4      10  br-
           5      11  ca++
           6      14  cl-
           7      22  f-
           8      23  fe++
           9      26  h+
          10      28  hco3-
          11      32  hpo4--
          12      33  i-
          13      35  k+
          14      40  mg++
          15      43  na+
          16      60  sio2(aq)
          17      63  so4--
          18      64  sr++
          19      79  o2(g)
          20      94  dolomite-ord
          21     113  fluorapatite
          22     130  hematite
          23     201  muscovite
          24       1  smectitebeidellite-ca
          25       2  smectitebeidellite-k
          26       3  smectitebeidellite-mg
          27       4  smectitebeidellite-na
          28       5  smectitemontmor-ca
```

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29	6	smectitemontmor-k
30	7	smectitemontmor-mg
31	8	smectitemontmor-na
32	9	smectitenontronite-ca
33	10	smectitenontronite-k
34	11	smectitenontronite-mg
35	12	smectitenontronite-na

--- iteration has gone sour (iter= 14) ---
the phase to be dropped is hematite (130)

attempted species assemblage no. 7

1	1	h2o
2	3	al+++
3	7	b(oh)3(aq)
4	10	br-
5	11	ca++
6	14	cl-
7	22	f-
8	23	fe++
9	26	h+
10	28	hco3-
11	32	hpo4--
12	33	i-
13	35	k+
14	40	mg++
15	43	na+
16	60	sio2(aq)
17	63	so4--
18	64	sr++
19	79	o2(g)
20	94	dolomite-ord
21	113	fluorapatite
22	201	muscovite
23	1	smectitebeidellite-ca
24	2	smectitebeidellite-k
25	3	smectitebeidellite-mg
26	4	smectitebeidellite-na
27	5	smectitemontmor-ca
28	6	smectitemontmor-k
29	7	smectitemontmor-mg
30	8	smectitemontmor-na
31	9	smectitenontronite-ca
32	10	smectitenontronite-k
33	11	smectitenontronite-mg
34	12	smectitenontronite-na

iter = 12

- -

reaction progress = 0.00000000000000E+00
log of reaction progress = -999.0000000

temperature = 25.000 degrees c
total pressure = 1.013 bars

computing units remaining = 0.000

change in the product phase assemblage

start or re-start of run

maximum number of steps

--- element totals for the aqueous phase ---

element	mg/kg soln.	molal conc.	moles
o	8.598075E+05	5.562758E+01	5.562784E+01
al	3.943528E-05	1.512902E-09	1.512909E-09
b	4.455977E+00	4.266480E-04	4.266500E-04
br	6.501602E+01	8.422568E-04	8.422607E-04
ca	3.889233E+02	1.004501E-02	1.004506E-02
cl	1.869621E+04	5.458797E-01	5.458823E-01
f	1.338935E+00	7.295164E-05	7.295198E-05
fe	2.623868E-08	4.863342E-13	4.863365E-13
h	1.081038E+05	1.110195E+02	1.110200E+02
c	1.786183E+01	1.539358E-03	1.539365E-03
p	5.618196E-04	1.877576E-08	1.877585E-08
i	5.989589E-02	4.885542E-07	4.885565E-07
k	3.855548E+02	1.020753E-02	1.020758E-02
mg	1.242294E+03	5.290799E-02	5.290824E-02
na	1.040256E+04	4.683801E-01	4.683822E-01
si	1.929133E+00	7.110049E-05	7.110082E-05
s	8.745426E+02	2.823117E-02	2.823130E-02
sr	7.863751E+00	9.290073E-05	9.290116E-05

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co3--	1.539358E-03	1.539365E-03
so4--	2.823117E-02	2.823130E-02
s--	6.180482-141	6.180511-141

warning-- co3--, so4--, and s-- totals require that routine compl have the names of non-carbonate carbon, sulfide sulfur, and non-sulfate sulfur aqueous species

single ion activities and activity coefficients are here defined with respect to the modified nbs ph scale

	ph	eh	pe
modified nbs ph scale	6.7579	0.8184	1.3835E+01
rational ph scale	6.6459	0.8251	1.3947E+01

phcl = 7.2231

oxygen fugacity = 1.78589E-01
log oxygen fugacity = -0.74815

activity of water = 0.98231
log activity of water = -0.00775

ionic strength = 6.224964E-01 molal
sum of molalities = 1.0819386403006
osmotic coefficient = 0.91584

mass of solution = 1.035129 kg
mass of solutes = 0.035125 kg
conc of solutes = 3.393277 per cent (w/w)

moles of solvent h2o = 5.55087E+01
mass of solvent h2o = 1.00000E+00 kg

species	moles	grams	conc	log conc	log g	log act
h2o	5.55087E+01	1.00000E+03	9.80881E-01	-0.00838	0.00063	-0.00775
cl-	5.24365E-01	1.85902E+01	5.24363E-01	-0.28037	-0.18479	-0.46516
na+	4.44970E-01	1.02297E+01	4.44967E-01	-0.35167	-0.18908	-0.54075
mg++	4.06169E-02	9.87193E-01	4.06167E-02	-1.39130	-0.53245	-1.92375
nacl(aq)	1.64852E-02	9.63433E-01	1.64851E-02	-1.78291	0.00000	-1.78291
so4--	1.32289E-02	1.27081E+00	1.32288E-02	-1.87848	-0.73336	-2.61184
k+	9.98095E-03	3.90238E-01	9.98090E-03	-2.00083	-0.21797	-2.21880
ca++	9.08389E-03	3.64064E-01	9.08384E-03	-2.04173	-0.63896	-2.68069
mgso4(aq)	7.51825E-03	9.04961E-01	7.51821E-03	-2.12389	0.00000	-2.12389
naso4-	6.65764E-03	7.92614E-01	6.65760E-03	-2.17668	-0.15590	-2.33259
mgcl+	4.62671E-03	2.76481E-01	4.62669E-03	-2.33473	-0.18908	-2.52381
hco3-	9.05631E-04	5.52590E-02	9.05626E-04	-3.04305	-0.15590	-3.19895
br-	8.34815E-04	6.67050E-02	8.34811E-04	-3.07841	-0.15590	-3.23432
caso4(aq)	6.58529E-04	8.96532E-02	6.58526E-04	-3.18143	0.00000	-3.18143
b(oh)3(aq)	4.21666E-04	2.60729E-02	4.21664E-04	-3.37503	0.00000	-3.37503
nahco3(aq)	2.59655E-04	2.18128E-02	2.59654E-04	-3.58560	0.00000	-3.58560
cacl+	2.22654E-04	1.68172E-02	2.22653E-04	-3.65237	-0.18908	-3.84145
co2(aq)	2.21217E-04	9.73571E-03	2.21216E-04	-3.65518	0.05076	-3.60443
o2(aq)	2.00817E-04	6.42589E-03	2.00816E-04	-3.69720	0.05076	-3.64645
kso4-	1.60278E-04	2.16635E-02	1.60278E-04	-3.79513	-0.15590	-3.95103
mghco3+	1.26496E-04	1.07929E-02	1.26495E-04	-3.89793	-0.18908	-4.08700
sr++	8.05516E-05	7.05793E-03	8.05512E-05	-4.09393	-0.71026	-4.80418
sio2(aq)	7.02069E-05	4.21833E-03	7.02065E-05	-4.15362	0.00000	-4.15362
kcl(aq)	6.62900E-05	4.94198E-03	6.62897E-05	-4.17855	0.00000	-4.17855
cacl2(aq)	5.56408E-05	6.17520E-03	5.56405E-05	-4.25461	0.00000	-4.25461
f-	5.52305E-05	1.04929E-03	5.52303E-05	-4.25782	-0.15590	-4.41373
cahco3+	2.27057E-05	2.29543E-03	2.27056E-05	-4.64387	-0.18908	-4.83295
mgf+	1.59957E-05	6.92669E-04	1.59957E-05	-4.79600	-0.18908	-4.98508
srso4(aq)	7.65564E-06	1.40622E-03	7.65560E-06	-5.11602	0.00000	-5.11602
nabr(aq)	7.38136E-06	7.59495E-04	7.38132E-06	-5.13187	0.00000	-5.13187
srcl+	4.69069E-06	5.77296E-04	4.69067E-06	-5.32877	-0.18908	-5.51784
bo2-	2.00286E-06	8.57420E-05	2.00285E-06	-5.69835	-0.15590	-5.85426
mgb(oh)4+	1.96684E-06	2.02871E-04	1.96684E-06	-5.70623	-0.18908	-5.89531
mgco3(aq)	1.92896E-06	1.62639E-04	1.92895E-06	-5.71468	0.00000	-5.71468
naf(aq)	1.11667E-06	4.68869E-05	1.11667E-06	-5.95208	0.00000	-5.95208
caco3(aq)	7.52629E-07	7.53286E-05	7.52626E-07	-6.12342	0.00000	-6.12342
co3--	7.48308E-07	4.49054E-05	7.48304E-07	-6.12592	-0.64391	-6.76983
nab(oh)4(aq)	7.25089E-07	7.38359E-05	7.25085E-07	-6.13961	0.00000	-6.13961
caf+	5.97533E-07	3.53001E-05	5.97531E-07	-6.22364	-0.18908	-6.41272
nahsio3(aq)	5.64680E-07	5.65139E-05	5.64677E-07	-6.24820	0.00000	-6.24820
io3-	4.88556E-07	8.54498E-05	4.88554E-07	-6.31109	-0.15590	-6.46699
cab(oh)4+	2.89287E-07	3.44015E-05	2.89285E-07	-6.53867	-0.18908	-6.72775
nah3sio4(aq)	2.43472E-07	2.87533E-05	2.43471E-07	-6.61355	0.00000	-6.61355
naco3-	2.28942E-07	1.90020E-05	2.28941E-07	-6.64028	-0.15590	-6.79618
h+	2.26014E-07	2.27809E-07	2.26013E-07	-6.64587	-0.11206	-6.75793
oh-	8.70694E-08	1.48082E-06	8.70690E-08	-7.06014	-0.18479	-7.24493
kbr(aq)	6.45195E-08	7.67796E-06	6.45192E-08	-7.19031	0.00000	-7.19031

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hsio3-	6.30894E-08	4.86366E-06	6.30891E-08	-7.20005	-0.15590	-7.35595
hso4-	5.82432E-08	5.65375E-06	5.82429E-08	-7.23476	-0.15590	-7.39066
mgh3sio4+	2.05366E-08	2.45231E-06	2.05365E-08	-7.68747	-0.18908	-7.87655
hcl(aq)	1.27914E-08	4.66383E-07	1.27913E-08	-7.89308	0.00000	-7.89308
naoh(aq)	1.07010E-08	4.28009E-07	1.07010E-08	-7.97058	0.00000	-7.97058
hf(aq)	9.91859E-09	1.98435E-07	9.91854E-09	-8.00355	0.00000	-8.00355
mghpo4(aq)	6.85575E-09	8.24638E-07	6.85572E-09	-8.16395	0.00000	-8.16395
hpo4--	3.82967E-09	3.67569E-07	3.82966E-09	-8.41684	-0.73336	-9.15020
h2po4-	2.83912E-09	2.75358E-07	2.83910E-09	-8.54682	-0.15590	-8.70272
caoh+	2.56190E-09	1.46247E-07	2.56189E-09	-8.59144	-0.18908	-8.78052
nahpo4-	2.42638E-09	2.88664E-07	2.42637E-09	-8.61504	-0.15590	-8.77095
cah3sio4+	2.02110E-09	2.73222E-07	2.02109E-09	-8.69442	-0.18908	-8.88349
srco3(aq)	1.95563E-09	2.88709E-07	1.95563E-09	-8.70871	0.00000	-8.70871
mgh2po4+	1.66958E-09	2.02507E-07	1.66958E-09	-8.77739	-0.18908	-8.96647
srf+	1.28964E-09	1.37499E-07	1.28963E-09	-8.88953	-0.18908	-9.07861
al(oh)4-	1.16173E-09	1.10377E-07	1.16172E-09	-8.93490	-0.15590	-9.09080
cahpo4(aq)	8.11173E-10	1.10366E-07	8.11169E-10	-9.09089	0.00000	-9.09089
cah2po4+	1.60571E-10	2.20086E-08	1.60570E-10	-9.79434	-0.18908	-9.98341
al(oh)3(aq)	1.40938E-10	1.09937E-08	1.40938E-10	-9.85097	0.00000	-9.85097
mgpo4-	1.27963E-10	1.52629E-08	1.27962E-10	-9.89292	-0.15590	-10.04882
koh(aq)	1.17863E-10	6.61281E-09	1.17863E-10	-9.92862	0.00000	-9.92862
alf2+	1.04192E-10	6.77023E-09	1.04192E-10	-9.98217	-0.18908	-10.17125

--- summary of solid product phases---

product	log moles	moles	grams	volume, cc
dolomite-ord	-3.6174110	2.41318E-04	4.44993E-02	1.55264E-02
fluorapatite	-6.6735111	2.12075E-07	1.06950E-04	3.34145E-05
muscovite	-7.6530418	2.22310E-08	8.85477E-06	3.12812E-06
smectite-di	-7.7468600	1.79118E-08	7.60343E-06	2.35613E-06
beidellite-ca	-14.8476376	1.42024E-15	5.20607E-13	1.83964E-13
beidellite-k	-14.8697238	1.34982E-15	5.03283E-13	1.80471E-13
beidellite-mg	-14.3546213	4.41956E-15	1.60854E-12	5.44445E-13
beidellite-na	-14.2171330	6.06551E-15	2.22929E-12	7.91791E-13
montmor-ca	-12.3805923	4.16301E-13	1.52384E-10	5.54780E-11
montmor-k	-12.1893451	6.46629E-13	2.40761E-10	8.88675E-11
montmor-mg	-11.6766669	2.10539E-12	7.65186E-10	2.76326E-10
montmor-na	-11.5482695	2.82964E-12	1.03852E-09	3.79938E-10
nontronite-ca	-8.7167566	1.91974E-09	8.14534E-07	2.51678E-07
nontronite-k	-8.7391459	1.82328E-09	7.85074E-07	2.46636E-07
nontronite-mg	-8.2240433	5.96976E-09	2.51739E-06	7.74636E-07
nontronite-na	-8.0865551	8.19304E-09	3.48423E-06	1.08238E-06

	mass, grams	volume, cc
created	4.462271E-02	1.556527E-02
destroyed	0.000000E+00	0.000000E+00
net	4.462271E-02	1.556527E-02

warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base

--- mineral saturation state summary ---

mineral	affinity, kcal	state	mineral	affinity, kcal	state
albite	-2.5089		albite high	-4.3080	
albite low	-2.5089		alunite	-7.9958	
analcime	-2.4146		andalusite	-7.8474	
anhydrite	-1.3454		aragonite	-1.5209	
arcanite	-7.1606		artinite	-8.8234	
bassanite	-2.2305		beidellite-ca	-3.1969	
beidellite-h	-4.3291		beidellite-k	-3.2068	
beidellite-mg	-2.9749		beidellite-na	-2.9130	
bischofite	-9.9496		bloedite	-7.8886	
boehmite	-2.8881		boric acid	-4.3873	
brucite	-6.4413		calcite	-1.3239	
caso4:0.5h2o(beta)	-2.4598		celadonite	-1.0738	
celestite	-2.3724		chalcedony	-0.5805	
chrysotile	-6.4055		clinoptilolite-na	-9.5927	
coesite	-1.3156		corundum	-8.7539	
cristobalite	-0.9616		cristobalite-a	-0.9616	
cristobalite-b	-1.5666		dawsonite	-1.2509	
diaspore	-1.7359		diopside	-9.3587	
dolomite	0.0000		dolomite-dis	-2.1070	
dolomite-ord	0.0000	satd	enstatite	-5.3155	
epsomite	-3.5847		fe(oh)3	-8.2804	
fluorapatite	0.0000	satd	fluorite	-2.0071	
gibbsite	-0.6682		glauberite	-4.7980	
goethite	-1.2832		gypsum	-1.1265	
halite	-3.5354		hematite	-1.2456	
hexahydrite	-3.8954		huntite	-6.1626	
ice	-0.1995		illite	-1.9866	
jadeite	-4.5155		k-feldspar	-0.6511	
kainite	-9.4564		kalicinite	-7.7784	

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kalsilite	-4.5622	kaolinite	-1.0733	
kbr	-8.8982	kieserite	-5.8341	
kyanite	-7.4783	lansfordite	-4.4263	
laumontite	-7.0106	lawsonite	-7.3160	
magnesite	-0.8982	maximum microcline	-0.6511	
mesolite	-0.7557	mg1.25so4(oh)0.5:0	-9.2178	
mirabilite	-3.5895	monohydrocalcite	-2.4719	
montmor-ca	-2.0862	montmor-k	-2.0001	
montmor-mg	-1.7693	montmor-na	-1.7114	
mordenite	-5.0849	muscovite	0.0000	satd
na4ca(so4)3:2h2o	-9.2784	nabr	-9.2075	
nabr:2h2o	-8.0419	nahcolite	-4.9480	
natrolite	-5.7628	natron	-9.8368	
nepheline	-6.2320	nesquehonite	-4.6161	
nontronite-ca	-0.4367	nontronite-h	-1.5689	
nontronite-k	-0.4467	nontronite-mg	-0.2148	
nontronite-na	-0.1529	paragonite	-3.0809	
pentahydrite	-4.3482	phlogopite	-4.7031	
picromerite	-9.8118	pseudowollastonite	-9.9931	
pyrophyllite	-3.7052	quartz	-0.2105	
sanidine high	-2.2872	saponite-ca	-3.5948	
saponite-h	-4.7270	saponite-k	-3.6047	
saponite-mg	-3.3728	saponite-na	-3.3111	
scolecite	-4.3485	sellaite	-1.8571	
sillimanite	-8.3434	sio2(am)	-1.9646	
srcl2:6h2o	-9.9386	srf2	-6.9464	
starkeyite	-4.8660	stilbite	-2.5873	
strontianite	-1.2709	sylvite	-4.8157	
syngenite	-6.4798	talc	-4.1031	
thenardite	-4.6171	tridymite	-0.4445	
wollastonite	-9.6683			

--- summary of solid solutions ---

mineral	aff. kcal/mol	mole frac.	lambda	state
biotite	-4.7031			
annite	-4.70305	0.1236E-16	0.1527E-33	
phlogopite	-4.70305	1.000	1.000	
carbonate-calcite	-0.4814			
calcite	-0.48144	0.2412	1.000	
magnesite	-0.48144	0.4949	1.000	
siderite	-0.48144	0.4123E-17	1.000	
strontianite	-0.48144	0.2639	1.000	
chlorite-ss	-10.1820			
clinochlore-14a	-10.18197	1.000	1.000	
daphnite-14a	-10.18197	0.2670E-16	0.5082E-66	
clinoptilolite-ss	-8.8706			
clinoptilolite-ca	-8.87055	0.1021	0.3652E-02	
clinoptilolite-k	-8.87055	0.1851	0.1577E-01	
clinoptilolite-na	-8.87055	0.7031	0.4204	
clinoptilolite-sr	-8.87055	0.9674E-02	0.1108E-04	
epidote-ss	-13.3630			
clinozoisite	-13.36297	0.1766E-02	1.000	
epidote	-13.36297	0.9982	1.000	
garnet-ss	-19.2389			
andradite	-19.23887	0.9812	0.9812	
grossular	-19.23887	0.1876E-01	0.1876E-01	
olivine	-12.0705			
fayalite	-12.07055	0.6468E-15	2.174	
forsterite	-12.07055	1.000	1.000	
orthopyroxene	-5.3155			
enstatite	-5.31549	1.000	1.000	
ferrosilite	-5.31549	0.2065E-15	1.000	
plagioclase	-2.2679			
albite high	-2.26792	0.3196E-01	1.000	
anorthite	-2.26792	0.8925E-08	1.000	
sanidine high	-2.26792	0.9680	1.000	
sanidine-ss	-2.2679			
albite high	-2.26792	0.3196E-01	1.000	
sanidine high	-2.26792	0.9680	1.000	
anorthite	-2.26792	0.8925E-08	1.000	
saponite-tri	-3.1581			
saponite-ca	-3.15807	0.1071	4.466	
saponite-h	-3.15807	0.3274E-03	216.2	
saponite-k	-3.15807	0.1018	4.621	
saponite-mg	-3.15807	0.3334	2.087	
saponite-na	-3.15807	0.4573	1.689	
smectite-di	0.0000			saturated
beidellite-ca	0.00000	0.7929E-07	0.5722E+05	
beidellite-k	0.00000	0.7536E-07	0.5920E+05	

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    beidellite-mg                 0.00000    0.2467E-06   0.2674E+05
    beidellite-na                 0.00000    0.3386E-06   0.2163E+05
    montmor-ca                    0.00000    0.2324E-04    1272.
    montmor-k                     0.00000    0.3610E-04    947.3
    montmor-mg                    0.00000    0.1175E-03    429.5
    montmor-na                    0.00000    0.1580E-03    352.3
    nontronite-ca                 0.00000    0.1072        4.465
    nontronite-k                  0.00000    0.1018        4.622
    nontronite-mg                 0.00000    0.3333        2.088
    nontronite-na                 0.00000    0.4574        1.689

solid solution product phases

          xbar      lambda    activity  log xbar  log lambda log activity

  smectite-di
ideal solution

    beidellite-ca
       0.7929E-07  0.5722E+05  0.4537E-02  -7.101       4.758      -2.343
    beidellite-k
       0.7536E-07  0.5920E+05  0.4461E-02  -7.123       4.772      -2.351
    beidellite-mg
       0.2467E-06  0.2674E+05  0.6598E-02  -6.608       4.427      -2.181
    beidellite-na
       0.3386E-06  0.2163E+05  0.7325E-02  -6.470       4.335      -2.135
    montmor-ca
       0.2324E-04   1272.      0.2957E-01  -4.634       3.105      -1.529
    montmor-k
       0.3610E-04   947.3      0.3420E-01  -4.442       2.976      -1.466
    montmor-mg
       0.1175E-03   429.5      0.5049E-01  -3.930       2.633      -1.297
    montmor-na
       0.1580E-03   352.3      0.5566E-01  -3.801       2.547      -1.254
    nontronite-ca
       0.1072       4.465      0.4786     -0.9699      0.6498     -0.3201
    nontronite-k
       0.1018       4.622      0.4705     -0.9923      0.6648     -0.3275
    nontronite-mg
       0.3333       2.088      0.6959     -0.4772      0.3197     -0.1575
    nontronite-na
       0.4574       1.689      0.7725     -0.3397      0.2276     -0.1121


- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


        start time = 18:52       5Dec91
          end time = 18:54       5Dec91

        user time =      63.330
         cpu time =       8.290

--- no further input found ---
```

6.3. Calculating High Temperature pH from Quench pH

This example illustrates EQ6's capability to calculate high temperature properties from measurements of fluid samples that have been quenched (cooled to room temperature). The problem here is to calculate the *in situ* (at temperature) *pH* of the fluid in an autoclave experiment from a measurement of quench *pH* (the value measured at room temperature). This calculation also yields other *in situ* properties, such as redox potential and mineral saturation indices. The activity coefficients of the aqueous species are computed from the B-dot equation (**iopg1** = 0). The supporting data file is the **com** file.

The quenched fluid in the present example is taken from Knauss and Peifer (1986). The EQ3NR **input** file which initializes this calculation is **quenchfl.3i** (see Appendix F). The EQ3NR calculation pertains to the quench temperature, which is taken to be 25°C. Note that the analysis of the fluid must be essentially complete. The **pickup** file from this run was used as the bottom part of the EQ6 **input** file **heatqf.6i**, which is presented below in both formats.

Information Only

This EQ6 run steps the temperature from the quench value of 25°C to the *in situ* value of 150°C. In this example, the temperature was stepped up to 150°C. To do this, the **input** file variable **tempc0** was set to 25. The variable **jtemp** was set to 0, and **tk1** was set to 125. This **jtemp** option means that the temperature is computed from the formula: **tempc = tempc0 + tk1*zi1 + tk2*zi1**2 + tk3*zi1**3**. In this case, the temperature follows a path from 25 °C to 150°C. No minerals are precipitated in this EQ6 run because precipitation is globally suppressed by means of the **nxopt** subset selection suppression option "**all**". This option should generally be employed in extrapolating fluid quench chemistries to *in situ* conditions.

It is also possible to compute the properties of a fluid at different temperature using a temperature jump, as opposed to stepping the temperature up (or down) to the desired value (see Chapter 7). This can be done by setting **tempc0** to the desired value. The present version of EQ6 often has difficulty converging for temperature jumps greater than about 25 °C, although the actual limit varies with the fluid chemistry.

Parts of the **output** file for this example (**heatqf.6o**) are presented below. Included are the print points for 25°C and 150°C (the *in situ* temperature). The measured quench *pH* is 6.17. The calculated *in situ* value is 6.38. The solution is calculated to be multiply-supersaturated under *in situ* conditions. This is a realistic result, considering that the fluid was sampled after only one day of reaction with ground tuff.

The EQ6 **input** file (**heatqf.6i**), heat quenched fluid to 150°C ("W" format):

```
EQ6 input file name= heatqf.6i
Description= "Heat a quenched fluid to find the in situ pH"
Version number= 3245   Stage number= 01
Created 10/29/90     Creator= T.J. Wolery
Revised 10/29/90     Revisor= T.J. Wolery

  Heat quenched fluid from a hydrothermal experiment involving the
reaction of water with vitric tuff. This fluid is for day 16
of the 150 C experiment reported by Knauss and Peifer (1986,
Appendix B2, p. 31). In Table 4, p. 12, they report a calculated
in situ pH of 6.39.

  Purpose: to test the ability of the code to compute the high
temperature, in situ pH of a fluid from the measured quench pH.

  Note that unit change in the reaction progress variable
corresponds to an increase of 100 C in the temperature.

  The "all" mineral subset-selection suppression option is used
to prevent the formation of any pure mineral precipitates. The
option switch iopt4 is set to 0 to prevent the formation of any
solid solutions.

                          References

Knauss, K. G., and Peifer, D. W., 1986, Reaction of Vitric Topopah
  Spring Tuff and J-13 Ground Water under Hydrothermal Conditions
  Using Dickson-Type, Gold-Bag Rocking Autoclaves: UCRL-53795,
  Lawrence Livermore National Laboratory, Livermore, California,
  39 p.

endit.
    nmodl1=  2              nmodl2=  0
    tempc0=  2.50000E+01     jtemp=  0
       tk1=  100.000E+00       tk2=  0.00000E+00       tk3=  0.00000E+00
    zistrt=  0.00000E+00     zimax=  1.25000E+00
     tstrt=  0.00000E+00   timemax=  1.00000E+38
    kstpmx=          200     cplim=  0.00000E+00
    dzprnt=  1.00000E+38   dzprlg=  1.00000E+38    ksppmx=   100
    dzplot=  1.00000E+38   dzplig=  1.00000E+38    ksplmx= 10000
     ifile= 60
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
```

Information Only

```
  iodb1-10=     0    0    0    0    0    0    0    0    0    0
     11-20=     0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
     nxopt=  1
    option= all
    nxopex=  0
* nffg = number of gas species with fixed fugacities
     nffg =  0
* nrct = number of reactants
      nrct=  0
*-----------------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00     tolsl=  0.00000E+00      tolx=  0.00000E+00
    tolsat=  0.00000E+00    tolsst=  0.00000E+00
    screw1=  0.00000E+00    screw2=  0.00000E+00    screw3=  0.00000E+00
    screw4=  0.00000E+00    screw5=  0.00000E+00    screw6=  0.00000E+00
    zklogu=        0.000    zklogl=        0.000     zkfac=        0.000
    dlzmx1=  0.00000E+00    dlzmx2=  0.00000E+00    nordlm=  0
    itermx=  0              ntrymx=  0
    nps1mx=  0              nss1mx=  0              ioscan=  0
*-----------------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= quenchfl.3i
Description= "Quenched fluid from a hydrothermal experiment"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Quenched fluid from a hydrothermal experiment involving the
reaction of water with vitric tuff. This fluid is for day 16
of the 150 C experiment reported by Knauss and Peifer (1986,
Appendix B2, p. 31).

  Purpose: to test the ability of the code to compute the high
temperature, in situ pH of a fluid from the measured quench pH.
This test case produces a model of the quenched solution, which
is used to initialize the EQ6 test case input file heatqf.6i,
which takes the fluid up to the in situ temperature and gives
the in situ pH.

  Data for the following was originally specified as:

    SiO2(aq) :   Si          = 156 mg/L

                          References

Knauss, K. G., and Peifer, D. W., 1986, Reaction of Vitric Topopah
  Spring Tuff and J-13 Ground Water under Hydrothermal Conditions
  Using Dickson-Type, Gold-Bag Rocking Autoclaves: UCRL-53795,
  Lawrence Livermore National Laboratory, Livermore, California,
  39 p.

endit.
    tempci=  0.25000E+02
     nxmod=  0
     iopg1=  0               iopg2=  0               iopg3=  0
     iopg4=  0               iopg5=  0               iopg6=  0
     iopg7=  0               iopg8=  0               iopg9=  0
    iopg10=  0
       kct= 13                 ksq= 14                 kmt= 14
       kxt= 14                kdim= 14                kprs=  0
  o                  0.555269815717476E+02
  al                 0.518873275376966E-04
  ca                 0.134737262343943E-03
  cl                 0.211549472959789E-03
  f                  0.121062826533055E-03
  h                  0.111017869724876E+03
  c                  0.233049271133101E-02
  k                  0.409224953515136E-03
  mg                 0.617156963631210E-05
  na                 0.254200020270319E-02
  n                  0.106443131789226E-03
  si                 0.555386348846496E-02
  s                  0.238383737448853E-03
  electr             0.147080043065439E-02
  h2o                h2o                     0.174435898352698E+01
  al+++              al+++                  -0.795715886948377E+01
  ca++               ca++                   -0.308252699125854E+01
  cl-                cl-                    -0.367476711288551E+01
  f-                 f-                     -0.448269911100242E+01
  h+                 h+                     -0.614579779615327E+01
  hco3-              hco3-                  -0.301555046817940E+01
  k+                 k+                     -0.338864222507918E+01
  mg++               mg++                   -0.522955964427169E+01
  na+                na+                    -0.259591848324627E+01
  no3-               no3-                   -0.397310892845145E+01
  sio2(aq)           sio2(aq)               -0.225549180379597E+01
  so4--              so4--                  -0.363442314484525E+01
  o2(g)              o2(g)                  -0.700000000000000E+00
```

Information Only

The EQ6 input file (heatqf.6i), heat quenched fluid to 150°C ("D" format):

```
EQ6 input file name= heatqf.6i
Description= "Heat a quenched fluid to find the in situ pH"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Heat quenched fluid from a hydrothermal experiment involving the
reaction of water with vitric tuff. This fluid is for day 16
of the 150 C experiment reported by Knauss and Peifer (1986,
Appendix B2, p. 31). In Table 4, p. 12, they report a calculated
in situ pH of 6.39.

  Purpose: to test the ability of the code to compute the high
temperature, in situ pH of a fluid from the measured quench pH.

  Note that unit change in the reaction progress variable
corresponds to an increase of 100 C in the temperature.

  The "all" mineral subset-selection suppression option is used
to prevent the formation of any pure mineral precipitates. The
option switch iopt4 is set to 0 to prevent the formation of any
solid solutions.

                          References

Knauss, K. G., and Peifer, D. W., 1986, Reaction of Vitric Topopah
  Spring Tuff and J-13 Ground Water under Hydrothermal Conditions
  Using Dickson-Type, Gold-Bag Rocking Autoclaves: UCRL-53795,
  Lawrence Livermore National Laboratory, Livermore, California,
  39 p.

 calculational mode   |*normal     | economy          | super economy
 model type           | titration  |*closed           | open
 temperature model    |*power      | fluid mixing
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c
 tstart(c)|  25.00    |tk1|  100.0    |tk2|     0.    |tk3|     0.
 starting value of zi |      0.    |max. value of zi    |  1.2500
 starting time (sec)  |      0.    |max. time (sec)     | 1.00000E+38
 max. steps           |       200  |max. steps w/o print|       100
 linear print interval| 1.00000E+38|log print interval  | 1.00000E+38
 suppress mineral phases
 phases w/ elements|  all                  |                        n
 phases except     |                       |                        n
 fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
 none                              |                |                n
c                 R A T E     L A W S
c 1 = relative                  rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory   rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate        rate = CHECK DOCUMENTATION

c                 R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                 S U R F A C E    T Y P E
c 0 = fixed surface area     1 = fixed specific surface area
c
c                 N O T E S
c status and jreac are normally not set by the user
 reactants   (ss) solid solution only     (sp) special reactant only
 REACTANT          | none                  |status   |
 options
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * don't print
     lists species loaded into memory
 - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
   * don't print
```

Information Only

```
    print
- LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
  * don't print
    print
- LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
  * only species > 10**-12 molal
    all species
    don't print
- LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
  * don't print
    print
- LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
  * don't print
    print
- MINERAL SATURATION STATES -
  * print if affinity > -10 kcals
    print all
    don't print
- LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
  * don't print
    print
- PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
  * don't print
    print
- TAB FILES -
  * write
    append to previous tabx file
    don't write
- WRITE PICKUP FILE -
  * write pickup file at end of run
    don't write pickup file
    write pickup file for each print point
- PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    transfer minerals but leave trivial mass in the system
    transfer minerals
- CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    clear p.r.s. before first reaction progress advance
- PHASE BOUNDARY SEARCH -
  * step size constrained by predicted phase boundaries
    phase boundaries estimated from Taylor's series and printed
    locations of phase boundaries ignored
- AUTO BASIS SWITCHING -
  * off
    on
- SUPPRESS REDOX REACTIONS -
  * does nothing
    suppress all redox reactions
- LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
  * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
    logarithmic for kcol = 1,kbt
    linear for kcol = 1,kdim
- AZERO AND HYDRATION NUMBERS -
  * no change
    read in new azero and hydration numbers
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
  * does nothing
    print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
    print summary information
    print detailed information
- PRINT STEP SIZE AND ORDER -
  * don't print
    print scale factor
    print orders and step size scaling factors
- CONTROL STEP SIZE AND ORDER PRINT -
  * does nothing
    print step size and order when delzi .le. dlzmx1
- NEWTON ITERATIONS -
  * don't print
    print summary of newton iterations
    print summary, residual functions and correction terms
    print summary, residual functions, correction terms and matrix
- PRINT SEARCH ITERATIONS -
  * don't print
    print
- PRINT HPSAT ITERATIONS -
  * don't print
    print
- PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
  * don't print
    print computations from RDERIV, and RTAYLR
    print computations from RDERIV, RTAYLR, DERIV and TAYLOR
```

Information Only

```
 - PRINT KINETICS DIAGNOSTIC MESSAGES -
   * don't print
     print level 1 diagnostics
     print level 1 and level 2 diagnostics
 - PRINT AKMATR -
   * don't print
     print level 1 diagnostics
 - KILL ITERATION VARIABLES -
   * does nothing
     allow selection of variables to remove
-----------------------------------------------------------------------
 development options  (used for code development)
-----------------------------------------------------------------------
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
-----------------------------------------------------------------------
 tolerances                          desired values - defaults info-only
-----------------------------------------------------------------------
 number of N-R iterations            |                | 40      itermx
 p.r.s. transfer interval            |                | varies  dlzidp
 residual magnitude                  |                | 1.0e-06 tolbt
 correction magnitude                |                | 1.0e-06 toldl
 search/find tolerance               |                | varies  tolx
 supersaturation                     |                | varies  tolsat
 supersaturation set size            |                | varies  tolsst
 max. size Taylor's series term      |                | 1.0e-04 screw1
 max. initial value betamx           |                | n/a     screw2
 max. Taylor's series term (kin.)    |                | 1.0e-04 screw3
 corrector iteration                 |                | 1.0e-04 screw4
 max. size of N-R correction term    |                | 4.0     screw5
 step size (economy mode)            |                | 4.0     screw6
 log mass of phases                  |                | varies  zklogu
 decrement mass (p.r.s.)             |                | 2.0     zklogl
 min. left after p.r.s.              |                | .98     zkfac
 initial step size                   |                | varies  dlzmx1
 upper limit step size               |                | varies  dlzmx2
 maximum order                       |                | 6       nordlm
 num. attempted assemblages          |                | 25      ntrymx
 slide -> over phase bound.          |                | 8       npslmx
 slide -> over redox insta.          |                | 3       nsslmx
 fo2 scan control                    |                | none    ioscan
-----------------------------------------------------------------------
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= quenchfl.3i
Description= "Quenched fluid from a hydrothermal experiment"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Quenched fluid from a hydrothermal experiment involving the
reaction of water with vitric tuff. This fluid is for day 16
of the 150 C experiment reported by Knauss and Peifer (1986,
Appendix B2, p. 31).

  Purpose: to test the ability of the code to compute the high
temperature, in situ pH of a fluid from the measured quench pH.
This test case produces a model of the quenched solution, which
is used to initialize the EQ6 test case input file heatqf.6i,
which takes the fluid up to the in situ temperature and gives
the in situ pH.

  Data for the following was originally specified as:

    SiO2(aq) :   Si          = 156 mg/L

                            References

Knauss, K. G., and Peifer, D. W., 1986, Reaction of Vitric Topopah
  Spring Tuff and J-13 Ground Water under Hydrothermal Conditions
  Using Dickson-Type, Gold-Bag Rocking Autoclaves: UCRL-53795,
  Lawrence Livermore National Laboratory, Livermore, California,
  39 p.

-----------------------------------------------------------------------
 temperature (C)                    |     25.000
-----------------------------------------------------------------------
 electrical imbalance               |     1.470800430654390E-03
-----------------------------------------------------------------------
 number of aqueous master species   |     14
-----------------------------------------------------------------------
 position of last pure mineral      |     14
-----------------------------------------------------------------------
 position of last solid solution    |     14
-----------------------------------------------------------------------
 suppressed species     (suppress,replace,augmentk,augmentg)  value
-----------------------------------------------------------------------
 none                   |
-----------------------------------------------------------------------
 iopg options
-----------------------------------------------------------------------
 - pH SCALE CONVENTION -
    * modified NBS
```

Information Only

```
      internal
      rational
 - ACTIVITY COEFFICIENT OPTIONS -
    * use B-dot equation
      Davies' equation
      Pitzer's equations
-----------------------------------------------------------------------
 elements, moles and moles aqueous
-----------------------------------------------------------------------
          o        |   5.552698157174760E+01|    0.000000000000000E+00
          al       |   5.188732753769660E-05|    0.000000000000000E+00
          ca       |   1.347372623439430E-04|    0.000000000000000E+00
          cl       |   2.115494729597890E-04|    0.000000000000000E+00
          f        |   1.210628265330550E-04|    0.000000000000000E+00
          h        |   1.110178697248760E+02|    0.000000000000000E+00
          c        |   2.330492711331010E-03|    0.000000000000000E+00
          k        |   4.092249535151360E-04|    0.000000000000000E+00
          mg       |   6.171569636312100E-06|    0.000000000000000E+00
          na       |   2.542000202703190E-03|    0.000000000000000E+00
          n        |   1.064431317892260E-04|    0.000000000000000E+00
          si       |   5.553863488464960E-03|    0.000000000000000E+00
          s        |   2.383837374488530E-04|    0.000000000000000E+00
-----------------------------------------------------------------------
 master species and logarithmic basis variables
-----------------------------------------------------------------------
h2o                 |h2o                     |    1.744358983526980E+00
al+++               |al+++                   |   -7.957158869483770E+00
ca++                |ca++                    |   -3.882526991258540E+00
cl-                 |cl-                     |   -3.674767112885510E+00
f-                  |f-                      |   -4.482699111002420E+00
h+                  |h+                      |   -6.145797796153270E+00
hco3-               |hco3-                   |   -3.015550468179400E+00
k+                  |k+                      |   -3.388642225079180E+00
mg++                |mg++                    |   -5.229559644271690E+00
na+                 |na+                     |   -2.595918483246270E+00
no3-                |no3-                    |   -3.973108928451450E+00
sio2(aq)            |sio2(aq)                |   -2.255491803795970E+00
so4--               |so4--                   |   -3.634423144845250E+00
o2(g)               |o2(g)                   |   -7.000000000000000E-01
-----------------------------------------------------------------------
 physically removed subsystem  (solid solution, mineral, moles)
-----------------------------------------------------------------------
 none               |                        |
-----------------------------------------------------------------------
```

The EQ6 **output** file (**heatqf.6o**), heat quenched fluid to 150°C (partial reproduction)

```
                    .
                    .
                    .
              (Material deleted)
                    .
                    .
                    .
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

stepping to zi=  0.0000E+00, delzi=  0.0000E+00, nord= 0

  attempted species assemblage no.   1

             1      1  h2o
             2      3  al+++
             3     11  ca++
             4     14  cl-
             5     22  f-
             6     26  h+
             7     28  hco3-
             8     35  k+
             9     40  mg++
            10     43  na+
            11     47  no3-
            12     60  sio2(aq)
            13     63  so4--
            14     79  o2(g)

iter =    1

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                  reaction progress        =  0.00000000000000E+00
                  log of reaction progress =    -999.0000000
```

Information Only

```
temperature     =      25.000 degrees c
total pressure =        1.013 bars

computing units remaining =       0.000
```

start or re-start of run

--- element totals for the aqueous phase ---

element	mg/kg soln.	molal conc.	moles
o	8.878816E+05	5.552698E+01	5.552698E+01
al	1.399186E+00	5.188733E-05	5.188733E-05
ca	5.396859E+00	1.347373E-04	1.347373E-04
cl	7.495637E+00	2.115495E-04	2.115495E-04
f	2.298662E+00	1.210628E-04	1.210628E-04
h	1.118343E+05	1.110179E+02	1.110179E+02
c	2.797527E+01	2.330493E-03	2.330493E-03
k	1.599069E+01	4.092250E-04	4.092250E-04
mg	1.499127E-01	6.171570E-06	6.171570E-06
na	5.840601E+01	2.542000E-03	2.542000E-03
n	1.490054E+00	1.064431E-04	1.064431E-04
si	1.558923E+02	5.553863E-03	5.553863E-03
s	7.639566E+00	2.383837E-04	2.383837E-04
co3--		2.330493E-03	2.330493E-03
so4--		2.383837E-04	2.383837E-04
s--		9.978163-142	9.978163-142

warning-- co3--, so4--, and s-- totals require that routine compl
have the names of non-carbonate carbon, sulfide sulfur,
and non-sulfate sulfur aqueous species

single ion activities and activity coefficients are here defined
with respect to the modified nbs ph scale

	ph	eh	pe
modified nbs ph scale	6.1700	0.8537	1.4431E+01
rational ph scale	6.1458	0.8551	1.4455E+01

phcl = 9.8703

```
oxygen fugacity =  1.99526E-01
log oxygen fugacity =  -0.70000

activity of water =    0.99979
log activity of water =  -0.00009

ionic strength =  2.904497E-03 molal
sum of molalities =   0.0118537298584
osmotic coefficient =   0.99072

mass of solution =   1.000582 kg
mass of solutes  =   0.000582 kg
conc of solutes  =   0.058170 per cent (w/w)

moles of solvent h2o =  5.55084E+01
mass of solvent h2o  =  1.00000E+00 kg
```

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	1.00000E+03	9.99786E-01	-0.00009	0.00000	-0.00009
sio2(aq)	5.55275E-03	3.33633E-01	5.55275E-03	-2.25549	0.00000	-2.25549
na+	2.53560E-03	5.82930E-02	2.53560E-03	-2.59592	-0.02617	-2.62209
co2(aq)	1.36130E-03	5.99106E-02	1.36130E-03	-2.86605	0.00022	-2.86583
hco3-	9.64827E-04	5.88710E-02	9.64827E-04	-3.01555	-0.02507	-3.04062
k+	4.08656E-04	1.59778E-02	4.08656E-04	-3.38864	-0.02660	-3.41524
o2(aq)	2.52046E-04	8.06517E-03	2.52046E-04	-3.59852	0.00022	-3.59830
so4--	2.32047E-04	2.22913E-02	2.32047E-04	-3.63442	-0.10173	-3.73615
cl-	2.11462E-04	7.49691E-03	2.11462E-04	-3.67477	-0.02550	-3.70027
ca++	1.31061E-04	5.25266E-03	1.31061E-04	-3.88253	-0.10063	-3.98316
no3-	1.06388E-04	6.59656E-03	1.06388E-04	-3.97311	-0.02550	-3.99861
f-	3.29080E-05	6.25198E-04	3.29080E-05	-4.48270	-0.02507	-4.50777
alf2+	2.74165E-05	1.78148E-03	2.74165E-05	-4.56199	-0.02617	-4.58816
alf3(aq)	1.00943E-05	8.47690E-04	1.00943E-05	-4.99592	0.00000	-4.99592
mg++	5.89441E-06	1.43264E-04	5.89441E-06	-5.22956	-0.09754	-5.32710
nahco3(aq)	3.10024E-06	2.60442E-04	3.10024E-06	-5.50860	0.00000	-5.50860
naso4-	3.06782E-06	3.65235E-04	3.06782E-06	-5.51317	-0.02507	-5.53824
alf++	2.64664E-06	1.21692E-04	2.64664E-06	-5.57730	-0.10309	-5.68039
caso4(aq)	2.46485E-06	3.35569E-04	2.46485E-06	-5.60821	0.00000	-5.60821
al(oh)4-	2.42312E-06	2.30223E-04	2.42312E-06	-5.61563	-0.02507	-5.64069

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al(oh)3(aq)	1.51147E-06	1.17900E-04	1.51147E-06	-5.82060	0.00000	-5.82060
al(oh)2+	1.24240E-06	7.57815E-05	1.24240E-06	-5.90574	-0.02617	-5.93191
cahco3+	1.11968E-06	1.13194E-04	1.11968E-06	-5.95091	-0.02617	-5.97708
hsio3-	9.70472E-07	7.48153E-05	9.70472E-07	-6.01302	-0.02507	-6.03808
h+	7.14829E-07	7.20505E-07	7.14829E-07	-6.14580	-0.02420	-6.17000
kso4-	5.66596E-07	7.65822E-05	5.66596E-07	-6.24673	-0.02507	-6.27179
al13o4(oh)24(7+)	4.87249E-07	4.00974E-04	4.87249E-07	-6.31225	-1.22444	-7.53669
mgso4(aq)	2.23075E-07	2.68513E-05	2.23075E-07	-6.65155	0.00000	-6.65155
aloh++	1.22735E-07	5.39898E-06	1.22735E-07	-6.91103	-0.10309	-7.01412
nahsio3(aq)	9.73484E-08	9.74277E-06	9.73484E-08	-7.01167	0.00000	-7.01167
alf4-	8.34409E-08	8.59234E-06	8.34409E-08	-7.07862	-0.02507	-7.10369
nacl(aq)	7.95510E-08	4.64916E-06	7.95510E-08	-7.09935	0.00000	-7.09935
co3--	7.95487E-08	4.77365E-06	7.95487E-08	-7.09937	-0.10005	-7.19942
caho3+	5.55138E-08	5.66701E-06	5.55138E-08	-7.25560	-0.02617	-7.28177
mghco3+	4.94484E-08	4.21905E-06	4.94484E-08	-7.30585	-0.02617	-7.33202
nah3sio4(aq)	4.27206E-08	5.04516E-06	4.27206E-08	-7.36936	0.00000	-7.36936
hf(aq)	3.09267E-08	6.18731E-07	3.09267E-08	-7.50967	0.00000	-7.50967
caf+	1.64795E-08	9.73548E-07	1.64795E-08	-7.78306	-0.02617	-7.80923
oh-	1.58602E-08	2.69739E-07	1.58602E-08	-7.79969	-0.02550	-7.82519
caco3(aq)	1.39484E-08	1.39605E-06	1.39484E-08	-7.85548	0.00000	-7.85548
hso4-	1.25319E-08	1.21649E-06	1.25319E-08	-7.90198	-0.02507	-7.92705
al+++	1.10367E-08	2.97788E-07	1.10367E-08	-7.95716	-0.21547	-8.17262
naf(aq)	7.45670E-09	3.13093E-07	7.45670E-09	-8.12745	0.00000	-8.12745
cacl+	4.43754E-09	3.35171E-07	4.43754E-09	-8.35286	-0.02617	-8.37903
mgf+	3.49707E-09	1.51435E-07	3.49707E-09	-8.45630	-0.02617	-8.48246
kcl(aq)	2.45408E-09	1.82954E-07	2.45408E-09	-8.61011	0.00000	-8.61011
cah3sio4+	1.46465E-09	1.97999E-07	1.46465E-09	-8.83427	-0.02617	-8.86044
also4+	1.34090E-09	1.64991E-07	1.34090E-09	-8.87261	-0.02617	-8.89877
mgcl+	7.30976E-10	4.36814E-08	7.30976E-10	-9.13610	-0.02617	-9.16227
naco3-	5.22351E-10	4.33546E-08	5.22351E-10	-9.28204	-0.02507	-9.30710
mgco3(aq)	2.83389E-10	2.38938E-08	2.83389E-10	-9.54762	0.00000	-9.54762
mgh3sio4+	1.17976E-10	1.40878E-08	1.17976E-10	-9.92821	-0.02617	-9.95437

	mass, grams	volume, cc
created	0.000000E+00	0.000000E+00
destroyed	0.000000E+00	0.000000E+00
net	0.000000E+00	0.000000E+00

warning-- these volume totals may be incomplete because of missing partial molar volume data in the data base

--- mineral saturation state summary ---

mineral	affinity, kcal	state	mineral	affinity, kcal	state
albite	7.1063	ssatd	albite high	5.3072	ssatd
albite low	7.1063	ssatd	alf3	-4.9439	
alunite	6.1748	ssatd	amesite-14a	-9.7540	
analcime	4.6513	ssatd	analcime-dehy	-4.0291	
andalusite	5.7080	ssatd	anhydrite	-4.6562	
anorthite	-0.4753		aragonite	-3.8840	
bassanite	-5.5361		beidellite-ca	18.5364	ssatd
beidellite-h	17.9620	ssatd	beidellite-k	18.2810	ssatd
beidellite-mg	18.2854	ssatd	beidellite-na	18.1764	ssatd
boehmite	2.6000	ssatd	caal2o4:10h2o	-9.8977	
calcite	-3.6869		caso4:0.5h2o(beta)	-5.7654	
celadonite	6.1119	ssatd	chalcedony	2.0091	ssatd
clinozoisite	0.3626	ssatd	coesite	1.2740	ssatd
cordierite anhyd	-6.5318		cordierite hydr	-3.1485	
corundum	2.2119	ssatd	cristobalite	1.6280	ssatd
cristobalite-a	1.6280	ssatd	cristobalite-b	1.0230	ssatd
dawsonite	1.6137	ssatd	diaspore	3.7522	ssatd
dolomite	-7.5922		dolomite-dis	-9.6992	
dolomite-ord	-7.5922		enstatite	-8.9628	
epsomite	-9.6886		fluorite	-4.0406	
gibbsite	4.8304	ssatd	gismondine	14.6543	ssatd
gypsum	-4.4165		ice	-0.1891	
illite	16.6813	ssatd	jadeite	2.5102	ssatd
k-feldspar	10.1714	ssatd	kalicinite	-9.1947	
kalsilite	1.0811	ssatd	kaolinite	15.0926	ssatd
kyanite	6.0770	ssatd	lansfordite	-9.6033	
laumontite	10.9847	ssatd	lawsonite	5.4792	ssatd
magnesite	-6.1274		margarite	10.2971	ssatd
maximum microcline	10.1714	ssatd	mesolite	13.3049	ssatd
monohydrocalcite	-4.8245		montmor-ca	14.8248	ssatd
montmor-k	14.6654	ssatd	montmor-mg	14.6688	ssatd
montmor-na	14.5556	ssatd	mordenite	10.9201	ssatd
mordenite-dehy	-9.7193		muscovite	21.7988	ssatd
nahcolite	-7.5715		natrolite	5.7198	ssatd
nepheline	-1.7959		nesquehonite	-9.8140	
niter	-9.8319		okenite	-8.9170	
paragonite	17.5106	ssatd	prehnite	-0.8183	
pyrophyllite	17.6295	ssatd	quartz	2.3791	ssatd
sanidine high	8.5353	ssatd	scolecite	11.0467	ssatd
sellaite	-6.7568		sillimanite	5.2120	ssatd
sio2(am)	0.6250	ssatd	stilbite	23.1592	ssatd
tridymite	2.1451	ssatd	wairakite	4.9691	ssatd
zoisite	0.3016	ssatd			

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stepping to zi=  1.0000E-02, delzi=  1.0000E-02, nord= 0
steps completed =     1, iter =  4, ncorr = 0
most rapidly changing is zvclgl(o2(g)              ) =     -0.6928

stepping to zi=  2.0000E-02, delzi=  1.0000E-02, nord= 0
steps completed =     2, iter =  4, ncorr = 0
most rapidly changing is zvclgl(o2(g)              ) =     -0.6857

stepping to zi=  3.0000E-02, delzi=  1.0000E-02, nord= 0
steps completed =     3, iter =  4, ncorr = 0
most rapidly changing is zvclgl(o2(g)              ) =     -0.6789

stepping to zi=  4.0000E-02, delzi=  1.0000E-02, nord= 0
steps completed =     4, iter =  4, ncorr = 0
most rapidly changing is zvclgl(al+++              ) =     -7.9747

                    .
                    .
                    .
            (Material deleted)
                    .
                    .
                    .

stepping to zi=  1.1790E+00, delzi=  2.7956E-02, nord= 6
steps completed =    47, iter =  1, ncorr = 0
most rapidly changing is zvclgl(al+++              ) =    -15.8720

stepping to zi=  1.2070E+00, delzi=  2.8005E-02, nord= 6
steps completed =    48, iter =  1, ncorr = 0
most rapidly changing is zvclgl(al+++              ) =    -16.0847

stepping to zi=  1.2350E+00, delzi=  2.8058E-02, nord= 6
steps completed =    49, iter =  1, ncorr = 0
most rapidly changing is zvclgl(al+++              ) =    -16.2972

stepping to zi=  1.2500E+00, delzi=  1.4985E-02, nord= 6
steps completed =    50, iter =  1, ncorr = 0
most rapidly changing is zvclgl(al+++              ) =    -16.4104
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                reaction progress        =  1.25000000000000E+00
                log of reaction progress =       0.0969100

                temperature    =    150.000 degrees c
                total pressure =      4.757 bars

                computing units remaining =      0.000

maximum value of reaction progress
```

--- element totals for the aqueous phase ---

element	mg/kg soln.	molal conc.	moles
o	8.878816E+05	5.552698E+01	5.552698E+01
al	1.399186E+00	5.188733E-05	5.188733E-05
ca	5.396859E+00	1.347373E-04	1.347373E-04
cl	7.495637E+00	2.115495E-04	2.115495E-04
f	2.298662E+00	1.210628E-04	1.210628E-04
h	1.118343E+05	1.110179E+02	1.110179E+02
c	2.797527E+01	2.330493E-03	2.330493E-03
k	1.599069E+01	4.092250E-04	4.092250E-04
mg	1.499127E-01	6.171570E-06	6.171570E-06
na	5.840601E+01	2.542000E-03	2.542000E-03
n	1.490054E+00	1.064431E-04	1.064431E-04
si	1.558923E+02	5.553864E-03	5.553863E-03
s	7.639566E+00	2.383837E-04	2.383837E-04
co3--		2.330493E-03	2.330493E-03
so4--		2.383837E-04	2.383837E-04
s--		1.833352E-95	1.833352E-95

warning-- co3--, so4--, and s-- totals require that routine compl
have the names of non-carbonate carbon, sulfide sulfur,
and non-sulfate sulfur aqueous species

single ion activities and activity coefficients are here defined
with respect to the modified nbs ph scale

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	ph	eh	pe
modified nbs ph scale	6.3840	0.6673	7.9485E+00
rational ph scale	6.3525	0.6700	7.9799E+00

phcl = 10.0928

oxygen fugacity = 2.73360E-01
log oxygen fugacity = -0.56326

activity of water = 0.99979
log activity of water = -0.00009

ionic strength = 2.790310E-03 molal
sum of molalities = 0.0119353889244
osmotic coefficient = 0.98841

mass of solution = 1.000582 kg
mass of solutes = 0.000582 kg
conc of solutes = 0.058175 per cent (w/w)

moles of solvent h2o = 5.55084E+01
mass of solvent h2o = 1.00000E+00 kg

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	1.00000E+03	9.99785E-01	-0.00009	0.00000	-0.00009
sio2(aq)	5.53269E-03	3.32428E-01	5.53269E-03	-2.25706	0.00000	-2.25706
na+	2.53584E-03	5.82984E-02	2.53584E-03	-2.59588	-0.03418	-2.63006
co2(aq)	1.55657E-03	6.85041E-02	1.55657E-03	-2.80783	-0.00014	-2.80798
hco3-	7.68057E-04	4.68646E-02	7.68057E-04	-3.11461	-0.03296	-3.14756
k+	4.07068E-04	1.59157E-02	4.07068E-04	-3.39033	-0.03478	-3.42511
o2(aq)	2.52046E-04	8.06517E-03	2.52046E-04	-3.59852	-0.00014	-3.59866
so4--	2.16380E-04	2.07862E-02	2.16380E-04	-3.66478	-0.13345	-3.79823
cl-	2.11228E-04	7.48861E-03	2.11228E-04	-3.67525	-0.03355	-3.70880
f-	1.19449E-04	2.26934E-03	1.19449E-04	-3.92282	-0.03296	-3.95577
ca++	1.17583E-04	4.71249E-03	1.17583E-04	-3.92966	-0.13138	-4.06103
no3-	1.06443E-04	6.60000E-03	1.06443E-04	-3.97288	-0.03355	-4.00643
al(oh)4-	4.62702E-05	4.39618E-03	4.62702E-05	-4.33470	-0.03296	-4.36766
hsio3-	2.04224E-05	1.57440E-03	2.04224E-05	-4.68989	-0.03296	-4.72285
caso4(aq)	1.12418E-05	1.53048E-03	1.12418E-05	-4.94916	0.00000	-4.94916
oh-	6.11878E-06	1.04064E-04	6.11878E-06	-5.21334	-0.03355	-5.24689
al(oh)3(aq)	5.61476E-06	4.37971E-04	5.61476E-06	-5.25067	0.00000	-5.25067
cahco3+	4.83374E-06	4.88668E-04	4.83374E-06	-5.31572	-0.03418	-5.34990
naso4-	4.73444E-06	5.63651E-04	4.73444E-06	-5.32473	-0.03296	-5.35769
mgso4(aq)	3.51544E-06	4.23149E-04	3.51545E-06	-5.45402	0.00000	-5.45402
mg++	2.50995E-06	6.10044E-05	2.50995E-06	-5.60033	-0.12716	-5.72749
kso4-	2.13707E-06	2.88851E-04	2.13707E-06	-5.67018	-0.03296	-5.70314
hf(aq)	9.96141E-07	1.99291E-05	9.96141E-07	-6.00168	0.00000	-6.00168
nahsio3(aq)	6.49368E-07	6.49897E-05	6.49368E-07	-6.18751	0.00000	-6.18751
caco3(aq)	5.09457E-07	5.09901E-05	5.09457E-07	-6.29289	0.00000	-6.29289
caf+	4.64059E-07	2.74149E-05	4.64059E-07	-6.33343	-0.03418	-6.36761
h+	4.44108E-07	4.47634E-07	4.44108E-07	-6.35251	-0.03149	-6.38401
hso4-	3.75079E-07	3.64095E-05	3.75079E-07	-6.42588	-0.03296	-6.45884
nacl(aq)	2.79989E-07	1.63633E-05	2.79989E-07	-6.55286	0.00000	-6.55286
nahco3(aq)	2.68582E-07	2.25628E-05	2.68582E-07	-6.57092	0.00000	-6.57092
co3--	1.46991E-07	8.82083E-06	1.46991E-07	-6.83271	-0.13115	-6.96386
naf(aq)	1.19088E-07	5.00028E-06	1.19088E-07	-6.92413	0.00000	-6.92413
mghco3+	1.09529E-07	9.34521E-06	1.09529E-07	-6.96047	-0.03418	-6.99465
nah3sio4(aq)	9.68721E-08	1.14403E-05	9.68721E-08	-7.01380	0.00000	-7.01380
caoh+	8.49885E-08	4.85160E-06	8.49885E-08	-7.07064	-0.03418	-7.10482
mgf+	3.30231E-08	1.43001E-06	3.30231E-08	-7.48118	-0.03418	-7.51536
cacl+	2.01487E-08	1.52185E-06	2.01487E-08	-7.69575	-0.03418	-7.72993
kcl(aq)	1.95610E-08	1.45829E-06	1.95610E-08	-7.70861	0.00000	-7.70861
naoh(aq)	9.46355E-09	3.78515E-07	9.46355E-09	-8.02395	0.00000	-8.02395
mgco3(aq)	2.01628E-09	1.70001E-07	2.01628E-09	-8.69545	0.00000	-8.69545
al(oh)2+	1.80509E-09	1.10104E-07	1.80509E-09	-8.74350	-0.03418	-8.77768
mgcl+	1.60211E-09	9.57382E-08	1.60211E-09	-8.79531	-0.03418	-8.82949
alf2+	3.42236E-10	2.22379E-08	3.42236E-10	-9.46567	-0.03418	-9.49986
h2sio4--	1.81974E-10	1.71236E-08	1.81974E-10	-9.73999	-0.13345	-9.87344
alf3(aq)	1.49029E-10	1.25150E-08	1.49029E-10	-9.82673	0.00000	-9.82673

	mass, grams	volume, cc
created	0.000000E+00	0.000000E+00
destroyed	0.000000E+00	0.000000E+00
net	0.000000E+00	0.000000E+00

warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base

--- mineral saturation state summary ---

Information Only

mineral	affinity, kcal	state	mineral	affinity, kcal	state
albite	1.7699	ssatd	albite high	0.3196	ssatd
albite low	1.7699	ssatd	amesite-14a	2.4341	ssatd
analcime	0.4134	ssatd	analcime-dehy	-7.6562	
andalusite	0.3359	ssatd	anhydrite	-3.0693	
anorthite	-0.1466		aragonite	-2.0743	
bassanite	-4.3622		beidellite-ca	8.0961	ssatd
beidellite-h	6.3611	ssatd	beidellite-k	6.5757	ssatd
beidellite-mg	7.9186	ssatd	beidellite-na	6.8570	ssatd
boehmite	0.2072	ssatd	brucite	-7.0818	
ca-al pyroxene	-8.9317		calcite	-1.7901	
caso4:0.5h2o(beta)	-4.4782		celadonite	3.1118	ssatd
chalcedony	0.5246	ssatd	chrysotile	-5.4255	
clinochlore-14a	-1.4665		clinochlore-7a	-6.7459	
clinozoisite	1.8345	ssatd	coesite	-0.2441	
cordierite anhyd	-6.9053		cordierite hydr	-4.0018	
corundum	-1.6891		cristobalite	0.2078	ssatd
cristobalite-a	0.2078	ssatd	cristobalite-b	-0.2695	
dawsonite	-6.9094		diaspore	0.9657	ssatd
diopside	-3.9705		dolomite	-3.8074	
dolomite-dis	-5.5680		dolomite-ord	-3.8046	
enstatite	-3.7069		fluorite	-3.3057	
forsterite	-9.9088		gibbsite	0.7664	ssatd
grossular	-6.1716		gypsum	-4.6975	
ice	-1.3571		illite	6.8175	ssatd
jadeite	-2.3064		k-feldspar	3.4522	ssatd
kalsilite	-2.5527		kaolinite	5.7289	ssatd
kyanite	0.4263	ssatd	laumontite	5.2841	ssatd
lawsonite	2.1121	ssatd	magnesite	-4.1418	
margarite	4.7070	ssatd	maximum microcline	3.4910	ssatd
mesolite	7.4991	ssatd	monohydrocalcite	-4.8108	
montmor-ca	7.4433	ssatd	montmor-k	6.0890	ssatd
montmor-mg	7.3409	ssatd	montmor-na	6.2954	ssatd
mordenite	2.7984	ssatd	muscovite	9.6249	ssatd
natrolite	-2.9407		nepheline	-4.1275	
okenite	-9.9708		paragonite	6.5440	ssatd
phlogopite	-0.5342		prehnite	1.5673	ssatd
pseudowollastonite	-5.8258		pyrophyllite	6.2028	ssatd
quartz	0.8946	ssatd	sanidine high	2.2800	ssatd
saponite-ca	1.8730	ssatd	saponite-h	0.1392	ssatd
saponite-k	0.3524	ssatd	saponite-mg	1.6756	ssatd
saponite-na	0.6325	ssatd	scolecite	6.7598	ssatd
sellaite	-5.4702		sillimanite	-0.0500	
sio2(am)	-0.5372		spinel	-8.2886	
stilbite	11.5963	ssatd	talc	0.0789	ssatd
tremolite	-5.3092		tridymite	0.4595	ssatd
wairakite	2.3787	ssatd	wollastonite	-5.6633	
zoisite	1.7861	ssatd			

```
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                    --- maximum value of reaction progress ---

---  the reaction path has terminated normally ---


         50 steps were taken
      zi increased from
              0.00000E+00 to  1.25000E+00
      the average value of delzi was  2.50000E-02
      the average matrix dimension was   14


         start time = 17:52       5Dec91
           end time = 17:54       5Dec91

         user time =     116.380
          cpu time =      11.630

--- no further input found ---
```

6.4. Microcline Dissolution in pH 4 HCl.

The dissolution of microcline (a polymorph of $KAlSi_3O_8$) in $pH\ 4\ HCl$ solution is an example of a relatively simple reaction path calculation. This is test problem 3 of INTERA (1983, p. 65-73), who conducted a comparison of EQ3/6 with PHREEQE (Parkhurst, Thorstenson, and Plummer, 1980). The activity coefficients of the aqueous species in this example are computed from the B-

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dot equation (**iopg1** = 0). The name of the microcline in the supporting **com** data file is "maximum microcline." The EQ6 **input** file for this example is **microhcl.6i**. The initializing EQ3NR **input** file is **ph4hcl.3i** (see Appendix F).

This test problem calls for the precipitation of quartz (a polymorph of SiO_2) to be suppressed. It is also necessary here to suppress two other SiO_2 polymorphs, chalcedony and tridymite, which were apparently not on the supporting data file used by INTERA (1983).

The reaction for the dissolution of microcline is:

$$KAlSi_3O_{8\,(c)} + 4H^+ = K^+ + Al^{3+} + 3SiO_{2\,(aq)} + 2H_2O_{\,(l)} \tag{63}$$

Thus, reaction of microcline with the dilute HCl solution puts silica and aluminum into solution (Figure 6), while increasing the *pH* due to neutralization of the acid (Figure 7). As the reaction proceeds, the solution becomes saturated with gibbsite ($Al(OH)_3$), which then precipitates according to partial equilibrium (Figure 8). With further reaction, the solution becomes saturated with kaolinite ($Al_2Si_2O_5(OH)_4$), which also then precipitates according to partial equilibrium. The kaolinite competes with the gibbsite for available aluminum. This competition is so successful that once kaolinite forms, the gibbsite redissolves, again following partial equilibrium. Eventually, the gibbsite disappears entirely. The solution later becomes saturated with muscovite ($KAl_3Si_3O_{10}(OH)_2$), which then precipitates according to partial equilibrium. When the muscovite appears, the kaolinite also starts redissolving. However, before it can disappear, the solution becomes saturated with the microcline. The reaction path then terminates, as no more microcline can dissolve. The final mineral assemblage consists of kaolinite, muscovite, and microcline.

The approach to equilibrium is shown in Figure 9, in which the affinity to dissolve is plotted as a function of reaction progress. Note that this is positive, and trends toward (and eventually reaches) zero. This follows the classical notion of the affinity function as a driving force: it must be positive for the process to proceed. The affinity to dissolve is the negative of the affinity to precipitate. The latter affinity has the same sign as the saturation index.

The results obtained by running this example are also illustrated below by selected parts of the **output** file, **microhcl.6o**, and by the complete **tab** file, **microhcl.6t**. The data in Figures 6-9 were extracted from this **tab** file and edited using the UNIX editor **vi** to create a set of X-Y and X-multiple Y data files. In the case of the X-multiple Y file created to plot the amounts of secondary minerals, the log number of moles of a mineral was set to -100 for points at which the mineral was not present. These X-Y and X-multiple Y data files were subsequently plotted using TempleGraph, version 2.4.

The solid phases *al*, *k*, and *si* are shown on the **output** file as having large supersaturations. This is a minor bug in the code which is related to the fact that the log oxygen fugacity variable is set to -999.0 when the code is operating without a redox variable. These phases are technically suppressed and can not be precipitated. They are actually irrelevant to the current problem.

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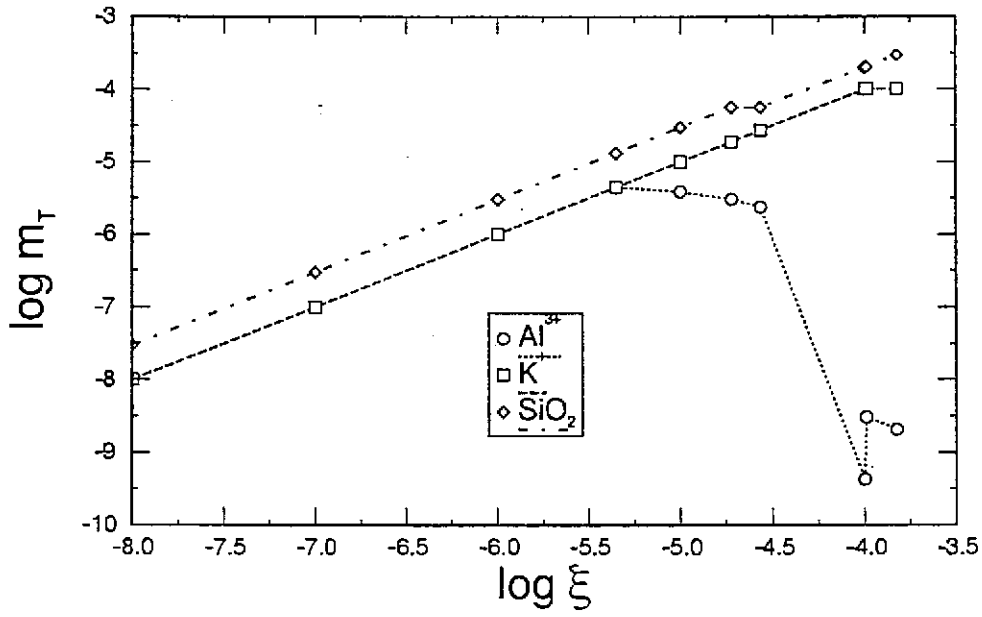

Figure 6. Changes in the total molalities of dissolved aluminum, potassium, and silica as a function of reaction progress (ξ) in closed system reaction of microcline with *pH* 4.0 *HCl* solution.

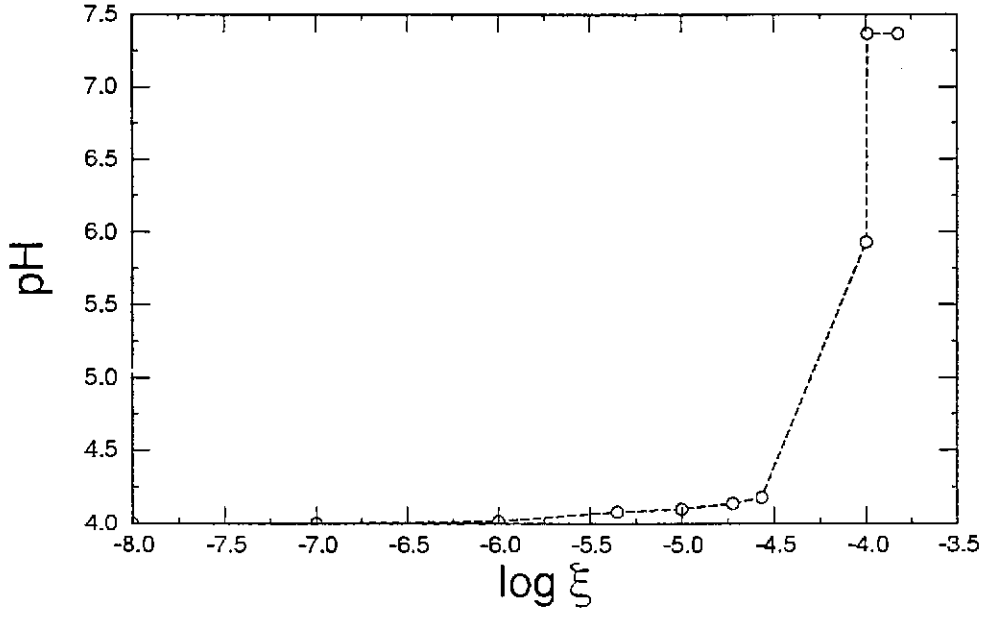

Figure 7. Change in the *pH* as a function of reaction progress (ξ) in closed system reaction of microcline with *pH* 4.0 *HCl* solution.

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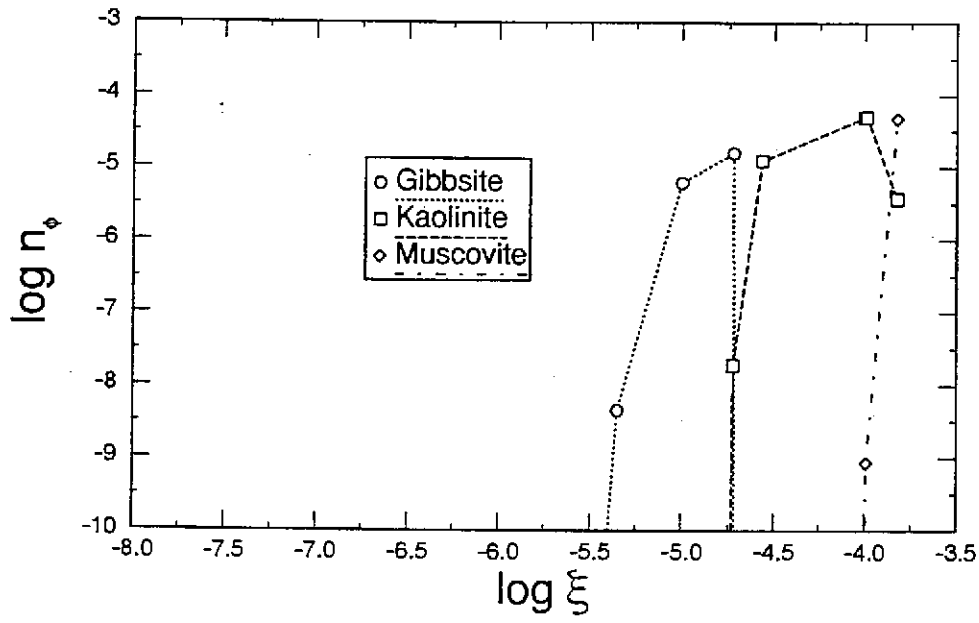

Figure 8. The number of moles of secondary minerals (n_ϕ) as a function of reaction progress (ξ) in closed system reaction of microcline with *pH* 4.0 *HCl* solution. The reacting system originally contains 1 kg of solvent water.

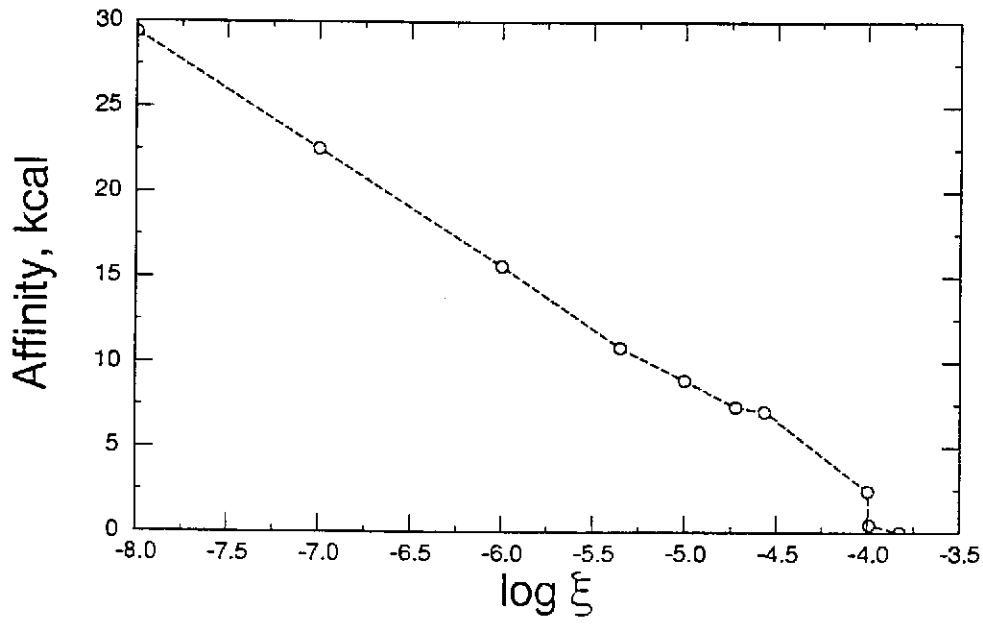

Figure 9. The affinity to dissolve of microcline as a function of reaction progress (ξ) in closed system reaction of microcline with *pH* 4.0 *HCl* solution.

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The EQ6 **input** file (**microhcl.6i**), microcline dissolution in pH 4 HCl ("W" format):

```
EQ6 input file name= microhcl.6i
Description= "Microcline dissolution in pH 4 HCl"
Version number= 3245   Stage number= 01
Created 10/31/90    Creator= T.J. Wolery
Revised 10/31/90    Revisor= T.J. Wolery

  React microcline (KAlSi3O8) with a dilute (pH 4.0) HCl solution
at 25 C. There is no time frame in this calculation. Precipitation
of quartz, chalecedony, and tridymite is suppressed by means of an
"nxmod" option that is inherited from the initializing EQ3NR input
file ph4hcl.3i. This is test problem 3 of INTERA (1983, p. 65-73);
it is similar to test problem 5 of Parkhurst, Thorstenson, and
Plummer (1980). INTERA (1983) reported that the product minerals
formed were gibbsite, kaolinite, and muscovite. The run terminates
when the solution becomes saturated with microcline.

  The original problem called for suppression of quartz. Chalcedony
and tridymite were apparently not the supporting data file used
by INTERA (1983).

  Purpose: to compare against results obtained in a previous
comparison of EQ3/6 with PHREEQE (Parkhurst, Thorstenson, and
Plummer, 1980) made by INTERA (1983).

  This problem has no redox aspect. The option switch ioptl1 is
set to 1 to indicate this to the code.

                          References

INTERA Environmental Consultants, Inc., 1983, Geochemical Models
  Suitable for Performance Assessment of Nuclear Waste Storage:
  Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste
  Isolation, Battelle Project Management Division, Columbus, Ohio,
  ONWI-473, 114 p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980,
  PHREEQE- A Computer Program for Geochemical Calculations: Water
  Resources Investigations Report 80-96, U.S. Geological Survey,
  Reston, Virginia, 210 p.

endit.
    nmodl1=  2                nmodl2=  0
    tempc0=  2.50000E+01       jtemp=  0
       tk1=  0.00000E+00         tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.                zimax=  1.0
     tstrt=  0.               timemx=  1.00000E+38
    kstpmx=          200       cplim=  0.00000E+00
    dzprnt=  1.00000E+00     dzprlg=  1.00000E+00     ksppmx=   100
    dzplot=  1.00000E+38     dzpllg=  1.00000E+38     ksplmx= 10000
     ifile= 60
*               1    2    3    4    5    6    7    8    9   10
  iopt1-10=     0    0    0    0    0    0    0    0    0    0
    11-20=      1    0    0    0    0    0    0    0    0    0
  iopr1-10=     0    0    0    0    0    0    0    0    0    0
 iopr11-20=     0    0    0    0    0    0    0    0    0    0
  iodb1-10=     0    0    0    0    0    0    0    0    0    0
    11-20=      0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
    nxopt=  0
* nffg = number of gas species with fixed fugacities
     nffg=  0
* nrct = number of reactants
     nrct=  1
*-----------------------------------------------------------------------
  reactant= maximum microcline
     jcode=  0                jreac=  0
      morr=  1.00000E+00       modr=  0.00000E+00
       nsk=  0                   sk=  0.00000E+00         fk=  0.00000E+00
       nrk=  1                 nrpk=  0
       rk1=  1.00000E+00        rk2=  0.00000E+00        rk3=  0.00000E+00
*-----------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00      toldl=  0.00000E+00       tolx=  0.00000E+00
    tolsat=  0.00000E+00     tolsst=  0.00000E+00
    screw1=  0.00000E+00     screw2=  0.00000E+00     screw3=  0.00000E+00
    screw4=  0.00000E+00     screw5=  0.00000E+00     screw6=  0.00000E+00
    zklogu=        0.000     zklogl=        0.000      zkfac=        0.000
    dlzmx1=  0.00000E+00     dlzmx2=  0.00000E+00     nordlm=  0
    itermx=  0               ntrymx=  0
    npslmx=  0               nsslmx=  0               ioscan=  0
*-----------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= ph4hcl.3i
Description= "A pH 4 HCl solution, with traces of K, Al, and Si"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery
```

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```
  Dilute HCl solution, pH 4.00, with traces of potassium, aluminum,
and silica. This problem is part of test problem 3 of INTERA
(1983), who report a comparison study of EQ3/6 with PHREEQE
(Parkhurst, Thorstenson, and Plummer, 1980). Note that quartz,
chalcedony, and tridymite are suppressed by means of "nxmod"
options. This has no effect on the EQ3NR calculation. It is simply
needed for the subsequent EQ6 problem. EQ3NR passes this on to
EQ6 on the pickup file.

  Purpose: to provide a pickup file for construction of the EQ6 test
cases microhcl.6i and microhclft.6i. It also tests the "nxmod"
suppress option.

  This problem is actually redox-indifferent. The auxiliary basis
species O2(aq) and H2(aq) have therefore been suppressed. The EQ6
option switch iopt11 should be set to 1.

                          References

INTERA Environmental Consultants, Inc., 1983, Geochemical Models
  Suitable for Performance Assessment of Nuclear Waste Storage:
  Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste
  Isolation, Battelle Project Management Division, Columbus, Ohio,
  ONWI-473, 114 p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980,
  PHREEQE- A Computer Program for Geochemical Calculations: Water
  Resources Investigations Report 80-96, U.S. Geological Survey,
  Reston, Virginia, 210 p.

endit.
    tempci=  0.25000E+02
     nxmod=  3
   species= quartz
      type=  1              option= -1              xlkmod=  0.00000E+00
   species= chalcedony
      type=  1              option= -1              xlkmod=  0.00000E+00
   species= tridymite
      type=  1              option= -1              xlkmod=  0.00000E+00
     iopg1=  0               iopg2=  0               iopg3=  0
     iopg4=  0               iopg5=  0               iopg6=  0
     iopg7=  0               iopg8=  0               iopg9=  0
    iopg10=  0
       kct=  6                 ksq=  7                 kmt=  7
       kxt=  7                kdim=  7                kprs=  0
   o                  0.555084350618964E+02
   al                 0.100000000000005E-11
   cl                 0.101162909259305E-03
   h                  0.111016971286694E+03
   k                  0.999999999999999E-12
   si                 0.100000000000000E-11
   electr             0.271050543121376E-19
   h2o                h2o                     0.174435898352698E+01
   al+++              al+++                  -0.120411346756320E+02
   cl-                cl-                    -0.399498786688732E+01
   h+                 h+                     -0.399498744436686E+01
   k+                 k+                     -0.120000013741135E+02
   sio2(aq)           sio2(aq)               -0.120000004901545E+02
   o2(g)              o2(g)                  -0.700000000000000E+00
```

The EQ6 input file (microhcl.6i), microcline dissolution in pH 4 HCl ("D" format):

```
-----------------------------------------------------------------------
EQ6 input file name= microhcl.6i
Description= "Microcline dissolution in pH 4 HCl"
Version number= 3245   Stage number= 01
Created 10/31/90    Creator= T.J. Wolery
Revised 10/31/90  . Revisor= T.J. Wolery

  React microcline (KAlSi3O8) with a dilute (pH 4.0) HCl solution
at 25 C. There is no time frame in this calculation. Precipitation
of quartz, chalecedony, and tridymite is suppressed by means of an
"nxmod" option that is inherited from the initializing EQ3NR input
file ph4hcl.3i. This is test problem 3 of INTERA (1983, p. 65-73);
it is similar to test problem 5 of Parkhurst, Thorstenson, and
Plummer (1980). INTERA (1983) reported that the product minerals
formed were gibbsite, kaolinite, and muscovite. The run terminates
when the solution becomes saturated with microcline.

  The original problem called for suppression of quartz. Chalcedony
and tridymite were apparently not the supporting data file used
by INTERA (1983).

  Purpose: to compare against results obtained in a previous
comparison of EQ3/6 with PHREEQE (Parkhurst, Thorstenson, and
Plummer, 1980) made by INTERA (1983).
```

Information Only

```
  This problem has no redox aspect. The option switch ioptl1 is
set to 1 to indicate this to the code.

                          References

INTERA Environmental Consultants, Inc., 1983, Geochemical Models
  Suitable for Performance Assessment of Nuclear Waste Storage:
  Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste
  Isolation, Battelle Project Management Division, Columbus, Ohio,
  ONWI-473, 114 p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980,
  PHREEQE- A Computer Program for Geochemical Calculations: Water
  Resources Investigations Report 80-96, U.S. Geological Survey,
  Reston, Virginia, 210 p.

 ------------------------------------------------------------------------
 calculational mode   |*normal     | economy          | super economy
 ------------------------------------------------------------------------
 model type           | titration  |*closed           | open
 ------------------------------------------------------------------------
 temperature model    |*power      | fluid mixing
 ------------------------------------------------------------------------
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c------------------------------------------------------------------------
 tstart(c)|  25.00    |tk1|     0.    |tk2|     0.    |tk3|     0.
 ------------------------------------------------------------------------
 starting value of zi |      0.    |max. value of zi    |  1.0000
 ------------------------------------------------------------------------
 starting time (sec)  |      0.    |max. time (sec)     | 1.00000E+38
 ------------------------------------------------------------------------
 max. steps           |       200  |max. steps w/o print|       100
 ------------------------------------------------------------------------
 linear print interval|  1.0000    |log print interval  |  1.0000
 ------------------------------------------------------------------------
 suppress mineral phases
 ------------------------------------------------------------------------
 phases w/ elements|                      |                          n
 phases except     |                      |                          n
 ------------------------------------------------------------------------
 fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
 ------------------------------------------------------------------------
 none                                |                |                n
 ------------------------------------------------------------------------
c                  R A T E     L A W S
c 1 = relative                  rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory   rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate        rate = CHECK DOCUMENTATION

c                  R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                  S U R F A C E    T Y P E
c 0 = fixed surface area     1 = fixed specific surface area
c
c                  N O T E S
c status and jreac are normally not set by the user
 ------------------------------------------------------------------------
 reactants   (ss) solid solution only     (sp) special reactant only
 ------------------------------------------------------------------------
 REACTANT          |  maximum microcline    |status    | 0
 moles remaining   |  1.0000                |destroyed |      0.
 reactant type     |  mineral               |sk        |      0.
 surface type      |   0                    |fk        |  1.0000
 end-member        |                        |mole fr   |                ss,n
 volume            |                        |          |                sp
 element           |                        |moles     |                sp,n
 DISSOLUTION LAW   |    1                   |          |
 rate constant rk1 |  1.0000                |csigma1   |
 rate constant rk2 |      0.                |csigma2   |
 rate constant rk3 |      0.                |csigma3   |
 PRECIPITATION LAW |    0                   |          |
 ------------------------------------------------------------------------
 options
 ------------------------------------------------------------------------
  - SOLID SOLUTIONS -
    * ignore solid solutions
      process solid solutions
  - LOADING OF SPECIES INTO MEMORY -
    * don't print
      lists species loaded into memory
  - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
    * don't print
      print
  - LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
    * don't print
      print
  - LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
    * only species > 10**-12 molal
      all species
      don't print
```

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```
- LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
  * don't print
    print
- LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
  * don't print
    print
- MINERAL SATURATION STATES -
  * print if affinity > -10 kcals
    print all
    don't print
- LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
  * don't print
    print
- PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
  * don't print
    print
- TAB FILES -
  * write
    append to previous tabx file
    don't write
- WRITE PICKUP FILE -
  * write pickup file at end of run
    don't write pickup file
    write pickup file for each print point
- PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    transfer minerals but leave trivial mass in the system
    transfer minerals
- CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    clear p.r.s. before first reaction progress advance
- PHASE BOUNDARY SEARCH -
  * step size constrained by predicted phase boundaries
    phase boundaries estimated from Taylor's series and printed
    locations of phase boundaries ignored
- AUTO BASIS SWITCHING -
  * off
    on
- SUPPRESS REDOX REACTIONS -
    does nothing
  * suppress all redox reactions
- LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
  * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
    logarithmic for kcol = 1,kbt
    linear for kcol = 1,kdim
- AZERO AND HYDRATION NUMBERS -
  * no change
    read in new azero and hydration numbers
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
  * does nothing
    print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
    print summary information
    print detailed information
- PRINT STEP SIZE AND ORDER -
  * don't print
    print scale factor
    print orders and step size scaling factors
- CONTROL STEP SIZE AND ORDER PRINT -
  * does nothing
    print step size and order when delzi .le. dlzmx1
- NEWTON ITERATIONS -
  * don't print
    print summary of newton iterations
    print summary, residual functions and correction terms
    print summary, residual functions, correction terms and matrix
- PRINT SEARCH ITERATIONS -
  * don't print
    print
- PRINT HPSAT ITERATIONS -
  * don't print
    print
- PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
  * don't print
    print computations from RDERIV, and RTAYLR
    print computations from RDERIV, RTAYLR, DERIV and TAYLOR
- PRINT KINETICS DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 diagnostics
    print level 1 and level 2 diagnostics
- PRINT AKMATR -
  * don't print
    print level 1 diagnostics
- KILL ITERATION VARIABLES -
```

Information Only

```
   * does nothing
     allow selection of variables to remove
-------------------------------------------------------------------------
 development options  (used for code development)
-------------------------------------------------------------------------
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
-------------------------------------------------------------------------
 tolerances                        desired values - defaults info-only
-------------------------------------------------------------------------
 number of N-R iterations          |                  | 40      itermx
 p.r.s. transfer interval          |                  | varies  dlzidp
 residual magnitude                |                  | 1.0e-06 tolbt
 correction magnitude              |                  | 1.0e-06 toldl
 search/find tolerance             |                  | varies  tolx
 supersaturation                   |                  | varies  tolsat
 supersaturation set size          |                  | varies  tolsst
 max. size Taylor's series term    |                  | 1.0e-04 screw1
 max. initial value betamx         |                  | n/a     screw2
 max. Taylor's series term (kin.)  |                  | 1.0e-04 screw3
 corrector iteration               |                  | 1.0e-04 screw4
 max. size of N-R correction term  |                  | 4.0     screw5
 step size (economy mode)          |                  | 4.0     screw6
 log mass of phases                |                  | varies  zklogu
 decrement mass (p.r.s.)           |                  | 2.0     zklogl
 min. left after p.r.s.            |                  | .98     zkfac
 initial step size                 |                  | varies  dlzmx1
 upper limit step size             |                  | varies  dlzmx2
 maximum order                     |                  | 6       nordlm
 num. attempted assemblages        |                  | 25      ntrymx
 slide -> over phase bound.        |                  | 8       npslmx
 slide -> over redox insta.        |                  | 3       nsslmx
 fo2 scan control                  |                  | none    ioscan
-------------------------------------------------------------------------
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
 EQ3NR input file name= ph4hcl.3i
 Description= "A pH 4 HCl solution, with traces of K, Al, and Si"
 Version number= 3245   Stage number= 01
 Created 06/08/90    Creator= T.J. Wolery
 Revised 06/08/90    Revisor= T.J. Wolery

  Dilute HCl solution, pH 4.00, with traces of potassium, aluminum,
 and silica. This problem is part of test problem 3 of INTERA
 (1983), who report a comparison study of EQ3/6 with PHREEQE
 (Parkhurst, Thorstenson, and Plummer, 1980). Note that quartz,
 chalcedony, and tridymite are suppressed by means of "nxmod"
 options. This has no effect on the EQ3NR calculation. It is simply
 needed for the subsequent EQ6 problem. EQ3NR passes this on to
 EQ6 on the pickup file.

  Purpose: to provide a pickup file for construction of the EQ6 test
 cases microhcl.6i and microhclft.6i. It also tests the "nxmod"
 suppress option.

  This problem is actually redox-indifferent. The auxiliary basis
 species O2(aq) and H2(aq) have therefore been suppressed. The EQ6
 option switch iopt11 should be set to 1.

                          References

 INTERA Environmental Consultants, Inc., 1983, Geochemical Models
   Suitable for Performance Assessment of Nuclear Waste Storage:
   Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste
   Isolation, Battelle Project Management Division, Columbus, Ohio,
   ONWI-473, 114 p.

 Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980,
   PHREEQE- A Computer Program for Geochemical Calculations: Water
   Resources Investigations Report 80-96, U.S. Geological Survey,
   Reston, Virginia, 210 p.

-------------------------------------------------------------------------
 temperature (C)                      |     25.000
-------------------------------------------------------------------------
 electrical imbalance                 |     2.710505431213760E-20
-------------------------------------------------------------------------
 number of aqueous master species     |     7
-------------------------------------------------------------------------
 position of last pure mineral        |     7
-------------------------------------------------------------------------
 position of last solid solution      |     7
-------------------------------------------------------------------------
 suppressed species     (suppress,replace,augmentk,augmentg)  value
-------------------------------------------------------------------------
 quartz                 | mineral        | suppress |       0.
 chalcedony             | mineral        | suppress |       0.
 tridymite              | mineral        | suppress |       0.
-------------------------------------------------------------------------
 iopg options
-------------------------------------------------------------------------
 - pH SCALE CONVENTION -
    * modified NBS
```

Information Only

```
      internal
      rational
 - ACTIVITY COEFFICIENT OPTIONS -
    * use B-dot equation
      Davies' equation
      Pitzer's equations
-----------------------------------------------------------------------
 elements, moles and moles aqueous
-----------------------------------------------------------------------
          o        |  5.550843506189640E+01|   0.000000000000000E+00
          al       |  1.000000000000050E-12|   0.000000000000000E+00
          cl       |  1.011629092593050E-04|   0.000000000000000E+00
          h        |  1.110169712866940E+02|   0.000000000000000E+00
          k        |  9.999999999999990E-13|   0.000000000000000E+00
          si       |  1.000000000000000E-12|   0.000000000000000E+00
-----------------------------------------------------------------------
 master species and logarithmic basis variables
-----------------------------------------------------------------------
h2o                |h2o                    |   1.744358983526980E+00
al+++              |al+++                  |  -1.204113467563200E+01
cl-                |cl-                    |  -3.994987866BB7320E+00
h+                 |h+                     |  -3.994987444366860E+00
k+                 |k+                     |  -1.200000137411350E+01
sio2(aq)           |sio2(aq)               |  -1.200000049015450E+01
o2(g)              |o2(g)                  |  -7.000000000000000E-01
-----------------------------------------------------------------------
 physically removed subsystem  (solid solution, mineral, moles)
-----------------------------------------------------------------------
 none              |                       |
-----------------------------------------------------------------------
```

The EQ6 output file (microhcl.6o), microcline dissolution in pH 4 HCl (partial reproduction):

```
                    .
                    .
                    .
            (Material deleted)
                    .
                    .
                    .
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

stepping to zi=  0.0000E+00, delzi=  0.0000E+00, nord= 0

  attempted species assemblage no.   1

            1      1  h2o
            2      3  al+++
            3     14  cl-
            4     26  h+
            5     35  k+
            6     60  sio2(aq)

iter =    1

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                    reaction progress        =  0.00000000000000E+00
                    log of reaction progress =    -999.0000000

                    temperature    =     25.000 degrees c
                    total pressure =      1.013 bars

                    computing units remaining =      0.000

start or re-start of run

                            .
                             --- reactant summary ---

    definitions and conventions

         delta x = x now - x at start
         affinity is + for forward direction (dissolution),
                     - for reverse direction (precipitation)
         rates are + for forward direction (dissolution),
                   - for reverse direction (precipitation)

    reactant                  moles     delta moles      grams     delta grams
```

Information Only

```
maximum microcline          1.0000E+00   0.0000E+00   2.7833E+02   0.0000E+00

              current total mass =  2.78332E+02 grams
              delta total mass   =  0.00000E+00 grams
              delta total volume =      0.00000 cc

   reactant                  affinity   rel. rate
                             kcal/mol     mol/mol

maximum microcline            58.6114   1.0000E+00

        affinity of the overall irreversible reaction=    58.611 kcal
        contributions from irreversible reactions
        with no thermodynamic data are not included


    --- element totals for the aqueous phase ---

 element          mg/kg soln.          molal conc.          moles

    o          8.880984E+05         5.550844E+01         5.550844E+01
    al         2.698144E-08         1.000000E-12         1.000000E-12
    cl         3.586485E+00         1.011629E-04         1.011629E-04
    h          1.118980E+05         1.110170E+02         1.110170E+02
    k          3.909816E-08         1.000000E-12         1.000000E-12
    si         2.808540E-08         1.000000E-12         1.000000E-12

    co3--                           0.000000E+00         0.000000E+00
    so4--                           0.000000E+00         0.000000E+00
    s--                             0.000000E+00         0.000000E+00

  warning-- co3--, so4--, and s-- totals require that routine compl
  have the names of non-carbonate carbon, sulfide sulfur,
  and non-sulfate sulfur aqueous species


 single ion activities and activity coefficients are here defined
 with respect to the modified nbs ph scale


                                    ph

   modified nbs ph scale           4.0000
   rational ph scale               3.9950

 phcl =       8.0001


        redox parameters are not defined


                          activity of water =    1.00000
              log activity of water =    0.00000

                   ionic strength =  1.011609E-04 molal
                sum of molalities =    0.0002023238845
              osmotic coefficient =    0.99613

                        mass of solution =    1.000004 kg
                        mass of solutes  =    0.000004 kg
                        conc of solutes  =    0.000369 per cent (w/w)

                   moles of solvent h2o =  5.55084E+01
                   mass of solvent h2o  =  1.00000E+00 kg


 species                 moles        grams          conc        log conc      log g      log act

 h2o                   5.55084E+01   1.00000E+03   9.99996E-01     0.00000     0.00000     0.00000
 h+                    1.01161E-04   1.01964E-04   1.01161E-04    -3.99499    -0.00501    -4.00000
 cl-                   1.01161E-04   3.58642E-03   1.01161E-04    -3.99499    -0.00507    -4.00006
 hcl(aq)               2.13769E-09   7.79416E-08   2.13769E-09    -8.67006     0.00000    -8.67006
 oh-                   1.02321E-10   1.74021E-09   1.02321E-10    -9.99003    -0.00507    -9.99510


              --- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

    phase/end-member        log moles        moles        grams        volume, cc

 maximum microcline         0.0000000    1.00000E+00    2.78332E+02    1.08741E+02


                          mass, grams        volume, cc

         created          0.000000E+00       0.000000E+00
         destroyed        0.000000E+00       0.000000E+00
         net              0.000000E+00       0.000000E+00
```

Information Only

```
warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base


--- mineral saturation state summary ---

  mineral        affinity, kcal    state        mineral        affinity, kcal    state

al                   821.6586  ssatd         gibbsite               -9.3899
ice                   -0.1890                 k                    233.9523  ssatd
si                   1147.3536  ssatd


- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


stepping to zi=  1.0000E-08, delzi=  1.0000E-08, nord= 0
steps completed =     1, iter =  2, ncorr = 0
most rapidly changing is zvclgl(sio2(aq)          ) =     -7.5229

                    •
                    •
                    •
            (Material deleted)
                    •
                    •
                    •

stepping to zi=  1.8500E-06, delzi=  8.5000E-07, nord= 3
steps completed =    11, iter =  1, ncorr = 0
most rapidly changing is zvclgl(sio2(aq)          ) =     -5.2557

stepping to zi=  3.5500E-06, delzi=  1.7000E-06, nord= 4
steps completed =    12, iter =  1, ncorr = 0
most rapidly changing is zvclgl(sio2(aq)          ) =     -4.9726

stepping to zi=  4.4582E-06, delzi=  9.0819E-07, nord= 5
iter =    1
      1 supersaturated pure minerals
      0 supersaturated solid solutions

                        the most supersaturated phases     affinity, kcal

                          1      13   gibbsite                0.00085453

  attempted species assemblage no.   2

             1      1  h2o
             2      3  al+++
             3     14  cl-
             4     26  h+
             5     35  k+
             6     60  sio2(aq)
             8     13  gibbsite

steps completed =    13, iter = 11, ncorr = 0
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                reaction progress        =  4.45820300741969E-06
                log of reaction progress =      -5.3508402

                temperature    =     25.000 degrees c
                total pressure =      1.013 bars

                computing units remaining =      0.000

change in the product phase assemblage

                          --- reactant summary ---


   reactant                 moles     delta moles      grams     delta grams

maximum microcline        1.0000E+00   4.4582E-06   2.7833E+02   1.2409E-03


            current total mass =  2.78330E+02 grams
            delta total mass   =  1.24086E-03 grams
            delta total volume =      0.00048 cc
```

Information Only

reactant	affinity kcal/mol	rel. rate mol/mol
maximum microcline	10.8723	1.0000E+00

affinity of the overall irreversible reaction= 10.872 kcal
contributions from irreversible reactions
with no thermodynamic data are not included

--- element totals for the aqueous phase ---

element	mg/kg soln.	molal conc.	moles
o	8.880978E+05	5.550846E+01	5.550847E+01
al	1.201678E-01	4.453725E-06	4.453726E-06
cl	3.586481E+00	1.011629E-04	1.011629E-04
h	1.118979E+05	1.110170E+02	1.110170E+02
k	1.743073E-01	4.458203E-06	4.458204E-06
si	3.756308E-01	1.337461E-05	1.337461E-05
co3--		0.000000E+00	0.000000E+00
so4--		0.000000E+00	0.000000E+00
s--		0.000000E+00	0.000000E+00

warning-- co3--, so4--, and s-- totals require that routine compl
have the names of non-carbonate carbon, sulfide sulfur,
and non-sulfate sulfur aqueous species

single ion activities and activity coefficients are here defined
with respect to the modified nbs ph scale

	ph
modified nbs ph scale	4.0817
rational ph scale	4.0764

phcl = 8.0821

redox parameters are not defined

activity of water = 1.00000
log activity of water = 0.00000

ionic strength = 1.135163E-04 molal
sum of molalities = 0.0002073161051
osmotic coefficient = 0.99552

mass of solution = 1.000005 kg
mass of solutes = 0.000005 kg
conc of solutes = 0.000478 per cent (w/w)

moles of solvent h2o = 5.55084E+01
mass of solvent h2o = 1.00000E+00 kg

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	1.00000E+03	9.99996E-01	0.00000	0.00000	0.00000
cl-	1.01161E-04	3.58644E-03	1.01161E-04	-3.99499	-0.00536	-4.00035
h+	8.38666E-05	8.45325E-05	8.38666E-05	-4.07641	-0.00530	-4.08171
sio2(aq)	1.33746E-05	8.03603E-04	1.33746E-05	-4.87372	0.00000	-4.87372
k+	4.45819E-06	1.74308E-04	4.45819E-06	-5.35084	-0.00541	-5.35625
al+++	3.97168E-06	1.07162E-04	3.97168E-06	-5.40103	-0.04761	-5.44863
aloh++	4.39722E-07	1.93429E-05	4.39722E-07	-6.35682	-0.02150	-6.37832
al(oh)2+	4.17909E-08	2.54909E-06	4.17909E-08	-7.37892	-0.00539	-7.38431
hcl(aq)	1.76986E-09	6.45301E-08	1.76986E-09	-8.75206	0.00000	-8.75206
al(oh)3(aq)	4.35311E-10	3.39558E-08	4.35311E-10	-9.36120	0.00000	-9.36120
oh-	1.23587E-10	2.10189E-09	1.23587E-10	-9.90803	-0.00536	-9.91339

--- summary of solid product phases---

product	log moles	moles	grams	volume, cc
gibbsite	-8.3488731	4.47844E-09	3.49334E-07	1.43113E-07

--- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

phase/end-member	log moles	moles	grams	volume, cc
gibbsite	-8.3488731	4.47844E-09	3.49334E-07	1.43113E-07
maximum microcline	-0.0000019	9.99996E-01	2.78330E+02	1.08741E+02

Information Only

```
                    mass, grams        volume, cc

created          3.493344E-07       1.431131E-07
destroyed        1.240859E-03       4.847895E-04
net             -1.240509E-03      -4.846463E-04

warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base


--- mineral saturation state summary ---

  mineral        affinity, kcal    state        mineral        affinity, kcal    state

al                   831.0485  ssatd         andalusite             -7.5251
beidellite-h          -6.4023                beidellite-k           -7.8974
boehmite              -2.2305                chalcedony             -1.5630
coesite               -2.2980                corundum               -7.4493
cristobalite          -1.9440                cristobalite-a         -1.9440
cristobalite-b        -2.5491                diaspore               -1.0783
gibbsite               0.0000  satd          ice                    -0.1890
k                    243.1347  ssatd         kaolinite              -1.7124
kyanite               -7.1561                muscovite              -8.9059
pyrophyllite          -6.3196                quartz                 -1.1930
si                  1157.0758  ssatd         sillimanite            -8.0212
sio2(am)              -2.9470                tridymite              -1.4269


- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


stepping to zi=  4.4682E-06, delzi=  1.0000E-08, nord= 0
steps completed =    14, iter =  7, ncorr = 0
most rapidly changing is zvclgl(gibbsite          ) =     -7.8086

stepping to zi=  4.4782E-06, delzi=  1.0000E-08, nord= 0
steps completed =    15, iter =  5, ncorr = 0
most rapidly changing is zvclgl(gibbsite          ) =     -7.5752

stepping to zi=  4.4882E-06, delzi=  1.0000E-08, nord= 0
steps completed =    16, iter =  5, ncorr = 0
most rapidly changing is zvclgl(gibbsite          ) =     -7.4241

stepping to zi=  4.4982E-06, delzi=  1.0000E-08, nord= 0
steps completed =    17, iter =  4, ncorr = 0
most rapidly changing is zvclgl(gibbsite          ) =     -7.3123

                    .
                    .
                    .
            (Material deleted)
                    .
                    .
                    .

stepping to zi=  1.5176E-05, delzi=  5.1755E-06, nord= 4
steps completed =    21, iter =  2, ncorr = 0
most rapidly changing is zvclgl(gibbsite          ) =     -4.9285

stepping to zi=  1.8924E-05, delzi=  3.7487E-06, nord= 4
iter =    1
      1 supersaturated pure minerals
      0 supersaturated solid solutions

                        the most supersaturated phases     affinity, kcal

                          1      19   kaolinite               0.00079032


  attempted species assemblage no.   2

            1       1  h2o
            2       3  al+++
            3      14  cl-
            4      26  h+
            5      35  k+
            6      60  sio2(aq)
            8      13  gibbsite
            9      19  kaolinite

steps completed =    22, iter =  6, ncorr = 0
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
```

Information Only

```
                reaction progress        =  1.89242200387290E-05
                log of reaction progress =      -4.7229820

                temperature    =     25.000 degrees c
                total pressure =      1.013 bars

                computing units remaining =      0.000

change in the product phase assemblage

                          --- reactant summary ---

   reactant                  moles     delta moles      grams     delta grams

maximum microcline         9.9998E-01   1.8924E-05   2.7833E+02   5.2672E-03

             current total mass =  2.78326E+02 grams
             delta total mass   =  5.26721E-03 grams
             delta total volume =      0.00206 cc

   reactant                 affinity   rel. rate
                            kcal/mol     mol/mol

maximum microcline            7.3690   1.0000E+00

       affinity of the overall irreversible reaction=     7.369 kcal
       contributions from irreversible reactions
       with no thermodynamic data are not included


   --- element totals for the aqueous phase ---

 element        mg/kg soln.        molal conc.         moles

    o         8.880965E+05       5.550855E+01       5.550854E+01
    al        8.218842E-02       3.046122E-06       3.046122E-06
    cl        3.586471E+00       1.011629E-04       1.011629E-04
    h         1.118975E+05       1.110169E+02       1.110169E+02
    k         7.398992E-01       1.892422E-05       1.892422E-05
    si        1.593413E+00       5.673482E-05       5.673481E-05

    co3--                        0.000000E+00       0.000000E+00
    so4--                        0.000000E+00       0.000000E+00
    s--                          0.000000E+00       0.000000E+00

  warning-- co3--, so4--, and s-- totals require that routine compl
  have the names of non-carbonate carbon, sulfide sulfur,
  and non-sulfate sulfur aqueous species


 single ion activities and activity coefficients are here defined
 with respect to the modified nbs ph scale


                                  ph

   modified nbs ph scale         4.1389
   rational ph scale             4.1336

 phcl =      8.1391


       redox parameters are not defined


                        activity of water =    1.00000
            log activity of water =    0.00000

                ionic strength =  1.095133E-04 molal
              sum of molalities =    0.0002533794975
            osmotic coefficient =    0.99653

                     mass of solution =    1.000008 kg
                     mass of solutes  =    0.000008 kg
                     conc of solutes  =    0.000790 per cent (w/w)

                moles of solvent h2o =  5.55084E+01
                mass of solvent h2o  =  1.00000E+00 kg


 species              moles        grams          conc        log conc      log g      log act

 h2o                5.55084E+01   1.00000E+03   9.99995E-01     0.00000     0.00000     0.00000
 cl-                1.01161E-04   3.58644E-03   1.01161E-04    -3.99499    -0.00527    -4.00025
```

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h+	7.35113E-05	7.40950E-05	7.35113E-05	-4.13365	-0.00521	-4.13886
sio2(aq)	5.67347E-05	3.40887E-03	5.67347E-05	-4.24615	0.00000	-4.24615
k+	1.89242E-05	7.39903E-04	1.89242E-05	-4.72298	-0.00532	-4.72830
al+++	2.67131E-06	7.20760E-05	2.67131E-06	-5.57328	-0.04678	-5.62006
aloh++	3.37688E-07	1.48545E-05	3.37688E-07	-6.47148	-0.02112	-6.49261
al(oh)2+	3.66306E-08	2.23433E-06	3.66306E-08	-7.43616	-0.00530	-7.44145
hcl(aq)	1.55199E-09	5.65867E-08	1.55199E-09	-8.80911	0.00000	-8.80911
al(oh)3(aq)	4.35311E-10	3.39558E-08	4.35311E-10	-9.36120	0.00000	-9.36120
oh-	1.40936E-10	2.39695E-09	1.40936E-10	-9.85098	-0.00527	-9.85625

--- summary of solid product phases---

product	log moles	moles	grams	volume, cc
gibbsite	-4.8002380	1.58402E-05	1.23560E-03	5.06191E-04
kaolinite	-7.7229557	1.89254E-08	4.88578E-06	1.88345E-06

--- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

phase/end-member	log moles	moles	grams	volume, cc
gibbsite	-4.8002380	1.58402E-05	1.23560E-03	5.06191E-04
kaolinite	-7.7229557	1.89254E-08	4.88578E-06	1.88345E-06
maximum microcline	-0.0000082	9.99981E-01	2.78326E+02	1.08739E+02

	mass, grams	volume, cc
created	1.240482E-03	5.080744E-04
destroyed	5.267207E-03	2.057839E-03
net	-4.026726E-03	-1.549764E-03

warning-- these volume totals may be incomplete because of missing partial molar volume data in the data base

--- mineral saturation state summary ---

mineral	affinity, kcal	state	mineral	affinity, kcal	state
al	831.0485	ssatd	andalusite	-6.6690	
beidellite-h	-3.2601		beidellite-k	-4.4468	
boehmite	-2.2305		chalcedony	-0.7068	
coesite	-1.4418		corundum	-7.4493	
cristobalite	-1.0878		cristobalite-a	-1.0878	
cristobalite-b	-1.6929		diaspore	-1.0783	
gibbsite	0.0000	satd	ice	-0.1890	
k	244.0693	ssatd	k-feldspar	-7.3690	
kaolinite	0.0000	satd	kyanite	-6.2999	
maximum microcline	-7.3690		muscovite	-5.4027	
pyrophyllite	-2.8949		quartz	-0.3368	
sanidine high	-9.0051		si	1157.9320	ssatd
sillimanite	-7.1650		sio2(am)	-2.0908	
tridymite	-0.5708				

- -

```
stepping to zi=  1.8934E-05, delzi=  1.0000E-08, nord= 0
steps completed =     23, iter =  5, ncorr = 0
most rapidly changing is zvclgl(kaolinite          ) =      -7.4695

stepping to zi=  1.8944E-05, delzi=  1.0000E-08, nord= 0
steps completed =     24, iter =  5, ncorr = 0
most rapidly changing is zvclgl(kaolinite          ) =      -7.3105

stepping to zi=  1.8954E-05, delzi=  1.0000E-08, nord= 0
steps completed =     25, iter =  4, ncorr = 0
most rapidly changing is zvclgl(kaolinite          ) =      -7.1943

stepping to zi=  1.8964E-05, delzi=  1.0000E-08, nord= 0
steps completed =     26, iter =  4, ncorr = 0
most rapidly changing is zvclgl(kaolinite          ) =      -7.1028

stepping to zi=  1.9064E-05, delzi=  1.0000E-07, nord= 2
steps completed =     27, iter =  6, ncorr = 0
most rapidly changing is zvclgl(kaolinite          ) =      -6.6403

stepping to zi=  2.0064E-05, delzi=  1.0000E-06, nord= 3
steps completed =     28, iter =  1, ncorr = 0
most rapidly changing is zvclgl(kaolinite          ) =      -5.7622

stepping to zi=  2.1340E-05, delzi=  1.2755E-06, nord= 3
steps completed =     29, iter =  1, ncorr = 0
most rapidly changing is zvclgl(kaolinite          ) =      -5.4386
```

Information Only

```
stepping to zi=  2.7187E-05, delzi=  5.8477E-06, nord= 3
                   the phase to be dropped is gibbsite                    (    13)

  attempted species assemblage no.   2

            1      1  h2o
            2      3  al+++
            3     14  cl-
            4     26  h+
            5     35  k+
            6     60  sio2(aq)
            8     19  kaolinite

steps completed =    30, iter =  3, ncorr = 0
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                   reaction progress        =  2.71873977556321E-05
                   log of reaction progress =      -4.5656324

                   temperature    =     25.000 degrees c
                   total pressure =      1.013 bars

                   computing units remaining =      0.000

change in the product phase assemblage

                              --- reactant summary ---


    reactant                   moles     delta moles      grams     delta grams

 maximum microcline          9.9997E-01   2.7187E-05   2.7832E+02   7.5671E-03


              current total mass =  2.78324E+02 grams
              delta total mass   =  7.56711E-03 grams
              delta total volume =      0.00296 cc


    reactant                  affinity   rel. rate
                              kcal/mol     mol/mol

 maximum microcline             7.1016   1.0000E+00


        affinity of the overall irreversible reaction=     7.102 kcal
        contributions from irreversible reactions
        with no thermodynamic data are not included


    --- element totals for the aqueous phase ---

  element         mg/kg soln.         molal conc.          moles

     o          8.880962E+05        5.550855E+01        5.550854E+01
     al         6.367612E-02        2.360008E-06        2.360007E-06
     cl         3.586469E+00        1.011629E-04        1.011629E-04
     h          1.118975E+05        1.110169E+02        1.110169E+02
     k          1.062973E+00        2.718740E-05        2.718740E-05
     si         1.593412E+00        5.673481E-05        5.673480E-05

     co3--                          0.000000E+00        0.000000E+00
     so4--                          0.000000E+00        0.000000E+00
     s--                            0.000000E+00        0.000000E+00

   warning-- co3--, so4--, and s-- totals require that routine compl
   have the names of non-carbonate carbon, sulfide sulfur,
   and non-sulfate sulfur aqueous species


  single ion activities and activity coefficients are here defined
  with respect to the modified nbs ph scale


                                      ph

    modified nbs ph scale           4.1775
    rational ph scale               4.1723

  phcl =      8.1777


        redox parameters are not defined
```

Information Only

```
                    activity of water =    1.00000
          log activity of water =    0.00000

              ionic strength =  1.075748E-04 molal
            sum of molalities =    0.0002546904210
          osmotic coefficient =    0.99663

                 mass of solution =    1.000008 kg
                 mass of solutes  =    0.000008 kg
                 conc of solutes  =    0.000820 per cent (w/w)

              moles of solvent h2o =  5.55084E+01
              mass of solvent h2o  =  1.00000E+00 kg
```

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	1.00000E+03	9.99995E-01	0.00000	0.00000	0.00000
cl-	1.01161E-04	3.58644E-03	1.01161E-04	-3.99499	-0.00522	-4.00021
h+	6.72452E-05	6.77791E-05	6.72452E-05	-4.17234	-0.00516	-4.17750
sio2(aq)	5.67347E-05	3.40887E-03	5.67347E-05	-4.24615	0.00000	-4.24615
k+	2.71873E-05	1.06298E-03	2.71873E-05	-4.56563	-0.00527	-4.57090
al+++	2.04351E-06	5.51370E-05	2.04351E-06	-5.68962	-0.04638	-5.73600
aloh++	2.82511E-07	1.24273E-05	2.82511E-07	-6.54897	-0.02094	-6.56990
al(oh)2+	3.35081E-08	2.04387E-06	3.35081E-08	-7.47485	-0.00525	-7.48010
hcl(aq)	1.42000E-09	5.17741E-08	1.42000E-09	-8.84771	0.00000	-8.84771
al(oh)3(aq)	4.35311E-10	3.39558E-08	4.35311E-10	-9.36120	0.00000	-9.36120
oh-	1.54037E-10	2.61976E-09	1.54037E-10	-9.81238	-0.00522	-9.81760

--- summary of solid product phases---

product	log moles	moles	grams	volume, cc
kaolinite	-4.9060989	1.24137E-05	3.20473E-03	1.23541E-03

--- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

phase/end-member	log moles	moles	grams	volume, cc
kaolinite	-4.9060989	1.24137E-05	3.20473E-03	1.23541E-03
maximum microcline	-0.0000118	9.99973E-01	2.78324E+02	1.08738E+02

	mass, grams	volume, cc
created	3.204725E-03	1.235411E-03
destroyed	7.567110E-03	2.956385E-03
net	-4.362385E-03	-1.720974E-03

warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base

--- mineral saturation state summary ---

mineral	affinity, kcal	state	mineral	affinity, kcal	state
al	831.0485	ssatd	andalusite	-6.6690	
beidellite-h	-3.2601		beidellite-k	-4.3585	
boehmite	-2.2305		chalcedony	-0.7068	
coesite	-1.4418		corundum	-7.4493	
cristobalite	-1.0878		cristobalite-a	-1.0878	
cristobalite-b	-1.6929		diaspore	-1.0783	
gibbsite	0.0000	ssatd	ice	-0.1890	
k	244.3368	ssatd	k-feldspar	-7.1016	
kaolinite	0.0000	satd	kyanite	-6.2999	
maximum microcline	-7.1016		muscovite	-5.1352	
pyrophyllite	-2.8949		quartz	-0.3368	
sanidine high	-8.7376		si	1157.9320	ssatd
sillimanite	-7.1650		sio2(am)	-2.0908	
tridymite	-0.5708				

```
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


stepping to zi=  2.7197E-05, delzi=  1.0000E-08, nord= 0
steps completed =    31, iter =  3, ncorr = 0
most rapidly changing is zvclgl(al+++              ) =      -5.6899

stepping to zi=  2.7207E-05, delzi=  1.0000E-08, nord= 0
steps completed =    32, iter =  3, ncorr = 0
most rapidly changing is zvclgl(al+++              ) =      -5.6901

stepping to zi=  2.7217E-05, delzi=  1.0000E-08, nord= 0
```

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```
steps completed =    33, iter =  3, ncorr = 0
most rapidly changing is zvclg1(al+++              ) =     -5.6904
```

(Material deleted)

```
stepping to zi=  1.0182E-04, delzi=  5.7544E-08, nord= 6
steps completed =    62, iter =  3, ncorr = 0
most rapidly changing is zvclg1(al+++              ) =    -15.6951

stepping to zi=  1.0187E-04, delzi=  4.8700E-08, nord= 6
steps completed =    63, iter =  2, ncorr = 0
most rapidly changing is zvclg1(al+++              ) =    -15.7767

stepping to zi=  1.0189E-04, delzi=  2.3063E-08, nord= 6
steps completed =    64, iter =  2, ncorr = 0
most rapidly changing is zvclg1(al+++              ) =    -15.8137

stepping to zi=  1.0190E-04, delzi=  1.8832E-09, nord= 6
iter =    2
      1 supersaturated pure minerals
      0 supersaturated solid solutions

                        the most supersaturated phases     affinity, kcal

                          1      22   muscovite               0.00062491

  attempted species assemblage no.   2

            1      1  h2o
            2      3  al+++
            3     14  cl-
            4     26  h+
            5     35  k+
            6     60  sio2(aq)
            8     19  kaolinite
            9     22  muscovite

steps completed =    65, iter = 14, ncorr = 0
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                    reaction progress        =  1.01896734182593E-04
                    log of reaction progress =     -3.9918397

                    temperature    =     25.000 degrees c
                    total pressure =      1.013 bars

                    computing units remaining =      0.000

change in the product phase assemblage

                              --- reactant summary ---


    reactant                  moles     delta moles      grams     delta grams

 maximum microcline         9.9990E-01   1.0190E-04   2.7830E+02   2.8361E-02


               current total mass =  2.78303E+02 grams
               delta total mass   =  2.83611E-02 grams
               delta total volume =      0.01108 cc


    reactant                 affinity   rel. rate
                             kcal/mol     mol/mol

 maximum microcline            0.4542   1.0000E+00


         affinity of the overall irreversible reaction=     0.454 kcal
         contributions from irreversible reactions
         with no thermodynamic data are not included


     --- element totals for the aqueous phase ---

  element         mg/kg soln.         molal conc.          moles
```

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o	8.880906E+05	5.550884E+01	5.550879E+01
al	8.257125E-05	3.060347E-09	3.060345E-09
cl	3.586431E+00	1.011630E-04	1.011629E-04
h	1.118961E+05	1.110169E+02	1.110168E+02
k	3.983880E+00	1.018960E-04	1.018959E-04
si	5.723619E+00	2.037967E-04	2.037965E-04
co3--		0.000000E+00	0.000000E+00
so4--		0.000000E+00	0.000000E+00
s--		0.000000E+00	0.000000E+00

warning-- co3--, so4--, and s-- totals require that routine compl have the names of non-carbonate carbon, sulfide sulfur, and non-sulfate sulfur aqueous species

single ion activities and activity coefficients are here defined with respect to the modified nbs ph scale

	ph
modified nbs ph scale	7.3676
rational ph scale	7.3626

phcl = 11.3677

redox parameters are not defined

activity of water = 0.99999
log activity of water = 0.00000

ionic strength = 1.019390E-04 molal
sum of molalities = 0.0004071403885
osmotic coefficient = 0.99806

mass of solution = 1.000019 kg
mass of solutes = 0.000020 kg
conc of solutes = 0.001983 per cent (w/w)

moles of solvent h2o = 5.55084E+01
mass of solvent h2o = 9.99999E-01 kg

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	9.99999E+02	9.99993E-01	0.00000	0.00000	0.00000
sio2(aq)	2.03262E-04	1.22128E-02	2.03262E-04	-3.69194	0.00000	-3.69194
k+	1.01896E-04	3.98394E-03	1.01896E-04	-3.99184	-0.00513	-3.99697
cl-	1.01163E-04	3.58649E-03	1.01163E-04	-3.99498	-0.00509	-4.00007
hsio3-	5.34862E-07	4.12334E-05	5.34862E-07	-6.27176	-0.00507	-6.27683
oh-	2.38563E-07	4.05732E-06	2.38563E-07	-6.62240	-0.00509	-6.62748
h+	4.33921E-08	4.37367E-08	4.33922E-08	-7.36259	-0.00503	-7.36762
al(oh)4-	2.93277E-09	2.78645E-07	2.93277E-09	-8.53272	-0.00507	-8.53779
kcl(aq)	3.22373E-10	2.40333E-08	3.22374E-10	-9.49164	0.00000	-9.49164
al(oh)3(aq)	1.21504E-10	9.47778E-09	1.21505E-10	-9.91541	0.00000	-9.91541

--- summary of solid product phases---

product	log moles	moles	grams	volume, cc
kaolinite	-4.2928937	5.09456E-05	1.31521E-02	5.07010E-03
muscovite	-9.0671540	8.56734E-10	3.41244E-07	1.20551E-07

--- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

phase/end-member	log moles	moles	grams	volume, cc
kaolinite	-4.2928937	5.09456E-05	1.31521E-02	5.07010E-03
maximum microcline	-0.0000443	9.99898E-01	2.78303E+02	1.08730E+02
muscovite	-9.0671540	8.56734E-10	3.41244E-07	1.20551E-07

	mass, grams	volume, cc
created	1.315247E-02	5.070222E-03
destroyed	2.836107E-02	1.108035E-02
net	-1.520861E-02	-6.010131E-03

warning-- these volume totals may be incomplete because of missing partial molar volume data in the data base

--- mineral saturation state summary ---

Information Only

mineral	affinity, kcal	state	mineral	affinity, kcal	state
al	830.2924	ssatd	andalusite	-7.4251	
beidellite-h	-2.2470		beidellite-k	-1.6507	
boehmite	-2.9866		chalcedony	0.0493	ssatd
coesite	-0.6857		corundum	-8.9615	
cristobalite	-0.3317		cristobalite-a	-0.3317	
cristobalite-b	-0.9368		diaspore	-1.8344	
gibbsite	-0.7561		ice	-0.1890	
k	249.4720	ssatd	k-feldspar	-0.4542	
kalsilite	-5.6250		kaolinite	0.0000	satd
kyanite	-7.0560		maximum microcline	-0.4542	
muscovite	0.0000	satd	pyrophyllite	-1.3827	
quartz	0.4193	ssatd	sanidine high	-2.0902	
si	1158.6881	ssatd	sillimanite	-7.9211	
sio2(am)	-1.3347		tridymite	0.1853	ssatd

```
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


stepping to zi=  1.0191E-04, delzi=  1.0000E-08, nord= 0
steps completed =    66, iter = 13, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -7.9664

stepping to zi=  1.0192E-04, delzi=  1.0000E-08, nord= 0
steps completed =    67, iter =  5, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -7.6829

stepping to zi=  1.0193E-04, delzi=  1.0000E-08, nord= 0
steps completed =    68, iter =  5, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -7.5128

stepping to zi=  1.0194E-04, delzi=  1.0000E-08, nord= 0
steps completed =    69, iter =  4, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -7.3909

stepping to zi=  1.0204E-04, delzi=  1.0000E-07, nord= 2
steps completed =    70, iter =  7, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -6.8535

stepping to zi=  1.0304E-04, delzi=  1.0000E-06, nord= 2
steps completed =    71, iter =  2, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -5.9450

stepping to zi=  1.0555E-04, delzi=  2.5108E-06, nord= 3
steps completed =    72, iter =  2, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -5.4398

stepping to zi=  1.1033E-04, delzi=  4.7790E-06, nord= 3
steps completed =    73, iter =  2, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -5.0764

stepping to zi=  1.2075E-04, delzi=  1.0423E-05, nord= 4
steps completed =    74, iter =  2, ncorr = 0
most rapidly changing is zvclgl(muscovite         ) =     -4.7269

stepping to zi=  1.3798E-04, delzi=  1.7228E-05, nord= 5
steps completed =    75, iter =  2, ncorr = 0
most rapidly changing is zvclgl(kaolinite         ) =     -4.8197

stepping to zi=  1.4959E-04, delzi=  1.1612E-05, nord= 6
iter =    3
      2 supersaturated pure minerals
      0 supersaturated solid solutions

                        the most supersaturated phases     affinity, kcal

                          1      21   maximum microcline      0.00079466
                          2      16   k-feldspar              0.00079466


  attempted species assemblage no.   2

            1      1  h2o
            2      3  al+++
            3     14  cl-
            4     26  h+
            5     35  k+
            6     60  sio2(aq)
            8     19  kaolinite
            9     21  maximum microcline
           10     22  muscovite

--- reactant maximum microcline       has saturated and been transferred
      to the equilibrium system ---
steps completed =    76, iter =  9, ncorr = 0
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
```

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```
reaction progress          =  1.49588678790796E-04
log of reaction progress =       -3.8251013

temperature     =      25.000 degrees c
total pressure =        1.013 bars

computing units remaining =       0.000
```

change in the product phase assemblage

--- reactant summary ---

reactant	moles	delta moles	grams	delta grams
maximum microcline	0.0000E+00	1.4959E-04	0.0000E+00	4.1635E-02

```
current total mass =  0.00000E+00 grams
delta total mass   =  4.16352E-02 grams
delta total volume =       0.01627 cc
```

reactant	affinity kcal/mol	rel. rate mol/mol
maximum microcline	0.0000	0.0000E+00

```
affinity of the overall irreversible reaction=      0.000 kcal
contributions from irreversible reactions
with no thermodynamic data are not included
```

--- element totals for the aqueous phase ---

element	mg/kg soln.	molal conc.	moles
o	8.880885E+05	5.550903E+01	5.550903E+01
al	5.615486E-05	2.081286E-09	2.081286E-09
cl	3.586407E+00	1.011629E-04	1.011629E-04
h	1.118955E+05	1.110169E+02	1.110169E+02
k	3.993485E+00	1.021422E-04	1.021422E-04
si	8.396757E+00	2.989789E-04	2.989789E-04
co3--		0.000000E+00	0.000000E+00
so4--		0.000000E+00	0.000000E+00
s--		0.000000E+00	0.000000E+00

```
warning-- co3--, so4--, and s-- totals require that routine compl
have the names of non-carbonate carbon, sulfide sulfur,
and non-sulfate sulfur aqueous species
```

single ion activities and activity coefficients are here defined
with respect to the modified nbs ph scale

	ph
modified nbs ph scale	7.3666
rational ph scale	7.3615

```
phcl =      11.3666
```

redox parameters are not defined

```
activity of water =    0.99999
log activity of water =    0.00000

ionic strength =  1.021854E-04 molal
sum of molalities =    0.0005025672852
osmotic coefficient =    0.99842

mass of solution =    1.000025 kg
mass of solutes  =    0.000026 kg
conc of solutes  =    0.002556 per cent (w/w)

moles of solvent h2o =  5.55084E+01
mass of solvent h2o  =  1.00000E+00 kg
```

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	1.00000E+03	9.99991E-01	0.00000	0.00000	0.00000
sio2(aq)	2.98196E-04	1.79169E-02	2.98196E-04	-3.52550	0.00000	-3.52550

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k+	1.02142E-04	3.99357E-03	1.02142E-04	-3.99080	-0.00514	-3.99593
cl-	1.01163E-04	3.58649E-03	1.01163E-04	-3.99498	-0.00509	-4.00007
hsio3-	7.82799E-07	6.03472E-05	7.82799E-07	-6.10635	-0.00508	-6.11143
oh-	2.37993E-07	4.04764E-06	2.37993E-07	-6.62343	-0.00509	-6.62853
h+	4.34971E-08	4.38425E-08	4.34971E-08	-7.36154	-0.00504	-7.36658
al(oh)4-	1.99432E-09	1.89482E-07	1.99432E-09	-8.70021	-0.00508	-8.70528
kcl(aq)	3.23143E-10	2.40907E-08	3.23143E-10	-9.49060	0.00000	-9.49060

--- summary of solid product phases---

product	log moles	moles	grams	volume, cc
kaolinite	-5.4290056	3.72387E-06	9.61356E-04	3.70599E-04
maximum microcline	-0.0000649	9.99851E-01	2.78290E+02	1.08725E+02
muscovite	-4.3247149	4.73462E-05	1.88584E-02	6.66208E-03

--- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

phase/end-member	log moles	moles	grams	volume, cc
kaolinite	-5.4290056	3.72387E-06	9.61356E-04	3.70599E-04
maximum microcline	-0.0000649	9.99851E-01	2.78290E+02	1.08725E+02
muscovite	-4.3247149	4.73462E-05	1.88584E-02	6.66208E-03

	mass, grams	volume, cc
created	2.783098E+02	1.087318E+02
destroyed	4.163525E-02	1.626642E-02
net	2.782681E+02	1.087155E+02

warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base

--- mineral saturation state summary ---

mineral	affinity, kcal	state	mineral	affinity, kcal	state
al	830.0653	ssatd	andalusite	-7.6521	
beidellite-h	-1.9427		beidellite-k	-1.3465	
boehmite	-3.2136		chalcedony	0.2764	ssatd
coesite	-0.4587		corundum	-9.4156	
cristobalite	-0.1046		cristobalite-a	-0.1046	
cristobalite-b	-0.7097		diaspore	-2.0615	
gibbsite	-0.9832		ice	-0.1890	
k	249.4720	ssatd	k-feldspar	0.0000	
kalsilite	-5.6250		kaolinite	0.0000	satd
kyanite	-7.2831		maximum microcline	0.0000	satd
muscovite	0.0000	satd	pyrophyllite	-0.9285	
quartz	0.6464	ssatd	sanidine high	-1.6361	
si	1158.9152	ssatd	sillimanite	-8.1482	
sio2(am)	-1.1077		tridymite	0.4124	ssatd

- -

--- all rates are zero ---

--- each reactant is saturated or exhausted ---

--- the reaction path has terminated normally ---

76 steps were taken
zi increased from
0.00000E+00 to 1.49589E-04
the average value of delzi was 1.96827E-06
the average matrix dimension was 8

start time = 13:46 10Dec91
end time = 13:46 10Dec91

user time = 39.060
cpu time = 0.960

--- no further input found ---

Information Only

The EQ6 tab file (microhcl.6t), microcline dissolution in pH 4 HCl:

```
EQ6 input file name= microhcl.6i
Description= "Microcline dissolution in pH 4 HCl"
Version number= 3245    Stage number= 01
Created 10/31/90     Creator= T.J. Wolery
Revised 10/31/90     Revisor= T.J. Wolery

  React microcline (KAlSi3O8) with a dilute (pH 4.0) HCl solution
at 25 C. There is no time frame in this calculation. Precipitation
of quartz, chalecedony, and tridymite is suppressed by means of an
"nxmod" option that is inherited from the initializing EQ3NR input
file ph4hcl.3i. This is test problem 3 of INTERA (1983, p. 65-73);
it is similar to test problem 5 of Parkhurst, Thorstenson, and
Plummer (1980). INTERA (1983) reported that the product minerals
formed were gibbsite, kaolinite, and muscovite. The run terminates
when the solution becomes saturated with microcline.

  The original problem called for suppression of quartz. Chalcedony
and tridymite were apparently not the supporting data file used
by INTERA (1983).

  Purpose: to compare against results obtained in a previous
comparison of EQ3/6 with PHREEQE (Parkhurst, Thorstenson, and
Plummer, 1980) made by INTERA (1983).

  This problem has no redox aspect. The option switch iopt11 is
set to 1 to indicate this to the code.

                          References

INTERA Environmental Consultants, Inc., 1983, Geochemical Models
  Suitable for Performance Assessment of Nuclear Waste Storage:
  Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste
  Isolation, Battelle Project Management Division, Columbus, Ohio,
  ONWI-473, 114 p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980,
  PHREEQE- A Computer Program for Geochemical Calculations: Water
  Resources Investigations Report 80-96, U.S. Geological Survey,
  Reston, Virginia, 210 p.


eq6.3245R119x
  supported by eqlib.3245R153

data0.com.R10
THERMODYNAMIC DATABASE
generated by gembochs/INGRES  15-apr-91
+-----------------------------------------------------------------
         start time = 16:10     13Dec91
           end time = 16:11     13Dec91
```

zi	log zi	time, d	log days	tempc	press	ph	log fo2	eh	pe	kg h2o	tot aff
0.000E+00	-999.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0000	-999.0000	-999.0000	-999.0000	1.0000	58.6114
1.000E-08	-8.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0002	-999.0000	-999.0000	-999.0000	1.0000	29.3719
1.000E-07	-7.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0017	-999.0000	-999.0000	-999.0000	1.0000	22.5426
1.000E-06	-6.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0171	-999.0000	-999.0000	-999.0000	1.0000	15.6398
4.458E-06	-5.3508	0.000E+00	-999.0000	25.0000	1.0132	4.0817	-999.0000	-999.0000	-999.0000	1.0000	10.8723
1.000E-05	-5.0000	0.000E+00	-999.0000	25.0000	1.0132	4.1022	-999.0000	-999.0000	-999.0000	1.0000	8.9296
1.892E-05	-4.7230	0.000E+00	-999.0000	25.0000	1.0132	4.1389	-999.0000	-999.0000	-999.0000	1.0000	7.3690
2.719E-05	-4.5656	0.000E+00	-999.0000	25.0000	1.0132	4.1775	-999.0000	-999.0000	-999.0000	1.0000	7.1016
1.000E-04	-4.0000	0.000E+00	-999.0000	25.0000	1.0132	5.9292	-999.0000	-999.0000	-999.0000	1.0000	2.4469
1.019E-04	-3.9918	0.000E+00	-999.0000	25.0000	1.0132	7.3676	-999.0000	-999.0000	-999.0000	1.0000	0.4542
1.496E-04	-3.8251	0.000E+00	-999.0000	25.0000	1.0132	7.3666	-999.0000	-999.0000	-999.0000	1.0000	0.0000

log zi	time, d	log days	log alk	log tot co3--	log tot so4--	log tot s--	log a h2o
-999.0000	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-8.0000	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-7.0000	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-6.0000	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-5.3508	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-5.0000	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-4.7230	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-4.5656	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-4.0000	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-3.9918	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000
-3.8251	0.000E+00	-999.0000	-999.0000	-999.0000	-999.0000	-999.0000	0.0000

log molality of dissolved elements

log zi	time, d	log days	al	cl	k	si

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-999.0000	0.000E+00	-999.0000	-12.0000	-3.9950	-12.0000	-12.0000
-8.0000	0.000E+00	-999.0000	-8.0000	-3.9950	-8.0000	-7.5229
-7.0000	0.000E+00	-999.0000	-7.0000	-3.9950	-7.0000	-6.5229
-6.0000	0.000E+00	-999.0000	-6.0000	-3.9950	-6.0000	-5.5229
-5.3508	0.000E+00	-999.0000	-5.3513	-3.9950	-5.3508	-4.8737
-5.0000	0.000E+00	-999.0000	-5.4107	-3.9950	-5.0000	-4.5229
-4.7230	0.000E+00	-999.0000	-5.5163	-3.9950	-4.7230	-4.2462
-4.5656	0.000E+00	-999.0000	-5.6271	-3.9950	-4.5656	-4.2462
-4.0000	0.000E+00	-999.0000	-9.3678	-3.9950	-4.0000	-3.6990
-3.9918	0.000E+00	-999.0000	-8.5142	-3.9950	-3.9918	-3.6908
-3.8251	0.000E+00	-999.0000	-8.6817	-3.9950	-3.9908	-3.5244

ppm (mg/kg) of dissolved elements

log zi	time, d	log days	al	cl	k	si
-999.0000	0.000E+00	-999.0000	.270E-07	3.59	.391E-07	.281E-07
-8.0000	0.000E+00	-999.0000	.270E-03	3.59	.391E-03	.843E-03
-7.0000	0.000E+00	-999.0000	.270E-02	3.59	.391E-02	.843E-02
-6.0000	0.000E+00	-999.0000	.270E-01	3.59	.391E-01	.843E-01
-5.3508	0.000E+00	-999.0000	.120	3.59	.174	.376
-5.0000	0.000E+00	-999.0000	.105	3.59	.391	.843
-4.7230	0.000E+00	-999.0000	.822E-01	3.59	.740	1.59
-4.5656	0.000E+00	-999.0000	.637E-01	3.59	1.06	1.59
-4.0000	0.000E+00	-999.0000	.116E-04	3.59	3.91	5.62
-3.9918	0.000E+00	-999.0000	.826E-04	3.59	3.98	5.72
-3.8251	0.000E+00	-999.0000	.562E-04	3.59	3.99	8.40

solid solution product compositions

log of moles of product minerals (cumulative)

log zi	time, d	log days	gibbsite
-5.3508	0.000E+00	-999.0000	-8.3489
-5.0000	0.000E+00	-999.0000	-5.2136

log zi	time, d	log days	gibbsite	kaolinite
-4.7230	0.000E+00	-999.0000	-4.8002	-7.7230

log zi	time, d	log days	kaolinite
-4.5656	0.000E+00	-999.0000	-4.9061
-4.0000	0.000E+00	-999.0000	-4.3010

log zi	time, d	log days	kaolinite	muscovite
-3.9918	0.000E+00	-999.0000	-4.2929	-9.0672

log zi	time, d	log days	kaolinite	maximum microcline	muscovite
-3.8251	0.000E+00	-999.0000	-5.4290	-0.0001	-4.3247

log of destroyed moles of reactants

log zi	time, d	log days	maximum microcline
-999.0000	0.000E+00	-999.0000	-999.0000
-8.0000	0.000E+00	-999.0000	-8.0000

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-7.0000	0.000E+00	-999.0000	-7.0000
-6.0000	0.000E+00	-999.0000	-6.0000
-5.3508	0.000E+00	-999.0000	-5.3508
-5.0000	0.000E+00	-999.0000	-5.0000
-4.7230	0.000E+00	-999.0000	-4.7230
-4.5656	0.000E+00	-999.0000	-4.5656
-4.0000	0.000E+00	-999.0000	-4.0000
-3.9918	0.000E+00	-999.0000	-3.9918
-3.8251	0.000E+00	-999.0000	-3.8251

zi	log zi	time, d	log days	g des	g cre	g net	cc des	cc cre	cc net
0.000E+00	-999.0000	0.000E+00	-999.0000	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
1.000E-08	-8.0000	0.000E+00	-999.0000	2.783E-06	0.000E+00	-2.783E-06	1.087E-06	0.000E+00	-1.087E-06
1.000E-07	-7.0000	0.000E+00	-999.0000	2.783E-05	0.000E+00	-2.783E-05	1.087E-05	0.000E+00	-1.087E-05
1.000E-06	-6.0000	0.000E+00	-999.0000	2.783E-04	0.000E+00	-2.783E-04	1.087E-04	0.000E+00	-1.087E-04
4.458E-06	-5.3508	0.000E+00	-999.0000	1.241E-03	3.493E-07	-1.241E-03	4.848E-04	1.431E-07	-4.846E-04
1.000E-05	-5.0000	0.000E+00	-999.0000	2.783E-03	4.770E-04	-2.306E-03	1.087E-03	1.954E-04	-8.920E-04
1.892E-05	-4.7230	0.000E+00	-999.0000	5.267E-03	1.240E-03	-4.027E-03	2.058E-03	5.081E-04	-1.550E-03
2.719E-05	-4.5656	0.000E+00	-999.0000	7.567E-03	3.205E-03	-4.362E-03	2.956E-03	1.235E-03	-1.721E-03
1.000E-04	-4.0000	0.000E+00	-999.0000	2.783E-02	1.291E-02	-1.493E-02	1.087E-02	4.976E-03	-5.898E-03
1.019E-04	-3.9918	0.000E+00	-999.0000	2.836E-02	1.315E-02	-1.521E-02	1.108E-02	5.070E-03	-6.010E-03
1.496E-04	-3.8251	0.000E+00	-999.0000	4.164E-02	2.783E+02	2.783E+02	1.627E-02	1.087E+02	1.087E+02

affinities of irreversible reactions

log zi	time, d	log days	maximum microcline
-999.0000	0.000E+00	-999.0000	58.6114
-8.0000	0.000E+00	-999.0000	29.3719
-7.0000	0.000E+00	-999.0000	22.5426
-6.0000	0.000E+00	-999.0000	15.6398
-5.3508	0.000E+00	-999.0000	10.8723
-5.0000	0.000E+00	-999.0000	8.9296
-4.7230	0.000E+00	-999.0000	7.3690
-4.5656	0.000E+00	-999.0000	7.1016
-4.0000	0.000E+00	-999.0000	2.4469
-3.9918	0.000E+00	-999.0000	0.4542
-3.8251	0.000E+00	-999.0000	0.0000

6.5. Microcline Dissolution in a Fluid-Centered Flow-Through Open System

This example is a modification of the previous one. Here reaction takes place in a fluid-centered flow-through open system instead of in a closed system. The calculation describes the evolution of the "first" packet of dilute acid solution flowing through a microcline "medium." Results analogous to those plotted for the preceding example are plotted in Figures 10-13. The EQ6 **input** file for this example is **microhclft.6i**. This initializing EQ3NR **input** file is once more **ph4hcl.3i**. The results are illustrated below by selected parts of the corresponding **output** and **tab** files (**microhcftl.6o** and **microhclft.6t**, respectively). Only the final "print point" is presented here for the **output** file.

The reaction path is identical to that in the previous example up to the point at which kaolinite ($Al_2Si_2O_5(OH)_4$) begins to precipitate. Recall that the kaolinite competed with the previously precipitated gibbsite ($Al(OH)_3$) for available aluminum. This competition caused the gibbsite to redissolve. In the present model system, however, the gibbsite is taken to be physically separated from the moving packet of fluid. Hence, it can not redissolve. In the code, it is protected from redissolving by transfer from the equilibrium system to the physically removed system. In practice, a very small amount is left in the equilibrium system and permitted to redissolve. Because redissolution is not permitted (except as previously noted), it is the cumulative amount of secondary minerals that is plotted in Figure 12. As before, muscovite ($KAl_3Si_3O_{10}(OH)_2$) later begins to precipitate, though at an earlier point of reaction progress (less microcline dissolved).

Information Only

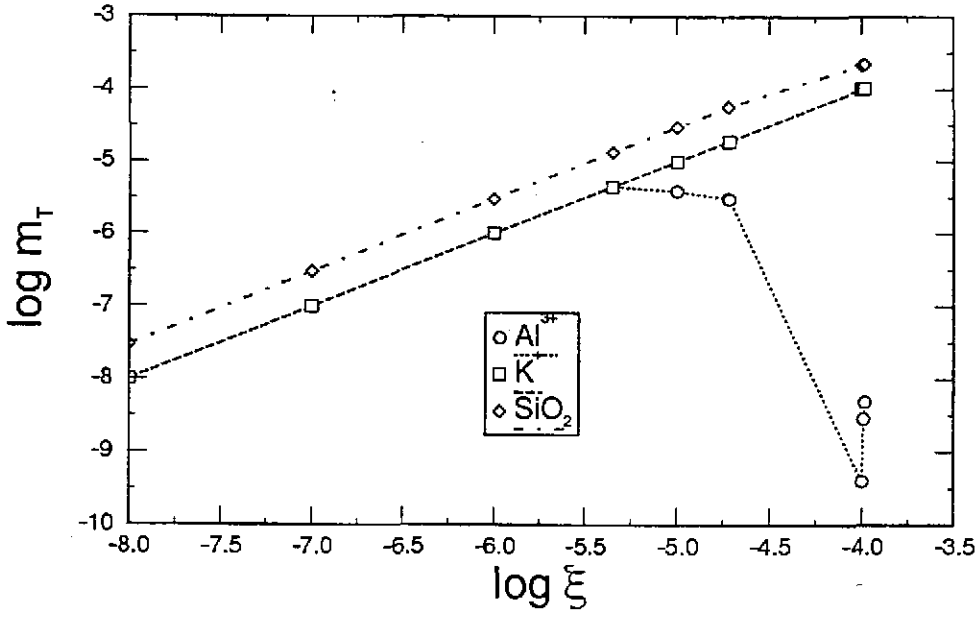

Figure 10. Changes in the total molalities of dissolved aluminum, potassium, and silica as a function of reaction progress (ξ) in fluid-centered flow-through open system reaction of microcline with *pH* 4.0 *HCl* solution.

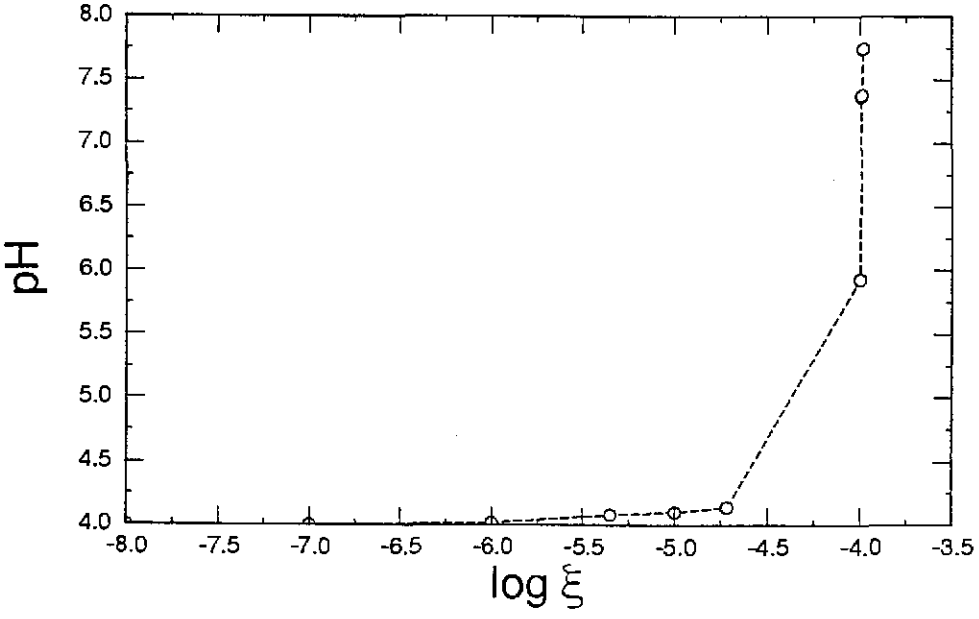

Figure 11. Change in the *pH* as a function of reaction progress (ξ) in fluid-centered flow-through open system reaction of microcline with *pH* 4.0 *HCl* solution.

Information Only

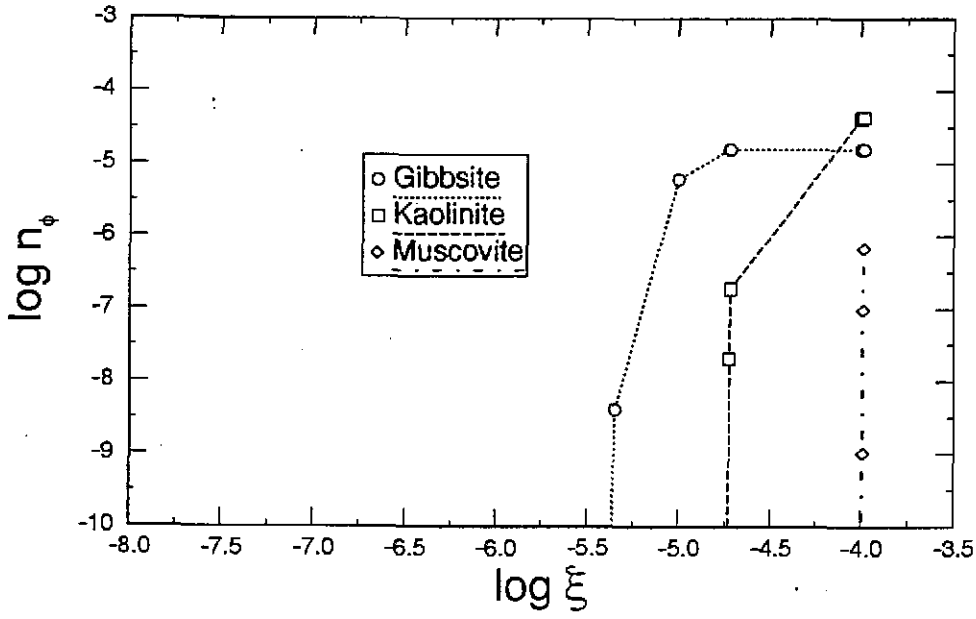

Figure 12. The cumulative number of moles of secondary minerals (n_ϕ) as a function of reaction progress (ξ) in fluid-centered flow-through open system reaction of microcline with *pH* 4.0 *HCl* solution. The reacting system originally contains 1 kg of solvent water.

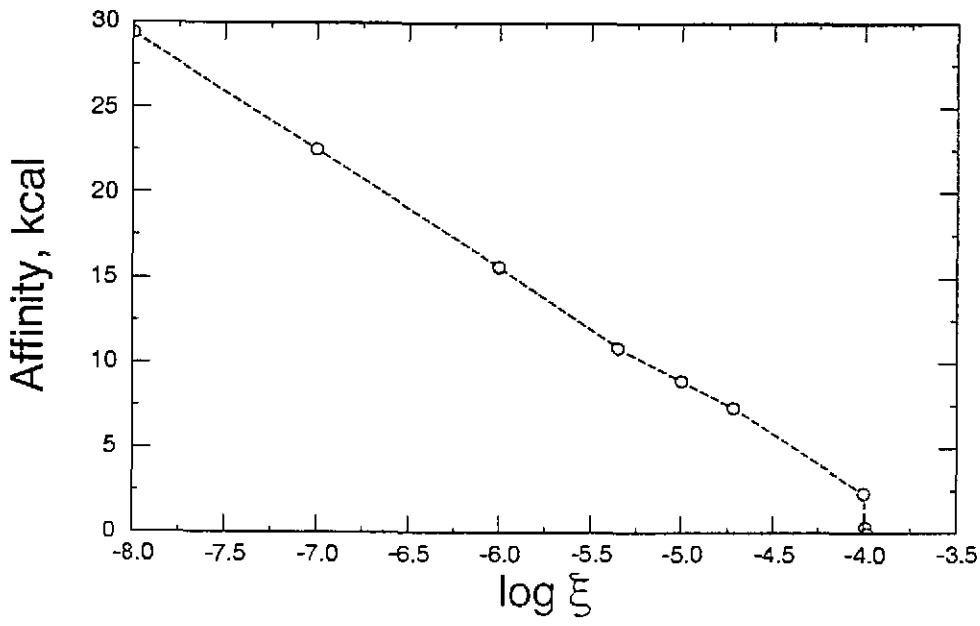

Figure 13. The affinity to dissolve of microcline as a function of reaction progress (ξ) in fluid-centered flow-through open system reaction of microcline with *pH* 4.0 *HCl* solution.

Information Only

It competes with the kaolinite for aluminum and silicon. In the previous example, some but not all of the kaolinite redissolved. Here the precipitated kaolinite is protected in the same manner as was the gibbsite. The solution eventually saturates with microcline, and reaction stops.

Note that the reaction path is similar to, but different from, that obtained in the closed system model. The final value of reaction progress (1.038×10^{-4} moles) is about two thirds that obtained in closed system (1.496×10^{-4} moles). The *pH*, which was initially 4.0, is 7.75 at this point. It was 7.37 for the closed system. Other small but significant differences in the water chemistry may also be noted.

<u>The EQ6 **input** file (**microhclft.6i**), microcline dissolution in pH 4 HCl, fluid-centered flow-through open system ("W" format)</u>:

```
EQ6 input file name= microhclft.6i
Description= "Microcline dissolution in flowing HCl solution"
Version number= 3245    Stage number= 01
Created 10/31/90     Creator= T.J. Wolery
Revised 10/31/90     Revisor= T.J. Wolery

  React microcline (KAlSi3O8) with a dilute (pH 4.0) HCl solution
at 25 C. This case is identical to that in the EQ6 test case input
file microhcl.6i, except that reaction here takes place in a
fluid-centered flow-through open system (nmodl1 = 3). There is no
time frame in this calculation. Precipitation of quartz,
chalecedony, and tridymite is suppressed by means of an "nxmod"
option that is inherited from the initializing EQ3NR input file
ph4hcl.3i.

  Purpose: to test the fluid-centered flow-through open system
model. The results may be compared and contrasted with those
obtained using the EQ6 test case input file microhcl.6i, which
is used to model the same reaction in a closed system.

  This problem has no redox aspect. The option switch ioptl1 is
set to 1 to indicate this to the code.

                              References

None

endit.
    nmodl1=  3                nmodl2=  0
    tempc0=  2.50000E+01       jtemp=  0
       t'1=  0.00000E+00         tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.               zimax=  1.0
     tstrt=  0.              timemx=  1.00000E+38
    kstpmx=          200      cplim=  0.00000E+00
    dzprnt=  1.00000E+00    dzprlg=  1.00000E+00    ksppmx=   100
    dzplot=  1.00000E+38    dzpllg=  1.00000E+38    ksplmx= 10000
     ifile= 60
*              1    2    3    4    5    6    7    8    9   10
  ioptl-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    1    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
    nxopt=  0
* nffg = number of gas species with fixed fugacities
     nffg=  0
* nrct = number of reactants
     nrct=  1
*-----------------------------------------------------------------------
  reactant= maximum microcline
    jcode=  0                 jreac=  0
     morr=  1.00000E+00        modr=  0.00000E+00
      nsk=  0                    sk=  0.00000E+00        fk=  0.00000E+00
      nrk=  1                 nrpk=  0
      rk1=  1.00000E+00         rk2=  0.00000E+00       rk3=  0.00000E+00
*-----------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00      toldl=  0.00000E+00      tolx=  0.00000E+00
    tolsat=  0.00000E+00     tolsst=  0.00000E+00
    screw1=  0.00000E+00     screw2=  0.00000E+00    screw3=  0.00000E+00
    screw4=  0.00000E+00     screw5=  0.00000E+00    screw6=  0.00000E+00
```

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```
    zklogu=        0.000     zklogl=        0.000     zkfac=        0.000
    dlzmx1=  0.00000E+00     dlzmx2=  0.00000E+00     nordlm=  0
    itermx=  0               ntrymx=  0
    npslmx=  0               nsslmx=  0               ioscan=  0
*-----------------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= ph4hcl.3i
Description= "A pH 4 HCl solution, with traces of K, Al, and Si"
Version number= 3245   Stage number= 01
Created 06/08/90     Creator= T.J. Wolery
Revised 06/08/90     Revisor= T.J. Wolery

  Dilute HCl solution, pH 4.00, with traces of potassium, aluminum,
and silica. This problem is part of test problem 3 of INTERA
(1983), who report a comparison study of EQ3/6 with PHREEQE
(Parkhurst, Thorstenson, and Plummer, 1980). Note that quartz,
chalcedony, and tridymite are suppressed by means of "nxmod"
options. This has no effect on the EQ3NR calculation. It is simply
needed for the subsequent EQ6 problem. EQ3NR passes this on to
EQ6 on the pickup file.

  Purpose: to provide a pickup file for construction of the EQ6 test
cases microhcl.6i and microhclft.6i. It also tests the "nxmod"
suppress option.

  This problem is actually redox-indifferent. The auxiliary basis
species O2(aq) and H2(aq) have therefore been suppressed. The EQ6
option switch iopt11 should be set to 1.

                              References

INTERA Environmental Consultants, Inc., 1983, Geochemical Models
  Suitable for Performance Assessment of Nuclear Waste Storage:
  Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste
  Isolation, Battelle Project Management Division, Columbus, Ohio,
  ONWI-473, 114 p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980,
  PHREEQE- A Computer Program for Geochemical Calculations: Water
  Resources Investigations Report 80-96, U.S. Geological Survey,
  Reston, Virginia, 210 p.

endit.
    tempci=  0.25000E+02
     nxmod=  3
   species= quartz
      type=  1              option= -1              xlkmod=  0.00000E+00
   species= chalcedony
      type=  1              option= -1              xlkmod=  0.00000E+00
   species= tridymite
      type=  1              option= -1              xlkmod=  0.00000E+00
     iopg1=  0               iopg2=  0               iopg3=  0
     iopg4=  0               iopg5=  0               iopg6=  0
     iopg7=  0               iopg8=  0               iopg9=  0
    iopg10=  0
       kct=  6                 ksq=  7                 kmt=  7
       kxt=  7                kdim=  7                kprs=  0
   o                  0.555084350618964E+02
   al                 0.100000000000005E-11
   cl                 0.101162909259305E-03
   h                  0.111016971286694E+03
   k                  0.999999999999999E-12
   si                 0.100000000000000E-11
   electr             0.271050543121376E-19
   h2o                h2o                    0.174435898352698E+01
   al+++              al+++                 -0.120411346756320E+02
   cl-                cl-                   -0.399498786688732E+01
   h+                 h+                    -0.399498744436686E+01
   k+                 k+                    -0.120000013741135E+02
   sio2(aq)           sio2(aq)              -0.120000004901545E+02
   o2(g)              o2(g)                 -0.700000000000000E+00
```

The EQ6 **input** file (**microhclft.6i**), microcline dissolution in pH 4 HCl, fluid-centered flow-through open system ("W" format):

```
-----------------------------------------------------------------------
EQ6 input file name= microhclft.6i
Description= "Microcline dissolution in flowing HCl solution"
Version number= 3245   Stage number= 01
Created 10/31/90     Creator= T.J. Wolery
Revised 10/31/90     Revisor= T.J. Wolery

  React microcline (KAlSi3O8) with a dilute (pH 4.0) HCl solution
at 25 C. This case is identical to that in the EQ6 test case input
file microhcl.6i, except that reaction here takes place in a
```

Information Only

```
fluid-centered flow-through open system (nmodl1 = 3). There is no
time frame in this calculation. Precipitation of quartz,
chalecedony, and tridymite is suppressed by means of an "nxmod"
option that is inherited from the initializing EQ3NR input file
ph4hcl.3i.

  Purpose: to test the fluid-centered flow-through open system
model. The results may be compared and contrasted with those
obtained using the EQ6 test case input file microhcl.6i, which
is used to model the same reaction in a closed system.

  This problem has no redox aspect. The option switch iopt11 is
set to 1 to indicate this to the code.

                          References

None

-------------------------------------------------------------------
 calculational mode   |*normal     | economy          | super economy
-------------------------------------------------------------------
 model type           | titration  | closed           |*open
-------------------------------------------------------------------
 temperature model    |*power      | fluid mixing
-------------------------------------------------------------------
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c-------------------------------------------------------------------
 tstart(c)| 25.00    |tk1|     0.    |tk2|     0.    |tk3|     0.
-------------------------------------------------------------------
 starting value of zi |      0.    |max. value of zi    | 1.0000
-------------------------------------------------------------------
 starting time (sec)  |      0.    |max. time (sec)     | 1.00000E+38
-------------------------------------------------------------------
 max. steps           |       200  |max. steps w/o print|       100
-------------------------------------------------------------------
 linear print interval| 1.0000     |log print interval  | 1.0000
-------------------------------------------------------------------
 suppress mineral phases
-------------------------------------------------------------------
 phases w/ elements|                      |                      n
 phases except     |                      |                      n
-------------------------------------------------------------------
 fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
-------------------------------------------------------------------
 none                                |                |                n
-------------------------------------------------------------------
c                  R A T E     L A W S
c 1 = relative                  rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory   rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate        rate = CHECK DOCUMENTATION

c                  R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                  S U R F A C E    T Y P E
c 0 = fixed surface area     1 = fixed specific surface area
c
c                  N O T E S
c status and jreac are normally not set by the user
-------------------------------------------------------------------
 reactants   (ss) solid solution only     (sp) special reactant only
-------------------------------------------------------------------
 REACTANT          | maximum microcline   |status   | 0
 moles remaining   | 1.0000               |destroyed|      0.
 reactant type     | mineral              |sk       |      0.
 surface type      |  0                   |fk       |  1.0000
 end-member        |                      |mole fr  |                ss,n
 volume            |                      |         |                sp
 element           |                      |moles    |                sp,n
 DISSOLUTION LAW   |    1                 |         |
 rate constant rk1 | 1.0000               |csigma1  |
 rate constant rk2 |      0.              |csigma2  |
 rate constant rk3 |      0.              |csigma3  |
 PRECIPITATION LAW |    0                 |         |
-------------------------------------------------------------------
 options
-------------------------------------------------------------------
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * don't print
     lists species loaded into memory
 - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
   * don't print
     print
 - LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
   * don't print
     print
 - LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
   * only species > 10**-12 molal
     all species
```

Information Only

```
    don't print
- LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
  * don't print
    print
- LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
  * don't print
    print
- MINERAL SATURATION STATES -
  * print if affinity.> -10 kcals
    print all
    don't print
- LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
  * don't print
    print
- PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
  * don't print
    print
- TAB FILES -
  * write
    append to previous tabx file
    don't write
- WRITE PICKUP FILE -
  * write pickup file at end of run
    don't write pickup file
    write pickup file for each print point
- PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    transfer minerals but leave trivial mass in the system
    transfer minerals
- CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    clear p.r.s. before first reaction progress advance
- PHASE BOUNDARY SEARCH -
  * step size constrained by predicted phase boundaries
    phase boundaries estimated from Taylor's series and printed
    locations of phase boundaries ignored
- AUTO BASIS SWITCHING -
  * off
    on
- SUPPRESS REDOX REACTIONS -
    does nothing
  * suppress all redox reactions
- LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
  * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
    logarithmic for kcol = 1,kbt
    linear for kcol = 1,kdim
- AZERO AND HYDRATION NUMBERS -
  * no change
    read in new azero and hydration numbers
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
  * does nothing
    print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
    print summary information
    print detailed information
- PRINT STEP SIZE AND ORDER -
  * don't print
    print scale factor
    print orders and step size scaling factors
- CONTROL STEP SIZE AND ORDER PRINT -
  * does nothing
    print step size and order when delzi .le. dlzmxl
- NEWTON ITERATIONS -
  * don't print
    print summary of newton iterations
    print summary, residual functions and correction terms
    print summary, residual functions, correction terms and matrix
- PRINT SEARCH ITERATIONS -
  * don't print
    print
- PRINT HPSAT ITERATIONS -
  * don't print
    print
- PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
  * don't print
    print computations from RDERIV, and RTAYLR
    print computations from RDERIV, RTAYLR, DERIV and TAYLOR
- PRINT KINETICS DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 diagnostics
    print level 1 and level 2 diagnostics
- PRINT AKMATR -
  * don't print
    print level 1 diagnostics
```

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```
- KILL ITERATION VARIABLES -
  * does nothing
    allow selection of variables to remove
```

development options (used for code development)

```
   0 check finite difference and Taylor series expression
   0 check reaction rate finite difference and Taylor series
```

tolerances	desired values - defaults info-only	
number of N-R iterations	40	itermx
p.r.s. transfer interval	varies	dlzidp
residual magnitude	1.0e-06	tolbt
correction magnitude	1.0e-06	toldl
search/find tolerance	varies	tolx
supersaturation	varies	tolsat
supersaturation set size	varies	tolsst
max. size Taylor's series term	1.0e-04	screw1
max. initial value betamx	n/a	screw2
max. Taylor's series term (kin.)	1.0e-04	screw3
corrector iteration	1.0e-04	screw4
max. size of N-R correction term	4.0	screw5
step size (economy mode)	4.0	screw6
log mass of phases	varies	zklogu
decrement mass (p.r.s.)	2.0	zklogl
min. left after p.r.s.	.98	zkfac
initial step size	varies	dlzmx1
upper limit step size	varies	dlzmx2
maximum order	6	nordlm
num. attempted assemblages	25	ntrymx
slide -> over phase bound.	8	npslmx
slide -> over redox insta.	3	nsslmx
fo2 scan control	none	ioscan

```
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= ph4hcl.3i
Description= "A pH 4 HCl solution, with traces of K, Al, and Si"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  Dilute HCl solution, pH 4.00, with traces of potassium, aluminum,
and silica. This problem is part of test problem 3 of INTERA
(1983), who report a comparison study of EQ3/6 with PHREEQE
(Parkhurst, Thorstenson, and Plummer, 1980). Note that quartz,
chalcedony, and tridymite are suppressed by means of "nxmod"
options. This has no effect on the EQ3NR calculation. It is simply
needed for the subsequent EQ6 problem. EQ3NR passes this on to
EQ6 on the pickup file.

  Purpose: to provide a pickup file for construction of the EQ6 test
cases microhcl.6i and microhclft.6i. It also tests the "nxmod"
suppress option.

  This problem is actually redox-indifferent. The auxiliary basis
species O2(aq) and H2(aq) have therefore been suppressed. The EQ6
option switch iopt11 should be set to 1.
```

References

INTERA Environmental Consultants, Inc., 1983, Geochemical Models Suitable for Performance Assessment of Nuclear Waste Storage: Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste Isolation, Battelle Project Management Division, Columbus, Ohio, ONWI-473, 114 p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980, PHREEQE- A Computer Program for Geochemical Calculations: Water Resources Investigations Report 80-96, U.S. Geological Survey, Reston, Virginia, 210 p.

temperature (C)	25.000
electrical imbalance	2.710505431213760E-20
number of aqueous master species	7
position of last pure mineral	7
position of last solid solution	7

suppressed species	(suppress,replace,augmentk,augmentg)		value
quartz	mineral	suppress	0.
chalcedony	mineral	suppress	0.
tridymite	mineral	suppress	0.

iopg options

- pH SCALE CONVENTION -

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```
    * modified NBS
      internal
      rational
 - ACTIVITY COEFFICIENT OPTIONS -
    * use B-dot equation
      Davies' equation
      Pitzer's equations
-------------------------------------------------------------------------
 elements, moles and moles aqueous
-------------------------------------------------------------------------
          o        |   5.550843506189640E+01|   0.000000000000000E+00
          al       |   1.000000000000050E-12|   0.000000000000000E+00
          cl       |   1.011629092593050E-04|   0.000000000000000E+00
          h        |   1.110169712866940E+02|   0.000000000000000E+00
          k        |   9.999999999999990E-13|   0.000000000000000E+00
          si       |   1.000000000000000E-12|   0.000000000000000E+00
-------------------------------------------------------------------------
 master species and logarithmic basis variables
-------------------------------------------------------------------------
h2o                |h2o                     |   1.744358983526980E+00
al+++              |al+++                   |  -1.204113467563200E+01
cl-                |cl-                     |  -3.994987866887320E+00
h+                 |h+                      |  -3.994987444366860E+00
k+                 |k+                      |  -1.200000137411350E+01
sio2(aq)           |sio2(aq)                |  -1.200000049015450E+01
o2(g)              |o2(g)                   |  -7.000000000000000E-01
-------------------------------------------------------------------------
 physically removed subsystem  (solid solution, mineral, moles)
-------------------------------------------------------------------------
 none              |                        |
-------------------------------------------------------------------------
```

The EQ6 **input** file (**microhclft.6o**), microcline dissolution in pH 4 HCl, fluid-centered flow-through open system (partial reproduction):

•
•
•
(Material deleted)
•
•
•

```
stepping to zi=  1.0346E-04, delzi=  2.0071E-07, nord= 6
steps completed =    99, iter =  3, ncorr = 0
most rapidly changing is zvclg1(al+++              ) =    -16.9470

stepping to zi=  1.0367E-04, delzi=  2.1639E-07, nord= 6
steps completed =   100, iter =  2, ncorr = 0
most rapidly changing is zvclg1(al+++              ) =    -17.0598

stepping to zi=  1.0378E-04, delzi=  1.0953E-07, nord= 6
steps completed =   101, iter =  2, ncorr = 0
most rapidly changing is zvclg1(al+++              ) =    -17.1138

stepping to zi=  1.0380E-04, delzi=  1.8408E-08, nord= 6
iter =    2
      2 supersaturated pure minerals
      0 supersaturated solid solutions

                        the most supersaturated phases     affinity, kcal

                          1      21   maximum microcline      0.00069027
                          2      16   k-feldspar              0.00069027

  attempted species assemblage no.   2

            1      1  h2o
            2      3  al+++
            3     14  cl-
            4     26  h+
            5     35  k+
            6     60  sio2(aq)
            8     21  maximum microcline
            9     22  muscovite

steps completed =   102, iter = 17, ncorr = 0
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                    reaction progress        =  1.03802104305174E-04
                    log of reaction progress =      -3.9837938
```

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temperature = 25.000 degrees c
total pressure = 1.013 bars

computing units remaining = 0.000

change in the product phase assemblage

--- reactant summary ---

reactant	moles	delta moles	grams	delta grams
maximum microcline	9.9990E-01	1.0380E-04	2.7830E+02	2.8891E-02

current total mass = 2.78303E+02 grams
delta total mass = 2.88914E-02 grams
delta total volume = 0.01129 cc

reactant	affinity kcal/mol	rel. rate mol/mol
maximum microcline	0.0000	0.0000E+00

affinity of the overall irreversible reaction= 0.000 kcal
contributions from irreversible reactions
with no thermodynamic data are not included

--- element totals for the aqueous phase ---

element	mg/kg soln.	molal conc.	moles
o	8.880901E+05	5.550888E+01	5.550882E+01
al	1.315509E-04	4.875691E-09	4.875686E-09
cl	3.586427E+00	1.011630E-04	1.011629E-04
h	1.118960E+05	1.110169E+02	1.110168E+02
k	4.031780E+00	1.031212E-04	1.031211E-04
si	6.272759E+00	2.233498E-04	2.233496E-04
co3--		0.000000E+00	0.000000E+00
so4--		0.000000E+00	0.000000E+00
s--		0.000000E+00	0.000000E+00

warning-- co3--, so4--, and s-- totals require that routine compl
have the names of non-carbonate carbon, sulfide sulfur,
and non-sulfate sulfur aqueous species

single ion activities and activity coefficients are here defined
with respect to the modified nbs ph scale

	ph
modified nbs ph scale	7.7472
rational ph scale	7.7421

phcl = 11.7473

redox parameters are not defined

activity of water = 0.99999
log activity of water = 0.00000

ionic strength = 1.031390E-04 molal
sum of molalities = 0.0004282284953
osmotic coefficient = 0.99812

mass of solution = 1.000020 kg
mass of solutes = 0.000021 kg
conc of solutes = 0.002107 per cent (w/w)

moles of solvent h2o = 5.55084E+01
mass of solvent h2o = 9.99999E-01 kg

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	9.99999E+02	9.99992E-01	0.00000	0.00000	0.00000
sio2(aq)	2.21950E-04	1.33357E-02	2.21950E-04	-3.65374	0.00000	-3.65374
k+	1.03121E-04	4.03185E-03	1.03121E-04	-3.98665	-0.00516	-3.99181
cl-	1.01163E-04	3.58649E-03	1.01163E-04	-3.99498	-0.00512	-4.00010
hsio3-	1.39974E-06	1.07908E-04	1.39974E-06	-5.85395	-0.00510	-5.85905

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oh-	5.71754E-07	9.72402E-06	5.71755E-07	-6.24279	-0.00512	-6.24791
h+	1.81076E-08	1.82514E-08	1.81077E-08	-7.74214	-0.00506	-7.74720
al(oh)4-	4.79114E-09	4.55211E-07	4.79115E-09	-8.31956	-0.00510	-8.32466
kcl(aq)	3.26205E-10	2.43189E-08	3.26205E-10	-9.48651	0.00000	-9.48651

--- summary of instantaneously precipitated solid phases ---
(defined by derivatives)

phase/end-member	d mol/d zi	d grams/d zi	d vol (cc)/d zi
maximum microcline	3.33000E-01	9.26845E+01	3.62108E+01
muscovite	9.94707E-01	3.96200E+02	1.39965E+02

--- summary of solid phases (e.s.+p.r.s.) ---

phase/end-member	log moles	moles	grams	volume, cc
gibbsite	-4.8027113	1.57503E-05	1.22858E-03	5.03316E-04
kaolinite	-4.3664619	4.30069E-05	1.11027E-02	4.28005E-03
maximum microcline	-8.3098522	4.89945E-09	1.36367E-06	5.32772E-07
muscovite	-6.1700012	6.76081E-07	2.69289E-04	9.51314E-05

--- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

phase/end-member	log moles	moles	grams	volume, cc
gibbsite	-4.8027113	1.57503E-05	1.22858E-03	5.03316E-04
kaolinite	-4.3664619	4.30069E-05	1.11027E-02	4.28005E-03
maximum microcline	-0.0000451	9.99896E-01	2.78303E+02	1.08730E+02
muscovite	-6.1700012	6.76081E-07	2.69289E-04	9.51314E-05

	mass, grams	volume, cc
created	1.260191E-02	4.879027E-03
destroyed	2.889140E-02	1.128754E-02
net	-1.628949E-02	-6.408518E-03

warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base

--- mineral saturation state summary ---

mineral	affinity, kcal	state	mineral	affinity, kcal	state
al	830.0653	ssatd	andalusite	-7.8271	
beidellite-h	-2.5848		beidellite-k	-1.8154	
boehmite	-3.2136		chalcedony	0.1014	ssatd
coesite	-0.6336		corundum	-9.4156	
cristobalite	-0.2796		cristobalite-a	-0.2796	
cristobalite-b	-0.8847		diaspore	-2.0615	
gibbsite	-0.9832		ice	-0.1890	
k	249.9969	ssatd	k-feldspar	0.0000	
kalsilite	-5.2750		kaolinite	-0.3499	
kyanite	-7.4581		maximum microcline	0.0000	satd
muscovite	0.0000	satd	pyrophyllite	-1.6284	
quartz	0.4714	ssatd	sanidine high	-1.6361	
si	1158.7402	ssatd	sillimanite	-8.3232	
sio2(am)	-1.2826		tridymite	0.2375	ssatd

- -

--- all rates are zero ---

--- each reactant is saturated or exhausted ---

--- the reaction path has terminated normally ---

102 steps were taken
zi increased from
0.00000E+00 to 1.03802E-04
the average value of delzi was 1.01767E-06
the average matrix dimension was 8

start time = 16:11 13Dec91
end time = 16:12 13Dec91

user time = 53.380
cpu time = 1.080

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--- no further input found ---

The EQ6 tab file (**microhclft.6t**), microcline dissolution in pH 4 HCl, fluid-centered flow-through open system (partial reproduction):

•
•
•
(Material deleted)
•
•
•

zi	log zi	time, d	log days	tempc	press	ph	log fo2	eh	pe	kg h2o	tot aff
0.000E+00	-999.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0000	-999.0000	-999.0000	-999.0000	1.0000	58.6114
1.000E-09	-9.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0000	-999.0000	-999.0000	-999.0000	1.0000	36.1925
1.000E-08	-8.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0002	-999.0000	-999.0000	-999.0000	1.0000	29.3719
1.000E-07	-7.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0017	-999.0000	-999.0000	-999.0000	1.0000	22.5426
1.000E-06	-6.0000	0.000E+00	-999.0000	25.0000	1.0132	4.0171	-999.0000	-999.0000	-999.0000	1.0000	15.6398
4.458E-06	-5.3509	0.000E+00	-999.0000	25.0000	1.0132	4.0817	-999.0000	-999.0000	-999.0000	1.0000	10.8724
1.000E-05	-5.0000	0.000E+00	-999.0000	25.0000	1.0132	4.1022	-999.0000	-999.0000	-999.0000	1.0000	8.9296
1.893E-05	-4.7230	0.000E+00	-999.0000	25.0000	1.0132	4.1389	-999.0000	-999.0000	-999.0000	1.0000	7.3690
1.914E-05	-4.7180	0.000E+00	-999.0000	25.0000	1.0132	4.1396	-999.0000	-999.0000	-999.0000	1.0000	7.3547
1.000E-04	-4.0000	0.000E+00	-999.0000	25.0000	1.0132	5.9287	-999.0000	-999.0000	-999.0000	1.0000	2.3578
1.019E-04	-3.9917	0.000E+00	-999.0000	25.0000	1.0132	7.3674	-999.0000	-999.0000	-999.0000	1.0000	0.3655
1.021E-04	-3.9912	0.000E+00	-999.0000	25.0000	1.0132	7.3782	-999.0000	-999.0000	-999.0000	1.0000	0.3545
1.038E-04	-3.9838	0.000E+00	-999.0000	25.0000	1.0132	7.7472	-999.0000	-999.0000	-999.0000	1.0000	0.0000

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log molality of dissolved elements

log zi	time, d	log days	al	cl	k	si
-999.0000	0.000E+00	-999.0000	-12.0000	-3.9950	-12.0000	-12.0000
-9.0000	0.000E+00	-999.0000	-8.9996	-3.9950	-8.9996	-8.5227
-8.0000	0.000E+00	-999.0000	-8.0000	-3.9950	-8.0000	-7.5229
-7.0000	0.000E+00	-999.0000	-7.0000	-3.9950	-7.0000	-6.5229
-6.0000	0.000E+00	-999.0000	-6.0000	-3.9950	-6.0000	-5.5229
-5.3509	0.000E+00	-999.0000	-5.3513	-3.9950	-5.3509	-4.8738
-5.0000	0.000E+00	-999.0000	-5.4107	-3.9950	-5.0000	-4.5229
-4.7230	0.000E+00	-999.0000	-5.5163	-3.9950	-4.7230	-4.2462
-4.7180	0.000E+00	-999.0000	-5.5208	-3.9950	-4.7180	-4.2437
-4.0000	0.000E+00	-999.0000	-9.4006	-3.9950	-4.0000	-3.6660
-3.9917	0.000E+00	-999.0000	-8.5469	-3.9950	-3.9917	-3.6583
-3.9912	0.000E+00	-999.0000	-8.5407	-3.9950	-3.9916	-3.6578
-3.9838	0.000E+00	-999.0000	-8.3120	-3.9950	-3.9867	-3.6510

ppm (mg/kg) of dissolved elements

log zi	time, d	log days	al	cl	k	si
-999.0000	0.000E+00	-999.0000	.270E-07	3.59	.391E-07	.281E-07
-9.0000	0.000E+00	-999.0000	.270E-04	3.59	.391E-04	.843E-04
-8.0000	0.000E+00	-999.0000	.270E-03	3.59	.391E-03	.843E-03
-7.0000	0.000E+00	-999.0000	.270E-02	3.59	.391E-02	.843E-02
-6.0000	0.000E+00	-999.0000	.270E-01	3.59	.391E-01	.843E-01
-5.3509	0.000E+00	-999.0000	.120	3.59	.174	.376
-5.0000	0.000E+00	-999.0000	.105	3.59	.391	.843
-4.7230	0.000E+00	-999.0000	.822E-01	3.59	.740	1.59
-4.7180	0.000E+00	-999.0000	.813E-01	3.59	.748	1.60
-4.0000	0.000E+00	-999.0000	.107E-04	3.59	3.91	6.06
-3.9917	0.000E+00	-999.0000	.766E-04	3.59	3.99	6.17
-3.9912	0.000E+00	-999.0000	.777E-04	3.59	3.99	6.17
-3.9838	0.000E+00	-999.0000	.132E-03	3.59	4.03	6.27

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Information Only

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log of moles of product minerals (cumulative)

log zi	time, d	log days	gibbsite
-5.3509	0.000E+00	-999.0000	-8.3882
-5.0000	0.000E+00	-999.0000	-5.2136

log zi	time, d	log days	gibbsite	kaolinite
-4.7230	0.000E+00	-999.0000	-4.8003	-7.6833

log zi	time, d	log days	kaolinite
-4.7180	0.000E+00	-999.0000	-6.7236
-4.0000	0.000E+00	-999.0000	-4.3755

log zi	time, d	log days	kaolinite	muscovite
-3.9917	0.000E+00	-999.0000	-4.3656	-8.9970

log zi	time, d	log days	muscovite
-3.9912	0.000E+00	-999.0000	-7.0179

log zi	time, d	log days	maximum microcline	muscovite
-3.9838	0.000E+00	-999.0000	-8.3099	-6.1700

log of destroyed moles of reactants

log zi	time, d	log days	maximum microcline
-999.0000	0.000E+00	-999.0000	-999.0000
-9.0000	0.000E+00	-999.0000	-9.0000
-8.0000	0.000E+00	-999.0000	-8.0000
-7.0000	0.000E+00	-999.0000	-7.0000
-6.0000	0.000E+00	-999.0000	-6.0000
-5.3509	0.000E+00	-999.0000	-5.3509
-5.0000	0.000E+00	-999.0000	-5.0000
-4.7230	0.000E+00	-999.0000	-4.7230
-4.7180	0.000E+00	-999.0000	-4.7180
-4.0000	0.000E+00	-999.0000	-4.0000
-3.9917	0.000E+00	-999.0000	-3.9917
-3.9912	0.000E+00	-999.0000	-3.9912
-3.9838	0.000E+00	-999.0000	-3.9838

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•
•

(Material deleted)

•
•
•

affinities of irreversible reactions

log zi	time, d	log days	maximum microcline

Information Only

```
-999.0000 0.000E+00 -999.0000   58.6114
  -9.0000 0.000E+00 -999.0000   36.1925
  -8.0000 0.000E+00 -999.0000   29.3719
  -7.0000 0.000E+00 -999.0000   22.5426
  -6.0000 0.000E+00 -999.0000   15.6398
  -5.3509 0.000E+00 -999.0000   10.8724
  -5.0000 0.000E+00 -999.0000    8.9296
  -4.7230 0.000E+00 -999.0000    7.3690
  -4.7180 0.000E+00 -999.0000    7.3547
  -4.0000 0.000E+00 -999.0000    2.3578
  -3.9917 0.000E+00 -999.0000    0.3655
  -3.9912 0.000E+00 -999.0000    0.3545
  -3.9838 0.000E+00 -999.0000    0.0000
```

6.6. Pitzer's Equations: Gypsum Solubility in NaCl Solutions.

This example involves computing the solubility of gypsum ($CaSO_4.2H_2O$) in the system $CaSO_4$-$NaCl$-H_2O as a function of the $NaCl$ concentration. Because the ionic strength exceeds the range in which a simple extended Debye-Hückel model can be successfully applied, Pitzer's (1973, 1975, 1979, 1987) equations are employed in conjunction with the model of Harvie, Møller, and Weare (1984). This model is selected by setting **iopg1** = 1 and the **hmw** data file. This choice of the **iopg1** variable is first made on the initializing EQ3NR **input** file **caso4naclB.3i** (see Appendix F). This creates a model of a dilute solution containing a trace each of calcium sulfate and sodium chloride. The choice of **iopg1** then carries through on the EQ3NR **pickup** file.

This problem is completed in two successive EQ6 runs. The first, represented by the EQ6 **input** file **gypsumB.6i**, involves adding an excess of gypsum to the solution This essentially gives the solubility of gypsum at an $NaCl$ concentration of zero. This **input** file is given below in both "W" and "D" formats. The only output of interest is the bottom part of the corresponding **pickup** file, which is incorporated into the other EQ6 **input** file, **gypnacl.6i**. This **input** file directs the addition of sodium chloride via dissolution of halite ($NaCl$). The run terminates at the point of halite saturation.

The results are plotted in Figure 14. Also shown in this figure are the experimental data of Marshall and Slusher (1966) and Block and Waters (1968). This figure may be compared with Figure 4 of Harvie and Weare (1980), which presents a model solubility showing slightly better correspondence with the same experimental data near the point of halite saturation. The model of Harvie, Møller, and Weare (1984) is not identical to that of Harvie and Weare (1980), not generally and not for this particular electrolyte system. The results of the present example are also illustrated below by parts of the corresponding **tab** file, **gypnacl.6t**.

Note that it is important to begin the second EQ6 calculation with an excess of gypsum present in the system. This is because the solubility initially increases as the $NaCl$ concentration increases. It then passes through a maximum and decreases as shown in Figure 14.

Information Only

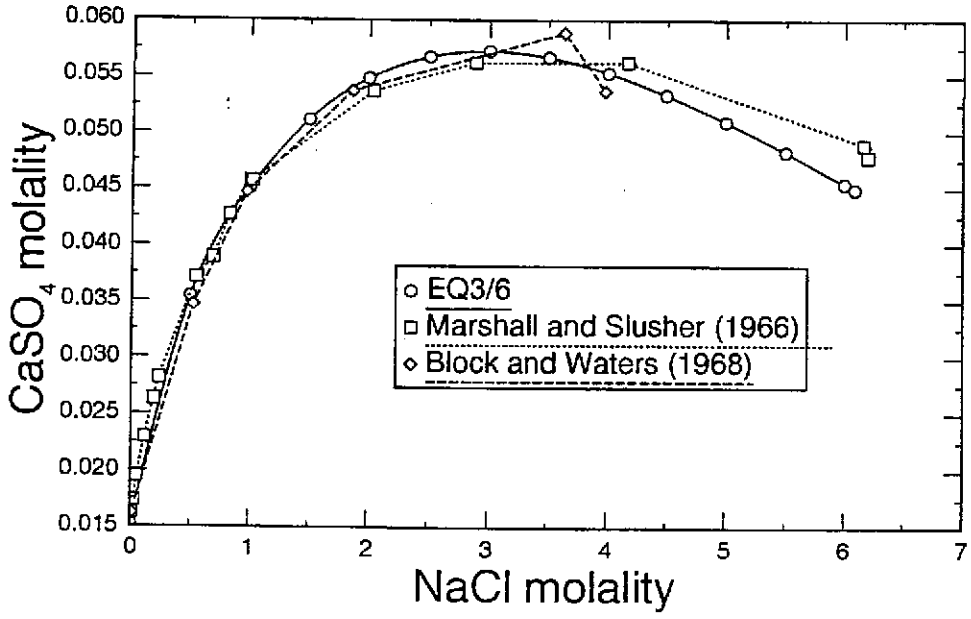

Figure 14. The solubility of gypsum in the system $CaSO_4$-$NaCl$-H_2O as a function of the molality of $NaCl$. The experimental data reported by Marshall and Slusher (1966) and Block and Waters (1968) are shown for comparison.

The EQ6 **input** file (**gypsumB.6i**), add gypsum to dilute NaCl solution ("W" format):

```
EQ6 input file name= gypsumB.6i
Description= "Gypsum sol'y, trace NaCl, anhydrite suppresssd"
Version number= 3245    Stage number= 01
Created 10/29/90     Creator= T.J. Wolery
Revised 10/29/90     Revisor= T.J. Wolery

  Add gypsum (CaSO4.2H2O) to water containing traces of CaSO4 and
NaCl.

  Purpose: to find the solubility of gypsum (CaSO4.2H2O) in the
system CaSO4-H2O, and to initialize the EQ6 test case input files
gypnacl.6i (compute the solubility of gypsum in the system
CaSO4-NaCl-H2O, results to be compared with Figure 4 of Harvie and
Weare, 1980). Anhydrite is suppressed using an "nxmod" option on
the initializing EQ3NR input file, caso4naclB.3i. This test case
uses Pitzer's equations to calculate the activity of water and
the activity coefficients of the aqueous solute species. The
Harvie- Moller-Weare (hmw) data file (after Harvie, Moller, and
Weare, 1984) should be employed.

  The print option switch iopr9 is set to 1 to direct the code to
also include a table of mean ionic activity coefficients.

                          References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
  of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-
  OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:
  Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

Harvie, C. E., and Weare, J. H., 1980, The prediction of mineral
  solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO4-H2O system
  from zero to high ionic strengths at 25 C: Geochimica et
  Cosmochimica Acta, v. 44, p. 981-987.

endit.
    nmodl1=  2                nmodl2=  0
    tempc0=  2.50000E+01       jtemp=  0
       tk1=  0.00000E+00         tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.00000E+00      zimax=  0.10000E+00
     tstrt=  0.00000E+00     timemx=  1.00000E+38
```

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```
    kstpmx=          200     cplim=  0.00000E+00
    dzprnt=  1.00000E+38    dzprlg=  1.00000E+38    ksppmx=   100
    dzplot=  1.00000E+38    dzpllg=  1.00000E+38    ksplmx= 10000
     ifile= 60
*              1    2    3    4    5    6    7    8    9   10
  ioptl-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
  ioprl-10=    0    0    0    0    0    0    0    0    1    0
 ioprl1-20=    0    0    0    0    0    0    0    0    0    0
  iodbl-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
    nxopt=  0
* nffg = number of gas species with fixed fugacities
    nffg =  0
* nrct = number of reactants
     nrct=  1
*-----------------------------------------------------------------------
  reactant= gypsum
     jcode=  0                jreac=  0
      morr=  0.10000E+00       modr=  0.00000E+00
       nsk=  0                   sk=  0.00000E+00        fk=  0.00000E+00
       nrk=  1                 nrpk=  0
       rk1=  1.00000E+00        rk2=  0.00000E+00       rk3=  0.00000E+00
*-----------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00      toldl=  0.00000E+00      tolx=  0.00000E+00
    tolsat=  0.00000E+00     tolsst=  0.00000E+00
    screw1=  0.00000E+00     screw2=  0.00000E+00    screw3=  0.00000E+00
    screw4=  0.00000E+00     screw5=  0.00000E+00    screw6=  0.00000E+00
    zklogu=        0.000     zklogl=        0.000     zkfac=        0.000
    dlzmx1=  0.00000E+00     dlzmx2=  0.00000E+00    nordlm=  0
    itermx=  0               ntrymx=  0
    npslmx=  0               nsslmx=  0              ioscan=  0
*-----------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= caso4naclB.3i
Description= "Trace CaSO4-NaCl solution, anhydrite suppressed"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Nearly pure water, with traces of calcium sulfate and sodium
chloride.

  Purpose: to initialize the EQ6 test case input file gypsumB.6i,
which in turn initializes the EQ6 test case input file gypnacl.6i.
This test case is identical to that in the EQ3NR test case input
file caso4nacl.3i, except that anhydrite is suppressed by an "nxmod"
option. This test case uses Pitzer's equations to calculate the
activity of water and the activity coefficients of the aqueous
solute species. The Harvie- Moller-Weare (hmw) data file (after
Harvie, Moller, and Weare, 1984) should be employed.

                              References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
  of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-
  OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:
  Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

endit.
    tempci=  0.25000E+02
     nxmod=  1
   species= anhydrite
      type=  1               option= -1              xlkmod=  0.00000E+00
     iopg1=  1                iopg2=  0               iopg3=  0
     iopg4=  0                iopg5=  0               iopg6=  0
     iopg7=  0                iopg8=  0               iopg9=  0
    iopg10=  0
       kct=  6                  ksq=  7                 kmt=  7
       kxt=  7                 kdim=  7                kprs=  0
   o                  0.555084351626101E+02
   ca                 0.999999999999996E-10
   cl                 0.999999999999996E-10
   h                  0.111016870324420E+03
   na                 0.999999999999996E-10
   s                  0.999999999999998E-10
   electr             0.579158777685128E-19
   h2o                h2o                     0.174435898352698E+01
   ca++               ca++                   -0.100000000000000E+02
   cl-                cl-                    -0.100000000000000E+02
   h+                 h+                     -0.699818779726878E+01
   na+                na+                    -0.100000000000000E+02
   so4--              so4--                  -0.100000041451921E+02
   o2(g)              o2(g)                   0.000000000000000E+00
```

Information Only

The EQ6 input file (gypsumB.6i), add gypsum to dilute NaCl solution ("D" format):

```
EQ6 input file name= gypsumB.6i
Description= "Gypsum sol'y, trace NaCl, anhydrite suppressed"
Version number= 3245   Stage number= 01
Created 10/29/90     Creator= T.J. Wolery
Revised 10/29/90     Revisor= T.J. Wolery

  Add gypsum (CaSO4.2H2O) to water containing traces of CaSO4 and
NaCl.

  Purpose: to find the solubility of gypsum (CaSO4.2H2O) in the
system CaSO4-H2O, and to initialize the EQ6 test case input files
gypnacl.6i (compute the solubility of gypsum in the system
CaSO4-NaCl-H2O, results to be compared with Figure 4 of Harvie and
Weare, 1980). Anhydrite is suppressed using an "nxmod" option on
the initializing EQ3NR input file, caso4naclB.3i. This test case
uses Pitzer's equations to calculate the activity of water and
the activity coefficients of the aqueous solute species. The
Harvie- Moller-Weare (hmw) data file (after Harvie, Moller, and
Weare, 1984) should be employed.

  The print option switch iopr9 is set to 1 to direct the code to
also include a table of mean ionic activity coefficients.

                          References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
  of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-
  OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:
  Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

Harvie, C. E., and Weare, J. H., 1980, The prediction of mineral
  solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO4-H2O system
  from zero to high ionic strengths at 25 C: Geochimica et
  Cosmochimica Acta, v. 44, p. 981-987.

 calculational mode   |*normal     | economy          | super economy
 model type           | titration  |*closed           | open
 temperature model    |*power      | fluid mixing
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c
 tstart(c)|  25.00    |tk1|     0.    |tk2|     0.    |tk3|     0.
 starting value of zi |      0.    |max. value of zi    | 0.10000
 starting time (sec)  |      0.    |max. time (sec)     | 1.00000E+38
 max. steps           |      200   |max. steps w/o print|      100
 linear print interval| 1.00000E+38|log print interval  | 1.00000E+38
 suppress mineral phases
 phases w/ elements |                        |                        n
 phases except      |                        |                        n
 fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
 none                                |                  |             n
c                   R A T E     L A W S
c 1 = relative                  rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory   rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate        rate = CHECK DOCUMENTATION

c                   R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                   S U R F A C E    T Y P E
c 0 = fixed surface area      1 = fixed specific surface area
c
c                   N O T E S
c status and jreac are normally not set by the user
 reactants   (ss) solid solution only     (sp) special reactant only
 REACTANT          | gypsum              | status     | 0
 moles remaining   | 0.10000             | destroyed  |      0.
 reactant type     | mineral             | sk         |      0.
 surface type      | 0                   | fk         | 1.0000
 end-member                              | mole fr    |                ss,n
 volume                                  |            |                sp
 element                                 | moles      |                sp,n
 DISSOLUTION LAW   |  1                  |            |
```

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```
rate constant rk1|  1.0000                  |csigma1  |
rate constant rk2|      0.                  |csigma2  |
rate constant rk3|      0.                  |csigma3  |
PRECIPITATION LAW|    0                     |         |
-----------------------------------------------------------------------
options
-----------------------------------------------------------------------
- SOLID SOLUTIONS -
  * ignore solid solutions
    process solid solutions
- LOADING OF SPECIES INTO MEMORY -
  * don't print
    lists species loaded into memory
- LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
  * don't print
    print
- LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
  * don't print
    print
- LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
  * only species > 10**-12 molal
    all species
    don't print
- LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
  * don't print
    print
- LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
  * don't print
    print
- MINERAL SATURATION STATES -
  * print if affinity > -10 kcals
    print all
    don't print
- LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
  * don't print
    print
- PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
  * don't print
    print
- TAB FILES -
  * write
    append to previous tabx file
    don't write
- WRITE PICKUP FILE -
  * write pickup file at end of run
    don't write pickup file
    write pickup file for each print point
- PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    transfer minerals but leave trivial mass in the system
    transfer minerals
- CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    clear p.r.s. before first reaction progress advance
- PHASE BOUNDARY SEARCH -
  * step size constrained by predicted phase boundaries
    phase boundaries estimated from Taylor's series and printed
    locations of phase boundaries ignored
- AUTO BASIS SWITCHING -
  * off
    on
- SUPPRESS REDOX REACTIONS -
  * does nothing
    suppress all redox reactions
- LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
  * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
    logarithmic for kcol = 1,kbt
    linear for kcol = 1,kdim
- AZERO AND HYDRATION NUMBERS -
  * no change
    read in new azero and hydration numbers
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
    does nothing
  * print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 3 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
    print summary information
    print detailed information
- PRINT STEP SIZE AND ORDER -
  * don't print
    print scale factor
    print orders and step size scaling factors
- CONTROL STEP SIZE AND ORDER PRINT -
  * does nothing
    print step size and order when delzi .le. dlzmx1
```

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```
- NEWTON ITERATIONS -
  * don't print
    print summary of newton iterations
    print summary, residual functions and correction terms
    print summary, residual functions, correction terms and matrix
- PRINT SEARCH ITERATIONS -
  * don't print
    print
- PRINT HPSAT ITERATIONS -
  * don't print
    print
- PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
  * don't print
    print computations from RDERIV, and RTAYLR
    print computations from RDERIV, RTAYLR, DERIV and TAYLOR
- PRINT KINETICS DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 diagnostics
    print level 1 and level 2 diagnostics
- PRINT AKMATR -
  * don't print
    print level 1 diagnostics
- KILL ITERATION VARIABLES -
  * does nothing
    allow selection of variables to remove
-------------------------------------------------------------------------
development options  (used for code development)
-------------------------------------------------------------------------
   0 check finite difference and Taylor series expression
   0 check reaction rate finite difference and Taylor series
-------------------------------------------------------------------------
tolerances                          desired values - defaults info-only
-------------------------------------------------------------------------
number of N-R iterations                          40       itermx
p.r.s. transfer interval                          varies   dlzidp
residual magnitude                                1.0e-06  tolbt
correction magnitude                              1.0e-06  toldl
search/find tolerance                             varies   tolx
supersaturation                                   varies   tolsat
supersaturation set size                          varies   tolsst
max. size Taylor's series term                    1.0e-04  screw1
max. initial value betamx                         n/a      screw2
max. Taylor's series term (kin.)                  1.0e-04  screw3
corrector iteration                               1.0e-04  screw4
max. size of N-R correction term                  4.0      screw5
step size (economy mode)                          4.0      screw6
log mass of phases                                varies   zklogu
decrement mass (p.r.s.)                           2.0      zklogl
min. left after p.r.s.                            .98      zkfac
initial step size                                 varies   dlzmx1
upper limit step size                             varies   dlzmx2
maximum order                                     6        nordlm
num. attempted assemblages                        25       ntrymx
slide -> over phase bound.                        8        npslmx
slide -> over redox insta.                        3        nsslmx
fo2 scan control                                  none     ioscan
-------------------------------------------------------------------------
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= caso4nacl8.3i
Description= "Trace CaSO4-NaCl solution, anhydrite suppressed"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Nearly pure water, with traces of calcium sulfate and sodium
chloride.

  Purpose: to initialize the EQ6 test case input file gypsum8.6i,
which in turn initializes the EQ6 test case input file gypnacl.6i.
This test case is identical to that in the EQ3NR test case input
file caso4nacl.3i, except that anhydrite is suppressed by an "nxmod"
option. This test case uses Pitzer's equations to calculate the
activity of water and the activity coefficients of the aqueous
solute species. The Harvie- Moller-Weare (hmw) data file (after
Harvie, Moller, and Weare, 1984) should be employed.

                              References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
  of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-
  OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:
  Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

-------------------------------------------------------------------------
temperature (C)                        |      25.000
-------------------------------------------------------------------------
electrical imbalance                   |      5.791587776851288E-20
-------------------------------------------------------------------------
number of aqueous master species       |      7
-------------------------------------------------------------------------
position of last pure mineral          |      7
-------------------------------------------------------------------------
```

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```
| position of last solid solution     |      7
-------------------------------------------------------------------------
| suppressed species     (suppress,replace,augmentk,augmentg)  value
-------------------------------------------------------------------------
| anhydrite              | mineral        | suppress |       0.
-------------------------------------------------------------------------
| iopg options
-------------------------------------------------------------------------
| - pH SCALE CONVENTION -
|    * modified NBS
|      internal
|      rational
| - ACTIVITY COEFFICIENT OPTIONS -
|      use B-dot equation
|      Davies' equation
|    * Pitzer's equations
-------------------------------------------------------------------------
| elements, moles and moles aqueous
-------------------------------------------------------------------------
|          o       |    5.550843516261010E+01|    0.000000000000000E+00
|          ca      |    9.999999999999960E-11|    0.000000000000000E+00
|          cl      |    9.999999999999960E-11|    0.000000000000000E+00
|          h       |    1.110168703244200E+02|    0.000000000000000E+00
|          na      |    9.999999999999960E-11|    0.000000000000000E+00
|          s       |    9.999999999999980E-11|    0.000000000000000E+00
-------------------------------------------------------------------------
| master species and logarithmic basis variables
-------------------------------------------------------------------------
|h2o                |h2o                      |    1.744358983526980E+00
|ca++               |ca++                     |   -1.000000000000000E+01
|cl-                |cl-                      |   -1.000000000000000E+01
|h+                 |h+                       |   -6.998187797268780E+00
|na+                |na+                      |   -1.000000000000000E+01
|so4--              |so4--                    |   -1.000000414519210E+01
|o2(g)              |o2(g)                    |    0.000000000000000E+00
-------------------------------------------------------------------------
| physically removed subsystem  (solid solution, mineral, moles)
-------------------------------------------------------------------------
| none              |                         |
-------------------------------------------------------------------------
```

The EQ6 **input** file (**gypnacl.6i**), gypsum solubility in NaCl ("W" format):

```
EQ6 input file name= gypnacl.6i
Description= "Gypsum solubility in the system CaSO4-NaCl-H2O"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Add halite (NaCl) to gypsum-saturated water (containing a trace of
NaCl) to compute the solubility of gypsum in the system CaSO4-NaCl-H2O.

  Purpose: to allow comparison of the results with Figure 4 of Harvie
and Weare, 1980, p. 991). This test case is similar to those defined
in the EQ6 test case input files gypanhy.6i and gypanhyA.6i. Note
that in the present test case, precipitation of anhydrite is
suppressed by means of an "nxmod" option. This option was implemented
in the EQ3NR test case input file caso4naclB.3i and passed on to
the EQ6 test case input file gypsumB.6i, which initializes the present
input file. The activity coefficients of the aqueous species are
calculated from Pitzer's equations. The Harvie-Moller-Weare (hmw)
data file (after Harvie, Moller, and Weare, 1984) should be employed.

  The print option switch iopt9 is set to 1 to direct the code to
include a table of mean ionic properties at each print point.

                              References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
  of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-
  OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:
  Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

Harvie, C. E., and Weare, J. H., 1980, The prediction of mineral
  solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO4-H2O system
  from zero to high ionic strengths at 25 C: Geochimica et
  Cosmochimica Acta, v. 44, p. 981-987.

endit.
    nmodl1=  2              nmodl2=  0
    tempc0=  2.50000E+01     jtemp=  0
       tk1=  0.00000E+00       tk2=  0.00000E+00       tk3=  0.00000E+00
    zistrt=  0.00000E+00     zimax=  6.50000E+00
     tstrt=  0.00000E+00    timemx=  1.00000E+38
    kstpmx=          200     cplim=  0.00000E+00
    dzprnt=  5.00000E-01    dzprlg=  1.00000E+38    ksppmx=   100
    dzplot=  1.00000E+38    dzpllg=  1.00000E+38    ksplmx= 10000
```

Information Only

```
    ifile= 60
*                1    2    3    4    5    6    7    8    9   10
  iopt1-10=      0    0    0    0    0    0    0    0    0    0
     11-20=      0    0    0    0    0    0    0    0    0    0
  iopr1-10=      0    0    0    0    0    0    0    0    1    0
 iopr11-20=      0    0    0    0    0    0    0    0    0    0
  iodb1-10=      0    0    0    0    0    0    0    0    0    0
     11-20=      0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
    nxopt=  0
* nffg = number of gas species with fixed fugacities
    nffg =  0
* nrct = number of reactants
     nrct=  1
*-----------------------------------------------------------------------------
  reactant= halite
     jcode=  0                 jreac=  0
      morr=  6.50000E+00        modr=  0.00000E+00
       nsk=  0                    sk=  0.00000E+00          fk=  0.00000E+00
       nrk=  1                  nrpk=  0
       rk1=  1.00000E+00         rk2=  0.00000E+00         rk3=  0.00000E+00
*-----------------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00       toldl=  0.00000E+00        tolx=  0.00000E+00
    tolsat=  0.00000E+00      tolsst=  0.00000E+00
    screw1=  0.00000E+00      screw2=  0.00000E+00     screw3=  0.00000E+00
    screw4=  0.00000E+00      screw5=  0.00000E+00     screw6=  0.00000E+00
    zklogu=        0.000      zklog1=        0.000      zkfac=        0.000
    dlzmx1=  0.00000E+00      dlzmx2=  0.00000E+00     nordlm=  0
    itermx=  0                ntrymx=  0
    npslmx=  0                nsslmx=  0               ioscan=  0
*-----------------------------------------------------------------------------
* pickup file written by eq6.3245R119x
*  supported by eqlib.3245R153
EQ6 input file name= gypsumB.6i
Description= "Gypsum sol'y, trace NaCl, anhydrite suppresssd"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Add gypsum (CaSO4.2H2O) to water containing traces of CaSO4 and
NaCl.

  Purpose: to find the solubility of gypsum (CaSO4.2H2O) in the
system CaSO4-H2O, and to initialize the EQ6 test case input file
gypnacl.6i (compute the solubility of gypsum in the system
CaSO4-NaCl-H2O, results to be compared with Figure 4 of Harvie and
Weare, 1980). Anhydrite is suppressed using an "nxmod" option on
the initializing EQ3NR input file, caso4naclB.3i. This test case
uses Pitzer's equations to calculate the activity of water and
the activity coefficients of the aqueous solute species. The
Harvie- Moller-Weare (hmw) data file (after Harvie, Moller, and
Weare, 1984) should be employed.

  The print option switch iopr9 is set to 1 to direct the code to
also include a table of mean ionic activity coefficients.

                              References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
  of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-
  OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:
  Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

Harvie, C. E., and Weare, J. H., 1980, The prediction of mineral
  solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO4-H2O system
  from zero to high ionic strengths at 25 C: Geochimica et
  Cosmochimica Acta, v. 44, p. 981-987.

endit.
    tempci=  2.50000E+01
     nxmod=  1
   species= anhydrite
      type=  1                 option= -1                xlkmod=  0.00000E+00
     iopg1=  1                  iopg2=  0                 iopg3=  0
     iopg4=  0                  iopg5=  0                 iopg6=  0
     iopg7=  0                  iopg8=  0                 iopg9=  0
    iopg10=  0
       kct=  6                    ksq=  7                   kmt=  8
       kxt=  8                   kdim=  8                  kprs=  0
   o                    5.610843516261009E+01        5.560001290305884E+01
   ca                   1.000000001000001E-01        1.526295684144937E-02
   cl                   9.999999999999960E-11        9.999999999999960E-11
   h                    1.114168703244200E+02        1.110779221513859E+02
   na                   9.999999999999960E-11        9.999999999999960E-11
   s                    1.000000001000001E-01        1.526295684145153E-02
   electr               5.791587776851280E-20
   h2o                  h2o                        1.744597750257154E+00
   ca++                 ca++                      -1.816361323816837E+00
   cl-                  cl-                       -1.000000000000000E+01
   h+                   h+                        -6.970286673167660E+00
   na+                  na+                       -1.000000000000000E+01
```

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```
so4--          so4--          -1.816362726210342E+00
o2(g)          o2(g)          -9.990000000000000E+02
               gypsum         -1.071926693968132E+00
```

The EQ6 **input** file (**gypnacl.6i**), gypsum solubility in NaCl ("D" format):

```
EQ6 input file name= gypnacl.6i
Description= "Gypsum solubility in the system CaSO4-NaCl-H2O"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Add halite (NaCl) to gypsum-saturated water (containing a trace of
NaCl) to compute the solubility of gypsum in the system CaSO4-NaCl-H2O

  Purpose: to allow comparison of the results with Figure 4 of Harvie
and Weare, 1980, p. 991). This test case is similar to those defined
in the EQ6 test case input files gypanhy.6i and gypanhyA.6i. Note
that in the present test case, precipitation of anhydrite is
suppressed by means of an "nxmod" option. This option was implemented
in the EQ3NR test case input file caso4naclB.3i and passed on to
the EQ6 test case input file gypsumB.6i, which initializes the present
input file. The activity coefficients of the aqueous species are
calculated from Pitzer's equations. The Harvie-Moller-Weare (hmw)
data file (after Harvie, Moller, and Weare, 1984) should be employed.

  The print option switch iopt9 is set to 1 to direct the code to
include a table of mean ionic properties at each print point.

                          References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
  of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-
  OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:
  Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

Harvie, C. E., and Weare, J. H., 1980, The prediction of mineral
  solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO4-H2O system
  from zero to high ionic strengths at 25 C: Geochimica et
  Cosmochimica Acta, v. 44, p. 981-987.

 calculational mode   |*normal      | economy          | super economy
 model type           | titration   |*closed           | open
 temperature model    |*power       | fluid mixing
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
 tstart(c)|  25.00    |tk1|     0.    |tk2|     0.    |tk3|     0.
 starting value of zi |      0.    |max. value of zi    |  6.5000
 starting time (sec)  |      0.    |max. time (sec)     | 1.00000E+38
 max. steps           |       200  |max. steps w/o print|       100
 linear print interval| 0.50000    |log print interval  | 1.00000E+38
 suppress mineral phases
 phases w/ elements|                        |                        n
 phases except     |                        |                        n
 fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
 none                              |                |                n
c                 R A T E     L A W S
c 1 = relative                  rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory   rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate        rate = CHECK DOCUMENTATION

c                 R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                 S U R F A C E    T Y P E
c 0 = fixed surface area     1 = fixed specific surface area
c
c                 N O T E S
c status and jreac are normally not set by the user
 reactants   (ss) solid solution only     (sp) special reactant only
```

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```
REACTANT            halite                  status      0
moles remaining     6.5000                  destroyed       0.
reactant type       mineral                 sk              0.
surface type         0                      fk          1.0000
end-member                                  mole fr                     ss,n
volume                                                                  sp
element                                     moles                       sp,n
DISSOLUTION LAW        1
rate constant rk1   1.0000                  csigma1
rate constant rk2       0.                  csigma2
rate constant rk3       0.                  csigma3
PRECIPITATION LAW      0
-----------------------------------------------------------------------
options
-----------------------------------------------------------------------
- SOLID SOLUTIONS -
  * ignore solid solutions
    process solid solutions
- LOADING OF SPECIES INTO MEMORY -
  * don't print
    lists species loaded into memory
- LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
  * don't print
    print
- LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
  * don't print
    print
- LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
  * only species > 10**-12 molal
    all species
    don't print
- LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
  * don't print
    print
- LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
  * don't print
    print
- MINERAL SATURATION STATES -
  * print if affinity > -10 kcals
    print all
    don't print
- LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
  * don't print
    print
- PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
  * don't print
    print
- TAB FILES -
  * write
    append to previous tabx file
    don't write
- WRITE PICKUP FILE -
  * write pickup file at end of run
    don't write pickup file
    write pickup file for each print point
- PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    transfer minerals but leave trivial mass in the system
    transfer minerals
- CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    clear p.r.s. before first reaction progress advance
- PHASE BOUNDARY SEARCH -
  * step size constrained by predicted phase boundaries
    phase boundaries estimated from Taylor's series and printed
    locations of phase boundaries ignored
- AUTO BASIS SWITCHING -
  * off
    on
- SUPPRESS REDOX REACTIONS -
  * does nothing
    suppress all redox reactions
- LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
  * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
    logarithmic for kcol = 1,kbt
    linear for kcol = 1,kdim
- AZERO AND HYDRATION NUMBERS -
  * no change
    read in new azero and hydration numbers
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
    does nothing
  * print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
    print summary information
```

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```
      print detailed information
  - PRINT STEP SIZE AND ORDER -
    * don't print
      print scale factor
      print orders and step size scaling factors
  - CONTROL STEP SIZE AND ORDER PRINT -
    * does nothing
      print step size and order when delzi .le. dlzmx1
  - NEWTON ITERATIONS -
    * don't print
      print summary of newton iterations
      print summary, residual functions and correction terms
      print summary, residual functions, correction terms and matrix
  - PRINT SEARCH ITERATIONS -
    * don't print
      print
  - PRINT HPSAT ITERATIONS -
    * don't print
      print
  - PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
    * don't print
      print computations from RDERIV, and RTAYLR
      print computations from RDERIV, RTAYLR, DERIV and TAYLOR
  - PRINT KINETICS DIAGNOSTIC MESSAGES -
    * don't print
      print level 1 diagnostics
      print level 1 and level 2 diagnostics
  - PRINT AKMATR -
    * don't print
      print level 1 diagnostics
  - KILL ITERATION VARIABLES -
    * does nothing
      allow selection of variables to remove
-----------------------------------------------------------------------
 development options  (used for code development)
-----------------------------------------------------------------------
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
-----------------------------------------------------------------------
 tolerances                        desired values - defaults info-only
-----------------------------------------------------------------------
 number of N-R iterations                          40       itermx
 p.r.s. transfer interval                          varies   dlzidp
 residual magnitude                                1.0e-06  tolbt
 correction magnitude                              1.0e-06  toldl
 search/find tolerance                             varies   tolx
 supersaturation                                   varies   tolsat
 supersaturation set size                          varies   tolsst
 max. size Taylor's series term                    1.0e-04  screw1
 max. initial value betamx                         n/a      screw2
 max. Taylor's series term (kin.)                  1.0e-04  screw3
 corrector iteration                               1.0e-04  screw4
 max. size of N-R correction term                  4.0      screw5
 step size (economy mode)                          4.0      screw6
 log mass of phases                                varies   zklogu
 decrement mass (p.r.s.)                           2.0      zklogl
 min. left after p.r.s.                            .98      zkfac
 initial step size                                 varies   dlzmx1
 upper limit step size                             varies   dlzmx2
 maximum order                                     6        nordlm
 num. attempted assemblages                        25       ntrymx
 slide -> over phase bound.                        8        npslmx
 slide -> over redox insta.                        3        nsslmx
 fo2 scan control                                  none     ioscan
-----------------------------------------------------------------------
c pickup file written by eq6.3245R119
c supported by eqlib.3245R153
EQ6 input file name= gypsumB.6i
Description= "Gypsum sol'y, trace NaCl, anhydrite suppresssd"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Add gypsum (CaSO4.2H2O) to water containing traces of CaSO4 and
NaCl.

  Purpose: to find the solubility of gypsum (CaSO4.2H2O) in the
system CaSO4-H2O, and to initialize the EQ6 test case input file
gypnacl.6i (compute the solubility of gypsum in the system
CaSO4-NaCl-H2O, results to be compared with Figure 4 of Harvie and
Weare, 1980). Anhydrite is suppressed using an "nxmod" option on
the initializing EQ3NR input file, caso4naclB.3i. This test case
uses Pitzer's equations to calculate the activity of water and
the activity coefficients of the aqueous solute species. The
Harvie- Moller-Weare (hmw) data file (after Harvie, Moller, and
Weare, 1984) should be employed.

  The print option switch iopr9 is set to 1 to direct the code to
also include a table of mean ionic activity coefficients.

                          References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
```

Information Only

of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C: Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

Harvie, C. E., and Weare, J. H., 1980, The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-Cl-SO4-H2O system from zero to high ionic strengths at 25 C: Geochimica et Cosmochimica Acta, v. 44, p. 981-987.

temperature (C)	25.000
electrical imbalance	5.791587776851280E-20
number of aqueous master species	7
position of last pure mineral	8
position of last solid solution	8

suppressed species	(suppress,replace,augmentk,augmentg)	value
anhydrite	mineral	suppress	0.

iopg options

- pH SCALE CONVENTION -
  - * modified NBS
  - internal
  - rational
- ACTIVITY COEFFICIENT OPTIONS -
  - use B-dot equation
  - Davies' equation
  - * Pitzer's equations

elements, moles and moles aqueous

o	5.610843516261009E+01	5.560001290305884E+01
ca	1.000000001000001E-01	1.526295684144937E-02
cl	9.999999999999960E-11	9.999999999999960E-11
h	1.114168703244200E+02	1.110779221513859E+02
na	9.999999999999960E-11	9.999999999999960E-11
s	1.000000001000001E-01	1.526295684145153E-02

master species and logarithmic basis variables

h2o	h2o	1.744597750257154E+00
ca++	ca++	-1.816361323816837E+00
cl-	cl-	-1.000000000000000E+01
h+	h+	-6.970286673167660E+00
na+	na+	-1.000000000000000E+01
so4--	so4--	-1.816362726210342E+00
o2(g)	o2(g)	-9.990000000000000E+02
	gypsum	-1.071926693968132E+00

physically removed subsystem (solid solution, mineral, moles)

none

The EQ6 tab file (gypnacl.6t), gypsum solubility in NaCl (partial reproduction):

•
•
•
(Material deleted)
•
•
•

log zi	time, d	log days	log alk	log tot co3--	log tot so4--	log tot s--	log a h2o
-999.0000	0.000E+00	-999.0000	-999.0000	-999.0000	-1.8166	-999.0000	-0.0002
-0.3010	0.000E+00	-999.0000	-999.0000	-999.0000	-1.4505	-999.0000	-0.0075
0.0000	0.000E+00	-999.0000	-999.0000	-999.0000	-1.3464	-999.0000	-0.0151
0.1761	0.000E+00	-999.0000	-999.0000	-999.0000	-1.2914	-999.0000	-0.0230
0.3010	0.000E+00	-999.0000	-999.0000	-999.0000	-1.2610	-999.0000	-0.0314
0.3979	0.000E+00	-999.0000	-999.0000	-999.0000	-1.2462	-999.0000	-0.0404
0.4771	0.000E+00	-999.0000	-999.0000	-999.0000	-1.2422	-999.0000	-0.0499
0.5441	0.000E+00	-999.0000	-999.0000	-999.0000	-1.2465	-999.0000	-0.0601
0.6021	0.000E+00	-999.0000	-999.0000	-999.0000	-1.2571	-999.0000	-0.0708
0.6532	0.000E+00	-999.0000	-999.0000	-999.0000	-1.2728	-999.0000	-0.0823
0.6990	0.000E+00	-999.0000	-999.0000	-999.0000	-1.2926	-999.0000	-0.0944
0.7404	0.000E+00	-999.0000	-999.0000	-999.0000	-1.3159	-999.0000	-0.1072
0.7782	0.000E+00	-999.0000	-999.0000	-999.0000	-1.3420	-999.0000	-0.1207

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```
 0.7845 0.000E+00 -999.0000 -999.0000 -999.0000   -1.3467 -999.0000   -0.1231


                 log molality of dissolved elements

  log zi   time, d   log days      ca         cl         na         s

-999.0000 0.000E+00 -999.0000   -1.8166   -10.0002   -10.0002   -1.8166
  -0.3010 0.000E+00 -999.0000   -1.4505    -0.3016    -0.3016   -1.4505
   0.0000 0.000E+00 -999.0000   -1.3464    -0.0007    -0.0007   -1.3464
   0.1761 0.000E+00 -999.0000   -1.2914     0.1753     0.1753   -1.2914
   0.3010 0.000E+00 -999.0000   -1.2610     0.3002     0.3002   -1.2610
   0.3979 0.000E+00 -999.0000   -1.2462     0.3971     0.3971   -1.2462
   0.4771 0.000E+00 -999.0000   -1.2422     0.4762     0.4762   -1.2422
   0.5441 0.000E+00 -999.0000   -1.2465     0.5432     0.5432   -1.2465
   0.6021 0.000E+00 -999.0000   -1.2571     0.6012     0.6012   -1.2571
   0.6532 0.000E+00 -999.0000   -1.2728     0.6524     0.6524   -1.2728
   0.6990 0.000E+00 -999.0000   -1.2926     0.6982     0.6982   -1.2926
   0.7404 0.000E+00 -999.0000   -1.3159     0.7396     0.7396   -1.3159
   0.7782 0.000E+00 -999.0000   -1.3420     0.7774     0.7774   -1.3420
   0.7845 0.000E+00 -999.0000   -1.3467     0.7836     0.7836   -1.3467


                 ppm (mg/kg) of dissolved elements

  log zi   time, d   log days      ca         cl         na         s

-999.0000 0.000E+00 -999.0000 611.        .354E-05   .230E-05   489.
  -0.3010 0.000E+00 -999.0000 .142E+04   .177E+05   .115E+05   .114E+04
   0.0000 0.000E+00 -999.0000 .180E+04   .354E+05   .230E+05   .144E+04
   0.1761 0.000E+00 -999.0000 .205E+04   .531E+05   .344E+05   .164E+04
   0.3010 0.000E+00 -999.0000 .220E+04   .708E+05   .459E+05   .176E+04
   0.3979 0.000E+00 -999.0000 .227E+04   .885E+05   .574E+05   .182E+04
   0.4771 0.000E+00 -999.0000 .229E+04   .106E+06   .688E+05   .184E+04
   0.5441 0.000E+00 -999.0000 .227E+04   .124E+06   .803E+05   .182E+04
   0.6021 0.000E+00 -999.0000 .222E+04   .142E+06   .918E+05   .177E+04
   0.6532 0.000E+00 -999.0000 .214E+04   .159E+06   .103E+06   .171E+04
   0.6990 0.000E+00 -999.0000 .204E+04   .177E+06   .115E+06   .163E+04
   0.7404 0.000E+00 -999.0000 .194E+04   .195E+06   .126E+06   .155E+04
   0.7782 0.000E+00 -999.0000 .182E+04   .212E+06   .138E+06   .146E+04
   0.7845 0.000E+00 -999.0000 .180E+04   .215E+06   .140E+06   .144E+04

                      .
                      .
                      .
              (Material deleted)
                      .
                      .
                      .

                 affinities of irreversible reactions

  log zi   time, d   log days  halite


-999.0000 0.000E+00 -999.0000   29.6630
  -0.3010 0.000E+00 -999.0000    3.4526
   0.0000 0.000E+00 -999.0000    2.6635
   0.1761 0.000E+00 -999.0000    2.1767
   0.3010 0.000E+00 -999.0000    1.8101
   0.3979 0.000E+00 -999.0000    1.5077
   0.4771 0.000E+00 -999.0000    1.2446
   0.5441 0.000E+00 -999.0000    1.0080
   0.6021 0.000E+00 -999.0000    0.7903
   0.6532 0.000E+00 -999.0000    0.5865
   0.6990 0.000E+00 -999.0000    0.3933
   0.7404 0.000E+00 -999.0000    0.2084
   0.7782 0.000E+00 -999.0000    0.0301
   0.7845 0.000E+00 -999.0000    0.0000
```

6.7. Alkalinity Titration: An Example.

Chapter 2 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b) discussed the problem of dealing with alkalinity as a constraint on dissolved bicarbonate. Version 7.0 of EQ3/6 does not allow alkalinity to be used as an input to EQ3NR. Instead, one must input the total dissolved bicarbonate (total dissolved CO_2 expressed as bicarbonate). If this quantity has not been measured, it is possible to estimate it from the measured alkalinity and input this estimate to

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EQ3NR. It was suggested that such estimates be confirmed by simulation of the alkalinity titration.

The present example simulates the alkalinity titration of the water from the river water test case of Nordstrom et al. (1979). It uses the B-dot equation (**iopg1** = 0) to calculate the activity coefficients of aqueous species and the **com** data file. In this test case, the alkalinity is specified as 75.2 mg/L HCO_3^-. This is equivalent to 61.7 mg/L $CaCO_3$, the more usual way of expressing alkalinity (Standard Methods, 1976). As the *pH* in this test case is 8.01, the contribution to alkalinity from CO_3^{2-} and OH^- should be negligible. $CO_{2(aq)}$, which contributes to total HCO_3^- but not alkalinity, should also be essentially negligible. Therefore, the total HCO_3^- should be nearly equal to 75.2 mg/L. This value was used in the initializing EQ3NR **input** file, **rwpar.3i** (see Appendix F).

The EQ6 input file for this example, **rwtitr.6i**, was constructed using the 0.1 N H_2SO_4 required for the titration (see Standard Methods, 1976) as a special reactant. Its composition was obtained from the **pickup** file produced by the EQ3NR **input** file **h2so4p1N.3i** (see Appendix F). The relevant lines from that **pickup** file in "W" format may be inserted into the appropriate location in the EQ6 **input** file used to simulate the titration. However, the floating point number fields are not identical. The floating point numbers must be shifted 10 spaces to the left to line up correctly. The **pickup** file gives:

```
o                 0.557089536401029E+02
h                 0.111116870126555E+03
c                 0.105940546128471E-04
s                 0.500000027435395E-01
electr           -0.274337735861607E-08
```

The electrical balance is not included in the definition of the special reactant composition. However, it is crucial that it be negligible, as it is in this case. The special reactant composition lines are then given by:

```
o        0.557089536401029E+02
h        0.111116870126555E+03
c        0.105940546128471E-04
s        0.500000027435395E-01
```

The titrating solution is then defined such that one "mole" is essentially equal to one liter of solution. An increment of 0.001 in reaction progress (*zi*) then corresponds to the addition of 1 ml of titrating solution to 1 liter of sample solution.

Note that the **input** file contains the **nxopt** subset selection suppression option "**all**". This is important because it suppresses the precipitation of all pure minerals. The precipitation of solid solution minerals is suppressed by setting **iopt4** = 0. The titration is presumed to be made sufficiently rapidly that no mineral precipitation occurs.

The output of interest is the *pH* change. This is plotted in Figure 15, using data taken from the **tab** file **rwtitr.6p**. This tab file is reproduced below. The usual end point for the titration of a water such as this is *pH* 4.8 (Standard Methods, 1976). Other choices are possible, particularly *pH* 4.5 or the *pH* at the point of inflection (see Standard Methods, 1976; see also Section 2.3.5 of the EQ3NR Theoretical Manual and User's Guide, Wolery, 1992b). The actual end point *pH* used to

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define the reported alkalinity value in the present case is unknown. We will first assume that the value used was *pH* 4.8. Linear interpolation between the two closest points gives the addition of 11.57 ml per liter of sample. Multiplying this number by 5 gives the alkalinity in mg/L $CaCO_3$ (Standard Methods, 1976). This gives an alkalinity of 57.9 mg/L $CaCO_3$, or 70.5 mg/L HCO_3^-. This is somewhat less than the expected 61.7 mg/L $CaCO_3$ or 75.2 mg/L HCO_3^-. The difference is about 6.3%.

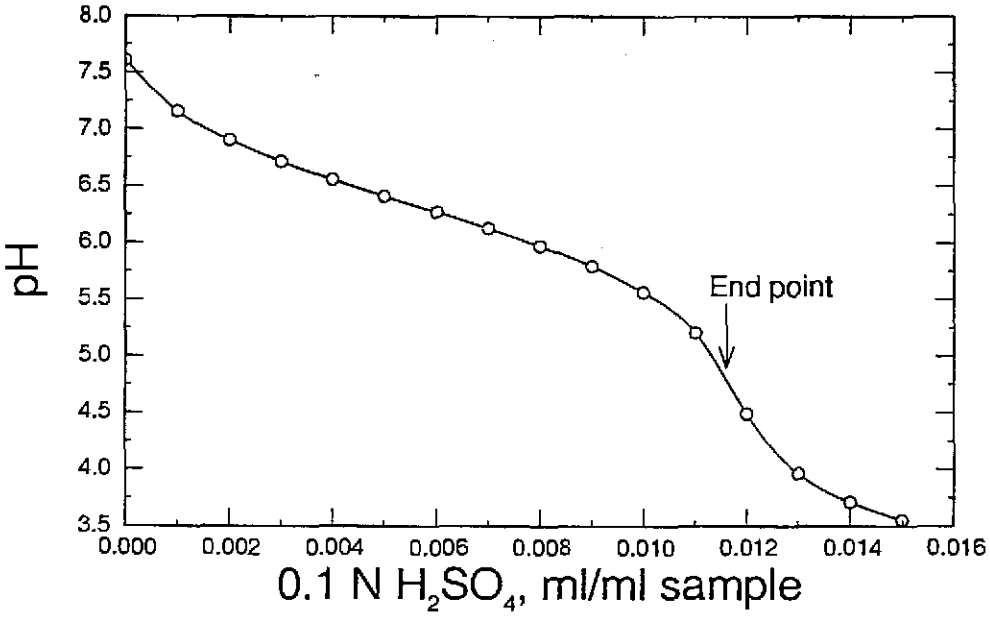

Figure 15. The pH curve for the titration of the test case river water. The ordinate (ml 0.1N sulfuric acid per ml sample) is equivalent to ξ,the reaction progress variable. The exact position of the end point depends on which of several criteria is chosen. Here, the end point is taken to correspond to *pH* 4.8.

Note from the **tab** file that the initial *pH* is 7.61. This is significantly lower than the *pH* of 8.01 specified on the initializing EQ3NR **input** file.What has happened is that some acid was created in the initial EQ6 calculation because of the necessary redox equilibration. In particular, the species $N_{2(aq)}$, NH_4^+, and $NH_{3(aq)}$ have been oxidized to NO_3^-, resulting in the creation of approximately 3.03 x 10^{-5} moles of H^+. This is the equivalent of adding about 0.30 ml of titrating solution. Correcting for this gives an alkalinity of 59.4 mg/L $CaCO_3$ or 72.4 mg/L HCO_3^-. The remaining difference is now about 3.7%. We have not corrected for the fact that the lost $NH_{3(aq)}$ contributes to alkalinity, but the amount lost is sufficiently small that this can be ignored. Thus, there is justification for a small upward correction to the assumed total dissolved HCO_3^-. However, considering the likely uncertainty in the end point (the criterion used to define it plus the likely measurement error), the present result is probably adequate. For example, an end point *pH* of 4.5 corresponds to 11.99 ml acid solution per liter of sample, and a corrected alkalinity of 61.4 mg/L $CaCO_3$, very close to the expected value of 61.7.

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It would be better to simulate alkalinity titrations in a mode which does not allow redox equilibration. It may be possible to do this in a future version of EQ6 which incorporates the auxiliary basis concept. Note that is not possible to solve this problem simply by setting the option switch **iopt11** equal to 1. Doing so suppresses all redox reactions (and associated species). However, this option does not necessarily preserve redox states. Rather, it forces the various chemical elements to take the redox state in the corresponding strict basis species. Thus, in the present problem, the species $N_{2(aq)}$, NH_4^+, and $NH_{3(aq)}$ would still be oxidized to NO_3^-.

The EQ6 input file (rwtitr.6i), Alkalinity titration of river water ("W" format):

```
EQ6 input file name= rwtitr.6i
Description= "Alkalinity titration of river water"
Version number= 3245   Stage number= 02
Created 12/05/90     Creator= T.J. Wolery
Revised 07/22/92     Revisor= T.J. Wolery

  Simulate a standard alkalinity titration of the water from the
the river water test case of Nordstrom et al. (1979, Table III).
This calculation is initialized by the EQ3NR input file rwpar.3i.
The model constraints on that file include all solute components
present above 0.05 mg/L, plus nitrite, sulfide, iron, and aluminum.
Other solutes are ignored (the full river water test case is in
the EQ3NR input file rwtst.3i). They are not significant with
regard to the alkalinity of this water.

  The analytical data relevent to the carbonate system is given
in terms of alkalinity. Nordstrom et al. (1979) report the total
alkalinity as 75.2 mg/L HCO3-. This is equivalent to 61.7 mg/L
CaCO3. The latter is the more standard way of reporting alkalinity
(Standard Methods, 1976). The total concentration of HCO3- has
been estimated from the total alkalinity and the pH. This is
simplified by the fact that for this water, the CO3 and OH
alkalinities are essentially zero, and the total alkalinity is
essentially equal to the HCO3 alkalinity (other sources of
alkalinity being negligible).

  Purpose: to confirm that the estimated value of total HCO3- is
consistent with the reported alkalinity data. If it doesn't match,
the estimated value of total HCO3- should be adjusted and the
problem re-run until a match is obtained.

  The temperature of the river water given by Nordstrom et al. (1979)
is 9.5 C. The alkalinity is presumed to be measured at room
temperature (25 C).

  The 0.1 N H2SO4 solution used in this titration simulation is
treated as a special reactant. Its gross composition was obtained
from EQ3NR using the input file h2so4pln.3i. Each unit of reaction
progress corresponds to the addition of an amount of this fluid
containing 1 kg of solvent water. To a very good approximation,
0.001 unit of reaction progress corresponds to the addition of
1 ml of solution to 1 L of sample fluid. Multiplying the value
of reaction progress at the titration end point by 5,000 gives
the alkalinity in units of mg/L CaCO3.

  The topic of alkalinity is unfortunately more complex than one
would intuitively think. It is very easy to misinterpret the data
reported as part of a chemical analysis. For more details, see the
section on alkalinity in Chapter 2 of the EQ3NR Theoretical
Manual and User's Guide (Wolery, 1992) and also the relevant
section of Standard Methods (1976).

                          References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical
  models for equilibrium calculations in aqueous systems, in Jenne,
  E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium
  Series, v. 93, American Chemical Society, Washington, D.C.,
  p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976,
  Prepared and jointly published by the American Public Health
  Association, the American Water Works Association, and the Water
  Pollution Control Federation: American Public Health Association,
  1015 Eighteenth Street NW, Washington, D.C.

Wolery, T. J., 1992, EQ3NR, A Computer Program for Geochemical
  Aqueous Speciation-Solubility Calculations: Theoretical Manual,
  User's Guide, and Related Documentation (Version 7.0):
  UCRL-MA-110662-PT-III, Lawrence Livermore National Laboratory,
```

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```
  Livermore, California.

endit.
    nmodl1=  2                 nmodl2=  0
    tempc0=  25.0000E+00        jtemp=  0
       tk1=  0.00000E+00          tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.00000E+00       zimax=  0.01500E+00
     tstrt=  0.00000E+00      timemx=  1.00000E+38
    kstpmx=          200       cplim=  0.00000E+00
    dzprnt=  0.00100E+00      dzprlg=  1.00000E+38     ksppmx=   100
    dzplot=  1.00000E+38      dzpllg=  1.00000E+38     ksplmx= 10000
     ifile= 60
*              1    2    3    4    5    6    7    8    9   10
  ioptl-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodbl-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
    nxopt=  1
   option= all
   nxopex=  0
* nffg = number of gas species with fixed fugacities
    nffg =  0
* nrct = number of reactants
     nrct=  1
*-----------------------------------------------------------------------
  reactant= Aqueous H2SO4, 0.1 N
     jcode=  2                 jreac=  0
      morr=  1.00000E+00        modr=  0.00000E+00
     vreac=  0.00000E+00
   o        0.557089536401029E+02
   h        0.111116870126555E+03
   c        0.105940546128471E-04
   s        0.500000027435395E-01
   endit.
       nsk=  0                    sk=  0.00000E+00         fk=  0.00000E+00
       nrk=  1                  nrpk=  0
       rk1=  1.00000E+00         rk2=  0.00000E+00        rk3=  0.00000E+00
*-----------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00       toldl=  0.00000E+00       tolx=  0.00000E+00
    tolsat=  0.00000E+00      tolsst=  0.00000E+00
    screw1=  0.00000E+00      screw2=  0.00000E+00     screw3=  0.00000E+00
    screw4=  0.00000E+00      screw5=  0.00000E+00     screw6=  0.00000E+00
    zklogu=        0.000      zklogl=        0.000      zkfac=        0.000
    dlzmx1=  0.00000E+00      dlzmx2=  0.00000E+00     nordlm=  0
    itermx=  0                ntrymx=  0
    npslmx=  0                nsslmx=  0               ioscan=  0
*-----------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= rwpar.3i
Description= "River water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/06/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  River water, including all solute components present above 0.05
mg/L, plus nitrite, sulfide, iron, and aluminum. This is a
moderately pared-down version of rwtst.3i, which contains the full
benchmark river water test case of Nordstrom et al. (1979, Table
III).

  Purpose: to test the code on an intermediate-sized problem
involving a dilute solution, and to initialize the EQ6 test case
input file rwtitr.6i (which simulates an alkalinity titration of
this water). The activity coefficients of the aqueous species are
calculated from the B-dot equation and related equations.

  Data for the following were originally specified as-

    HCO3-     :   alkalinity = 75.2  mg/L HCO3- (total alkalinity,
                                                 not the conventional
                                                 HCO3 alkalinity)
    SiO2(aq) :   Si          = 8.52  mg/L
    H3BO3(aq):   B           = 0.050 mg/L
    HPO4-     :   PO4---     = 0.210 mg/L
    HS-       :   H2S(aq)    = 0.002 mg/L

The pH (8.01) lies well in between the pKa values of carbonic
acid (-6.3 and -10.3), so equating the total molality of HCO3-
to the reported alkalinity is not likely to cause a problem.
This can be confirmed by simulating the alkalinity titration.
This is the purpose of the EQ6 test case represented by the
EQ6 input file rwtitr.6i.

  The total alkalinity of 75.2 mg/L HCO3- noted above is equivalent
to 61.7 mg/L CaCO3 (total alkalinity). This is the more standard
way of reporting alkalinity (see Standard Methods, 1976).
```

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References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.

```
endit.
    tempci=  0.95000E+01
     nxmod=  0
     iopg1=  0                iopg2=  0                iopg3=  0
     iopg4=  0                iopg5=  0                iopg6=  0
     iopg7=  0                iopg8=  0                iopg9=  0
    iopg10=  0
       kct= 16                  ksq= 17                  kmt= 17
       kxt= 17                 kdim= 17                 kprs=  0
   o                  0.555137378775316E+02
   al                 0.185311883608708E-06
   b                  0.462487518804552E-05
   ca                 0.304406407505495E-03
   cl                 0.279245304306866E-03
   f                  0.526360114536012E-05
   fe                 0.281125217113012E-06
   h                  0.111018114419475E+03
   c                  0.123244058964448E-02
   p                  0.221120918333949E-05
   k                  0.358071834325281E-04
   mg                 0.308578481794013E-03
   na                 0.521971294188688E-03
   n                  0.228786361714373E-04
   si                 0.303357116584516E-03
   s                  0.802139111342829E-04
   electr             0.132905378328183E-03
   h2o                h2o                     0.174435898352698E+01
   al+++              al+++                  -0.147198424391901E+02
   b(oh)3(aq)         b(oh)3(aq)             -0.535339687731229E+01
   ca++               ca++                   -0.352611022721331E+01
   cl-                cl-                    -0.355415234907870E+01
   f-                 f-                     -0.528165377314223E+01
   fe++               fe++                   -0.679713629173489E+01
   h+                 h+                     -0.798824636978119E+01
   hco3-              hco3-                  -0.292606308162218E+01
   hpo4--             hpo4--                 -0.578100664326632E+01
   k+                 k+                     -0.444623394341814E+01
   mg++               mg++                   -0.352048712612034E+01
   na+                na+                    -0.328350877286759E+01
   no3-               no3-                   -0.243009865491499E+02
   sio2(aq)           sio2(aq)               -0.352129777992280E+01
   so4--              so4--                  -0.412176543658063E+01
   o2(g)              o2(g)                  -0.244417932765032E+02
```

The EQ6 input file (rwtitr.6i), Alkalinity titration of river water ("D" format):

```
-----------------------------------------------------------------------
EQ6 input file name= rwtitr.6i
Description= "Alkalinity titration of river water"
Version number= 3245   Stage number= 02
Created 12/05/90     Creator= T.J. Wolery
Revised 07/22/92     Revisor= T.J. Wolery

  Simulate a standard alkalinity titration of the water from the
the river water test case of Nordstrom et al. (1979, Table III).
This calculation is initialized by the EQ3NR input file rwpar.3i.
The model constraints on that file include all solute components
present above 0.05 mg/L, plus nitrite, sulfide, iron, and aluminum.
Other solutes are ignored (the full river water test case is in
the EQ3NR input file rwtst.3i). They are not significant with
regard to the alkalinity of this water.

  The analytical data relevent to the carbonate system is given
in terms of alkalinity. Nordstrom et al. (1979) report the total
alkalinity as 75.2 mg/L HCO3-. This is equivalent to 61.7 mg/L
CaCO3. The latter is the more standard way of reporting alkalinity
(Standard Methods, 1976). The total concentration of HCO3- has
been estimated from the total alkalinity and the pH. This is
simplified by the fact that for this water, the CO3 and OH
alkalinities are essentially zero, and the total alkalinity is
essentially equal to the HCO3 alkalinity (other sources of
alkalinity being negligible).
```

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Purpose: to confirm that the estimated value of total HCO3- is consistent with the reported alkalinity data. If it doesn't match, the estimated value of total HCO3- should be adjusted and the problem re-run until a match is obtained.

The temperature of the river water given by Nordstrom et al. (1979) is 9.5 C. The alkalinity is presumed to be measured at room temperature (25 C).

The 0.1 N H2SO4 solution used in this titration simulation is treated as a special reactant. Its gross composition was obtained from EQ3NR using the input file h2so4pln.3i. Each unit of reaction progress corresponds to the addition of an amount of this fluid containing 1 kg of solvent water. To a very good approximation, 0.001 unit of reaction progress corresponds to the addition of 1 ml of solution to 1 L of sample fluid. Multiplying the value of reaction progress at the titration end point by 5,000 gives the alkalinity in units of mg/L CaCO3.

The topic of alkalinity is unfortunately more complex than one would intuitively think. It is very easy to misinterpret the data reported as part of a chemical analysis. For more details, see the section on alkalinity in Chapter 2 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992) and also the relevant section of Standard Methods (1976).

References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.

Wolery, T. J., 1992, EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation (Version 7.0): UCRL-MA-110662-PT-III, Lawrence Livermore National Laboratory, Livermore, California.

calculational mode	*normal	economy	super economy
model type	titration	*closed	open
temperature model	*power	fluid mixing	

```
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c
```

tstart(c)	25.00	tk1	0.	tk2	0.	tk3	0.
starting value of zi	0.	max. value of zi	1.50000E-02		
starting time (sec)	0.	max. time (sec)	1.00000E+38		
max. steps	200	max. steps w/o print	100		
linear print interval	1.00000E-03	log print interval	1.00000E+38		
suppress mineral phases					
phases w/ elements	all				n
phases except					n
fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)					
none					n

```
c                  R A T E     L A W S
c 1 = relative                 rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory  rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate       rate = CHECK DOCUMENTATION

c                  R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                  S U R F A C E    T Y P E
c 0 = fixed surface area     1 = fixed specific surface area
c
c                  N O T E S
c status and jreac are normally not set by the user
```

reactants	(ss) solid solution only	(sp) special reactant only	
REACTANT	Aqueous H2SO4, 0.1	status	0
moles remaining	1.0000	destroyed	0.

Information Only

```
reactant type      special                  sk          0.
surface type        0                       fk          1.0000
end-member                                  mole fr                  ss,n
volume                0.                                             sp
element            o            moles          5.570895364010290E+01 sp,n
element            h            moles          1.111168701265550E+02 sp,n
element            c            moles          1.059405461284710E-05 sp,n
element            s            moles          5.000000274353950E-02 sp,n
DISSOLUTION LAW     1
rate constant rk1   1.0000                  csigma1
rate constant rk2      0.                   csigma2
rate constant rk3      0.                   csigma3
PRECIPITATION LAW    0
-----------------------------------------------------------------------
options
-----------------------------------------------------------------------
- SOLID SOLUTIONS -
  * ignore solid solutions
    process solid solutions
- LOADING OF SPECIES INTO MEMORY -
  * don't print
    lists species loaded into memory
- LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
  * don't print
    print
- LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
  * don't print
    print
- LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
  * only species > 10**-12 molal
    all species
    don't print
- LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
  * don't print
    print
- LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
  * don't print
    print
- MINERAL SATURATION STATES -
  * print if affinity > -10 kcals
    print all
    don't print
- LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
  * don't print
    print
- PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
  * don't print
    print
- TAB FILES -
  * write
    append to previous tabx file
    don't write
- WRITE PICKUP FILE -
  * write pickup file at end of run
    don't write pickup file
    write pickup file for each print point
- PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    transfer minerals but leave trivial mass in the system
    transfer minerals
- CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    clear p.r.s. before first reaction progress advance
- PHASE BOUNDARY SEARCH -
  * step size constrained by predicted phase boundaries
    phase boundaries estimated from Taylor's series and printed
    locations of phase boundaries ignored
- AUTO BASIS SWITCHING -
  * off
    on
- SUPPRESS REDOX REACTIONS -
  * does nothing
    suppress all redox reactions
- LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
  * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
    logarithmic for kcol = 1,kbt
    linear for kcol = 1,kdim
- AZERO AND HYDRATION NUMBERS -
  * no change
    read in new azero and hydration numbers
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
  * does nothing
    print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
```

Information Only

```
      print summary information
      print detailed information
  - PRINT STEP SIZE AND ORDER -
    * don't print
      print scale factor
      print orders and step size scaling factors
  - CONTROL STEP SIZE AND ORDER PRINT -
    * does nothing
      print step size and order when delzi .le. dlzmxl
  - NEWTON ITERATIONS -
    * don't print
      print summary of newton iterations
      print summary, residual functions and correction terms
      print summary, residual functions, correction terms and matrix
  - PRINT SEARCH ITERATIONS -
    * don't print
      print
  - PRINT HPSAT ITERATIONS -
    * don't print
      print
  - PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
    * don't print
      print computations from RDERIV, and RTAYLR
      print computations from RDERIV, RTAYLR, DERIV and TAYLOR
  - PRINT KINETICS DIAGNOSTIC MESSAGES -
    * don't print
      print level 1 diagnostics
      print level 1 and level 2 diagnostics
  - PRINT AKMATR -
    * don't print
      print level 1 diagnostics
  - KILL ITERATION VARIABLES -
    * does nothing
      allow selection of variables to remove
-----------------------------------------------------------------------
 development options  (used for code development)
-----------------------------------------------------------------------
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
-----------------------------------------------------------------------
 tolerances                          desired values - defaults info-only
-----------------------------------------------------------------------
 number of N-R iterations                              40       itermx
 p.r.s. transfer interval                              varies   dlzidp
 residual magnitude                                    1.0e-06  tolbt
 correction magnitude                                  1.0e-06  toldl
 search/find tolerance                                 varies   tolx
 supersaturation                                       varies   tolsat
 supersaturation set size                              varies   tolsst
 max. size Taylor's series term                        1.0e-04  screw1
 max. initial value betamx                             n/a      screw2
 max. Taylor's series term (kin.)                      1.0e-04  screw3
 corrector iteration                                   1.0e-04  screw4
 max. size of N-R correction term                      4.0      screw5
 step size (economy mode)                              4.0      screw6
 log mass of phases                                    varies   zklogu
 decrement mass (p.r.s.)                               2.0      zklogl
 min. left after p.r.s.                                .98      zkfac
 initial step size                                     varies   dlzmxl
 upper limit step size                                 varies   dlzmx2
 maximum order                                         6        nordlm
 num. attempted assemblages                            25       ntrymx
 slide -> over phase bound.                            8        npslmx
 slide -> over redox insta.                            3        nsslmx
 fo2 scan control                                      none     ioscan
-----------------------------------------------------------------------
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= rwpar.3i
Description= "River water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  River water, including all solute components present above 0.05
mg/L, plus nitrite, sulfide, iron, and aluminum. This is a
moderately pared-down version of rwtst.3i, which contains the full
benchmark river water test case of Nordstrom et al. (1979, Table
III).

  Purpose: to test the code on an intermediate-sized problem
involving a dilute solution, and to initialize the EQ6 test case
input file rwtitr.6i (which simulates an alkalinity titration of
this water). The activity coefficients of the aqueous species are
calculated from the B-dot equation and related equations.

  Data for the following were originally specified as-

   HCO3-     :   alkalinity = 75.2  mg/L HCO3- (total alkalinity,
                                          not the conventional
                                          HCO3 alkalinity)
   SiO2(aq) :   Si          = 8.52  mg/L
   H3BO3(aq):   B           = 0.050 mg/L
```

Information Only

```
    HPO4-      :   PO4---      = 0.210 mg/L
    HS-        :   H2S(aq)     = 0.002 mg/L
```

The pH (8.01) lies well in between the pKa values of carbonic acid (~6.3 and ~10.3), so equating the total molality of HCO3- to the reported alkalinity is not likely to cause a problem. This can be confirmed by simulating the alkalinity titration. This is the purpose of the EQ6 test case represented by the EQ6 input file rwtitr.6i.

The total alkalinity of 75.2 mg/L HCO3- noted above is equivalent to 61.7 mg/L CaCO3 (total alkalinity). This is the more standard way of reporting alkalinity (see Standard Methods, 1976).

References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.

temperature (C)	9.5000
electrical imbalance	1.329053783281830E-04
number of aqueous master species	17
position of last pure mineral	17
position of last solid solution	17

suppressed species	(suppress,replace,augmentk,augmentg) value
none	

iopg options

```
 - pH SCALE CONVENTION -
    * modified NBS
      internal
      rational
 - ACTIVITY COEFFICIENT OPTIONS -
    * use B-dot equation
      Davies' equation
      Pitzer's equations
```

elements, moles and moles aqueous

o	5.551373787753160E+01	0.000000000000000E+00
al	1.853118836087080E-07	0.000000000000000E+00
b	4.624875188045520E-06	0.000000000000000E+00
ca	3.044064075054950E-04	0.000000000000000E+00
cl	2.792453043068660E-04	0.000000000000000E+00
f	5.263601145360120E-06	0.000000000000000E+00
fe	2.811252171130120E-07	0.000000000000000E+00
h	1.110181144194750E+02	0.000000000000000E+00
c	1.232440589644480E-03	0.000000000000000E+00
p	2.211209183339490E-06	0.000000000000000E+00
k	3.580718343252810E-05	0.000000000000000E+00
mg	3.085784817940130E-04	0.000000000000000E+00
na	5.219712941886880E-04	0.000000000000000E+00
n	2.287863617143730E-05	0.000000000000000E+00
si	3.033571165845160E-04	0.000000000000000E+00
s	8.021391113428290E-05	0.000000000000000E+00

master species and logarithmic basis variables

h2o	h2o	1.744358983526980E+00
al+++	al+++	-1.471984243919010E+01
b(oh)3(aq)	b(oh)3(aq)	-5.353396877312290E+00
ca++	ca++	-3.526110227213310E+00
cl-	cl-	-3.554152349078700E+00
f-	f-	-5.281653773142230E+00
fe++	fe++	-6.797136291734890E+00
h+	h+	-7.988246369781190E+00
hco3-	hco3-	-2.926063081622180E+00
hpo4--	hpo4--	-5.781006643266320E+00
k+	k+	-4.446233943418140E+00
mg++	mg++	-3.520487126120340E+00
na+	na+	-3.283508772867590E+00
no3-	no3-	-2.430098654914990E+01
sio2(aq)	sio2(aq)	-3.521297779922800E+00
so4--	so4--	-4.121765436580630E+00
o2(g)	o2(g)	-2.444179327650320E+01

Information Only

```
| physically removed subsystem  (solid solution, mineral, moles)      |
|-------------------------------------------------------------------------|
| none                |                          |                          |
|-------------------------------------------------------------------------|
```

The EQ6 **tab** file (**rwtitr.6o**), Alkalinity titration of river water (partial reproduction):

```
                    .
                    .
                    .
          (Material deleted)
                    .
                    .
                    .
```

zi	log zi	time, d	log days	tempc	press	ph	log fo2	eh	pe	kg h2o	tot aff
0.000E+00	-999.0000	0.000E+00	-999.0000	25.0000	1.0132	7.6101	-0.6137	0.7698	13.0127	1.0000	0.0000
1.000E-03	-3.0000	0.000E+00	-999.0000	25.0000	1.0132	7.1603	-0.6138	0.7964	13.4625	1.0010	0.0000
2.000E-03	-2.6990	0.000E+00	-999.0000	25.0000	1.0132	6.9050	-0.6139	0.8115	13.7178	1.0020	0.0000
3.000E-03	-2.5229	0.000E+00	-999.0000	25.0000	1.0132	6.7152	-0.6140	0.8227	13.9076	1.0030	0.0000
4.000E-03	-2.3979	0.000E+00	-999.0000	25.0000	1.0132	6.5551	-0.6141	0.8322	14.0676	1.0040	0.0000
5.000E-03	-2.3010	0.000E+00	-999.0000	25.0000	1.0132	6.4094	-0.6141	0.8408	14.2133	1.0050	0.0000
6.000E-03	-2.2218	0.000E+00	-999.0000	25.0000	1.0132	6.2685	-0.6142	0.8491	14.3541	1.0060	0.0000
7.000E-03	-2.1549	0.000E+00	-999.0000	25.0000	1.0132	6.1251	-0.6143	0.8576	14.4975	1.0070	0.0000
8.000E-03	-2.0969	0.000E+00	-999.0000	25.0000	1.0132	5.9707	-0.6144	0.8668	14.6519	1.0080	0.0000
9.000E-03	-2.0458	0.000E+00	-999.0000	25.0000	1.0132	5.7923	-0.6145	0.8773	14.8303	1.0090	0.0000
1.000E-02	-2.0000	0.000E+00	-999.0000	25.0000	1.0132	5.5634	-0.6145	0.8908	15.0592	1.0100	0.0000
1.100E-02	-1.9586	0.000E+00	-999.0000	25.0000	1.0132	5.2064	-0.6146	0.9120	15.4162	1.0110	0.0000
1.200E-02	-1.9208	0.000E+00	-999.0000	25.0000	1.0132	4.4903	-0.6147	0.9543	16.1322	1.0120	0.0000
1.300E-02	-1.8861	0.000E+00	-999.0000	25.0000	1.0132	3.9613	-0.6148	0.9856	16.6613	1.0130	0.0000
1.400E-02	-1.8539	0.000E+00	-999.0000	25.0000	1.0132	3.7105	-0.6148	1.0005	16.9120	1.0140	0.0000
1.500E-02	-1.8239	0.000E+00	-999.0000	25.0000	1.0132	3.5517	-0.6149	1.0098	17.0708	1.0150	0.0000

```
                    .
                    .
                    .
          (Material deleted)
                    .
                    .
                    .
```

6.8. Kinetics of Quartz Precipitation.

The following example models the growth kinetics of quartz according to the rate law model proposed by Rimstidt and Barnes (1980). This model pertains to an experiment conducted at 105°C. The rate constant used is the one fit to the experiment, so this example possesses elements of validation. This sample problem is taken from Delany, Puigdomenech, and Wolery (1986), who compared the results with those obtained using the rate constant computed from a temperature function proposed by Rimstidt and Barnes (1980). The rate law used here does not account for any *pH* dependency. The B-dot equation (**iopg1** = 1) is used to calculate the activity coefficients of the aqueous species, and the **com** data file is used. The **input** file for this example is **pquartz.6i**. The initializing EQ3NR **input** file is **sio2.3i**.

The results are plotted in Figure 16. They are also illustrated by selected parts of the **output** and **tab** files, (**pquartz.6o** and **pquartz.6t**, respectively). Note that this calculation takes place in a time frame, so time values now appear in addition to reaction progress values. The precipitation rate decreases with time, because the driving thermodynamic affinity also decreases. The concentration of dissolved silica (or elemental silicon) drops as time increases.

Information Only

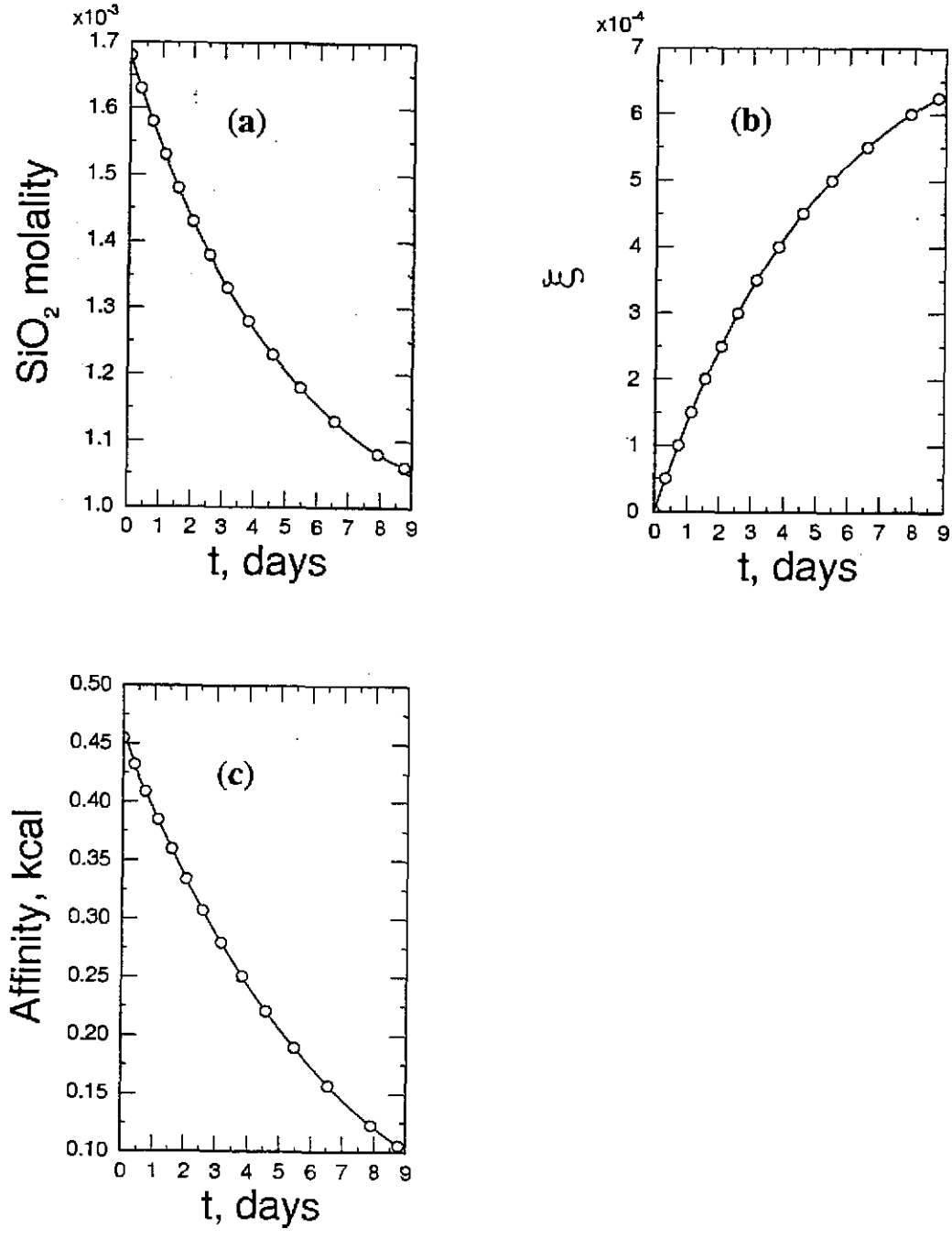

Figure 16. The precipiation kinetics of quartz in the system SiO_2-H_2O as a function of time (t): (a) the molality of aqueous silica; (b) the value of reaction progress (ξ, here equivalent to the number of moles of new quartz); (c) the affinity of quartz to precipitate.

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The experiment being modeled ran for 8 days. The maximum time value on the **input** file corresponds to this (6.92×10^5 seconds). The code oversteps this, stopping at 8.764 days (7.57×10^5 seconds). This occurs because the present version of EQ6 does not find the value of reaction progress that corresponds to the desired maximum time. Instead, it stops when it notices that the maximum time has been achieved or exceeded. Note also that the code does not provide for dealing with a user input print interval in terms of time.

A related but slightly more complex example is on the EQ6 **input** file **pquartzA.6i**, which is included in Appendix E. Its purpose is to model the same experiment. That example uses estimated activation energies to extrapolate the 70°C model for quartz dissolution proposed by Knauss and Wolery (1988) to 105°C. It also extrapolates this model to the case of precipitation. The first term of that model is essentially that appearing in the one-term model of Rimstidt and Barnes (1980). The second term accounts for the *pH* dependence of the dissolution rate at high *pH*. This second term improperly extrapolates to the case of precipitation (see Appendix E). It artificially accelerates the precipitation rate at low to moderate *pH*. Near-equilibrium is calculated to be achieved in about one day, a situation which is inconsistent with the experimental results. To obtain correct results, one should drop the second term (yielding a rate law essentially equivalent to that used in the present example) or set **nrpk** = 2 and enter a one-term rate law for the net rate of precipitation.

The EQ6 **input** file (**pquartz.6i**), kinetics of quartz precipitation at 105°C ("W" format):

```
EQ6 input file name= pquartz.6i
Description= "Precipitate quartz using Rimstidt and Barnes rate law"
Version number= 3245    Stage number= 01
Created 10/31/90     Creator= T.J. Wolery
Revised 10/31/90     Revisor= T.J. Wolery

  Precipitate quartz from supersaturated solution at 105 C, using the
rate law of Rimstidt and Barnes (1980). This is test problem 1 from
Delany, Puigdomenech, and Wolery (1986, p. 19-21, 31-33), which
simulates an experiment (Run 2E) reported by Rimstidt and Barnes
(1980, p. 1687-1688, Figure 2) and uses their rate law model, which
is independent of pH. Another EQ6 test case input file, pquartzA.6i,
runs the same problem, but uses a rate law model from Knauss and
Wolery (1988) that includes dependence on pH.

  Purpose: to test the kinetics mode of EQ6. Results may be compared
with Figure 2 of Rimstidt and Barnes (1980) and Figure 1 of Delany,
Puigdomenech, and Wolery (1986).

  The precipitation rate law is expressed in terms of a reversal of
the net rate form for dissolution, as the precipitation rate law code
"nprk" is set to -1. Thus, the specified rate constant is k(+) (the
dissolution rate constant) instead of k(-) (the precipitation rate
constant). The value chosen is 9.72e-16 mol/cm**2/s, is which the
value specifically fit by Rimstidt and Barnes (1980) to the data for
the corresponding experimental run (2E). Their master regression for
rate constants as functions of temperature yields a value of 2.53e-15
mol/cm**2/s, which does not do a good job of representing the data for
this particular run (See Figure 1 of Delany, Puigdomenech, and Wolery,
1986).

  The option switch ioptl1 is set to 1 to indicate that this problem
has no redox aspect.

  Note that the silica polymorphs tridymite, chalcedony, sio2(am),
and cristobalite have been suppressed by means of "nxmod" options.
These were set on the EQ3NR test case input file sio2.3i, which was
used to initialize this EQ6 test case.

                          References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986,
  Precipitation Kinetics Option for the EQ6 Geochemical Reaction
  Path Code: UCRL-53642, Lawrence Livermore National Laboratory,
  Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of
  quartz as a function of pH and time at 70 C: Geochimica et Cosmo-
  chimica Acta, v. 52, p. 43-53.
```

Information Only

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

```
endit.
    nmodl1=  2                 nmodl2=  0
    tempc0=  105.000E+00        jtemp=  0
       tk1=  0.00000E+00          tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.00000E+00        zimax=  1.00000E+00
     tstrt=  0.00000E+00       timemx=  6.92000E+05
    kstpmx=           500       cplim=  0.00000E+00
    dzprnt=  5.00000E-05      dzprlg=  10.0000E+00     ksppmx=    10
    dzplot=  1.00000E+38      dzpllg=  1.00000E+38     ksplmx= 10000
     ifile= 60
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=    1    0    0    0    0    0    0    0    0    0
     l1-20=    1    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     l1-20=    0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
    nxopt=  0
* nffg = number of gas species with fixed fugacities
     nffg =  0
* nrct = number of reactants
     nrct=  1
*-----------------------------------------------------------------------------
  reactant= quartz
     jcode=  0                  jreac=  0
      morr=  4.72000E+02         modr=  0.00000E+00
       nsk=  0                     sk=  2.61280E+06        fk=  1.00000E+00
       nrk=  2                   nrpk= -1
     imech=  1
       rk0=  7.92000E-16         trk0=  105.000E+00      iact=  0
      eact=  0.00000E-00         hact=  0.00000E+00
     ndact=  0                 csigma=  1.00000E+00
*-----------------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00        toldl=  0.00000E+00       tolx=  0.00000E+00
    tolsat=  0.00000E+00       tolsst=  0.00000E+00
    screw1=  0.00000E+00       screw2=  0.00000E+00     screw3=  0.00000E+00
    screw4=  0.00000E+00       screw5=  0.00000E+00     screw6=  0.00000E+00
    zklogu=          0.000     zklogl=          0.000    zkfac=          0.000
    dlzmx1=  0.00000E+00       dlzmx2=  0.00000E+00     nordlm=  0
    itermx=  0                 ntrymx=  0
    npslmx=  0                 nsslmx=  0               ioscan=  0
*-----------------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= sio2.3i
Description= "Solution containing 101.0 mg/L SiO2"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery
```

Solution containing 101.0 mg/L of dissolved SiO2. This test case is otherwise nearly identical to that in the EQ3NR test case input file deionw.3i.

Purpose: to initialize the EQ6 test case input files pquartz.6i and pquartzA.6i, both of which simulate the precipitation of quartz from supersaturated solution at 105 C. The former EQ6 test case is test problem 1 from Delany, Puigdomenech, and Wolery (1986, p. 19-21, 31-33), which simulates an experiment (Run 2E) reported by Rimstidt and Barnes (1980, p. 1687-1688, Figure 2) and uses their rate law model, which is independent of pH. The latter is the same problem, but uses a rate law model from Knauss and Wolery (1988) that does include a dependence on pH.

Note that the dissolved gases O2 and H2 have been suppressed. This is because this problem has no redox aspect. The EQ6 option switch iopt11 should be set to 1 in the EQ6 test case input files so that EQ6 knows this.

Note also that the silica polymorphs tridymite, chalcedony, sio2(am), and cristobalite have been suppressed by means of "nxmod" options.

References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986, Precipitation Kinetics Option for the EQ6 Geochemical Reaction Path Code: UCRL-53642, Lawrence Livermore National Laboratory, Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of quartz as a function of pH and time at 70 C: Geochimica et Cosmochimica Acta, v. 52, p. 43-53.

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

Information Only

```
endit.
    tempci=  0.25000E+02
     nxmod=  4
   species= tridymite
      type=  1              option= -1              xlkmod=  0.00000E+00
   species= chalcedony
      type=  1              option= -1              xlkmod=  0.00000E+00
   species= sio2(am)
      type=  1              option= -1              xlkmod=  0.00000E+00
   species= cristobalite
      type=  1              option= -1              xlkmod=  0.00000E+00
    iopg1=  0               iopg2=  0               iopg3=  0
    iopg4=  0               iopg5=  0               iopg6=  0
    iopg7=  0               iopg8=  0               iopg9=  0
   iopg10=  0
      kct=  4                 ksq=  5                 kmt=  5
      kxt=  5                kdim=  5                kprs=  0
   o                  0.555118250703269E+02
   h                  0.111016874628103E+03
   c                  0.129065694976057E-04
   si                 0.168097156827988E-02
   electr             0.196977511883988E-16
   h2o                h2o                     0.174435898352698E+01
   h+                 h+                     -0.564737292052235E+01
   hco3-              hco3-                  -0.566471043900596E+01
   sio2(aq)           sio2(aq)               -0.277446121770296E+01
   o2(g)              o2(g)                   0.000000000000000E+00
```

The EQ6 **input** file (**pquartz.6i**), kinetics of quartz precipitation at 105°C ("D" format):

```
-----------------------------------------------------------------------
EQ6 input file name= pquartz.6i
Description= "Precipitate quartz using Rimstidt and Barnes rate law"
Version number= 3245   Stage number= 01
Created 10/31/90    Creator= T.J. Wolery
Revised 10/31/90    Revisor= T.J. Wolery

  Precipitate quartz from supersaturated solution at 105 C, using the
rate law of Rimstidt and Barnes (1980). This is test problem 1 from
Delany, Puigdomenech, and Wolery (1986, p. 19-21, 31-33), which
simulates an experiment (Run 2E) reported by Rimstidt and Barnes
(1980, p. 1687-1688, Figure 2) and uses their rate law model, which
is independent of pH. Another EQ6 test case input file, pquartzA.6i,
runs the same problem, but uses a rate law model from Knauss and
Wolery (1988) that includes dependence on pH.

  Purpose: to test the kinetics mode of EQ6. Results may be compared
with Figure 2 of Rimstidt and Barnes (1980) and Figure 1 of Delany,
Puigdomenech, and Wolery (1986).

  The precipitation rate law is expressed in terms of a reversal of
the net rate form for dissolution, as the precipitation rate law code
"nprk" is set to -1. Thus, the specified rate constant is k(+) (the
dissolution rate constant) instead of k(-) (the precipitation rate
constant). The value chosen is 9.72e-16 mol/cm**2/s, is which the
value specifically fit by Rimstidt and Barnes (1980) to the data for
the corresponding experimental run (2E). Their master regression for
rate constants as functions of temperature yields a value of 2.53e-15
mol/cm**2/s, which does not do a good job of representing the data for
this particular run (See Figure 1 of Delany, Puigdomenech, and Wolery,
1986).

  The option switch iopt11 is set to 1 to indicate that this problem
has no redox aspect.

  Note that the silica polymorphs tridymite, chalcedony, sio2(am),
and cristobalite have been suppressed by means of "nxmod" options.
These were set on the EQ3NR test case input file sio2.3i, which was
used to initialize this EQ6 test case.

                          References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986,
  Precipitation Kinetics Option for the EQ6 Geochemical Reaction
  Path Code: UCRL-53642, Lawrence Livermore National Laboratory,
  Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of
  quartz as a function of pH and time at 70 C: Geochimica et Cosmo-
  chimica Acta, v. 52, p. 43-53.

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water
  reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

-----------------------------------------------------------------------
 calculational mode   |*normal      | economy          | super economy
```

Information Only

```
 model type            | titration  |*closed            | open
 temperature model     |*power      | fluid mixing
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
 tstart(c)|  105.0   |tk1|     0.    |tk2|     0.    |tk3|     0.
 starting value of zi |      0.    |max. value of zi    |  1.0000
 starting time (sec)  |      0.    |max. time (sec)     | 6.92000E+05
 max. steps           |       500  |max. steps w/o print|        10
 linear print interval| 5.00000E-05|log print interval  |  10.000
 suppress mineral phases
 phases w/ elements|                    |                    |n
 phases except     |                    |                    |n
 fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
 none                                  |                    |n
c                  R A T E     L A W S
c 1 = relative                    rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory     rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate          rate = CHECK DOCUMENTATION

c                  R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                  S U R F A C E    T Y P E
c 0 = fixed surface area      1 = fixed specific surface area
c
c                  N O T E S
c status and jreac are normally not set by the user
 reactants   (ss) solid solution only     (sp) special reactant only
 REACTANT          |  quartz                |status    | 0
 moles remaining   |  472.00                |destroyed |      0.
 reactant type     |  mineral               |sk        | 2.61280E+06
 surface type      |   0                    |fk        |  1.0000
 end-member        |                        |mole fr   |                ss,n
 volume            |                        |          |                sp
 element           |                        |moles     |                sp,n
 DISSOLUTION LAW   |    2                   |          |
 rate constant rk1 | 7.92000E-16            |csigmal   |    1.00000
 temperature (c)   |   105.00               |          |                234
 PRECIPITATION LAW |   -1                   |          |
 options
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * don't print
     lists species loaded into memory
 - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
   * don't print
     print
 - LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
   * don't print
     print
 - LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
   * only species > 10**-12 molal
     all species
     don't print
 - LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
   * don't print
     print
 - LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
   * don't print
     print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
   * don't print
     print
 - PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
   * don't print
     print
 - TAB FILES -
   * write
     append to previous tabx file
     don't write
```

Information Only

```
- WRITE PICKUP FILE -
  * write pickup file at end of run
    don't write pickup file
    write pickup file for each print point
- PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    transfer minerals but leave trivial mass in the system
    transfer minerals
- CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    clear p.r.s. before first reaction progress advance
- PHASE BOUNDARY SEARCH -
  * step size constrained by predicted phase boundaries
    phase boundaries estimated from Taylor's series and printed
    locations of phase boundaries ignored
- AUTO BASIS SWITCHING -
  * off
    on
- SUPPRESS REDOX REACTIONS -
    does nothing
  * suppress all redox reactions
- LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
  * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
    logarithmic for kcol = 1,kbt
    linear for kcol = 1,kdim
- AZERO AND HYDRATION NUMBERS -
  * no change
    read in new azero and hydration numbers
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
  * does nothing
    print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
    print summary information
    print detailed information
- PRINT STEP SIZE AND ORDER -
  * don't print
    print scale factor
    print orders and step size scaling factors
- CONTROL STEP SIZE AND ORDER PRINT -
  * does nothing
    print step size and order when delzi .le. dlzmx1
- NEWTON ITERATIONS -
  * don't print
    print summary of newton iterations
    print summary, residual functions and correction terms
    print summary, residual functions, correction terms and matrix
- PRINT SEARCH ITERATIONS -
  * don't print
    print
- PRINT HPSAT ITERATIONS -
  * don't print
    print
- PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
  * don't print
    print computations from RDERIV, and RTAYLR
    print computations from RDERIV, RTAYLR, DERIV and TAYLOR
- PRINT KINETICS DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 diagnostics
    print level 1 and level 2 diagnostics
- PRINT AKMATR -
  * don't print
    print level 1 diagnostics
- KILL ITERATION VARIABLES -
  * does nothing
    allow selection of variables to remove
-----------------------------------------------------------------------
development options  (used for code development)
-----------------------------------------------------------------------
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
-----------------------------------------------------------------------
tolerances                        desired values - defaults info-only
-----------------------------------------------------------------------
number of N-R iterations                          40       itermx
p.r.s. transfer interval                          varies   dlzidp
residual magnitude                                1.0e-06  tolbt
correction magnitude                              1.0e-06  toldl
search/find tolerance                             varies   tolx
supersaturation                                   varies   tolsat
supersaturation set size                          varies   tolsst
max. size Taylor's series term                    1.0e-04  screw1
max. initial value betamx                         n/a      screw2
max. Taylor's series term (kin.)                  1.0e-04  screw3
```

Information Only

corrector iteration	1.0e-04	screw4
max. size of N-R correction term	4.0	screw5
step size (economy mode)	4.0	screw6
log mass of phases	varies	zklogu
decrement mass (p.r.s.)	2.0	zklogl
min. left after p.r.s.	.98	zkfac
initial step size	varies	dlzmx1
upper limit step size	varies	dlzmx2
maximum order	6	nordlm
num. attempted assemblages	25	ntrymx
slide -> over phase bound.	8	npslmx
slide -> over redox insta.	3	nsslmx
fo2 scan control	none	ioscan

```
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= sio2.3i
Description= "Solution containing 101.0 mg/L SiO2"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Solution containing 101.0 mg/L of dissolved SiO2. This test
case is otherwise nearly identical to that in the EQ3NR test case
input file deionw.3i.

  Purpose: to initialize the EQ6 test case input files pquartz.6i
and pquartzA.6i, both of which simulate the precipitation of
quartz from supersaturated solution at 105 C. The former EQ6
test case is test problem 1 from Delany, Puigdomenech, and Wolery
(1986, p. 19-21, 31-33), which simulates an experiment (Run 2E)
reported by Rimstidt and Barnes (1980, p. 1687-1688, Figure 2)
and uses their rate law model, which is independent of pH. The
latter is the same problem, but uses a rate law model from Knauss
and Wolery (1988) that does include a dependence on pH.

  Note that the dissolved gases O2 and H2 have been suppressed.
This is because this problem has no redox aspect. The EQ6 option
switch ioptl1 should be set to 1 in the EQ6 test case input files
so that EQ6 knows this.

  Note also that the silica polymorphs tridymite, chalcedony,
sio2(am), and cristobalite have been suppressed by means of "nxmod"
options.

                          References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986,
  Precipitation Kinetics Option for the EQ6 Geochemical Reaction
  Path Code: UCRL-53642, Lawrence Livermore National Laboratory,
  Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of
  quartz as a function of pH and time at 70 C: Geochimica et
  Cosmochimica Acta, v. 52, p. 43-53.

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water
  reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.
```

temperature (C)	25.000
electrical imbalance	1.969775118839880E-17
number of aqueous master species	5
position of last pure mineral	5
position of last solid solution	5

suppressed species	(suppress,replace,augmentk,augmentg)		value
tridymite	mineral	suppress	0.
chalcedony	mineral	suppress	0.
sio2(am)	mineral	suppress	0.
cristobalite	mineral	suppress	0.

```
iopg options

 - pH SCALE CONVENTION -
    * modified NBS
      internal
      rational
 - ACTIVITY COEFFICIENT OPTIONS -
    * use B-dot equation
      Davies' equation
      Pitzer's equations
```

elements, moles and moles aqueous		
o	5.551182507032690E+01	0.000000000000000E+00
h	1.110168746281030E+02	0.000000000000000E+00
c	1.290656949760570E-05	0.000000000000000E+00

Information Only

```
|          si        |    1.680971568279880E-03|    0.000000000000000E+00|
|-----------------------------------------------------------------------|
| master species and logarithmic basis variables                        |
|-----------------------------------------------------------------------|
|h2o                 |h2o                      |    1.744358983526980E+00|
|h+                  |h+                       |   -5.647372920522350E+00|
|hco3-               |hco3-                    |   -5.664710439005960E+00|
|sio2(aq)            |sio2(aq)                 |   -2.774461217702960E+00|
|o2(g)               |o2(g)                    |    0.000000000000000E+00|
|-----------------------------------------------------------------------|
| physically removed subsystem  (solid solution, mineral, moles)        |
|-----------------------------------------------------------------------|
| none               |                         |                         |
|-----------------------------------------------------------------------|
```

The EQ6 **output** file (**pquartz.6o**), kinetics of quartz precipitation at 105°C (partial reproduction):

```
                    .
                    .
                    .
          (Material deleted)
                    .
                    .
                    .
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -

stepping to zi=  0.0000E+00, delzi=  0.0000E+00, nord= 0
  time =  0.0000E+00 d, dltime =  0.0000E+00 d

  attempted species assemblage no.   1

             1      1  h2o
             2     26  h+
             3     28  hco3-
             4     60  sio2(aq)

iter =    3

- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                    reaction progress        =  0.00000000000000E+00
                    log of reaction progress =    -999.0000000


                    time =  0.000E+00 sec
                         =  0.000E+00 days
                         =  0.000E+00 years

                    log sec =     -999.000
                    log days =    -999.000
                    log years =   -999.000

                    temperature    =    105.000 degrees c
                    total pressure =      1.210 bars

                    computing units remaining =      0.000

start or re-start of run


                              --- reactant summary ---

    definitions and conventions

         delta x = x now - x at start
         affinity is + for forward direction (dissolution),
                     - for reverse direction (precipitation)
         rates are + for forward direction (dissolution),
                   - for reverse direction (precipitation)


    reactant                  moles     delta moles      grams     delta grams

 quartz                     4.7200E+02   0.0000E+00   2.8360E+04   0.0000E+00


               current total mass =  2.83598E+04 grams
               delta total mass   =  0.00000E+00 grams
```

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delta total volume = 0.00000 cc

reactant	rel. rate mol/mol	rate mol/s	rate mol/s/cm2
quartz	-1.0000E+00	-1.7216E-09	-6.5891E-16

reactant	affinity kcal/mol	surface area mol/s/cm2
quartz	-0.4549	2.6128E+06

reactant	rate constants, mol/s/cm2
quartz	
forward	7.9200E-16

affinity of the overall irreversible reaction= 0.455 kcal
contributions from irreversible reactions
with no thermodynamic data are not included

--- element totals for the aqueous phase ---

element	mg/kg soln.	molal conc.	moles
o	8.880657E+05	5.551183E+01	5.551183E+01
h	1.118870E+05	1.110169E+02	1.110169E+02
c	1.550051E-01	1.290657E-05	1.290657E-05
si	4.720613E+01	1.680972E-03	1.680972E-03
co3--		1.290657E-05	1.290657E-05
so4--		0.000000E+00	0.000000E+00
s--		0.000000E+00	0.000000E+00

warning-- co3--, so4--, and s-- totals require that routine compl
have the names of non-carbonate carbon, sulfide sulfur,
and non-sulfate sulfur aqueous species

single ion activities and activity coefficients are here defined
with respect to the modified nbs ph scale

	ph
modified nbs ph scale	5.5939
rational ph scale	5.5930

redox parameters are not defined

activity of water = 0.99997
log activity of water = -0.00001

ionic strength = 2.552859E-06 molal
sum of molalities = 0.0016966923642
osmotic coefficient = 1.00000

mass of solution = 1.000102 kg
mass of solutes = 0.000102 kg
conc of solutes = 0.010160 per cent (w/w)

moles of solvent h2o = 5.55084E+01
mass of solvent h2o = 1.00000E+00 kg

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	1.00000E+03	9.99969E-01	-0.00001	0.00000	-0.00001
sio2(aq)	1.68038E-03	1.00965E-01	1.68038E-03	-2.77459	0.00000	-2.77459
co2(aq)	1.12059E-05	4.93168E-04	1.12059E-05	-4.95055	0.00000	-4.95055
h+	2.55280E-06	2.57307E-06	2.55280E-06	-5.59298	-0.00097	-5.59395
hco3-	1.70064E-06	1.03768E-04	1.70064E-06	-5.76939	-0.00097	-5.77035
hsio3-	5.90641E-07	4.55335E-05	5.90641E-07	-6.22868	-0.00097	-6.22964
oh-	2.61413E-07	4.44595E-06	2.61413E-07	-6.58267	-0.00097	-6.58364

--- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

phase/end-member	log moles	moles	grams	volume, cc
quartz	2.6739420	4.72000E+02	2.83598E+04	1.07087E+04

mass, grams volume, cc

Information Only

```
created          0.000000E+00        0.000000E+00
destroyed        0.000000E+00        0.000000E+00
net              0.000000E+00        0.000000E+00

warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base

--- mineral saturation state summary ---

 mineral        affinity, kcal    state        mineral        affinity, kcal    state

graphite            1629.1754  ssatd         chalcedony              0.0849  ssatd
coesite               -0.6707                cristobalite           -0.2556
cristobalite-a        -0.2556                cristobalite-b         -0.7673
ice                   -0.8437                o-phthalic acid     12136.6458  ssatd
quartz                 0.4549  ssatd         si                   1527.9178  ssatd
sio2(am)              -1.0612                tridymite               0.1525  ssatd


- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


stepping to zi=  1.0000E-09, delzi=  1.0000E-09, nord= 0
  time =  6.7229E-06 d, dltime =  6.7229E-06 d
steps completed =     1, iter =  1, ncorr = 0
most rapidly changing is zvclg1(sio2(aq)          ) =     -2.7746

                    •
                    •
                    •
          (Material deleted)
                    •
                    •
                    •

stepping to zi=  6.2500E-04, delzi=  2.5000E-05, nord= 5
  time =  8.7641E+00 d, dltime =  8.5220E-01 d
steps completed =    26, iter =  1, ncorr = 0
most rapidly changing is zvclg1(sio2(aq)          ) =     -2.9765
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                reaction progress        =  6.25000000000000E-04
                log of reaction progress =      -3.2041200


                time =  7.572E+05 sec
                     =  8.764E+00 days
                     =  2.399E-02 years

                log sec =        5.879
                log days =       0.943
                log years =     -1.620

                temperature    =    105.000 degrees c
                total pressure =      1.210 bars

                computing units remaining =      0.000

maximum value of time

                          --- reactant summary ---


   reactant                  moles     delta moles      grams     delta grams

 quartz                    4.7200E+02  -6.2500E-04   2.8360E+04  -3.7553E-02

              current total mass =  2.83598E+04 grams
              delta total mass   = -3.75527E-02 grams
              delta total volume =     -0.01418 cc

   reactant                rel. rate       rate        rate
                            mol/mol        mol/s     mol/s/cm2

 quartz                   -1.0000E+00  -3.1205E-10  -1.1943E-16
```

Information Only

reactant	affinity kcal/mol	surface area mol/s/cm2
quartz	-0.1056	2.6128E+06

reactant	rate constants, mol/s/cm2
quartz	
forward	7.9200E-16

affinity of the overall irreversible reaction= 0.106 kcal
contributions from irreversible reactions
with no thermodynamic data are not included

--- element totals for the aqueous phase ---

element	mg/kg soln.	molal conc.	moles
o	8.880790E+05	5.551058E+01	5.551058E+01
h	1.118912E+05	1.110169E+02	1.110169E+02
c	1.550109E-01	1.290657E-05	1.290657E-05
si	2.965559E+01	1.055972E-03	1.055972E-03
co3--		1.290657E-05	1.290657E-05
so4--		0.000000E+00	0.000000E+00
s--		0.000000E+00	0.000000E+00

warning-- co3--, so4--, and s-- totals require that routine comp1
have the names of non-carbonate carbon, sulfide sulfur,
and non-sulfate sulfur aqueous species

single ion activities and activity coefficients are here defined
with respect to the modified nbs ph scale

	ph
modified nbs ph scale	5.6145
rational ph scale	5.6135

redox parameters are not defined

activity of water = 0.99998
log activity of water = -0.00001

ionic strength = 2.434838E-06 molal
sum of molalities = 0.0010715869794
osmotic coefficient = 1.00000

mass of solution = 1.000064 kg
mass of solutes = 0.000064 kg
conc of solutes = 0.006406 per cent (w/w)

moles of solvent h2o = 5.55084E+01
mass of solvent h2o = 1.00000E+00 kg

species	moles	grams	conc	log conc	log g	log act
h2o	5.55084E+01	1.00000E+03	9.99981E-01	-0.00001	0.00000	-0.00001
sio2(aq)	1.05558E-03	6.34239E-02	1.05558E-03	-2.97651	0.00000	-2.97651
co2(aq)	1.11349E-05	4.90044E-04	1.11349E-05	-4.95331	0.00000	-4.95331
h+	2.43478E-06	2.45411E-06	2.43478E-06	-5.61354	-0.00094	-5.61448
hco3-	1.77162E-06	1.08099E-04	1.77162E-06	-5.75163	-0.00094	-5.75257
hsio3-	3.88979E-07	2.99870E-05	3.88979E-07	-6.41007	-0.00094	-6.41102
oh-	2.74060E-07	4.66103E-06	2.74060E-07	-6.56215	-0.00094	-6.56310

--- grand summary of solid phases (e.s.+p.r.s.+reactants) ---

phase/end-member	log moles	moles	grams	volume, cc
quartz	2.6739426	4.72001E+02	2.83598E+04	1.07088E+04

	mass, grams	volume, cc
created	0.000000E+00	0.000000E+00
destroyed	-3.755269E-02	-1.418000E-02
net	3.755269E-02	1.418000E-02

warning-- these volume totals may be incomplete because
of missing partial molar volume data in the data base

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```
          --- mineral saturation state summary ---

  mineral          affinity, kcal    state        mineral          affinity, kcal    state

graphite              1629.1707  ssatd         chalcedony              -0.2645
coesite                 -1.0201                  cristobalite            -0.6050
cristobalite-a          -0.6050                  cristobalite-b          -1.1167
ice                     -0.8437                  o-phthalic acid      12136.6077  ssatd
quartz                   0.1056  ssatd           si                    1527.5685  ssatd
sio2(am)                -1.4106                  tridymite               -0.1969


- - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - -


                    --- maximum value of time ---

---  the reaction path has terminated normally ---


         26 steps were taken
      zi increased from
             0.00000E+00 to  6.25000E-04
      the average value of delzi was  2.40385E-05
      the average matrix dimension was    5

      time increased from
             0.00000E+00 to  7.57220E+05 seconds
             0.00000E+00 to  8.76412E+00 days
             0.00000E+00 to  2.39948E-02 years


         start time = 10:34      18Dec91
           end time = 10:35      18Dec91

         user time =       8.480
          cpu time =       0.860

--- no further input found ---
```

The EQ6 **tab** file (**pquartz.6o**), kinetics of quartz precipitation at 105°C (partial reproduction):

```
                    .
                    .
                    .
              (Material deleted)
                    .
                    .
                    .

     zi     log zi    time, d  log days    tempc     press      ph     log fo2      eh       pe      kg h2o   tot aff

0.000E+00 -999.0000 0.000E+00 -999.0000 105.0000  1.2097  5.5939 -999.0000 -999.0000 -999.0000  1.0000   0.4549
1.000E-09   -9.0000 6.723E-06   -5.1724 105.0000  1.2097  5.5939 -999.0000 -999.0000 -999.0000  1.0000   0.4549
5.000E-05   -4.3010 3.477E-01   -0.4588 105.0000  1.2097  5.5955 -999.0000 -999.0000 -999.0000  1.0000   0.4322
1.000E-04   -4.0000 7.206E-01   -0.1423 105.0000  1.2097  5.5971 -999.0000 -999.0000 -999.0000  1.0000   0.4088
1.500E-04   -3.8239 1.123E+00    0.0503 105.0000  1.2097  5.5987 -999.0000 -999.0000 -999.0000  1.0000   0.3847
2.000E-04   -3.6990 1.559E+00    0.1929 105.0000  1.2097  5.6003 -999.0000 -999.0000 -999.0000  1.0000   0.3597
2.500E-04   -3.6021 2.036E+00    0.3088 105.0000  1.2097  5.6019 -999.0000 -999.0000 -999.0000  1.0000   0.3339
3.000E-04   -3.5229 2.562E+00    0.4086 105.0000  1.2097  5.6035 -999.0000 -999.0000 -999.0000  1.0000   0.3072
3.500E-04   -3.4559 3.148E+00    0.4980 105.0000  1.2097  5.6052 -999.0000 -999.0000 -999.0000  1.0000   0.2795
4.000E-04   -3.3979 3.810E+00    0.5809 105.0000  1.2097  5.6068 -999.0000 -999.0000 -999.0000  1.0000   0.2507
4.500E-04   -3.3468 4.569E+00    0.6598 105.0000  1.2097  5.6085 -999.0000 -999.0000 -999.0000  1.0000   0.2208
5.000E-04   -3.3010 5.461E+00    0.7373 105.0000  1.2097  5.6102 -999.0000 -999.0000 -999.0000  1.0000   0.1896
5.500E-04   -3.2596 6.542E+00    0.8157 105.0000  1.2097  5.6119 -999.0000 -999.0000 -999.0000  1.0000   0.1571
6.000E-04   -3.2218 7.912E+00    0.8983 105.0000  1.2097  5.6136 -999.0000 -999.0000 -999.0000  1.0000   0.1231
6.250E-04   -3.2041 8.764E+00    0.9427 105.0000  1.2097  5.6145 -999.0000 -999.0000 -999.0000  1.0000   0.1056

                    .
                    .
                    .
              (Material deleted)
                    .
                    .
                    .

                 log molality of dissolved elements

   log zi   time, d   log days      c          si
```

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-999.0000	0.000E+00	-999.0000	-4.8892	-2.7744
-9.0000	6.723E-06	-5.1724	-4.8892	-2.7744
-4.3010	3.477E-01	-0.4588	-4.8892	-2.7876
-4.0000	7.206E-01	-0.1423	-4.8892	-2.8011
-3.8239	1.123E+00	0.0503	-4.8892	-2.8150
-3.6990	1.559E+00	0.1929	-4.8892	-2.8295
-3.6021	2.036E+00	0.3088	-4.8892	-2.8444
-3.5229	2.562E+00	0.4086	-4.8892	-2.8598
-3.4559	3.148E+00	0.4980	-4.8892	-2.8758
-3.3979	3.810E+00	0.5809	-4.8892	-2.8925
-3.3468	4.569E+00	0.6598	-4.8892	-2.9098
-3.3010	5.461E+00	0.7373	-4.8892	-2.9278
-3.2596	6.542E+00	0.8157	-4.8892	-2.9465
-3.2218	7.912E+00	0.8983	-4.8892	-2.9662
-3.2041	8.764E+00	0.9427	-4.8892	-2.9763

ppm (mg/kg) of dissolved elements

log zi	time, d	log days	c	si
-999.0000	0.000E+00	-999.0000	.155	47.2
-9.0000	6.723E-06	-5.1724	.155	47.2
-4.3010	3.477E-01	-0.4588	.155	45.8
-4.0000	7.206E-01	-0.1423	.155	44.4
-3.8239	1.123E+00	0.0503	.155	43.0
-3.6990	1.559E+00	0.1929	.155	41.6
-3.6021	2.036E+00	0.3088	.155	40.2
-3.5229	2.562E+00	0.4086	.155	38.8
-3.4559	3.148E+00	0.4980	.155	37.4
-3.3979	3.810E+00	0.5809	.155	36.0
-3.3468	4.569E+00	0.6598	.155	34.6
-3.3010	5.461E+00	0.7373	.155	33.2
-3.2596	6.542E+00	0.8157	.155	31.8
-3.2218	7.912E+00	0.8983	.155	30.4
-3.2041	8.764E+00	0.9427	.155	29.7

•
•
•

(Material deleted)

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•

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7. Thermodynamic Calculational Methods

7.1. Introduction

The governing equations for reaction path calculations were introduced in Chapter 3. This chapter and the following one continue the development begun there, to show how EQ6 actually solves the system composed of these equations. As was pointed out in Chapter 3, the governing equations fall into two categories. The first deals with the equations that present themselves in the calculation of thermodynamic equilibrium. These equations are fundamentally algebraic (e.g., mass balance, mass action). The second problem deals with rate equations, which are by nature ordinary differential equations (ODEs). The calculational problem involving these is integration, generally numerical integration.

This chapter discusses the means by which EQ6 carries out thermodynamic equilibrium calculations. The methodology is very similar to that used in EQ3NR (see Chapter 9 of the EQ3NR Theoretical Manual and User's Guide, Wolery, 1992b). The reader of the present chapter is presumed to be familiar with methodology used in EQ3NR. The following chapter in the present report deals with the integration of rate equations.

7.2. The Set of Master Iteration Variables

In the EQ6 code, the set of master iteration variables is similar to that used in EQ3NR, with two key differences. First, concentration variables are replaced by number of moles variables. In the case of the solvent, water, the concentration is expressed by the mole fraction (x_w); the number of moles is represented by n_w. In the case of aqueous solute species, the concentration is expressed by the molality (m_i); the corresponding number of moles is represented by n_i. When no product minerals are present, the vector of master iteration variables (z) has the following structure:

$$z = \begin{bmatrix} \log n_w \\ \cdot \\ \cdot \\ \log n_{s'} \ , \ s' = 1, s_B - 1 \ , \ s \neq w \\ \cdot \\ \cdot \\ \log f_{O_2} \\ \cdot \\ \cdot \\ \log n_{s'} \ , \ s' = s_B + 1, s_Q \end{bmatrix} \tag{64}$$

This is exactly analogous to that used in EQ3NR. All of these variables formally correspond to mass balance relations, expect the fictive redox species $O_{2(g)}$, which formally corresponds to the charge balance equation. The first part of this vector contains entries for the s_B strict basis species. The last of these is $O_{2(g)}$, which continues to be represented in the set of master iteration variables

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by the corresponding fugacity. The second part contains entries for any auxiliary basis variables for which **jflag** $\neq 30$ (those with **jflag** = 30 are treated as non-basis species). The structure is further simplified if $s_Q = s_B$ (no active auxiliary basis set), which implies that the aqueous solution is in a state of complete internal (homogeneous) equilibrium. Otherwise, partial internal disequilibrium is implied. In the present version of EQ3/6, the code's internal data structure differs from that of EQ3NR and does not permit the use of an auxiliary basis set. For conceptual reasons, however, we include it in the present discussion. Some EQ6 problems are redox indifferent. In this case, the redox variable is automatically dropped from the basis set (the option switch **iopt11** can be set to 1 to suppress all aqueous redox reactions to avoid problems caused by the presence of insignificant amounts of the species $O_{2(aq)}$ and $H_{2(aq)}$).

If product minerals are present in the equilibrium system, the vector of master iteration variables is expanded to include the number of moles of the relevant species:

$$z = \begin{bmatrix} log\, n_w \\ \cdot \\ \cdot \\ log\, n_{s'} \;,\; s' = 1, s_B - 1 \;,\; s \neq w \\ \cdot \\ \cdot \\ log\, f_{O_2} \\ \cdot \\ \cdot \\ log\, n_{s'} \;,\; s' = s_B + 1, s_Q \\ \cdot \\ \cdot \\ log\, n_{\phi} \;,\; \phi = 1, \phi_T \\ \cdot \\ \cdot \\ log\, n_{\sigma\psi} \;,\; \sigma = 1, \sigma_{T,\psi} \;,\; \psi = 1, \psi_T \end{bmatrix} \tag{65}$$

These additional master iteration variables formally correspond to the associated mass action equations. Here ϕ denotes a pure mineral in the equilibrium system, n_ϕ is the corresponding number of moles, and ϕ_T is the number of such pure minerals. If ϕ_T is zero, this block is simply deleted. Here also ψ denotes a solid solution in the same system, and ψ_T is the number of such phases. If ψ_T is zero, this block is also simply deleted. Here σ denotes an end member component, $n_{\sigma\psi}$ is the number of moles of the σ-th component of the ψ-th solid solution, and $\sigma_{T,\psi}$ is the number of such components belonging to the ψ-th solid solution present in the equilibrium system.

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7.3. Expanding the System from the Set of Master Iteration Variables

One may "expand the system" from the vector of master iteration variables $\underline{z}$ by computing the number of moles, concentrations, and activity coefficients of all species present in the equilibrium system. As was pointed in the case of EQ3NR (Wolery, 1992b, Chapter 9), this is not a straightforward process when non-basis species are present in the model. The problem is that for any phase containing such species, the concentrations of the non-basis species are generally required to compute the activity coefficients, one must evaluate the corresponding mass action equations. The activity coefficients appear in these equations. Hence, the activity coefficients must be evaluated first. However, the activity coefficients depend in general on the concentrations of all solute species, both basis and non-basis. So to deal with these, one must compute the concentrations of the non-basis species first.

The approach to resolving this conundrum is nearly the same as that taken in the case of EQ3NR (see Wolery, 1992b, Chapter 9). The system is expanded by first calculating the new concentrations of the non-basis species, using the existing values of the activity coefficients. The activity coefficients are then recalculated. In the pre-Newton-Raphson optimization algorithm, the computed concentrations of the basis and non-basis species may be adjusted several times before the activity coefficients are recalculated. In the hybrid Newton-Raphson method, they are recalculated between each Newton-Raphson step. The expansion itself technically calls for a process of repeated steps, each consisting of recalculation of the concentrations of non-basis species, followed by recalculation of the activity coefficients. However, EQ3/6 uses a one step or single update method in hybrid Newton-Raphson iteration, because there seems to be no definite advantage to the use of repeated steps (Wolery, 1992b, Chapter 9).

7.4. Beginning the Process: Computing Starting Values

The problem of assigning starting values is very different in EQ6 than it is in EQ3NR. Starting values at the initial point of reaction progress are read from the **input** file. These originate from either an EQ3NR **pickup** file or an EQ6 **pickup** file. Starting values at subsequent points are calculated using finite-difference based predictor functions. If a calculation then requires precipitation of a new product phase to eliminate a corresponding supersaturation, the starting value for the number of moles of this phase is taken as 5% of the possible maximum value, as computed from the aqueous phase composition. If the phase is a solid solution, the starting value for the number of moles of each end member component is assigned by taking the product of 5% of the maximum number of moles of the phase and the mole fraction of the component corresponding to the composition which maximizes the affinity function for the phase.

7.5. Methods to Aid Convergence

Several techniques are used in EQ6 to aid convergence of the thermodynamic equilibrium calculations. They include:

- Use of logarithmic iteration variables
- Under-relaxation techniques
- Automatic and user-specified basis switching

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These methods are also used in EQ3NR and have been discussed in Chapter 9 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b). The implementation of these methods is very similar, but not identical in all respects.

The physical quantities that correspond to the iteration variables (number of moles) used by EQ6 are intrinsically positive. Use of logarithmic iteration variables prevents iteration from producing negative numbers. Other than the fact that EQ6 uses numbers of moles rather than concentrations as master variables, the usage of this technique is the same as in EQ3NR.

Under-relaxation is the technique of judiciously reducing the magnitude of the computed correction terms. Assume that the unmodified method involves adding a correction term vector (δ_k), where k is the iteration number. This is typical in Newton-Raphson iteration,. The new vector of master iteration variables is obtained thusly:

$$z_{k+1} = z_k + \underline{\delta}_k \tag{66}$$

If the new vector of master iteration variables is obtained instead by evaluating some set of corresponding equations not in this format, one can still utilize under-relaxation by defining a correction term vector as follows:

$$\underline{\delta}_k = z_{k+1} - z_k \tag{67}$$

Global under-relaxation is effected by replacing the correction equation given above by

$$z_{i+1} = z_i + \kappa \underline{\delta}_i \tag{68}$$

where κ is a positive number less than one. Non-global under-relaxation is also possible. This does not involve the use of an under-relaxation factor. Rather it involves truncating the magnitudes of individual correction terms to satisfy specified limits, which may be different depending on the species involved and on the direction of change.

There are several methods of applying global under-relaxation, distinguished by different methods of choosing a value for the under-relaxation factor. EQ6 uses two simple ones in making Newton-Raphson steps. These are identical to those used in EQ3NR (Wolery, 1992b).

The first of these limits the size of the largest correction term:

$$\kappa = \frac{\delta'}{\delta_{max}} \tag{69}$$

where δ' is the imposed limit and δ_{max} is the max norm of δ. In a Newton-Raphson iteration step (which occurs in the EQLIB module **nrstep.f**), this limit is represented by the variable **screwd**. In EQ3NR, this is set in the main program (module **eq3nr.f**) at a value of 2.0. In EQ6, it is set on the **input** file through the variable **screw5**. This has a default value of 4.0. This method of under-relaxation not only aids convergence, but is very helpful in inducing iteration to provide helpful information about the nature of the problem when it diverges. This information may be used by

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EQ6 to pick a phase to delete from the equilibrium phase assemblage or to enter the redox scan mode.

The other global under-relaxation method is applied for only the first 8 iterations. The under-relaxation factor is cut in half if the residual vector max norm β_{max} exceeds the value of the variable **screwn**. Initially, κ is set to a value of unity; when the current method of under-relaxation is applied, this factor may have been reduced as a result of applying the method described above. In EQ3NR, **screwn** is set to 0.5 in the main program (module **eq3nr.f**). In EQ6, it is set in the module **eqcalc.f**, which directs the equilibrium calculation at a given point of reaction progress. Initially, it is set to a value of 0.10. If the phase assemblage is changed, the value of **screwn** is temporarily reduced to 0.005. In practice, this under-relaxation method comes into play relatively infrequently in EQ6 compared to the one described above.

Some degree of non-global under-relaxation is also employed in pre-Newton-Raphson optimization. This optimization function takes place in EQ6 in module **optmzr.f**. Here under-relaxation is effected by imposing truncation limits on changes for individual master variables. The master variables for water and the hydrogen ion may not change in a given step by more than certain limits, which are specific to each species (0.05 and 2.0 log units, respectively) Other master variables are not subject to truncation limits. The limits imposed in EQ6 differ from those imposed in EQNR (see Chapter 9 of Wolery, 1992b).

Some truncation limits also apply to the activity coefficients and the functions Σm and the ionic strength. These limits are applied during both pre-Newton-Raphson optimization and hybrid Newton-Raphson iteration, and, in EQ6, during calculations involving the use of predictor functions. These limits are defined in the variable **chgfac**, which is in the calling sequence of the EQLIB module **ngcadv.f**. The value of this variable is set in the calling modules, and is usually scaled inversely with the value of Σm. Values range from 1.3 to 100.

Basis switching, the practice of changing the aqueous species in the basis set during execution of EQ3NR or EQ6, is often a very beneficial and sometimes also necessary device in order to achieve convergence. The general rule is that it is best to choose a basis species that makes up a significant fraction of the corresponding mass balance. For example, if $UO_2(CO_3)_2^{2-}$ makes up most of the total balance of uranium, then it is a better choice for the corresponding basis species than the data file master species, UO_2^{2+}. Experience with the Newton-Raphson method in EQ3NR and EQ6 has shown that basis-switching is occasionally critical to achieving convergence. It is not necessary for the chosen basis species to dominate the corresponding mass balance. However, it is critical that it not compose an extremely scarce fraction of that mass balance. The present version of EQ6 does not allow water, the hydrogen ion, or O_2 (the fictive redox species) to be switched out of the active basis set. Also, it does not allow non-aqueous species(e.g., pure minerals and solid solution end member components) to be switched into the active basis set.

The user may specify certain basis switches on the **input** file (see Chapter 5). These switches are executed prior to calculation of the state of the system at the initial point of reaction progress. This appears on the part of the **input** file that corresponds to the EQ3NR **pickup** file. If the user specifies certain basis switches on the EQ3NR **input** file, these switches will be listed on the cor-

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responding **pickup** file. It is probably best to make such switches at this point. However, it is possible to direct such switches later by modifying the appropriate part of the EQ6 **input** file.

There is also an automatic basis switching mode, specified by setting **iopt7** = 1 (**iopt2** is used for this specification in EQ3NR). It is not necessary to invoke automatic basis switching for most reaction path runs. Automatic basis switching does not operate in EQ6 as part of the pre-Newton-Raphson optimization method, as it does in EQ3NR. Instead, automatic basis switching is made after a successful calculation of the state of the system at a given point of reaction progress.

7.6. The Pre-Newton-Raphson Optimization Algorithm

The pre-Newton-Raphson optimization algorithm employed in EQ6 is patterned after that used in EQ3NR (see Chapter 9 of Wolery, 1992b). It is carried out in the module **optmzr.f**. The algorithm is simplified in comparison to that used in EQ3NR in that there is a much smaller number of kinds of constraints corresponding to the set of master iteration variables. Also, no automatic basis switching is employed in the optimization stage (if selected, automatic basis switching takes place after the state of the system at a given point of reaction progress has been calculated). The module **optmzr.f** is called by fellow EQ6 module **eqcalc.f**, which oversees thermodynamic calculations.

The optimization process begins by recalculating the Σm, the ionic strength, and the activity coefficients. It then re-expands the system and computes a full suite of residual functions. It then utilizes a loop structure similar to that employed in EQ3NR. The primary loop structure consists of *passes*. At the end of a pass, Σm, the ionic strength, and the activity coefficients are recomputed. Within each pass is another loop structure, the times through which are called *cycles*. Here, adjustments are made to the number of moles of the basis species corresponding to balance equations. A pass is completed after some number of cycles. The cycles within a pass terminate if some rather rough convergence criteria are satisfied, or if the maximum number of cycles in a pass have been completed. This is determined by the variable **ncylim**, which is currently set to 15 in a data statement in **optmzr.f**. The passes terminate if rough convergence criteria applying to both the cycles and passes are satisfied, or if the maximum number of passes has been completed. This is determined by the variable **nplim**, which is currently set to 5 in a data statement in **optmzr.f**.

To illustrate the cycle algorithm, we again consider the case of aluminum (compare the corresponding case for EQ3NR described in Chapter 9 of Wolery (1992b). The total aluminum in EQ6 is presently expressed as total elemental aluminum. This includes aluminum in both the aqueous solution and any other phases present in the equilibrium system. The normalized mass balance residual is:

$$\beta_{Al} = \frac{n_{T,calc,Al} - n_{T,Al}}{n_{T,Al}} \tag{70}$$

where: $n_{T,calc,Al}$ is the total number of moles of aluminum as calculated from a mass balance expression, using the current values of the master iteration variables. Here $n_{T,Al}$ is the total number of moles of aluminum in the equilibrium system.

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The basic cycle algorithm is based on that employed in EQ3NR (see Chapter 9 of Wolery, 1992b) and is modified principally only in that numbers of moles replace molalities. As applied to basis species other than water or O_2 (the fictive redox species), this assumption assumes that there is little change in the number of moles of water. Assuming that the basis species is that Al^{3+} and that it dominates the calculated mass balance, the cycle algorithm is illustrated by the equation:

$$n_{Al^{3+},k+1} = \frac{n_{Al^{3+},k}}{\beta_{Al,k}+1} \tag{71}$$

If the basis species is Al^{3+} and the aluminum mass balance is dominated by the complex $Al_{13}O_4(OH)_{24}^{7+}$, the equation is modified to the form:

$$n_{Al^{3+},k+1} = \frac{13^{\frac{1}{13}} n_{Al^{3+},k}}{(\beta_{Al,k}+1)^{\frac{1}{13}}} \tag{72}$$

where the "13" is the ratio of the reaction coefficients of Al^{3+} and $Al_{13}O_4(OH)_{24}^{7+}$ in the reaction for the dissociation of $Al_{13}O_4(OH)_{24}^{7+}$:

$$Al_{13}O_4(OH)_{24}^{7+} + 32H^+ = 13Al^{3+} + 28H_2O_{(l)} \tag{73}$$

This algorithm is applied to all basis species corresponding to mass balance equations, including water and the hydrogen ion. Special under-relaxation truncation limits apply to these latter two species, as was discussed earlier in this chapter.

There are two principle deficiencies to the cycle algorithm described above. First, it is not complete. The master variable corresponding to O_2 (the fictive redox species) is not optimized. Neither are any master variables defined for pure minerals and solid solutions. Second, the optimization equations illustrated above were derived on the assumption that the dominant species is an aqueous species. They do not work well when all aqueous species contribute insignificantly to a mass balance. Thus, on both counts, the optimization algorithm tends to perform poorly in rock dominated systems.

At the end of a cycle, a full set of residual functions is computed. This includes the β array and its max norm, β_{max}. A pass (sequence of cycles) ends when one of the following occurs:

- The non-zero (mass balance) elements of β satisfy a loose convergence test (all fall in the range -10% to +10%).
- The maximum number of cycles per pass have been completed.

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- A convergence function β_{func} (**betfnc**) indicates that iteration in the present cycle is diverging. This convergence function will be discussed later in this chapter.

At the end of a pass, the Σm function, the ionic strength, and the activity coefficients are recalculated. The code defines residual functions based on the magnitude of the changes in Σm, the ionic strength, and the activity coefficients from the values pertaining to the previous pass. The sequence of passes is stops when one of the following occurs:

- The residuals defined for Σm, the ionic strength, and the activity coefficients satisfy a loose convergence test (-10% to +10%).

- The maximum number of passes have been completed.

The optimization is deemed successful if both sets of loose convergence tolerances are satisfied. Following optimization, the code executes hybrid Newton-Raphson iteration, whether or not the optimization was successful.

The incomplete nature of the cycle algorithm in EQ6 is a major weakness in the present version of this code. This makes it difficult for the code to successfully deal with large steps in reaction progress. In particular, it causes the code some difficulty in dealing with large changes in temperature, such as are encountered in a temperature jump. This problem is basically responsible for the very limited usefulness of "economy mode" and "super economy mode," as the code in these modes tries to take large steps. The deficiencies of the present cycle algorithm sometimes also cause the code to spend a lot of run time trying to optimize starting estimates with little result, thus causing long run times.

7.7. The Newton-Raphson Method

The Newton-Raphson method and the methods for implementing it in EQ3NR were discussed in Chapter 9 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b). The methods for implementing it in EQ6 are very similar and in many aspects exactly the same. The differences that do exist come about because the Given a set n governing equations and n unknowns (represented by a vector $\underline{z}$ of iteration variables), one may construct a set of residual functions, represented by the vector α, which provides a measure of the degree to which the governing equations are not satisfied. Each element of this array has a value of zero when the $\underline{n}$ equations are satisfied. Both $\underline{z}$ and α are of length n.

Let k be the number of iterations, such that z_k and α_k are the iteration variable and residual function vectors on the k-th iteration. Let z_0 represent the set of starting estimates. An iteration step is made by calculating z_{k+1} from z_k. The Newton-Raphson method does this by computing a vector of correction terms, δ, by solving the matrix equation

$$\underline{J}\underline{\delta} = -\underline{\alpha} \tag{74}$$

Here $\underline{J}$ is the Jacobian matrix, defined as

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$$\underline{J} = \left(\frac{\partial \alpha_i}{\partial z_j}\right) \tag{75}$$

where i and j are the matrix coordinates. The correction term is then used to generate a new iteration variable vector by adding it to the old one:

$$\underline{z}_{k+1} = \underline{z}_k + \underline{\delta}_k \tag{76}$$

If the iteration converges, all elements of both α and δ approach zero. It is useful to define another residual function vector β, which is identical to α, except that some elements may be normalized to provide a better measure of convergence. Such relative residuals for mass balances are defined by dividing the absolute residual by the corresponding total number of moles. The relative residual for the charge balance is defined as the absolute residual divided by the calculated total number of charge equivalents. It is then convenient to define β_{max} and δ_{max} as the largest absolute values of the elements of β and δ, respectively. Both β_{max} and δ_{max} may then be used in tests to determine if the iteration has converged satisfactorily.

Useful measures of how well convergence is proceeding may be constructed. The Newton-Raphson method is a so-called second-order method, meaning that convergence should be very rapid in a close neighborhood of the solution. This behavior suggests that in a such a region, $\delta_{max,k+1}$ should be much less than $\delta_{max,k}$. The function δ_{conv} (the variable **delfnc** in EQ3NR and EQ6) defined as

$$\delta_{conv,\,k+1} = 1 - \left(\frac{\delta_{max,\,k+1}}{\delta_{max,\,k}}\right) \tag{77}$$

therefore tends to approach (from below) a value of unity when convergence is rapid. Convergence to a significantly lesser apparent limiting value, say 0.72 instead of 0.99, may imply an error in the Jacobian matrix. Similar behavior is expected from an analogous function defined in terms of the β_{max} residual (β_{conv}, the variable **betfnc** in EQ3NR and EQ6):

$$\beta_{conv,\,k+1} = 1 - \left(\frac{\beta_{max,\,k+1}}{\beta_{max,\,k}}\right) \tag{78}$$

The EQLIB routine **newton.f** oversees Newton-Raphson iteration for EQ6, just as it does for EQ3NR. Fellow EQLIB module **nrstep.f** is called to make a single Newton-Raphson step, and fellow EQLIB module **ngcadv.f** recomputes activity coefficients and computes the number of moles of dependent species. The latter module is called between Newton-Raphson steps, in accordance with the single update method that was discussed earlier in this chapter. The EQ6 module **betaz.f** computes the residual functions. Fellow EQ6 module **matrxz.f**, with the assistance of a few subordinate routines, writes the Jacobian matrix. The EQ6 modules **betaz.f** and **matrxz.f** are respective analogues of the EQ3NR modules **betas.f** and **matrix.f**.

The maximum number of iterations in a Newton-Raphson calculation is determined by the **input** file variable **itermx**. This has a default value of 40 in EQ6. Convergence is achieved when β_{max}

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is less than the tolerance parameter **tolbt**, δ_{max} is less than the tolerance parameter **toldl**, and max norms on the changes in the Σm function, the ionic strength, and the activity coefficients are all less than **tolbt**. The tolerance parameters **tolbt** and **toldl** both appear on the **input** file, and both have a default value of 1×10^{-6}.

7.8. Derivation of Residual Functions and the Jacobian Matrix

In this section, we shall derive the residual functions and the Jacobian matrix for the Newton-Raphson iteration procedures used by the EQ3NR code. Given a set of governing equations and an equal number of unknowns, there is no unique way to formulate residuals and Jacobians. The number of equations and unknowns may be reduced by means of substitutions. Furthermore, one may then construct the residual functions in any number of ways. Once the residual functions have been chosen, the form of the Jacobian is determined according to the partial derivatives of these functions.

We will now take each remaining governing equation, construct a corresponding pair of residual functions (α and β), and derive the corresponding row of elements in the Jacobian matrix by partial differentiation. The α residuals are the true Newton-Raphson residual functions and are the subject of partial differentiation to define the Jacobian matrix. The β residuals are better measures of satisfactory convergence. In the hybrid Newton-Raphson method currently used in EQ3/6, the activity coefficients of aqueous species are treated as known constants in a Newton-Raphson step. The partial differentiation of the α residuals therefore does not flow through these variables.

The Jacobian matrix for EQ6 is computed by the EQ6 module **matrxz.f**, which is analogous to the EQ3NR module **matrix.f**. Module **matrxz.f** calls other EQ6 modules to write the various kinds of rows in the matrix. The mass and charge balance rows are computed by module **balcnz.f**, the pure mineral mass action rows by module **balcmz.f**, and the solid solution end member component mass action rows by module **balcsz.f**. The residual functions are computed by the EQ6 module **betaz.f**, which is analogous to the EQ3NR module **betas.f**.

7.8.1. Mass Balance

As was pointed out in Chapter 3, mass balances can be defined in two ways: in terms of basis species (excluding the fictive redox species O_2, which is the s_B-th species), and in terms of chemical elements. The former treatment is more general, and permits the use of an auxiliary basis set. The latter, however, is the basis for the treatment in the present version of EQ6. The former treatment is equivalent to the latter if an auxiliary basis set is not used. Otherwise, they are not equivalent and the number of basis species minus one is greater than the number of chemical elements and there is hence a greater number of corresponding mass balance equations. As the former treatment is likely to be incorporated into future versions of EQ6, the equations for both treatments will be presented here.

Mass balance for the s'-th basis species is expressed by eq (4):

$$\sum_{s=1}^{s_T} u_{s's} n_s + \sum_{\phi=1}^{\phi_T} u_{s'\phi} n_\phi + \sum_{\psi=1}^{\psi_T} \sum_{\sigma=1}^{\sigma_{T,\psi}} u_{s'\sigma\psi} n_{\sigma\psi} = n_{T,s'} \tag{79}$$

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(see Chapter 3). The corresponding residual functions are defined by:

$$\alpha_{s'} = -n_{T,s'} + \sum_{s=1}^{s_T} u_{s's} n_s + \sum_{\phi=1}^{\phi_T} u_{s'\phi} n_\phi + \sum_{\psi=1}^{\psi_T} \sum_{\sigma=1}^{\sigma_{T,\psi}} u_{s'\sigma\psi} n_{\sigma\psi} \tag{80}$$

$$\beta_{s'} = \frac{\alpha_{s'}}{n_{T,s'}} \tag{81}$$

Mass balance for the ε-th chemical element is expressed by eq (5):

$$\sum_{s=1}^{s_T} c_{\varepsilon s} n_s + \sum_{\phi=1}^{\phi_T} c_{\varepsilon\phi} n_\phi + \sum_{\psi=1}^{\psi_T} \sum_{\sigma=1}^{\sigma_{T,\psi}} c_{\varepsilon\sigma\psi} n_{\sigma\psi} = n_{T,\varepsilon} \tag{82}$$

(see Chapter 3). The corresponding residual functions are defined by:

$$\alpha_\varepsilon = -n_{T,\varepsilon} + \sum_{s=1}^{s_T} c_{\varepsilon s} n_s + \sum_{\phi=1}^{\phi_T} c_{\varepsilon\phi} n_\phi + \sum_{\psi=1}^{\psi_T} \sum_{\sigma=1}^{\sigma_{T,\psi}} c_{\varepsilon\sigma\psi} n_{\sigma\psi} \tag{83}$$

$$\beta_\varepsilon = \frac{\alpha_\varepsilon}{n_{T,\varepsilon}} \tag{84}$$

The corresponding rows of the Jacobian matrix are obtained by partial differentiation of the α residuals with respect to the algebraic master variables. The numbers of moles variables appearing in the above equations are all directly related to the algebraic master variables, except those pertaining to the non-basis aqueous species. In deriving the Jacobian matrix, it is helpful to isolate the corresponding terms by rewriting eq (80) as:

$$\alpha_{s'} = -n_{T,s'} + u_{s's'} n_{s'} + \sum_{s''=s_Q+1}^{s_T} u_{s's''} n_{s''} + \sum_{\phi=1}^{\phi_T} u_{s'\phi} n_\phi$$

$$+ \sum_{\psi=1}^{\psi_T} \sum_{\sigma=1}^{\sigma_{T,\psi}} u_{s'\sigma\psi} n_{\sigma\psi} \tag{85}$$

Here s_Q is the number of basis species and s'' denotes a non-basis aqueous species Eq (83) can be similarly rewritten as:

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$$\alpha_\varepsilon = -n_{T,\varepsilon} + \sum_{s'''=1}^{s_Q} c_{\varepsilon s'''} n_{s'''} + \sum_{s''=s_Q+1}^{s_T} c_{\varepsilon s''} n_{s''} + \sum_{\phi=1}^{\phi_T} c_{\varepsilon\phi} n_\phi$$

$$+ \sum_{\psi=1}^{\psi_T} \sum_{\sigma=1}^{\sigma_{T,\psi}} c_{\varepsilon\sigma\psi} n_{\sigma\psi} \tag{86}$$

It is then necessary to find the $n_{s''}$ as functions of the $n_{s'}$. The relevant mass action equation can be written in the following form:

$$logK_r = b_{wr}(logx_w + log\lambda_w) + b_{s_B r} logf_{O_2} + b_{s''r}(logm_{s''} + log\gamma_{s''})$$

$$+ \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'r}(logm_{s'} + log\gamma_{s'}) \tag{87}$$

where r is the reaction for the s''-th aqueous species, K_r is the thermodynamic equilibrium constant for the reaction b_{sr} is the reaction coefficient for the s-th species, λ_w is the activity coefficient of water, and γ_s $(s \neq w)$ is the molal activity coefficient of the s-th species. As index labels, r and s'' are related in the present version of EQ3/6 by:

$$r = s'' - s_B \tag{88}$$

(recall that s_B is the number of strict basis species). Eq (87) can be rearranged to give:

$$logm_{s''} = \frac{logK_r}{b_{s''r}} - log\gamma_{s''} - \frac{b_{wr}}{b_{s''r}}(logx_w + log\lambda_w) - \frac{b_{s_B r}}{b_{s''r}} logf_{O_2}$$

$$- \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} \frac{b_{s'r}}{b_{s''r}}(logm_{s'} + log\gamma_{s'}) \tag{89}$$

Because EQ6 deals directly with the number of moles instead of the molality, it is useful for the purpose of deriving the Jacobian matrix to substitute eq (3) into eq (89) to obtain:

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$$log n_{s''} = \frac{log K_r}{b_{s''r}} - log\gamma_{s''} - \frac{b_{wr}}{b_{s''r}}(log x_w + log\lambda_w) - \frac{b_{s_B r}}{b_{s''r}} log f_{O_2}$$

$$- b_{T,r} log\Omega - log n_w - \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} \frac{b_{s'r}}{b_{s''r}}(log n_{s'} + log\gamma_{s'}) \tag{90}$$

Here we have that:

$$b_{T,r} = b_{s''r} + \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\phi} \tag{91}$$

Note that x_w appearing in eq (90) depends on the $n_{s'}$: This can be first expressed by the following equation:

$$log x_w = log\left(\frac{\Omega}{\Omega + \sum_{\substack{s'=1 \\ s' \neq w}}^{s_Q} m_{s'} + \sum_{s''=s_Q+1}^{s_T} m_{s''}}\right) \tag{92}$$

We could proceed by substituting eq (3) into eq (92) and then carry out partial differentiation. Instead, we will take a different route and use results that were obtained for EQ3NR. in Chapter 9 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b). There is was necessary to find the following:

$$W_{s'} = \frac{\partial log x_w}{\partial log m_{s'}}, \qquad s' \neq w, s_B \tag{93}$$

$$W_{s_B} = \frac{\partial log x_w}{\partial log f_{O_2}} \tag{94}$$

It was shown that:

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$$W_{s'} = \frac{-\frac{x_w}{\Omega}\left(m_{s'} - \sum_{s''=s_Q+1}^{s_T} \frac{b_{s'r}m_{s''}}{b_{s''r}}\right)}{\left(1 - \frac{x_w}{\Omega}\sum_{s''=s_Q+1}^{s_T} \frac{b_{wr}m_{s''}}{b_{s''r}}\right)}, \qquad s' \neq w, s_B \tag{95}$$

$$W_{s_B} = \frac{-\frac{x_w}{\Omega}\left(-\sum_{s''=s_Q+1}^{s_T} \frac{b_{s'r}m_{s''}}{b_{s''r}}\right)}{\left(1 - \frac{x_w}{\Omega}\sum_{s''=s_Q+1}^{s_T} \frac{b_{wr}m_{s''}}{b_{s''r}}\right)} \tag{96}$$

In EQ3/6, the $\underline{W}$ vector corresponds to the **dlogxw** array. It is computed by the EQLIB module **gdlgxw.f**. This module is called by the EQ6 module **matrix.f**.

For EQ6 the following related quantities are required:

$$\tilde{W}_{s'} = \frac{\partial log x_w}{\partial log n_{s'}}, \qquad s' \neq s_B \tag{97}$$

$$\tilde{W}_{s_B} = \frac{\partial log x_w}{\partial log f_{O_2}} \tag{98}$$

Note that a $\tilde{W}$ parameter is required for water. Using the chain rule and eq (3), it can be shown that:

$$\frac{\partial log x_w}{\partial log n_{s'}} = \frac{\partial log x_w}{\partial log m_{s'}}, \qquad s' \neq w, s_B \tag{99}$$

$$\frac{\partial log x_w}{\partial log n_w} = -\sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} \frac{\partial log x_w}{\partial log n_{s'}} \tag{100}$$

Therefore, the following results may be obtained:

$$\tilde{W}_w = -\sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} W_{s'} \tag{101}$$

$$\tilde{W}_{s'} = W_{s'}, \qquad s' \neq w \tag{102}$$

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The $\underline{\tilde{W}}$ vector is computed from $\underline{W}$ by the EQ6 module **matrxz.f**. Because of the near-identity of these vectors (only the entry for water differs), the former is also represented by the **dlogxw** array.

Partial differentiation of the mass balance equation gives the elements of the corresponding row of the Jacobian matrix: Using mass balances for basis species, the Jacobian elements are given by:

$$J_{s'w} = 2.303\left[u_{s'w}n_w + \sum_{s''=s_Q+1}^{s_T} \tilde{H}_{s'r}(b_{T,r} - b_{wr}\tilde{W}_w)\right] \tag{103}$$

$$J_{s's_B} = 2.303\left[-\sum_{s''=s_Q+1}^{s_T} \tilde{H}_{s'r}(b_{s_Br} + b_{wr}\tilde{W}_{s_B})\right] \tag{104}$$

$$J_{s's'''} = 2.303\left(u_{s's'''}m_{s'''} - \sum_{s''=s_Q+1}^{s_T} \tilde{H}_{s'r}(b_{s'''r} + b_{wr}\tilde{W}_{s'''})\right), \quad s' \neq w, s_B \tag{105}$$

where:

$$\tilde{H}_{s'r} = \frac{n_{s''}u_{s's''}}{b_{s''r}}, \quad s' = 1, s_Q, \quad s' \neq w \tag{106}$$

Note that $\tilde{H}_{s'r}$ is analogous to the $H_{s'r}$ used in EQ3NR. The difference is that the former is defined in terms of a number of moles variable instead of the corresponding molality. Note that $u_{s's'''} = 1$ if $s' = s'''$, otherwise $u_{s's'''} = 0$.

Using mass balances for chemical elements and taking the ε-th chemical element to be associated with the s'-th basis species, the Jacobian elements are given by:

$$J_{s'w} = 2.303\left[c_{\varepsilon w}n_w + \sum_{s''=s_Q+1}^{s_T} \tilde{H}_{s'r}(b_{T,r} - b_{wr}\tilde{W}_w)\right] \tag{107}$$

$$J_{s's_B} = 2.303\left[-\sum_{s''=s_Q+1}^{s_T} \tilde{H}_{s'r}(b_{s_Br} + b_{wr}\tilde{W}_{s_B})\right] \tag{108}$$

$$J_{s's'''} = 2.303\left(c_{\varepsilon s'''}m_{s'''} - \sum_{s''=s_Q+1}^{s_T} \tilde{H}_{s'r}(b_{s'''r} + b_{wr}\tilde{W}_{s'''})\right), \quad s' \neq w, s_B \tag{109}$$

where:

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$$\tilde{H}_{s'r} = \frac{n_{s''} c_{\varepsilon s''}}{b_{s''r}} \quad , \quad s' = 1, s_Q \ , \ s' \neq w \tag{110}$$

7.8.2. Electrical Balance

In the present version of EQ6, the fictive redox species O_2 (the s_B-th species) is formally associated with the charge balance equation. We will use a subscript z to denote items having to do with this equation. The treatment is closely analogous to that for a mass balance equation. The electrical charge z_s takes the place of the stoichiometric equivalence factor $u_{s's}$ or the composition coefficient $c_{\varepsilon s}$. The fixed charge imbalance (Δ_z; see Chapter 3) is included in the treatment. The governing equation can be written as:

$$\sum_{s'=1}^{s_Q} z_{s'} n_{s'} + \sum_{s''=s_Q+1}^{s_T} z_{s''} n_{s''} = \Delta_z \tag{111}$$

The corresponding residual functions are defined by:

$$\alpha_z = -\Delta_z + \sum_{s'=1}^{s_Q} z_{s'} n_{s'} + \sum_{s''=s_Q+1}^{s_T} z_{s''} n_{s''} \tag{112}$$

$$\beta_z = \frac{\alpha_z}{\sum_{s'=1}^{s_Q} |z_{s'}| n_{s'} + \sum_{s''=s_Q+1}^{s_T} |z_{s''}| n_{s''}} \tag{113}$$

The Jacobian elements are as follows:

$$J_{zw} = 2.303 \left[\sum_{s''=s_Q+1}^{s_T} \tilde{H}_{zr} (b_{T,r} - b_{wr} \tilde{W}_w) \right] \tag{114}$$

$$J_{zs_B} = 2.303 \left[- \sum_{s''=s_Q+1}^{s_T} \tilde{H}_{zr} (b_{s_B r} + b_{wr} \tilde{W}_{s_B}) \right] \tag{115}$$

$$J_{zs'''} = 2.303 \left(z_{s'''} m_{s'''} - \sum_{s''=s_Q+1}^{s_T} \tilde{H}_{zr} (b_{s'''r} + b_{wr} \tilde{W}_{s'''}) \right) , \qquad s' \neq w, s_B \tag{116}$$

where:

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$$\tilde{H}_{zr} = \frac{n_{s''} z_{s''}}{b_{s'' r}} \tag{117}$$

7.8.3. Mass Action For Pure Minerals

The governing mass action equation for pure minerals can be written as:

$$logK_{\phi} = b_{w\phi}(logx_w + log\lambda_w) + b_{s_B\phi} logf_{O_2} + \sum_{\substack{s' = 1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\phi}(logm_{s'} + log\gamma_{s'}) \tag{118}$$

The corresponding residual functions are defined by:

$$\alpha_{\phi} = -logK_{\phi} + b_{w\phi}(logx_w + log\lambda_w) + b_{s_B\phi} logf_{O_2} + \sum_{\substack{s' = 1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\phi}(logm_{s'} + log\gamma_{s'}) \tag{119}$$

$$\beta_{\phi} = \alpha_{\phi} \tag{120}$$

The residual function α_{ϕ} defined above is equivalent to the saturation index (*SI*).To facilitate the derivation of the corresponding elements of the Jacobian matrix, eq (87) can be written as:

$$\alpha_{\phi} = -logK_{\phi} + b_{w\phi}(logx_w + log\lambda_w) + b_{s_B\phi} logf_{O_2} + b_{T,\phi}(log\Omega - logn_w)$$

$$+ \sum_{\substack{s' = 1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\phi}(logn_{s'} + log\gamma_{s'}) \tag{121}$$

where:

$$b_{T,\phi} = \sum_{\substack{s' = 1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\phi} \tag{122}$$

Note that $b_{T,\phi}$ differs slightly in form from $b_{T,r}$: there is no term analogous to $b_{s'' r}$. Similar forms can be written for components of solid solutions and for gas species ($b_{T,\sigma\psi}$ and $b_{T,g}$ being defined analogously to $b_{T,\phi}$, not $b_{T,r}$).

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Each part of the equation for α_ϕ is now explicit in terms of the algebraic master variables, with one exception, the term in $log\ x_w$. The partial differentiation flowing through this term has been discussed previously. The corresponding Jacobian elements are as follows:

$$J_{\phi w} = -b_{T,\phi} + b_{w\phi}\tilde{W}_w \tag{123}$$

$$J_{\phi s_B} = b_{s_B\phi} + b_{w\phi}\tilde{W}_{s_B} \tag{124}$$

$$J_{\phi s'} = b_{s'\phi} + b_{w\phi}\tilde{W}_{s'} \quad , \ s \neq w, \ s_B \tag{125}$$

7.8.4. Mass Action For End Member Components Of Solid Solutions

The governing mass action equation for the σ-th end member component of the ψ-th solid solution is:

$$logK_{\sigma\psi} = b_{\sigma\psi\sigma\psi}(logx_{\sigma\psi} + log\lambda_{\sigma\psi}) + b_{w\sigma\psi}(logx_w + log\lambda_w)$$

$$+ b_{s_B\sigma\psi}logf_{O_2} + \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\sigma\psi}(logm_{s'} + log\gamma_{s'}) \tag{126}$$

The corresponding residual functions are defined by:

$$\alpha_{\sigma\psi} = -logK_{\sigma\psi} + b_{\sigma\psi\sigma\psi}(logx_{\sigma\psi} + log\lambda_{\sigma\psi}) + b_{w\sigma\psi}(logx_w + log\lambda_w)$$

$$+ b_{s_B\sigma\psi}logf_{O_2} + \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\sigma\psi}(logm_{s'} + log\gamma_{s'}) \tag{127}$$

$$\beta_{\sigma\psi} = \alpha_{\sigma\psi} \tag{128}$$

Here $x_{\sigma\psi}$ is the mole fraction of the end member component and $\lambda_{\sigma\psi}$ is the corresponding activity coefficient. The residual function $\alpha_{\sigma\psi}$ defined above is again equivalent to the saturation index (*SI*). For the purpose of deriving the corresponding elements of the Jacobian matrix, it is more convenient to write the equation for this residual function in the form:

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$$\alpha_{\sigma\psi} = -\log K_{\sigma\psi} + b_{\sigma\psi\sigma\psi}(\log x_{\sigma\psi} + \log\lambda_{\sigma\psi}) + b_{w\sigma\psi}(\log x_w + \log\lambda_w)$$

$$+ b_{s_B\sigma\psi}\log f_{O_2} + b_{T,\sigma\psi}(\log\Omega - \log n_w) + \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\sigma\psi}(\log n_{s'} + \log\gamma_{s'}) \quad (129)$$

where:

$$b_{T,\sigma\psi} = \sum_{\substack{s'=1 \\ s' \neq w, s_B}}^{s_Q} b_{s'\sigma\psi} \quad (130)$$

Each part of the equation for $\alpha_{\sigma\psi}$ is now explicit in terms of the master iteration variables, with two exception, the terms in $\log x_w$ and $\log x_{\sigma\psi}$. We have dealt previously with the flow of partial differentiation through the former, and will now deal with it through the latter.

The mole fraction of the end member component can be written as:

$$x_{\sigma\psi} = \frac{n_{\sigma\psi}}{\sum_{i=1}^{\sigma_{T,\psi}} n_{i\psi}} \quad (131)$$

where $\sigma_{T,\psi}$ is the number of end member components in the ψ-th solid solution. It follows that:

$$\frac{\partial \log x_{\sigma\psi}}{\partial \log n_{\sigma\psi}} = 1 - x_{\sigma\psi} \quad (132)$$

$$\frac{\partial \log x_{\sigma\psi}}{\partial \log n_{i\psi}} = -x_{i\psi} \quad (133)$$

The Jacobian elements are as follows:

$$J_{\sigma\psi w} = -b_{T,\sigma\psi} + b_{w\sigma\psi}\tilde{W}_w \quad (134)$$

$$J_{\sigma\psi s_B} = b_{s_B\sigma\psi} + b_{1\sigma\psi}\tilde{W}_{s_B} \quad (135)$$

$$J_{\sigma\psi s'} = b_{s'\sigma\psi} + b_{1\sigma\psi}\tilde{W}_{s'}, \quad s \neq w, s_B \quad (136)$$

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$$J_{\sigma\psi\sigma\psi} = b_{\sigma\psi\sigma\psi}\left((\Lambda_{\sigma\sigma\psi} + 1)\ (1 - x_{\sigma\psi}) - \sum_{\substack{i=1 \\ i \neq \sigma}}^{\sigma_{T,\psi}} \Lambda_{\sigma i\psi} x_{i\psi} \right) \tag{137}$$

$$J_{\sigma\psi j\psi} = b_{\sigma\psi\sigma\psi}\left(- x_{j\psi} + \Lambda_{\sigma j\psi} 1 - x_{j\psi} - \sum_{\substack{i=1 \\ i \neq j}}^{\sigma_{T,\psi}} \Lambda_{\sigma i\psi} x_{i\psi} \right) \tag{138}$$

where:

$$\Lambda_{\sigma i\psi} = \frac{\partial log \lambda_{\sigma\psi}}{\partial log n_{i\psi}} \tag{139}$$

These $\Lambda_{\sigma i\psi}$ parameters are specific to the solid solution thermodynamic models being employed. For examples, see Wolery (1979) where the notation uses "S" in place of Λ. The presence of such factors in the Jacobian matrix places the correction of activity coefficients of solid solution components in Newton-Raphson iteration; i.e., these activity coefficients are not corrected in the same manner as those of aqueous species.This is likely to be changed in a future version of EQ6.

7.9. Find Phases to Precipitate to Satisfy Partial Equilibrium

Each hybrid Newton-Raphson calculation requires that a phase assemblage be specified in advance. EQ6 finds the correct phase assemblage by making a sequence of calculations in which the phase assemblage is changed from calculation to calculation using algorithms previously described by Wolery (1979).

If such a Newton-Raphson calculation converges, EQ6 searches for cases of supersaturation, the extent of which is measured by the precipitation affinity ($A_{-,j}$, where j denotes a phase such as the ϕ-th pure mineral or the ψ-th solid solution. Phases which are suppressed or whose affinity functions are less than a specified tolerance (**tolsst**) are ignored. The code picks one supersaturated phase, adds it to the phase assemblage, and tries again. In principle, more than one such phase could be added simultaneously, but it is not generally profitable to do so. The number of supersaturations may far exceed the number of new phases that actually need to be precipitated. This is because precipitation of a phase reduces not only its own affinity, but also the affinities of other phases that are made of the same components.

EQ6 chooses the phase to be added as the one with the greatest scaled precipitation affinity. The scaled affinity is calculated by dividing the standard affinity by a scaling factor:

$$A_{-,j,scaled} = \frac{A_{-,j}}{b_{j,scale}} \tag{140}$$

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The scaling factor is arbitrarily defined as the sum of the absolute values of the reaction coefficients:

$$b_{j,scale} = \sum_{s'=1}^{s_Q} |b_{s'j}| \tag{141}$$

Other definitions (i.e., the sum of the molecular weights of the species appearing in the reaction, the number of atoms appearing in the reaction) are possible and might work as well. The justification for scaling is that it improves the probability, as shown by experience, of choosing the right phases. About 80% or more of the choices are correct when there is a large number of supersaturations, say twenty or more, and the figure gets better when there are only a few. Scaling helps because it tends to remove a bias in the unscaled affinity that favors phases with large molecular formulas, such as clay minerals.

EQ6 also must occasionally delete phases from the phase assemblage. This is needed in part because the algorithm for choosing phases to precipitate is not 100% accurate. This capability is also needed in reaction path calculations, where a phase in the equilibrium system may become exhausted.

There are two paths in EQ6 leading to deletion from the phase assemblage. One occurs when the matrix is singular at the start of the iteration, indicating that the phase assemblage being tried probably violates the so-called "apparent" or "mineralogic" phase rule (Wolery, 1979). In this case, EQ6 looks for linear dependence in the rows of the Jacobian that describe heterogeneous equilibria (e.g., mineral solubilities). If such dependence is found, the code calculates conditional affinities for the phases involved, scales them, and deletes the phase with the most negative scaled conditional affinity.

A "conditional" affinity is the affinity of a phase which is uniquely determined by mutual solubility for a subset of other phases. Violation of the mineralogic phase rule means that such subsets exist. Mathematically, conditional affinities can always be defined for linearly dependent sets. For example, if a solution is in equilibrium with cristobalite (a form of SiO_2), this is sufficient to fix the affinity of quartz, its polymorph. See Wolery (1979) for further discussion of this topic.

In the second path, the iteration proceeds for one or more iterations and subsequently diverges. Divergence generally is due to one of the following conditions: (a) a mineral should be deleted, (b) the starting value for the oxygen fugacity is too far off the mark, or (c) the system is so ill-poised that the oxygen fugacity can not be defined with acceptable precision. Experience with the code shows that the use of the convergence enhancement features described earlier usually limits the possibilities to one of these.

EQ6 analyzes the situation to determine what action to take in response to divergence. It uses four independent algorithms to attempt to pick candidate phases for deletion. An object function (O_{nj}) is calculated for the n-th algorithm and the j-th phase in the assemblage. Each algorithm produces a candidate phase for removal from the phase assemblage. This is the phase with the most negative value of the object function for that algorithm. This value (denoted simply as O_n) must be negative, otherwise no candidate is produced. The overall choice for deletion, if any, is

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the candidate among the possible four with the most negative object function. EQ6 deletes this phase, unless it determines that the problem lies instead with the redox variable and takes other corrective action (see below).

One of the four deletion algorithms referred to above is much more important than the other three. Recall that one of the under-relaxation controls (**screw5**) limits the magnitude of the Newton-Raphson correction terms. This causes the calculation to diverge more slowly than it would otherwise. If a mineral does not belong in the phase assemblage, the strongest indication of this, after a mineralogic phase rule violation, is that its logarithmic mass variable plunges downward. The corresponding correction term commonly approaches a value of -**screw5** (the **screw5** default is 4.0, so this value is usually -4.0) before the matrix becomes numerically singular and the iteration crashes. The object function for the j-th phase for the first algorithm is:

$$O_{1,j} = logn_{j,k} - logn_{j,0} \tag{142}$$

where $logn_{j,k}$ is the value of $logn_j$ at the last successful (k-th) iteration and $logn_{j,0}$ is the value prior to the start of iteration.

The other three algorithms were programmed into EQ6 prior to the full development of the convergence enhancement techniques that are now in the code. No study has been made of their significance to the operation of the code in its present state. Casual observation suggests that their current role may be largely vestigial. See Wolery (1979) for a description of these algorithms.

If the starting value of the oxygen fugacity variable is more than about five log units away from the correct value, experience has shown that convergence is not highly probable. This divergence tends to show up most strongly in the correction term for the log oxygen fugacity variable. Commonly, this correction term is at or near either ±**screw5** the last couple of iterations. This condition indicates that a better value for the starting value of this variable is required. The code goes into the redox scan mode in an attempt to find a good starting value if the magnitude of the last correction term for the log oxygen fugacity variable is **screw5**. This condition overrides any choice for phase deletion.

If the correction terms for the log oxygen fugacity variable oscillate in sign with magnitudes of the order of **screw5**, the system is probably ill-poised. If the residual functions have small magnitudes at this point, ill-poising is almost a certainty. The problem then is that the oxygen fugacity is so sensitive to the masses of the components in the system that the addition or subtraction of even one molecule of O_2 per kilogram of solvent can change the oxygen fugacity by orders of magnitude (or the corresponding Eh by hundreds of millivolts). An extremely ill-poised system causes trouble in the calculation because the machine floating point precision, even at 64 bits, is insufficient to handle the situation.

There are two methods of trying to deal with this condition. One would be to accept the results of the iteration process if the residual functions are all close to zero, even if the correction terms are not. The code presently does not do this. The second way, which the code does employ, is to assume that the ill-poising is limited to a very narrow range of reaction progress (encountered at a so-called redox jump), and make several attempts to step over it, using the redox scan feature to pick up the calculation on the other side of the jump.

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7.10. The Redox Scan Feature

The redox scan feature is used to try to generate a starting value for the log oxygen fugacity variable that will lead to convergence. As noted above, the starting value normally must be within about five log units to obtain convergence. A redox scan is a sequence of Newton-Raphson calculations with increasing or decreasing starting values for this variable. It terminates when either convergence is achieved or the whole range of the stability of water at the specified temperature and pressure has been covered.

The upper range of the stability field of water is taken to correspond to an oxygen fugacity of 1 bar. Thus:

$$logf_{O_2}\{upper\ \ limit\} = 0 \tag{143}$$

The lower range is taken to correspond to a hydrogen fugacity of one bar and is determined by reference to the reaction:

$$2H_{2\,(g)} + O_{2\,(g)} = 2H_2O_{\,(l)} \tag{144}$$

The corresponding mass action equation can be written as:

$$logf_{O_2} = -\,logK_{H_{2\,(g)}} - 2logf_{H_2} + 2log\,a_w \tag{145}$$

The lower limit is calculated by assuming that $log\,a_w = 0$. Thus,

$$logf_{O_2}\{lower\ \ limit\} = -logK_{H_{2\,(g)}} \tag{146}$$

At 25°C and 1.013 bar pressure, it has a value of about -83.1. It decreases in magnitude as the temperature is raised.

The above limits are what is in the present version of EQ6. They are calculated assuming a pressure limit of 1 bar and unit fugacity coefficients. For the purposes of establishing scan limits, assuming unit fugacity coefficients is not likely to be of much concern. However, the pressure limit should match the actual pressure (P), which may be considerably more than 1 bar. Thus, a better set of scanning limits would be:

$$logf_{O_2}\{upper\ \ limit\} = logP \tag{147}$$

$$logf_{O_2}\{lower\ \ limit\} = -logK_{H_{2\,(g)}} - 2logP \tag{148}$$

For P = 1000 bars, the upper limit of the scanning range would be increased by 3 log units, and the lower limit would be decreased by 6 log units. This is probably marginal in terms of affecting the outcome of the scanning process.

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8. Reaction Path Calculational Methods

8.1. Introduction

This chapter discusses the calculational methods that apply to reaction paths, apart from those used to make thermodynamic calculations. There are four topics to be covered. The first is continuous representation of the algebraic master variables (the vector $\underset{\sim}{z}$) with respect to reaction progress (ξ) by means of finite differences. This leads into the second topic, how EQ6 locates phase boundaries and other points of reaction progress at which something of interest occurs. A "phase boundary" in the sense used here is a point of reaction progress at which a phase appears or disappears. The third topic is the integration of the rate equations, which leads into the final topic, the finite difference representation of rate functions and how this is used to numerically integrate these ODEs.

In this chapter much use will be made of truncated Taylor's series. Such a series for a function $y(x)$ has the form:

$$y(x) = y(x_0) + \sum_{n=1}^{i} \frac{1}{n!} \left(\frac{d^n y}{dx^n} \right)_0 (x - x_0)^n \tag{149}$$

where x is any point, x_0 is a point at which the derivatives in the summation are evaluated, and i is the order of the series. An example of such a truncated Taylor's series is the representation of relative rates as a function of ξ discussed in Chapter 3.

The form of a truncated Taylor' series can be useful even if one does not have expressions for the necessary derivatives. One can estimate them using finite differences. If a calculation is proceeding along a sequence of points on the x axis, a finite difference equation can be used to make an equivalent prediction of the value of y at some new point, called x, using the values of y at the k most recent points. Here x_0 is the closest point, x_{-1} is the point immediately preceding it, and $x_{-(k+1)}$ is the point which is farthest back. The order of the calculation, i, is k - 1. A true finite difference function does not have the form of a truncated Taylor's series, but it is mathematically equivalent to one. See Carnahan, Luther, and Wilkes (1969) or any other introductory numerical methods text for a detailed introduction to finite differences.

Corresponding to the i derivatives of order 1 through i are i finite differences of order 1 through i. This is not a one-to-one correspondence, however. The finite differences are defined by the following equations:

$$f_0^{(0)}[y] = \frac{(y_0 - y_{-1})}{(x_0 - x_{-1})} \tag{150}$$

$$f_0^{(n+1)}[y] = \frac{(f_0^{(n)}[y] - f_{-1}^{(n)}[y])}{(x_0 - x_{-(n+1)})} \tag{151}$$

Here the superscript in parentheses denotes the order, the subscript denotes the point to which the differences correspond, and the symbol in the brackets denotes the function which is being treat-

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ed. Note the element of recursion in eq (151): finite differences of order greater than one at the most recent point (x_0) can be calculated from the finite differences at the immediately preceding point (x_{-1}), and so forth.

It is possible to use the following equation to estimate y as a function of x from these finite differences:

$$y(x) = y(x_0) + (x - x_0) \sum_{n=1}^{i} f_0^{(n)} [y] \prod_{j=1}^{n} (x - x_j) \tag{152}$$

This finite difference representation is one possible basis for deriving quadrature formulas for the numerical integration of ODEs (See for example Carnahan, Luther, and Wilkes, 1969). An equivalent representation, the Lagrangian, is more popular for deriving quadrature formulas and is more likely to be encountered by the reader in surveying such formulas in the literature. Instead of recording the information at previous points in the form of finite differences, it does so in the form of the values of y at those points. The approach used in EQ6 is based on storing finite differences, because it is easy to translate these functions into the derivatives appearing in an equivalent truncated Taylor's series. For further information on the Lagrangian representation and quadrature methods based on it, see Carnahan, Luther, and Wilkes (1969) or any other text dealing with numerical integration of ODEs.

EQ6 converts finite differences into the equivalent truncated Taylor's series primarily because the differential and integral forms are simpler and easier to manipulate. These truncated Taylor's series are used to represent the vector $\underline{z}$ of algebraic master variables in all modes and also, in time mode, the relative rates of the reactants and the inverse rate. This treatment of the algebraic master variables does not involve numerical integration; it is used only to provide a continuous representation of these variables. The treatment involving relative rates and the inverse rate is used for purposes of both continuous representation and numerical integration.

An array of finite differences ($\underline{f}$) whose elements increase in order from 1 to i can be converted into the equivalent array of derivatives ($\underline{d}$) by the simple linear transformation:

$$\underline{d} = \underline{D}\underline{f} \tag{153}$$

where $\underline{D}$ is an upper triangular matrix (Wolery, 1979). To construct this matrix, it is first convenient to define an array $\underline{w}$ of the same length as $\underline{d}$ and $\underline{f}$, where each element is defined by:

$$w_n = x_0 - x_{-n} \tag{154}$$

The matrix $\underline{D}$ being upper triangular, all the diagonal elements are ones and all elements in the lower triangle are zero. The following recursions permit calculation of the off-diagonal elements in the upper triangle. For the first row, we have that:

$$D_{1,n} = D_{1,n-1} w_n \tag{155}$$

where n goes from 2 to i. The remaining elements may be calculated from the following recursion formula:

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$$D_{m,n} = D_{m,n-1} w_n + D_{m-1,n-1} \quad , \; m = 2, \; i-2, \; n = m+1, \; i \tag{156}$$

The error in a truncated Taylor's series is usually estimated as a function of the step size, Δx (= $x - x_0$), from the magnitude of the first neglected term. Such an error expression is used to derive an algorithm for bounding the step size so as to keep the estimated error within some predetermined limit. In many finite difference algorithms, therefore, an estimate is constructed of this extra term. In EQ6, however, the last term in the truncated series is used instead, which has the effect of using a more conservative bound. Therefore, letting m be the order of the term used to estimate the error ($m = i$ in EQ6, $m = i + 1$ in the more traditional treatment):

$$Error\,[y] \cong \frac{1}{m!} \left(\frac{d^m y}{dx^m} \right)_0 (\Delta x)^m \tag{157}$$

where *Error [y]* is the error in y. Requiring Δx to satisfy the condition:

$$|Error\,[y]| \leq Tolerance\,[y] \tag{158}$$

where *Tolerance [y]* is the required error tolerance on y, leads to the following limit on the step size:

$$\Delta x \leq \left(\frac{m!\; Tolerance\,[y]}{\left(\frac{d^m y}{dx^m} \right)_0} \right)^{\frac{1}{m}} \tag{159}$$

(See discussion of the setscrew variables **screw1** and **screw3** in Chapter 5.) The finite differences in EQ6 range up to order six. The order is initially zero, and must be reset to zero at points where the derivatives being represented are discontinuous. Discontinuities occur at phase boundaries for secondary phases in equilibrium with the aqueous solution, and at points where primary reactants become exhausted. Otherwise, the order progressively builds up to a maximum of six. The order itself is actually computed following the treatment of Gear (1971ab). The above equation for determining the step size is used to test each of the possible orders. The order chosen is that which gives the largest step size satisfying the specified error tolerance.

It will be understood in the following discussion that the term "finite difference representation" refers to expressions which in EQ6 usually in fact take the form of truncated Taylor's series, the derivatives for which have been estimated by means of finite differences. There are a few places in the code in which the first order difference function is used as a "two point" derivative, regardless of the actual order used for the truncated Taylor's series.

8.2. Finite Difference Representation of Algebraic Master Variables

Finite difference representations of the algebraic master variables permit forecasting or prediction of the values of these variables at a new point of reaction progress from knowledge of their values at immediately preceding points. There are multiple usages of the capabilities afforded by

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such representations of these quantities. One usage in EQ6 is to use these predicted values as starting estimates for the Newton-Raphson calculation at the new point. Experience has shown that this can be quite useful, usually giving better starting values than would be obtained by using the values at the last point of reaction progress. This is not always the case, however. If an algebraic master variable is changing quite radically, as happens for example in the case of the oxygen fugacity at a redox jump, the predicted values may be poorer starting estimates, even at relatively small step sizes. It is then necessary or desirable to drop the order to zero.

The finite difference representations of algebraic master variables have other uses, however. They can be used to predict the locations of interesting points. Such points include phase boundaries, at which minerals appear in or disappear from the equilibrium system. They also include points corresponding to maxima in the number of moles of secondary minerals in the equilibrium system, which are of interest in the fluid-centered flow-through mode. The finite difference representations can also be used as part of a search algorithm to find the exact location of such events (*a priori* predictions carry an element of inaccuracy). Furthermore, they provide a means for restricting the step size so as to provide greater information density in a region in which a quantity of interest, such as the oxygen fugacity or the number of moles of a mineral in the equilibrium system, is changing rapidly. The accuracy criterion described above tends to increase information density in such regions, but it is not reliable for this purpose.

The basic idea is to represent the k-th algebraic master variable by a truncated Taylor's series:

$$z_k(\xi) = z_k(\xi_0) + \sum_{n=1}^{i} \frac{1}{n!} \left(\frac{d^n z_k}{d\xi^n} \right)_0 (\Delta\xi)^n \tag{160}$$

where ξ is a point of reaction progress, ξ_0 is the most recent point at which the calculation has been completed, i is the order of the truncated series, the derivatives pertain to point 0 (ξ_0), and $\Delta\xi$ ($= \xi - \xi_0$) is the step size. The derivatives are estimated from finite differences, using the equations given previously to calculate the differences themselves. These results are then converted to derivative form by the linear transformation given above.

The $\underline{z}$ vector used in the thermodynamic calculations consists of logarithmic quantities. The finite difference representation of an algebraic master variable in EQ6, however, may be in terms of either the same logarithmic quantity (element of the **zvclg1** array) or the corresponding "linear" quantity (element of the **zvec1** array). Only elements corresponding to aqueous basis species can presently be represented by logarithmic quantities, so those corresponding to mineral species in the equilibrium system are always linear (i.e., numbers of moles). Which representation is used for aqueous basis species depends on the user and perhaps the floating point characteristics of the machine. If **iopt8** = -1, linear variables are represented; if **iopt8** = 1, logarithmic variables. If **iopt8** = 0, linear variables are used unless the exponent range of the machine is less than +100.

Truncated Taylor's series can be used to locate maxima in the number of moles minerals in the equilibrium system. This function is necessary in the fluid-centered flow-through model in order to locate phase disappearance boundaries. Recall that the maximum of a function on an interval is either at one of the ends of the interval or at a point within the interval at which the derivative is zero. Differentiation of eq (160) yields the following result:

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$$\frac{dz_k(\xi)}{d\xi} = \sum_{n=1}^{i} \frac{1}{(n-1)!} \left(\frac{d^n z_k}{d\xi^n}\right)_0 (\Delta\xi)^{n-1} \tag{161}$$

This is a truncated Taylor's series of one less order.

8.3. Locating Phase Boundaries and Other Points of Interest

Finding the value of reaction progress corresponding to a point of interest, such as a phase boundary, is an activity which can make good use of the finite difference representation of algebraic master variables. However, this representation is often not sufficiently accurate to locate such a value to within desired tolerances. The accuracy requirement imposed in choosing the order and maximum allowable step size is not sufficiently reliable to ensure that points of interest can be found with needed accuracy. Therefore, something additional is required. This is a larger search algorithm which encompasses the use of finite difference representation.

Consider the case of finding a phase boundary at which a mineral appears in the equilibrium system. At immediately preceding points of reaction progress, the affinity to precipitate is negative, indicating that the aqueous solution is undersaturated with this phase. However, the affinity is increasing at the base point (the most recent point of reaction progress). Given a step size determined by other considerations (such as the accuracy requirement, but possibly other, more restrictive requirements that have already been dealt with), one can use the finite difference representation of the algebraic master variables to predict the affinity to precipitate at the new value of reaction progress. If the predicted value fails to exceed a tolerance value (the **input** file variable **tolsat**), EQ6 ignores the supersaturation. If it exceeds a second, higher tolerance (the **input** file variable **tolsst**), EQ6 uses the finite difference representations to find the value of reaction progress at which the predicted affinity is mid-way between these two tolerances. The variable **tolsat** has a default value of 0.0005 kcal if **iopt4** = 0 (no solid solutions), of 0.005 kcal if **iopt4** = 1 (solid solutions). This type of phase boundary search and other searches are directed by the EQ6 module **search.f**, which employs a "higher order" extension of the secant method and also under certain circumstances employs an interval halving method.

Because of the inaccuracy inherent in the use of backward finite differences, it is possible that the actual affinity, determined by a thermodynamic calculation, at such a predicted phase boundary, does not lie between the two tolerances. If it lies below the lower tolerance, the solution is not sufficiently supersaturated at the new point and the phase boundary has not been reached. However, the new point becomes the base point. Hence the finite difference representation becomes more accurate closer to the actual phase boundary, and the next predicted value of the phase boundary will be more accurate. If the actual affinity exceeds the upper tolerance, the phase boundary has been stepped over and the step size is cut by a predetermined factor until this condition is no longer the case. A series of such cuts will either result in hitting the phase boundary or moving the base point closer to the phase boundary. The same action takes place if the code oversteps a phase boundary, having failed to predict it in the first place.

The same general scheme is also employed to find other points of interest. These include phase boundaries at which minerals in the equilibrium system disappear (the special case of such boundaries in the fluid-centered, flow-through open system mode is discussed below), points at which reactants saturate (which are also normal phase appearance boundaries), points at which

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reactants are exhausted, points at which the temperature crosses 100°C (which is significant because the set of polynomials for approximating thermodynamic data changes), and points at which relative rates change sign (because different rate laws may govern net mass transfer in the opposite direction). Not all of these cases involve finite difference representation of algebraic master variables. They may involve instead arbitrary expressions (e.g., a polynomial for temperature) or finite difference representation of rate functions (which is discussed in the following section). Some functions of the code also limit the step size to satisfy an arbitrary constraint, such as a predetermined limit on the predicted change in some quantity, such as the oxygen fugacity. These exist primarily for the purpose of ensuring information density in desired regions and do not employ the "go back" feature.

In the fluid-centered flow-through open system mode, minerals precipitating in the equilibrium system must be protected from redissolving. In the case of pure minerals, this can be treated rigorously by keeping the entire precipitated mass of such minerals in contact with the aqueous solution (i.e., in the equilibrium system) until the mass (as measured by the number of moles) starts to decline. In practice, however, periodic transfers of mass to the physically removed system are made anyway. In theory, when the mass of such a mineral maximizes, all of the remaining mass is transferred and the mineral is not present (does not grow) in the equilibrium system as reaction progress is further advanced. Thus, such a point is a kind of phase boundary in which the phase disappears. In the case of solid solutions, the maximum criterion is necessary applied to either the phase itself or its components, but the criterion is not rigorously sufficient to represent the effects of the aqueous fluid leaving its solid products behind. This is because the composition of the solid solution may evolve along the reaction path, but allowing any precipitated mass to remain in the equilibrium system allows mixing of newly precipitated component mass with previously precipitated mass. Using the fluid-centered flow-through open system with solid solutions therefore depends on making periodic partial transfers of mass to the physically removed system in order to maintain a correct representation. The user-defined "dump interval," specified by the input file parameter **dlzidp**, can be used to insure such periodic transfers. If **iopt4** = 0 (no solid solutions), the default value of this variable is 1×10^{38} (pseudo-infinite). If **iopt4** = 1 (solid solutions), its default value is the smaller of the values for the linear print and plot variables.

The effect of a transfer to the physically removed system on the finite difference representation depends on whether a shift is partial or total. If a mineral is entirely shifted, a mass action constraint is lost and the order of the method must drop to zero before stepping out to a new point of reaction progress. If only part of the mass of a mineral is so shifted, the order does not have to be dropped to zero. The corresponding elements of the $\underline{z}$ vector are changed, but the values of the derivatives are not.

In general, phase disappearance boundaries in the fluid-centered flow-through open system model are detected and accurately located using finite-difference representation (or in the case of solid solutions calculation dependent on such representation) of the number of moles of the phase in the equilibrium system. This occurs in two ways. The first is by detection of predicted location of maxima, using the truncated Taylor's series representation of the derivative of the number of moles of a phase with respect to reaction progress. If a predicted maximum is found, the step is made, and a thermodynamic calculation yields a calculated value of the mass at the new point. This is compared with the value at the previous point. If the mass destroyed exceeds a tolerance

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(10^{zklogu} moles), then the phase boundary has been overstepped. A "go back" instruction is issued, and a partial transfer of mass to the physically removed system is made at the base point before stepping out again. Unlike the case in other "go back" situations, the step size is not cut. It is possible for such a phase disappearance boundary to be overstepped without having been detected by means of analysis based on finite difference representations. The course of action is the same. The code's primary objective is to prevent redissolving a mass exceeding the tolerance (which can be set on the **input** file; the default value of **zklogu** is -6.0 if **iopt4** = 0, -7.0 if **iopt4** = 1). Repetitive use of the "go back" instruction guarantees that this objective can be met. The code does not otherwise adjust the step size to locate the boundary more precisely.

Various events may occur which cause the derivatives of the algebraic master variables to be discontinuous. For example, a reactant may stop dissolving because it has saturated or become exhausted (other events of interest that are searched for), or the phase assemblage in the equilibrium system may change. In such cases, the order of the finite differences must be dropped to zero. By stepping out one point (at the small zero order step size), a "two point" estimate of the derivatives of the number of moles of the minerals in the equilibrium system is possible. If this estimate is negative for any such mineral, it is no longer forming. The remaining mass in the equilibrium system is transferred in its entirety to the physically removed system.

8.4. Integrating Rate Equations

The rate equations which must be integrated are expressed as truncated Taylor's series. These include the relative rate ($d\xi_j/d\xi$ or v_j^{rel}) of each irreversible reaction and, in time mode, the inverse rate ($dt/d\xi$ or $v_{1/t}$). In reaction progress mode, relative rates are described by truncated Taylor's series specified by the user. In time mode, the relative rates and the inverse rate are described by truncated Taylor's series that are based on a finite difference representation like that described previously for the algebraic master variables. In order to obtain new values for the total number of moles of the components at a new point of reaction progress, one must obtain $\Delta\xi_j$ by integrating the relative rate of each irreversible reaction ($d\xi_j/d\xi$) from ξ_0 to ξ, If the code is operating in time mode, the inverse rate ($dt/d\xi$) must also be integrated to obtain the time increment, Δt.

The relative rate of the j-th irreversible reaction can be written in the form of a truncated Taylor's series:

$$v_j^{rel}(\xi) = v_j^{rel}(\xi_0) + \sum_{n=1}^{i} \frac{1}{n!}\left(\frac{d^n v_j^{rel}}{d\xi^n}\right)_0 (\Delta\xi)^n \tag{162}$$

The corresponding integrated form is given by:

$$\Delta\xi_j = v_j^{rel}(\xi_0)\Delta\xi + \sum_{n=1}^{i} \frac{1}{(n+1)!}\left(\frac{d^n v_j^{rel}}{d\xi^n}\right)_0 (\Delta\xi)^{n+1} \tag{163}$$

In reaction progress mode, the relative rate of each irreversible reaction is arbitrarily defined in the form of a truncated Taylor's series (see Chapter 3). In this case, the above integration yields an exact result. In time mode, relative rates are calculated from actual rate laws (see Chapter 3).

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The truncated Taylor's series representation of the corresponding relative rates is generated using finite differences. In this case, the above integration does not yield an exact result, and it is necessary to restrict the step size to control the error.

The inverse rate is also represented by a truncated Taylor's series:

$$v_{1/t}(\xi) = v_{1/t}(\xi_0) + \sum_{n=1}^{i} \frac{1}{n!} \left(\frac{d^n v_{1/t}}{d\xi^n} \right)_0 (\Delta\xi)^n \tag{164}$$

The corresponding integrated form is given by:

$$\Delta t = v_{1/t}(\xi_0)\,\Delta\xi + \sum_{n=1}^{i} \frac{1}{(n+1)!} \left(\frac{d^n v_{1/t}}{d\xi^n} \right)_0 (\Delta\xi)^{n+1} \tag{165}$$

The inverse rate is calculated from the actual rate laws (see Chapter 3). Hence, the truncated Taylor's series representation is not exact, and the step size must be restricted to maintain accuracy.

True kinetic modeling requires the actual integration of differential equations, and except for the case where the rates are defined as functions of only a time variable, this integration must be accomplished numerically. In EQ6, the finite difference functions described above act as predictor functions that are essentially equivalent to those in the Gear (1971ab) method. Unlike the case of algebraic master variables, any "correction" step must be made using corrector functions based on finite differences.

The need for a corrector cycle for the rate functions must be determined after the Newton-Raphson iteration does the "correcting" of the algebraic master variables. The code then evaluates the rate laws at the new point of reaction progress (ξ), using the corrected algebraic variables, and compares the resulting values with the values that were predicted from eqs (162) and (164). If the corresponding rate values differ by more than a specified tolerance, some corrective action is initiated. This may be either a corrector cycle, in which the finite difference representations used in the integrations represented by eqs (163) and (165) are improved, using the tentative calculated rate information at the new point, or a cut in the step size. The present version of EQ6 does not include coding for making corrector cycles. The only course of action is to cut the step size.

A simple i-th order corrector function can be generated by dropping the i+1-th point and adding the point just stepped to. Resetting the indexing of the points so that ξ becomes ξ_0, ξ_0 becomes ξ_{-1}, etc. (dropping the last point), the finite differences may be recalculated using eqs (150) and (151). The rates at the latest point are taken to be the provisional values that were calculated by evaluating the rate laws. The $\underline{w}$ array must be updated, the $\underline{D}$ matrix recalculated, and the new finite differences converted to derivative form by applying eq (153). This brings us back to the level of eqs (162) and (164). The integration is made over the same limits, but the point indexing has changed. Hence, the following equations must be used instead to compute the corrected individual extents of reaction progress and the time increment:

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$$\Delta\xi_j = v_j^{rel}(\xi_1)\Delta\xi + \sum_{n=1}^{i} \frac{1}{(n+1)!}\left(\frac{d^n v_j^{rel}}{d\xi^n}\right)_0 (-\Delta\xi)^{n+1} \tag{166}$$

$$\Delta t = v_{1/t}(\xi_1)\Delta\xi + \sum_{n=1}^{i} \frac{1}{(n+1)!}\left(\frac{d^n v_{1/t}}{d\xi^n}\right)_0 (-\Delta\xi)^{n+1} \tag{167}$$

Further correction cycles can be made in like manner. The only difference is that the point indices are not shifted again. A general rule of thumb is that if two corrector cycles are not sufficient, the step size should be cut.

The simple corrector described above is based on back-substitution and should give first order convergence behavior. This is not satisfactory in the case of "stiff" ODEs (See for example Carnahan, Luther, and Wilkes, 1969, or Gear, 1971ab). The practical definition of stiff equations is that they require a second-order method for corrector iteration (most such correctors are based on the Newton-Raphson method). See Gear (1971ab) for a discussion of corrector functions for stiff equations. It will probably become necessary to incorporate such functions into EQ6.

8.5. A More Economical Approach to Equilibrium Step Calculations

When the finite difference representation of algebraic master variables is kept generally accurate, EQ6 functions very analogously to the two "souped-up" versions of the old PATHI program noted in Chapter 1, both of which followed the differential equations approach and integrated by means of the Gear (1971ab) variable step-size, variable order, predictor-corrector method. The EQ6 finite-difference functions for algebraic master variables are predictor functions equivalent to the Gear predictors, but EQ6 "corrects" these predictions by means of the Newton-Raphson calculation to satisfy the governing algebraic equations (e.g., mass balance, mass action). The Gear corrector functions correct the predicted values to satisfy the differential counterparts of these governing equations. Better results are obtained with the EQ6 approach, but the cost of a run is about the same, and can be relatively high in terms of one's computing resources.

A question of considerable importance in terms of the cost of reaction path calculations is whether or not it is necessary to keep finite difference functions generally accurate by restricting the step size. Cost generally bears a close relationship to the number of points at which thermodynamic calculations are made. Other reaction path codes, for example PHREEQE (Parkhurst, Plummer, and Thorstenson, 1980), do not employ such functions. It has been pointed out above that these difference functions must be kept accurate in the case of the fluid-centered flow-through model and in time mode. If the calculation is just a sequence of equilibrium calculations, however, then a computationally more economical approach making less or no use of finite differences may be satisfactory.

The **nmodl2** parameter on the input file permits the user to choose a more economical mode, if the type of model permits. Otherwise, the code operates in the "normal" mode described previously in this chapter. If the model type permits, setting **nmodl2** = 1 selects "economy" model, **nmodl2** = 2, "super economy" mode. In economy mode, the maximum order is 2 and the step size restriction represented by eq (159) is replaced by one which restricts the step size so that no linear algebraic master variable is predicted to change by more than the setscrew variable **screw6**

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(whose default value is 4.0) log units. Otherwise, economy mode is much like normal mode. In super economy mode, no finite differences are used. Instead of the step size restriction represented by eq (159), the code initially sets the step size for a new step to **dlzmx1**, the zero-th order value specified on the **input** file. The idea is to take large step sizes. In super economy mode, the code forgoes most of the normal attempts to locate points of interest, including phase boundaries. Thus, if a mineral is present in the equilibrium system at one point of reaction progress but not at the preceding value, all one knows is that the actual phase boundary lies somewhere in between. This may be sufficient to meet the user's needs, however. In both economy and super economy mode, if the thermodynamic calculation fails to converge, the step size is cut until convergence is achieved.

In the present version of EQ6, the pre-Newton-Raphson optimization algorithm is generally insufficient to allow much useful application of economy mode or super economy mode, as the thermodynamic calculations tend not to converge for large step sizes. Real economy is usually not obtained. The use of these options in this version is therefore not recommended.

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9. Code Architecture and Flow of Execution

The purpose of the present chapter is to provide a narrative description of the structure of the software itself. This material is primarily included because it is required as part of the documentation to satisfy NUREG-0856 (Silling, 1983). It does not provide anything necessary for the typical code user. It may be helpful to those few users who desire to modify the code for whatever purpose.

In the present description, we will not make it a point to describe the role and function of every module in the source code. For such descriptions, the reader is referred to the relevant glossaries of modules. For EQ6 modules, see Appendix B of the present report. For EQLIB modules, see Appendix A of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a). The purpose here is to describe the main features and essential aspects of the structure of the code. The purpose is not to provide detailed design documentation. Readers who want more detailed information are invited to examine the source code itself, which is reasonably well-documented internally.

Many aspects of the architecture and operation of EQ6 are similar to those of EQ3NR (see the EQ3NR Theoretical Manual and User's Guide, Wolery, 1992b). For examples, both codes are directed by problems specified by **input** files, both use the same supporting data file, and both make extensive use of modules in the EQLIB library. Virtually all of the underlying science and associated submodels built into EQ3NR are also built into EQ6.

EQ6, however, also contains some underlying science and associated submodels that are not contained in EQ3NR. The type of thermodynamic calculation done by EQ6 is different in terms of the kinds of constraints imposed. Also, EQ6 calculates reaction path models, and so must deal with sequences of thermodynamic calculations. In computing reaction paths, it must deal with fundamental system constraints (e.g., closed systems, fluid-centered flow-through open systems, systems open to external gas reservoirs). It must also deal with irreversible mass transfer, as constrained by arbitrary relative rates or actual rate laws.

Recall that the fixed fugacity options work by creating fictive pure mineral phases in the equilibrium system corresponding to the gases whose fugacities are to be fixed. If such options are in connection with the fluid-centered flow-through system model (**nmodl1** = 3), these fictive pure minerals are not subject to the constraint of not redissolving. Indeed, if they were, they would be unable to keep the corresponding fugacities from decreasing when other processes would act to make them do so. To simplify further discussion of the **nmodl1** = 3 option in the rest of this chapter, the exceptional treatment of these phases will not be pointed out each time actions pertaining to this option are addressed.

When the code is operating in time mode (**iopt1** = 1), the time variable is considered to be infinite when the value of the inverse rate is calculated by module **rtcalc.f** as being greater than the pseudo-infinite value of $1 \times 10^{+38}$ inverse seconds. This condition is marked by setting the flag variable **qriinf** to "**.true.**". The module **timer.f**, which computes the time increment corresponding to a given step of reaction progress, then takes the increment and the new time value to be infinite.

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9.1. Overview

Execution begins in the main program, **eq6.f**. This module directs the overall process of code execution. The function of the main program is illustrated in the simplified flow diagram in Figure 17. The first step is to get the time and date, which the code does by calling the EQLIB module **timdat.f**. This module contains UNIX-dependent code. The main program then writes the code name and version identification, the copyright notice, and the time and date information to the screen and **output** files. Its next step is to initialize the dimensioning variables which correspond to the dimensioning parameters. Dimensioning variables are used to pass dimensioning data in the calling sequences of called modules; FORTRAN does not generally allow parameters (in the special FORTRAN sense) to be so passed.

EQ6 will run multiple problems stacked on a single **input** file. The line marked by label **25** is a return point in the main program to which execution flows after a single problem has been solved. After this point, the code initializes the relevant arrays and variables, setting their contents to zero or some other appropriate null value equivalent. The purpose of this is to provide a clean slate for the solution of the next problem. The main program then calls module **rd6inp.f** to read another problem on the **input** file. If no problem is found, the problem execution stage is presumed to be finished. The main program then gets the current time and date and writes the starting and ending times and dates to the screen and **output** files. After that, it makes a normal exit and execution stops.

In practice, the usage of this stacked input capability is usually impractical. Any problems so stacked should be very short ones. A typical reaction path problem is usually long enough that in fact it is recommended that it be run in segments, each corresponding to a single execution of the code (see discussion in Chapter 5).

Module **rd6inp.f** is analogous in function to the EQ3NR module **rdinp.f**. If the **input** file has not been opened on a previous call, **rd6inp.f** opens it. Using an EQLIB module called **stripl.f**, it copies the **input** file to a file called **inputs**, deleting any comment lines. The original **input** file is then closed. The code then subsequently reads the stripped input file instead. Module **rd6inp.f** looks at the first line of input to see if the input file is in "W" or "D" format. It then repositions the file pointer at the top of the file.

If the input file is in "W" format, **rd6inp.f** calls module **readz.f** to read the next problem. If it is in "D" format, it calls module **rd6new.f** to oversee the reading of the next problem. Module **readz.f** reads most of the **input** file itself. It uses one helper module, **readrt.f**, to read a block of rate law data for each irreversible reaction ("reactant"). Module **rd6new.f** carries out its function by calling a fairly large number of helper modules (most of which begin with "**rd**"). Calls to either **readz.f** or **rd6inp.f** result in the writing of an instant echo of the **input** file to the **output** file. If no problem is found at the current position of the file pointer, the main program is notified and it then proceeds as described above to make a normal exit.

If the code finds a problem on the **input** file, the main program then gets the name of the chosen activity coefficient option corresponding to the **iopg1** activity coefficient option switch. This is a descriptive character string that will be used subsequently. The code then calls module **indatz.f** to read the supporting data file, **data1**. This module is analogous (and nearly identical to)

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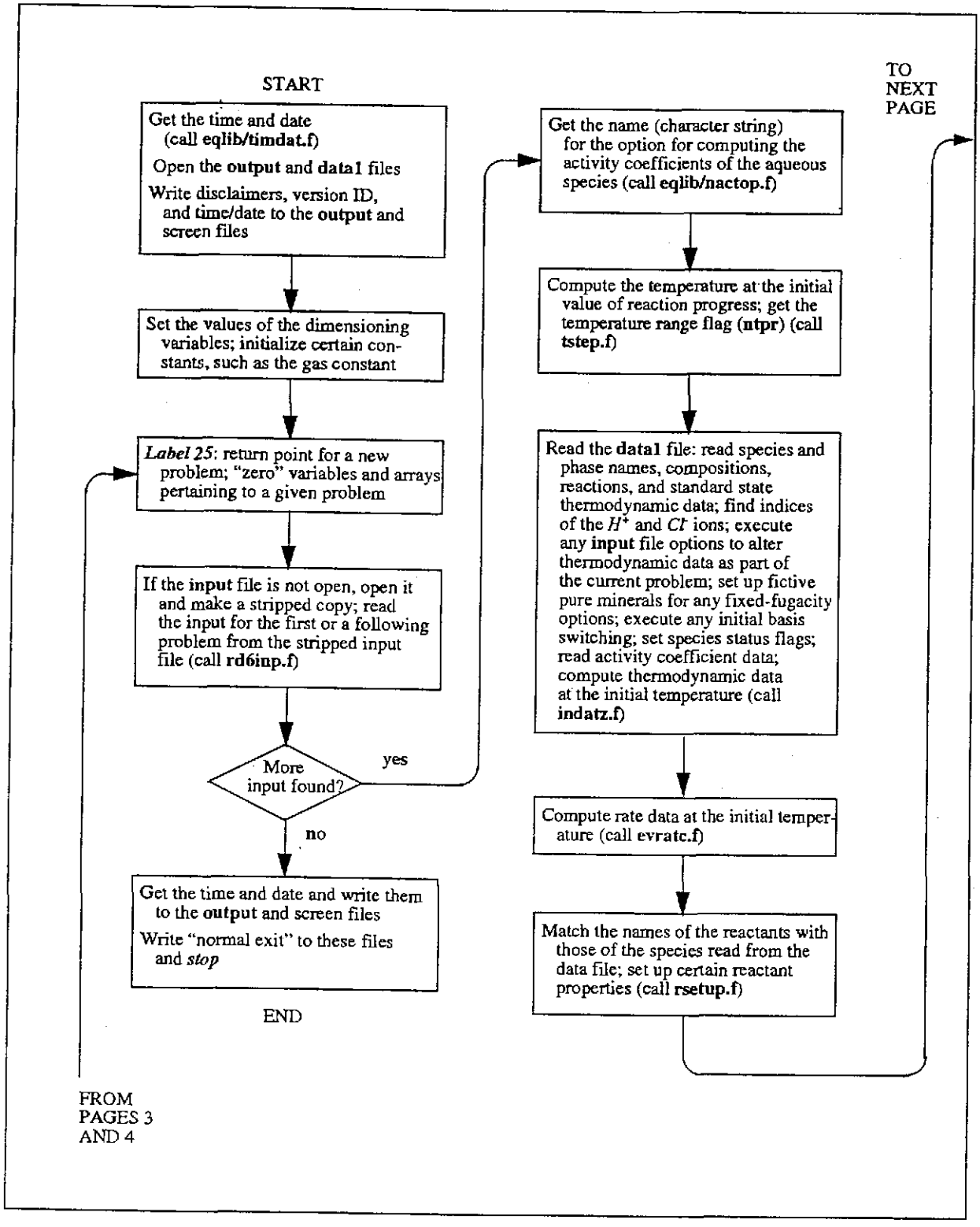

Figure 17 (page 1 of 4). Simplified flow diagram of the EQ6 main program (eq6.f).

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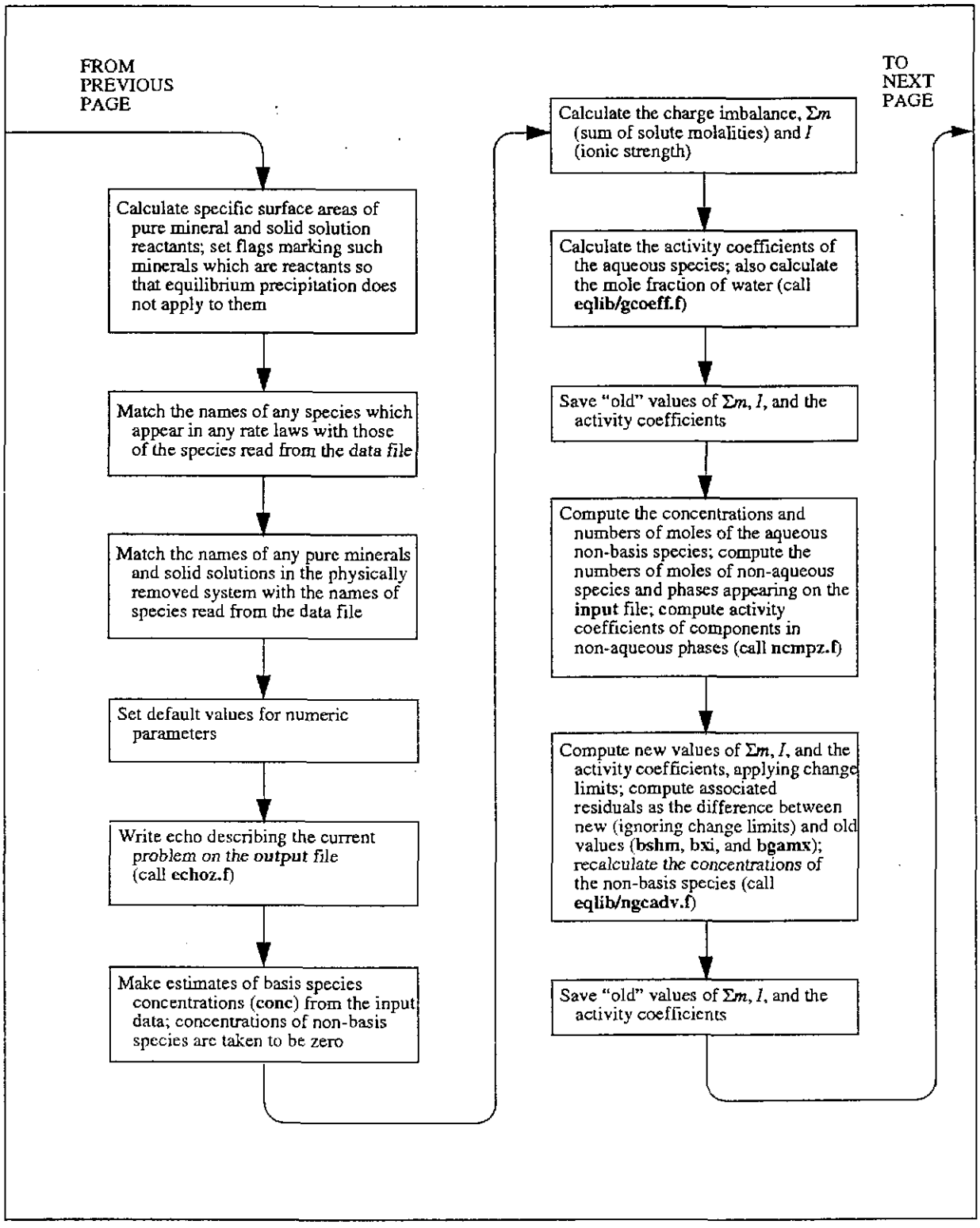

Figure 17 (continued, page 2 of 4). Simplified flow diagram of the EQ6 main program (**eq6.f**).

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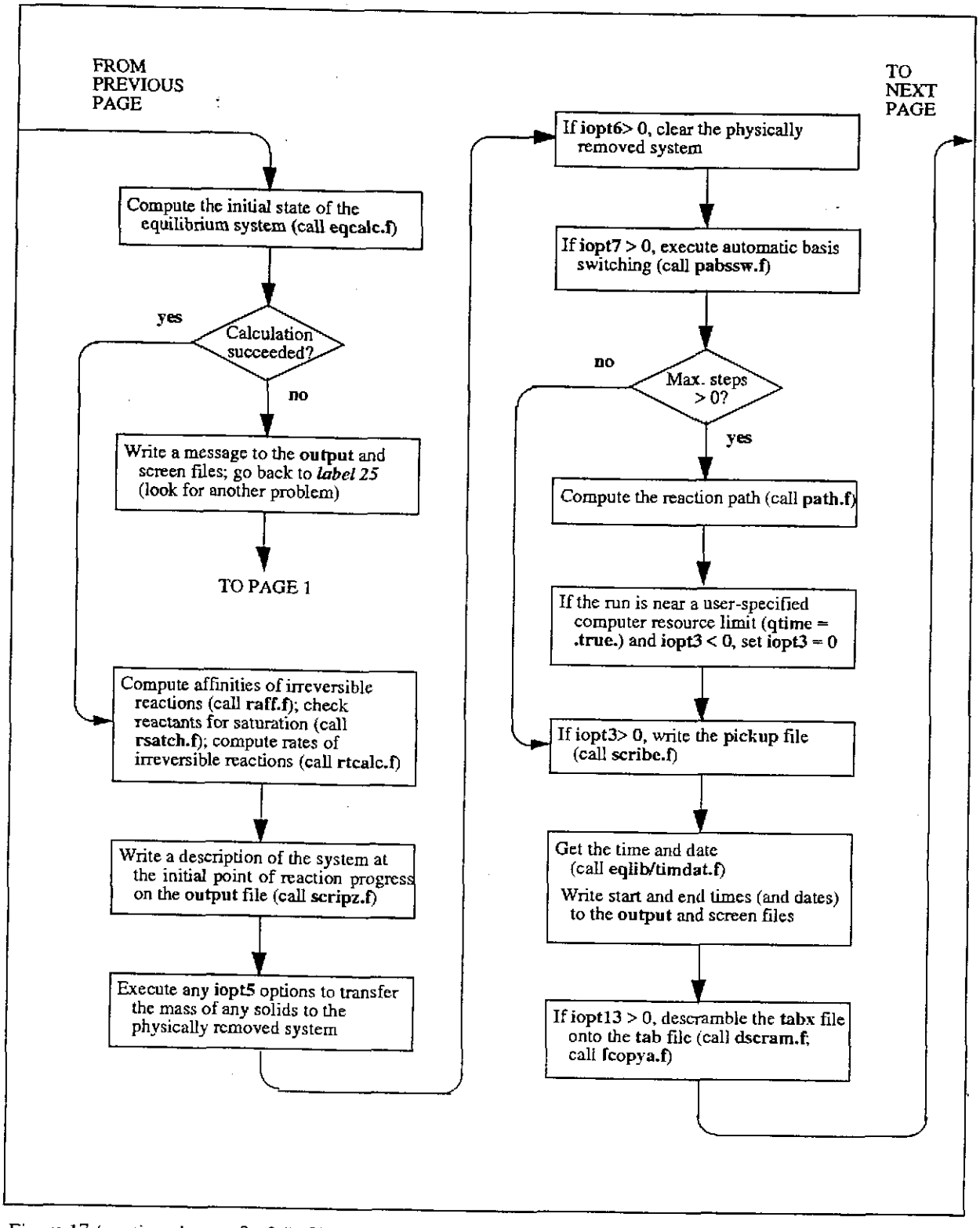

Figure 17 (continued, page 3 of 4). Simplified flow diagram of the EQ6 main program (eq6.f).

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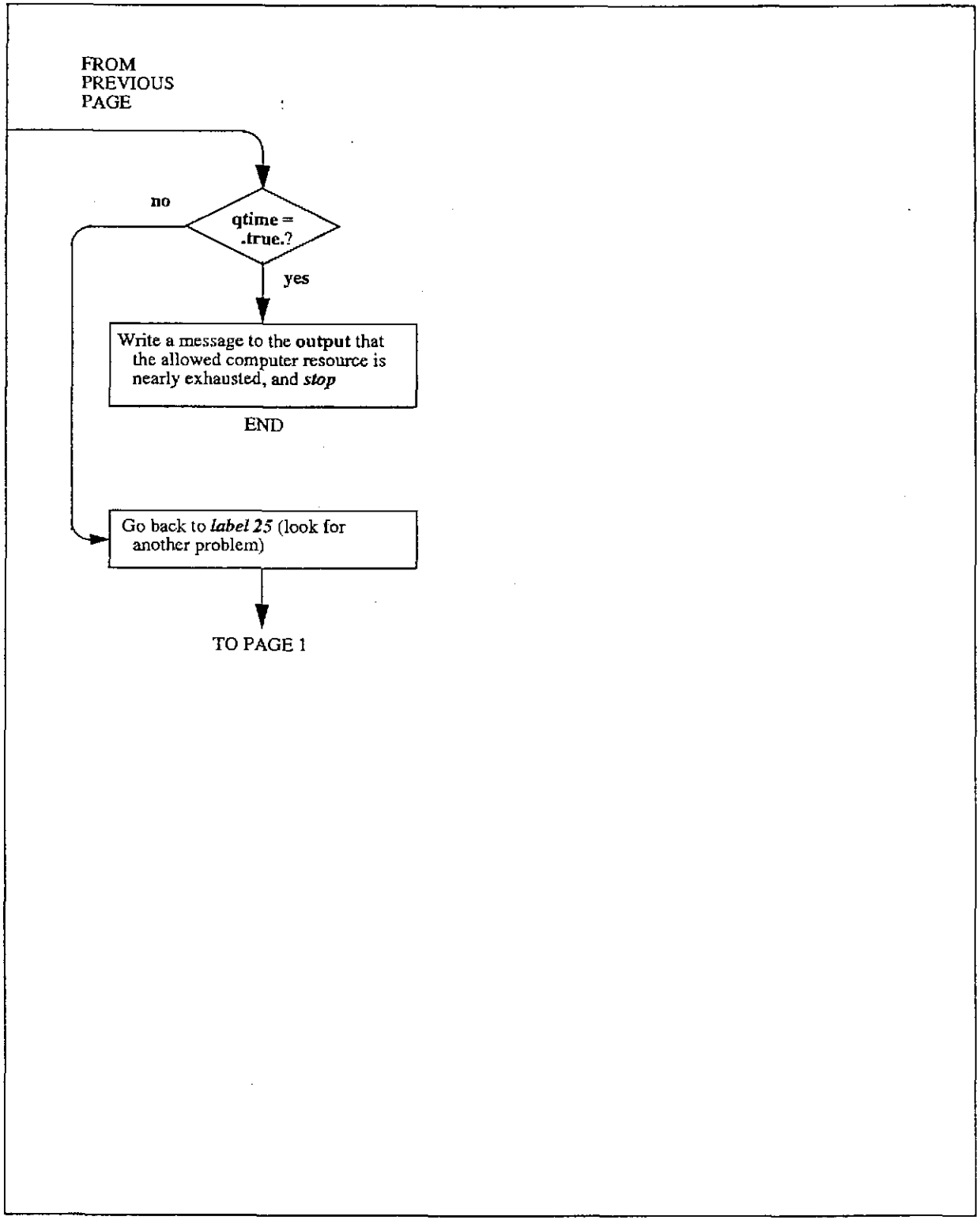

Figure 17 (continued, page 4 of 4). Simplified flow diagram of the EQ6 main program (**eq6.f**).

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the EQ3NR module **indatx.f**. It checks a flag contained on the data file to insure that the kind of data file provided is consistent with the activity coefficient option selected on the input file. If it is not, this module writes an error message to the screen and **output** files and execution stops. Otherwise, it proceeds to read the standard state thermodynamic data on the data file. All basis species are loaded into memory. All other types of species are loaded into memory only if they are relevant to the current problem. Module **indatz.f** then calls the EQLIB module **gspion.f** to find the indices of the hydrogen and chloride ions.

After completing the above actions, which includes finishing reading the **data1** file, **indatz.f** calls module **indat1.f**. This carries out several functions. The first of these is to call the EQLIB module **alters.f** to execute any **nxmod** "alter" options that may have been included on the **input** file. It then calls module **nlkffg.f** to set up the fictive pure minerals required for any fixed fugacity option. After that, **indat1.f** calls module **inndx.f** to decode the initial composition constraints for the initial equilibrium system. If there are any solid solution reactants or special reactants, it calls module **glxrn.f** to decode them. The next task of **indat1.f** is to call module **ibswch.f**, which executes any user-directed basis switches on the **input** file. Then it calls module **flgstz.f** (a close analogue of the EQ3NR module **flgstx.f**) to set the species status flags. This module may in turn call the EQLIB module **supprs.f** to execute any **nxmod** "suppress" options that may have been included on the **input** file. Module **indat1.f** then loads any fictive "fixed fugacity" minerals into the equilibrium system, if necessary. This is followed by a call to module **modexz.f**, which sets up the structure for the thermodynamic calculations for the equilibrium system. If **iopg1** = 0, **indat1.f** then calls the module **inbdot.f** to read from the data file the ion size and **insgfl** flag data required for the B-dot activity coefficient model. If **iopg1** = 1, it calls the module **inupt.f** to read from the data file the relevant interaction parameters needed for Pitzer's equations. Only the data needed for the current problem are loaded into memory by either **inbdot.f** or **inupt.f**.

After calling **indat1.f**,module **indatz.f** calls module **evdata.f** to evaluate all temperature-dependent thermodynamic data. It then calls module **gcdrst.f** to compute the **cdrst** ($b_{T,r}$), **cdrmt** ($b_{T,\phi}$), and **cdrgt** ($b_{T,g}$) arrays. This is followed by a call to module **gafscl.f**, which computes the array of affinity scaling factors ($b_{j,scale}$). Lastly, **indatz.f** computes the lower and upper limits on the oxygen fugacity corresponding to the stability field of liquid water.

The flow of execution then returns to the main program (**eq6.f**). It then sets up some arrays pertaining to the irreversible reactions ("reactants"). First, it calls module **evratc.f** to evaluate rate constants, which may be temperature-dependent. Secondly, it calls module **rsetup.f**, sets up the molecular weights and molar volumes of the reactants. Thirdly, it sets up some related pointer arrays and checks the identities of species names appearing in the activity products of rate laws to see if these species appear in the current model. The next action of **eq6.f** is to decode the input data for phases in the physically removed system. Following that, it checks the problem input. Default values are assigned and some input parameters are changed if necessary to fall within required ranges. Most of these parameters are tolerance and setscrew parameters.

The next action of **eq6.f** is to call module **echoz.f**. This module is analogous to the EQ3NR module **echox.f**. writes an echo of the current problem to the **output** file. This echo includes the actual values assigned to the relevant parameters, including any defaults or lower or upper limits assigned.

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The main program then begins to expand the description of the equilibrium system that was read from the **input** file. Essentially what is known initially is the number of moles of the basis species, including any mineral species present in this system. The expansion produces an estimate for the number of moles, the concentration (molality or mole fraction), activity coefficient, and thermodynamic activity of each species present. First, the molalities of the aqueous solute basis species are computed and used to estimate the Σm function (by a call to the EQLIB module **gsigm.f**) and the ionic strength (by a call to the EQLIB module **gxi.f**). The activity coefficients of the aqueous species are then estimated by a call to the EQLIB module **gcoeff.f**. That module also provides an estimate of the mole fraction of solvent water, which is calculated from Σm. The expansion is completed by a call to module **ncmpz.f** (analogous to the EQ3NR module **ncmpx.f**). This module in turn calls module **derspc.f** to compute the numbers of moles and the molalities of all non-basis aqueous species. It also calls module **ncmpz2.f** to complete the expansion for any mineral species in the equilibrium system. If any solid solutions are present, it calculates the mole fractions and activities of the end member components in any solid solutions present, calling the EQLIB module **lambda.f** to compute the relevant activity coefficients.

The main program follows up this initial expansion by calling the EQLIB module **ngcadv.f**. The function of this module is to expand the system by first recalculating the activity coefficients and then the concentrations of non-basis species. This module is called here to improve upon the initial expansion.

At this point, the main program calls module **eqcalc.f**. The function of this module is oversee a thermodynamic equilibrium calculation for the equilibrium system. The purpose of the present call is to make the calculation for the initial point of reaction progress. How this module makes a thermodynamic equilibrium calculation will be discussed below. We note, however, that this initial calculation commonly involves the precipitation of some originally supersaturated minerals. It may also involve a temperature jump. If the calculation for the initial point of reaction progress fails, the main program writes an error message (to both the **output** and screen files), terminates activity on the current program, and loops back to see if another problem is specified on the **input** file. If the calculation is successful, the main program computes data pertaining to the reactants (such as the values of reaction rates). It then calls module **scripz.f** to write a description of the state of the system on the **output** file. This module is analogous to the EQ3NR module **scripx.f**, and indeed writes many of the same tables of output data. Module **scripz.f** also writes data to the scrambled tab file, **tabx**.

The main program (**eq6.f**) then executes any options specified by the option switch **iopt5**. These options transfer minerals now present in the equilibrium system to the physically removed system. This provides a means of discarding initial precipitates. If **iopt6** = 1, **eq6.f** then clears the physically removed system. Then, if **iopt7** = 1, **eq6.f** calls module **pabssw.f** to execute automatic basis switching.

The next action of **eq6.f** is to call module **path.f** to compute the rest of the reaction path. This is a complex process which will be described in some detail below. After this call, **eq6.f** calls module **scribe.f** to oversee the writing of the **pickup** file. If the **input** file was in "W" format, **scribe.f** calls module **scribo.f**, which write the **pickup** file in the same format. Otherwise, it calls modules **writ6x.f** and **scribn.f**, which write this file in "D" format. The former module writes the top part, the latter, the bottom part. The main program then calls the EQLIB module **timdat.f** to get the

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time and date. Then it calls the UNIX system module **etime** to get the user and cpu times. The next action of **eq6.f** is to unscramble the **tabx** file, writing the results on the **tab** file. This file contains summary tables intended for post-run plotting.

The main program then loops back to see if there is another problem on the **input** file. If there is, it repeats the process. If not, a message announcing the end of the run is written to the **output** and screen files by module **rd6inp.f**.

9.2. Following the Reaction Path: Module path.f

Module **path.f** has the function of overseeing the calculation of the reaction path. As such, its major functions include choosing the step size (**delzi**) and detecting certain events, such as the appearance or disappearance of product minerals. When the code is operating in time mode, this module also oversees the integration of the relevant rate equations. This module is written to operate in one of three calculational modes:

- Normal: the step size is constrained to keep the finite difference based predictor functions accurate. This is required if the code is operating in time mode (**iopt1** = 1) or computing a model for the fluid-centered flow-through open system (**nmodl1** = 3). Normal mode is forced if **nmodl2** = 0 on the **input** file.

- Economy: the step size is allowed to become larger than in normal mode. The predictor functions are restricted to second order, and the step size is not constrained to keep them accurate. Economy mode is permitted if **nmodl2** = 1.

- Super economy: the step size is large, typically matching **dzprnt**, the linear print interval. Predictor functions are not used. Phase boundaries are not located.This mode is permitted if **nmodl2** = 2.

Use of the latter two modes is not recommended at the present time owing to deficiencies in the existing pre-Newton-Raphson optimization algorithm. Real economy is usually not obtained, because failure of the equilibrium calculations upon making large steps is frequent and results in the step size being cut.

The first function of **path.f** is to initialize the various arrays and variables associated with finite difference calculations. It also initializes certain other variables relevant to the computation of the reaction path. It then checks to see if the **input** constraints actually define a reaction path. Such a path is defined if there are one or more irreversible reactions ("reactants") or the temperature is defined as a function of reaction progress. If no path is defined, it writes a message to the **output** file and execution returns to the main program (**eq6.f**).

Otherwise, **path.f** computes the first "print points" corresponding to the linear (**dzprnt**) and logarithmic (**dzprlg**) print intervals. A "print point" is a point of reaction progress at which the code writes a detailed description of the state of the system by calling module **scripz.f**. Similarly **path.f** also computes the first "dump point" corresponding to the dump interval (**dlzidp**). A "dump point" is a point of reaction progress at which the code transfers all or part of the mass of solid phases in the equilibrium system to the physically removed system. This is relevant only to the fluid-centered flow-through system.

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Next in **path.f** comes label **20**. This is a return point for setting up to make a new step of reaction progress from the latest point to which the calculation has advanced (ξ_0). Here, the step counter, **kstep**, is incremented. Information describing the state of the system at the current or base point is saved, in case it is later necessary to fall back to this point.

After that, **path.f** computes the finite difference functions described in Chapter 8 for the current point of reaction progress. These are computed for the maximum possible order (**kord**), whose value ranges from zero to six. Initially, this has a value of zero, which is to say that no finite difference functions are actually calculated or used.

The next action of **path.f** takes place only if **nmodl1** = 3 (fluid- centered flow through system model). If the code is at the second point of reaction progress and the phase assemblage was changed on the first step, or a reactant saturated or exhausted, **path.f** examines the first order finite difference functions to see if any mineral phases are decreasing in number of moles. If so, **path.f** calls module **shftz.f** to shift each such phase in its entirely from the equilibrium system to the physically removed system. This complete shift removes representation of the phase in the set of algebraic master variables. Put another way, the phases themselves, in addition to their masses, are removed from the phase assemblage in the equilibrium system. This mechanism protects such phases from redissolving in an efficient manner. If it were not done, other mechanisms (see below) would suffice. The present coding here is somewhat vestigial. The action taken here was at one time taken at the first point of reaction progress after any of the relevant events, not just on the second point of reaction progress.

The next action of **path.f** also depends on the condition that **nmodl1** = 3. If the flag variable **qdump** is "**.true.**", **path.f** calls module **shftz.f**. It then makes a partial shift of the mass of the mineral phases in the equilibrium system is made to the physically removed system. The phases themselves are then largely but not completely protected from redissolving. They remain present in the phase assemblage of the equilibrium system. This presumes that they will grow, not redissolve. If they should redissolve on the next step of reaction progress, other protective mechanisms will come into play.

This is followed by label **215**, which is a return point for computing the step size and order for the next step. In normal calculational mode, the step size is computed for each potential order, using the accuracy requirement for finite difference based predictor functions discussed in Chapter 8. The step size for order zero is arbitrarily set to equal **dlzmx1** (the "zero order step size"). This is an **input** file parameter whose default value ranges from 1×10^{-9} (reactants, time mode) to 1×10^{-2} (no reactants, temperature change only), depending on circumstances. The order chosen is the one that gives the largest step size, and the step size is provisionally set to the corresponding value. Thus, the zero order step size is a minimum value at this point. The step size for a given order is actually the smallest for any of the algebraic master variables. In calculating this, no consideration is given to a result corresponding to a mineral species present in a trace amount. This condition is defined by the number of moles present being less than or equal to 10^{zklogu}, where **zklogu** is an **input** file parameter with a default value of -7.0 if **iopt4** =0 (no solid solutions) and -6.0 if **iopt4** = 1 (solid solutions enabled).

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In economy mode, the maximum order is 2 instead of 6. The order is chosen by the above procedure. The step size for order 1 or order 2, however, is computed so as to limit the degree of change to any algebraic master variable. It is limited so that none of these changes by more than **screw6** log units (**screw6** is a setscrew parameter that appears on the **input** file; it has a default value of 4.0). In super economy mode, the order is fixed at zero and the provisional step size is set to **dlzmx1**. In this mode, the default value of **dlzmx1** is usually set equal to **dzprnt**, the linear print interval.

If the chosen order (**nord**) is greater than zero, **path.f** then calls module **akmatr.f** to compute the $\underline{D}$ matrix required to compute derivatives from finite differences, calls module **deriv.f** to calculate derivatives of algebraic master variables, and, if the code is operating in time mode (**iopt1** = 1), calls module **rderiv.f** to calculate derivatives for rate functions (actual rates, relative rates, and the inverse rate function).

It is important to note that the step size at this point is only provisional. In general, before the step is actually made, many conditions may be encountered that will cause the step size to be decreased. Some of these conditions are associated with physical events, such as the appearance or disappearance of a product mineral. Others are numerical in nature. However, the step size may never decrease below the minimum allowed value represented by the variable **dlzimn** except for two cases which will be noted below. This variable is not an **input** file parameter. It is generally set at a value of 0.01 times **dlzmx1**. However, it is subject to other limits that depend on circumstances.

The step size may now be further reduced by the following mechanism. The variable **zilim** is used in conjunction with the process of locating points of reaction progress such as phase boundaries. It may happen that such a point may have previously been overstepped, and the step size subsequently cut. In such a case, the step may have been cut such that the last value of reaction progress was, within tolerances, the desired point. However, the final step size may have corresponded to a point of reaction progress preceding the desired point. In such a case, it would be inefficient to equal or exceed it on the next step, as the step size would have to be cut yet again. Thus, **zilim** is set equal to the point known to exceed than the desired point. On the subsequent (now current) step, **delzi** is restricted to 0.75 times the difference between **zilim** and the current value of reaction progress. This seems to work well. However, that **delzi** is not reduced to less than **dlzimn**. In other circumstances, **zilim** is set to a quasi-infinite value ($1 \times 10^{+38}$), which effectively turns off this step size control mechanism.

If the order **nord** is greater than zero, **path.f** calculates new values of the algebraic master species from the corresponding truncated Taylor's series (by calling module **taylor.f**) and repeatedly cuts the step size by one-fourth if any of the following conditions occur:

- The log number of moles of an aqueous basis species or the log oxygen fugacity has dropped to less than -100.0.
- The log number of moles of solvent water has changed by more than 1 log unit.
- The log oxygen fugacity has changed by more than 20.0 log units.

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- The max norm residual function β_{max} (**betamx**) calculated from the truncated Taylor's series is greater than 2.0.

However, **delzi** is not cut to less than **dlzimn.**

Other simple limits are then applied to the step size. It is restricted so that the resulting value of reaction progress does not exceed the following:

- The next "dump point" (which depends on the dump interval, **dlzidp**). This applies only if **nmodl1** = 3 (fluid-centered flow-through system model).

- Either of the next "print points" corresponding to the linear (**dzprnt**) and logarithmic (**dzprlg**) print intervals. This mechanism is one of two which may reduce **delzi** to less than **dlzimn.**

- The maximum value of reaction progress (**zimax**). This is an **input** file parameter. This mechanism is one of two which may reduce **delzi** to less than **dlzimn.**

- The maximum allowed value defined by **dlzmx2**, if the order **nord** is greater than zero. This is an **input** file parameter whose default value is quasi-infinite ($1 \times 10^{+38}$) under most circumstances (it is always greater than or equal to **dlzmx1**)

If **nord** is greater than zero and mineral phases are present in the equilibrium system, **path.f** then tries to limit the step size so that no more than about 90% of the existing mass of any species in such a phase is dissolved during the current step. This limit is computed for each species by looking at the first derivative of the corresponding algebraic master variable (the log number of moles of the species). This methodology is only approximate. Its purpose is not to locate the boundary at which a phase disappears. Rather, it is intended to slow down the advance of reaction progress prior to such a point, and by so doing to increase the accuracy of the relevant truncated Taylor's series in the immediate vicinity such a point. This helps to increase the efficiency of the actual methodology for locating the point.

If the order is greater than zero, **path.f** now steps out using the truncated Taylor's series for the algebraic variables and begins an earnest search for phase boundaries. The code first looks for points at which new mineral phases should appear. In stepping out, the code makes calls to the modules **taylor.f**, **ncmpz.f**, **tstep.f**, and **ngcadv.f**. These calculate all the variables needed to estimate the saturation indices at the new point of reaction progress. These indices are then obtained by a call to module **satchk.f**. If any phases are calculated to be supersaturated at the new point (apart from those which are suppressed or for which precipitation is to be controlled by a rate law), **path.f** reduces the step size so that the highest "unexcused" supersaturation falls within a target range (see references to **tolsat** and **tolsst** in the next section of this chapter). This reduction in the step size takes place by calling module **search.f** to find the step size corresponding to the target range for the mineral with the largest unexcused supersaturation. The code then loops back to evaluate the Taylor's series at the new step size, and rechecks the calculated saturation indices until no unexcused supersaturations remain.

The code then uses the truncated Taylor's series to constrain the step size so as not to skip over the point at which any existing mineral phase is completely redissolved (this mechanism is not

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relevant for the case of **nmodl1** = 3). Here **path.f** again calls **taylor.f**. It then looks to see if the predicted number of moles of any existing mineral phase is less than zero at the new point of reaction progress. If so, it again calls module **search.f**, which reduces the step size to the value corresponding to the phase boundary.

If **nmodl1** = 3, the code uses the truncated Taylor's series to see if the mass of any mineral species in the equilibrium system is decreasing. To do this, **path.f** calls modules **taylor.f** and **taylr2.f**. The latter module uses truncate Taylor's series to evaluate the first derivatives of the algebraic master variables corresponding to mineral species. The test focuses on these predicted first derivatives. If such a derivative is negative, the code calls **search.f** to reduce the step size for which the value is zero. This corresponds to the point at which the mass of the species is at a maximum. Such a reduction in the step size is done first for the mineral species with the most negative predicted first derivative. The code then loops back and steps out again using the new step size until no negative derivatives are encountered.

In actuality, it is necessary when **nmodl1** = 3 to allow some small mass of mineral species to redissolve. Thus, in the above mechanism, the condition of a negative predicted first derivative is ignored if the mass of the mineral species is already small, less than or equal to 10^{zklogu}, where **zklogu** is an **input** file parameter that has been noted previously in this section.Also, there is a possibility that the above search for the maximum (point where the derivative is zero) may fail, because the derivative is already negative at the previous point of reaction progress. This condition is possible owing to the approximate nature of finite differences. In such a case, the code steps back to the previous point of reaction progress, calls module **shftz.f** to make a partial shift of the minerals in the equilibrium system to the physically removed system, and execution flows back to label **215**. There, the process of stepping out begins over again.

Otherwise, the next action of **path.f** is to limit the step size so that the predicted inverse rate function (computed by a call to module **rtaylr.f**) does not become less than 100 times the machine floating point epsilon. Physically, the inverse rate must be positive. It may approach, but never reach, a value of zero. This check is made to avoid problems that might occur due to the approximate nature of finite differences. It is carried out if necessary by a call to **search.f**. This check is made only if **nord** is greater than zero and the code is operating in time mode.

The following action is similar and is done only under the same conditions. The code then limits the step size so that no predicted relative rate function (also obtained by a call to **rtaylr.f**), crosses from positive to negative or vice versa. This action also uses one or more calls to **search.f** as necessary.

If the code is operating is time mode, **path.f** then calls module **timer.f** to compute the time increment. This is checked to make sure that it is positive. This again is an action which is only necessary because of the approximate nature of finite differences. If the time increment is not positive, the step size is repeatedly cut by one-fourth until the time increment is positive or the step size is reduced to the minimum allowed value (**dlzimn**). If the time increment is still not positive, the order is repeatedly cut until the time increment is positive. This is guaranteed for order zero.

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The next action of **path.f** is to limit **delzi** if necessary by the points of exhaustion of any reactants. The code obtains the remaining amounts of reactants for a given step size by calling module **reacts.f**. If this is negative for any reactant, **search.f** is called to reduce the step size to coincide with the point of exhaustion of the reactant with the most negative value. This process is repeated until the step size coincides with the point of exhaustion that occurs first.

This point is followed by label **65**, which is a return point for computing the new value of reaction progress from the old one and the step size. Later events (to be described below) may cause the step size to be cut and execution to flow back to this point. There are two traps here, one to catch any case of repeated cycling of **delzi** at a value of zero, the other to catch any case of repeated cycling of **delzi** at the minimum allowed value. If either case is detected, an error message is written to the **output** and screen files, and execution stops.

The code now steps out using the truncated Taylor's series and calls module **eqcalc.f** to make a thermodynamic equilibrium calculation for the new point of reaction progress. This module is discussed in detail in the following section of this chapter. If the calculation fails, as noted by an error flag (**ier**), **path.f** restores the data for the previous point of reaction progress. Subsequent action depends on the value of the error flag.

If an attempt was made to increase the number of algebraic master variables beyond the dimensioned limit, execution flows to label **120**. Here an error message "Reaction path tracing has failed..." is written to the **output** and screen files, **delzi** is set to zero, **zimax** is set to the current value of reaction progress, and execution loops back to label **65**. This should terminate the run at the last value of reaction progress at which **eqcalc.f** could successfully make the calculations. It should also generate a usable **pickup** file.

If the calculation was otherwise successful but **nmodl1** = 3 and too much of a phase in the equilibrium system was redissolved, the code calls **shftz.f** to execute a partial transfer of the mineral phases in this system to the physically removed system. The step size is cut by one-fourth. Execution then loops back to label **65** for another try.

If the "sliding forward" mechanism for dealing with "incoming phase instability," "outgoing phase instability," or "critical redox instability" was engaged and failed, execution flows to label **120**, which has been discussed above. The sliding forward mechanism is discussed in the following section of this chapter.

For all other failure conditions associated with the equilibrium calculation, **path.f** cuts the step size by one-fourth and execution flows back to label **65** for another try. If the step size is already at the minimum allowed value, the order **nord** is reduced by one instead. If the step size is already at the minimum allowed value and the order is already zero, execution flows to label **120**, which has been discussed above.

If the thermodynamic equilibrium calculation was completed successfully, **path.f** calls module **raff.f** to compute the affinities of the irreversible reactions ("reactants"), and then calls module **rsatch.f** to check for any saturated reactants. If so, a flag (**qreq**) is set.

If the code is operating in time mode, a check is made on the accuracy of the ODE integration associated with the actual rate laws. Here **path.f** calls module **rtcalc.f** to evaluate the actual rates

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at the new point and from them the corresponding relative rates and the inverse rate. It calls module **rtaylr.f** to calculate the relative rates and the inverse rate at the new point from the corresponding truncated Taylor's series. These truncated Taylor's series comprise the basis for calculating the individual reaction progress increments of the irreversible reactions ($\Delta\xi_j$)and the time increment (Δt). The former are obtained by integration of the corresponding relative rate functions, the latter by integration of the inverse rate. Now **path.f** tests the accuracy of these integrations by comparing the calculated and predicted values of the relative rates and the inverse rate. The fractional error in any relative rate and in the inverse rate is required to be less than or equal to **screw4**. This an **input** file parameter with a normal default value of 1×10^{-3}. The test on the inverse rate is excused if the estimated fractional error in the time variable is less than or equal to **screw4**. This is an **input** file parameter with a normal default values of 1×10^{-4}. The test on any relative rate is excused if the fractional error in the amount of "reactant" created or destroyed is less than or equal to **screw4**2.

If the ODE accuracy test fails, **path.f** presently cuts the step size until the ODE accuracy test is satisfied. However, this is not done if the **delzi** is at the minimum allowed value or of the order **nord** is zero. If the step size is to be cut, execution flows to label **77**. The coding here is that which immediately follows the call to module **eqcalc.f** for the case of a returned error flag from that module. The value of **ier**, however, is zero in the present case.

Otherwise, **path.f** checks to see if any reactants have become exhausted. It sets a number of logical flags which denote conditions requiring the order **nord** to be reduced to zero. These conditions will be noted below

Module **path.f** then checks to see which algebraic master variable is changing most rapidly. It then writes a message to the **output** file which begins with, "steps completed =...". If a most rapidly changing algebraic master variable has been identified, it writes this information as part of the message.

If the **input** file parameter **iopt7** is set to 1, **path.f** then calls module **pabssw.f** to execute automatic basis switching. If any switches are made, a message is written to the **output** file.

The order of the finite difference based truncated Taylor's series for the next step is reduced to zero if any of the following events have occurred:

- The phase assemblage has just been modified.
- Automatic basis switching was just executed.
- One or more reactants has just saturated or become exhausted.
- The temperature has just crossed 100°C (the derivative of pressure with respect to temperature is not continuous here).

A counter is also set which delays any increase in the order for a few steps. If any of these events have occurred and **nmodl1** = 3, a flag is set to write on the **output** file an abbreviated table of system data at the next point of reaction progress. The events noted here require the order to be

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dropped to zero because they result in discontinuities in the derivatives of the variables represented by the finite difference based truncated Taylor's series.

Next, **path.f** calls module **scripz.f** to write a detailed description of the state o the system at the current point of reaction progress if one of the following conditions holds:

- Nothing is changing with respect to reaction progress.
- The phase assemblage has just been modified.
- One or more reactants has just saturated or become exhausted.
- The reaction progress variable is reached the maximum value (**zimax**).
- The time variable equals or exceeds the maximum value (**timemx**).
- The step counter (**kstep**) equals the maximum number of steps (**kstpmx**).
- The temperature has just crossed 100°C.
- The current point of reaction progress is a "print point" as defined by the linear print interval (**dzprnt**), the logarithmic print interval (**dzprlg**), or the maximum number of steps between print points (**kstppr**).
- If **nmodl1** = 3, the current point is a "dump point" as defined by the dump interval (**dlzidp**)
- If **nmodl1** =3, a transfer of mineral phases from the equilibrium system to the physically removed system was executed in the process of stepping out to the current point of reaction progress or if the current point of reaction progress corresponds to the maximum in the mass of a mineral phase.

If none of these conditions is met, execution flows back to label **20** to make another step of reaction progress. Otherwise, **path.f** makes the call to **scripz.f**.

After that, **path.f** must determine whether to stop the reaction path calculation or to go back and continue it. The following conditions cause normal termination of the calculation:

- The reaction progress variable is reached the maximum value (**zimax**).
- The time variable equals or exceeds the maximum value (**timemx**).
- The step counter (**kstep**) equals the maximum number of steps (**kstpmx**).
- Nothing is changing with respect to reaction progress.
- Each reactant is saturated or exhausted, and the run is for a constant temperature.

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If **path.f** stops the calculation at this point, it writes a message to the **output** and screen files ("the reaction path has terminated normally...") along with some summary run statistics. Execution then flows back to the main program (**eq6.f**).

If **path.f** does not stop the calculation, it then calculates as necessary new values for the print and dump points. It then determines whether to use the existing point of reaction progress as the next base point (the usual procedure) or to step out from the preceding point. The latter is done if the step size is small and the current value of reaction progress was determined only to meet the next print point as defined by the linear print interval (**dzprnt**), the logarithmic print interval (**dzprlg**), or the maximum number of steps between print points (**kstppr**). This procedure is increases efficiency and protects the integrity of the finite difference functions, for example in the case of two successive values of reaction progress which are nearly indistinguishable.If this is to be done, **path.f** then executes the necessary setup. Execution then flows back to label **215** (where the step size and order calculations for the next step begin).

9.3. Thermodynamic Equilibrium Calculations: Module eqcalc.f

Module **eqcalc.f** oversees thermodynamic equilibrium calculations at any given point of reaction progress. It is called once by the main program, **eq6.f**, to make these calculations at the initial point of reaction progress. It is also called by module **path.f** for each point of reaction progress the code steps to along the reaction path. Although **path.f** normally determines the step size, there are some conditions under which **eqcalc.f** may also cut or advance the step size.

The difference between a thermodynamic equilibrium calculation in EQ6 and one in EQ3NR is that EQ6 must find the equilibrium phase assemblage. If a solution is found to be supersaturated with respect to one or more phases, EQ3NR merely reports this condition. EQ6 must actually precipitate one or more such phases until no supersaturations remain. Supersaturation with respect to a phase may be ignored by EQ6 if the phase is suppressed or if precipitation is directed on the **input** file to be controlled by a rate law. EQ6 must also be able to delete phases.This is necessary for two reasons. First, the addition of a phase to the assemblage may turn out to be a mistake. Second, phases in the equilibrium system occasionally disappear (redissolve) along a reaction path,

Module **eqcalc.f** finds the equilibrium phase assemblage by a trial and error process. This involves making a sequence of thermodynamic equilibrium calculations, each for a provisional phase assemblage. The variable **ntry** is the number of phase assemblages that have been tried for the current point of reaction progress. Before the phase assemblage is modified, **eqcalc.f** compares the current value of **ntry** with the maximum allowed value (the **input** file variable **ntrymx**, which has a default value of 25). If **ntry** is already at this limit,**eqcalc.f** writes an error message to the **output** and screen files, sets an error flag, and returns execution to the calling module.

Module **eqcalc.f** makes a thermodynamic equilibrium calculation for a given phase assemblage in a two-step process. First, it may call module **optmzr.f**, which performs pre-Newton-Raphson optimization. This is not done if the starting values appear to be quite good (if the initial value of the residual max norm β_{max} is small).Module **optmzr.f** is crudely analogous to the EQ3NR module **arrset.f**. Such optimization is done only for the first provisional phase assemblage. In the case of the initial point of reaction progress, this assemblage is specified by what is on the **input** file.

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Otherwise, it is the assemblage that was found at the previous point of reaction progress. The second step is such a calculation is to call the EQLIB module **newton.f** to compute the final solution by means of the hybrid Newton-Raphson algorithm that was discussed in Chapter 7 of the present report. This module in turn calls the module **betaz.f** and **matrxz.f** to compute, respectively, the residual functions and the Jacobian matrix. These are analogous to the EQ3NR modules **betas.f** and **matrix.f**. They are known to **newton.f** as "**betae**" and "**matrxe**," respectively. Module **newton.f** also calls the module **ncmpz.f** to expand the system. This routine is known to it as "**ncmpe**." Module **newton.f** calls the EQLIB module **ngcadv.f** to recompute the activity coefficients, and EQLIB module **nrstep.f** to execute a single Newton-Raphson step. For additional description of the programming of this algorithm, see Chapter 9 of the EQ3NR Theoretical Manual and User's Guide (Wolery, 1992b).

The above description gives a good picture of the main functions of **eqcalc.f**. However, the actual structure and function of this module is somewhat more complicated. When this module is first entered, it initializes a number of flag variables and some arrays. It saves the entering phase assemblage in case it should become necessary to change the step size. This is followed by a return point (at label **15**) for making such a change. There are three cases in which this action occurs:

- The step size is cut if the aqueous solution is supersaturated with respect to more than three phases. This is done only if **iopt2** = 2 (the code is not locating phase boundaries); the rationale is to provide some degree of resolution. This is not done if the reaction progress variable is at the starting value or the step size is already at the minimum allowed value (**dlzimn**).

- The step size is advanced to step over a small region of computational singularity associated with critical redox instability.

- The step size is advanced to step over a small region of computational singularity associated with the appearance or disappearance of a phase.

Module **eqcalc.f** then steps out to the new point of reaction progress, using the finite difference based truncated Taylor's series. If the code is operating in time mode, it calls the module **timer.f** to compute the time increment. If there are any e irreversible reactions ("reactants"), it then calls module **reacts.f**. This module in turn calls module **integr.f** to compute the corresponding reaction progress increments. Module **reacts.f** then computes from these the component mass balance totals for the new point of reaction progress.

This action is followed in **eqcalc.f** by another major return point (label **35**). Code execution returns to this point when either the phase assemblage has been modified. It also returns to this point if the code is doing a a redox scan (trying to find a starting value for the oxygen fugacity which will lead to convergence).

At this point, **eqcalc.f** checks to see that each mineral in the phase assemblage has a log number of moles value greater than -999. This is in essence a test to insure that such a phase has a nonzero starting value for the number of moles (EQ3/6 uses -999 as though it were the log of zero). If a phase fails to satisfy this test, it is assumed to not be actually present. it is then deleted from the phase assemblage by means of a call to module **modexz.f** and execution flows to the return

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point at label **35**. This mechanism is present only because there is the possibility of the log number of moles of a mineral phase being -999 on an EQ6 **pickup** file.

Module **eqcalc.f** then completes expanding the system (via a call to **ncmpz.f**) and computes starting values for the residual functions (via a call to **betaz.f**). The code is then ready to make the thermodynamic equilibrium calculation for the current phase assemblage.

At this point, **eqcalc.f** calls module **optmzr.f** to carry out pre-Newton-Raphson optimization. It only does this, however, if the phase assemblage is the entering one. Even then, it is skipped if the max norm of the residuals (β_{max}) is less then or equal to the normal corresponding convergence tolerance (**tolbt**). Then **eqcalc.f** calls the EQLIB module **newton.f** to carry out hybrid Newton-Raphson iteration. The architectural details of how this is done were described earlier in this chapter. Code execution takes one flow if this iteration converges, and another if it fails to converge.

If hybrid Newton-Raphson iteration converges, execution then flows as follows. First, **eqcalc.f** recalculates the component mass balance totals for the aqueous solution. It then calls module **satchk.f** to check for supersaturated phases (ignoring phases for which supersaturation is permitted). Phases are considered to be supersaturated only if the corresponding affinities to precipitate exceed a small non-zero tolerance (**tolsat**). If any are found, **eqcalc.f** writes a message to that effect to the **output** file. It then orders the supersaturated phases in order of decreasing scaled affinity. It saves the current values of the $\underline{z}$ vector corresponding to the aqueous basis species so that the present state of the aqueous solution can later be recovered if necessary. It then defines the phase with the largest scaled affinity as the candidate to add to the phase assemblage.

Before adding this phase to the phase assemblage, however, **eqcalc.f** checks the phase assemblage modification history. If the same phase was added two cycles previously and deleted on the previous cycle, the calculation has entered a potential infinite loop in which this phase would be alternately added and deleted. The problem in such a case is that without the phase present in the assemblage, the supersaturation exceeds the tolerance. With it present in the assemblage, the corresponding number of moles variable during iteration becomes so small in relation to the machine epsilon and the mass balance totals to which the phase contributes that the Jacobian matrix is rendered computationally singular. Put another way, the phase should actually be present in the assemblage. However, the number of moles of this phase is too small to compute with the given floating point representation.

When this condition ("incoming phase instability") is recognized, **eqcalc.f** goes into a "sliding forward" mode in which the step size is increased one or more times in an attempt to step over the region of singularity (which is typically on the order of 1×10^{-8} units of reaction progress). The variable **nphasl** is the number of times the step size has been increased in a given slide forward sequence. Each time the step size is so increased, execution loops back to label **15**. The **input** file variable **npslmx** is the maximum number of steps in such a slide. The default value is 12. If the slide forward fails to succeed within **npslmx** tries, then **eqcalc.f** writes an error message to the **output** and screen files, sets an error flag, and returns execution to the calling module.

If **eqcalc.f** does not detect the condition of incoming phase instability, the code proceeds as follows. If **iopt2** = 2 (phase boundaries are not being located), the step size is cut if there are more

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than three supersaturations. This is not done, however, if the reaction progress value is at the starting value or if the step size is already at the minimum allowed value (**dlzimn**). If this step size cut is made, execution loops back to label **15**.

Otherwise, **eqcalc.f** is ready to add the candidate phase the phase assemblage. It estimates a starting value for the number of moles of this phase (and of its end member components if the phase is a solid solution). This is taken for a phase or a component species as 0.05 times the maximum amount that could be precipitated from solution. It then calls module **modexz.f** to add the candidate phase to the assemblage. It then checks the phase assemblage counter **ntry** against the limit **ntrymx**. If the limit has not been reached, **ntry** is incremented and execution flows back to label **35** and the code attempts an thermodynamic equilibrium calculation for the new phase assemblage.

If the calculation converges for a given phase assemblage and there are no remaining supersaturations (except those which may be permitted), then **eqcalc.f** does the following. If the code is computing a titration model (**nmodl1** = 1) or closed system mode(**nmodl1** = 2), the module has successfully completed its function and execution returns to the calling module. If the code is computing a fluid-centered flow-through model (**nmodl1** = 3), **eqcalc.f** checks to see if any product mineral mass has been redissolved beyond the allowable limit. If not, the module has successfully completed its function. If so, however, **eqcalc.f** writes a pertinent message to the **output** file, sets an error flag, and execution returns to the calling module (which in this particular case must be **path.f**). That module will then in turn go back to the previous point of reaction progress and partially transfer minerals in the equilibrium system to the physically removed system before stepping out again.

If the calculation for a given phase assemblage does not converge, **eqcalc.f** seeks to recover by one of several possible actions. It first checks the mineral phase assemblage to see if there is a violation of the mineralogic phase rule. This is done by calling the EQLIB module **lindep.f** to check for linear dependence in the mineral mass action rows of the Jacobian matrix. If such a violation is detected, **eqcalc.f** then calls module **jgibbs.f** to determine which phase to delete from the assemblage. Module **eqcalc.f** then resets the values of the $\underline{z}$ vector to their values at the start of the failed iteration. However, the entries corresponding to the deleted phase are removed. Also, **eqcalc.f** calls **modexz.f** to complete the deletion of this phase from the phase assemblage. The **ntry** counter is checked (as discussed above). If it has not already reached the maximum value, execution flows back to label **35** to make a thermodynamic equilibrium calculation for the new assemblage.

If there is no violation of the mineralogic phase rule, **eqcalc.f** calls module **phsdrp.f** to see if a phase should be deleted from the phase assemblage. This module uses four algorithms in an attempt to identify such a phase (see discussion in Chapter 7). The strongest of these algorithms identifies a candidate phase for deletion by noting a strong decrease in its calculated number of moles during the iteration process. Essentially, the number of moles of such a phase is trending toward zero. However, the use of logarithmic iteration variables does not permit this to actually become zero or negative.

If a candidate phase is identified, it is first checked to see if it was previously deleted and added in the two immediately previous changes to the phase assemblage. If so, the code has encountered

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the condition of "outgoing phase instability" This is similar to the condition of "incoming phase instability" discussed previously. The present condition differs in that a phase which has been present in the equilibrium system at previous points of reaction progress is redissolving as opposed to having been not present previously and now appearing. Once again, **eqcalc.f** goes into a "sliding forward" mode in which the step size is increased one or more times in an attempt to step over the region of singularity (the process is the same as that described previously).

If a candidate phase for is identified and is not involved in "outgoing phase instability," this phase is then deleted from the phase assemblage. This process is the same as that described above for the case of a violation of the mineralogic phase rule. However, there is a possible exception. if the deleted phase was added in the immediately preceding change to the phase assemblage and there were other candidates to add, the phase is not simply deleted. Rather, it is replaced by the phase which had been the second-place candidate. Execution then flows to label **370**, which is a point at which **eqcalc.f** estimates the starting value for the number of moles of the species corresponding to a phase to be added to the assemblage.

The oxygen fugacity can vary widely in value (over more than 80 orders of magnitude at 25°C). It can also change rapidly with respect to reaction progress. This condition is commonly encountered in the middle of a "redox jump," when a poising (redox buffering) component such as $O_{2(aq)}$ is exhausted, as by reaction with ferrous minerals. However, the existing pre-Newton-Raphson optimization algorithm is incomplete in that it has no capability to optimize the log oxygen fugacity, which is used in EQ3/6 as an algebraic master variable. If the starting value is off by more than 10 units, hybrid Newton-Raphson iteration has a tendency to not converge. For this reason, **eqcalc.f** incorporates the redox scan feature described in Chapter 7.

In order to enter the redox scan mode, the equilibrium calculation must diverge. The algorithms described above must all fail to find a candidate phase to delete from the phase assemblage. The step size must be zero (as it is when **eqcalc.f** is called by **eq6.f**) or the minimum allowed value (**dlzimn**). If this condition is not met, **eqcalc.f** sets an error flag and execution returns to the calling module. If this is **eq6.f**, the run terminates unsuccessfully. If the calling module is **path.f**, it responds by cutting the step size, which may eventually reach the minimum allowed value. There is an exception to the step size test if the code is attempting to "slide forward" over a region of critical redox instability (see below).

In redox scan mode, the starting value of the log oxygen fugacity is incremented 10 log units per step in the scan, which covers the range corresponding to the stability field of liquid water. After each increment, execution flows back to label **35** for a thermodynamic equilibrium calculation. The scan terminates if the calculation converges or if it diverges and one of the phase deletion algorithms produces a candidate. It also terminates when the scan has covered the allowed range. If this happens, the system is presumed to be so ill-poised relative to the floating point precision that the oxygen fugacity simply can not be calculated at the current point of reaction progress.

When this condition ("critical redox instability") is recognized, **eqcalc.f** goes into a "sliding forward" mode in which the step size is increased one or more times in an attempt to step over the region of singularity (which is typically on the order of 1×10^{-9} units of reaction progress). The variable **nslsc** is the number of times the step size has been increased in a given slide forward sequence. Each time the step size is so increased, execution loops back to label **15**. The **input** file

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variable **nsslmx** is the maximum number of steps in such a slide. The default value is 8. If the slide forward fails to succeed within **nsslmx** tries, then **eqcalc.f** writes an error message to the **output** and screen files, sets an error flag, and returns execution to the calling module.

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Appendix A: Glossary of Major Variables in EQ6

This glossary covers the major variables in EQ6 which are unique to this code. A roughly equal number are shared with EQ3NR. In fact, almost all of the variables used in EQ3NR are also used in EQ6. In order to save space, these variables will not be listed here unless there is some difference or nuance in the way in which they are used in EQ6, or unless it is desirable to include them to support immediate cross-reference with closely related variables which are only used in EQ6. Instead, the reader is referred to the descriptions of variables given in Appendix C of the EQ3NR User's Manual (Wolery, 1992b). None of these glossaries includes many variables which are of a purely local nature, such as a floating point variable used to accumulate sums in a do loop. Logarithmic quantities are frequently used in EQ3/6. These all refer to base ten, unless otherwise specified.

The variable names may be preceded by the corresponding algebraic symbols used in this report, if any. Following the conventions used universally in the EQ3/6 package, variables beginning with **i**, **j**, **k** or **n** are integer, those beginning with **q** are logical, and those beginning with **u** are character variables. Variables beginning with any other letters, including **l** and **m**, should be **real*8**. On 32-bit machines, this corresponds to **double precision**; on 64-bit machines, this corresponds to **single precision.**

Many entries in this glossary are described as either "data file ordered" or "input file ordered". The former refers to the indexing of arrays that have been filled by reading the data file, **data1**. The latter refers to the indexing of arrays that have been filled by reading the **input** file. Since the two forms of indexing are not equivalent, EQ6 must correlate them. This is done by mapping "input file ordered" data into a form which corresponds to "data file ordering," which is the ordering which is used in the code calculations. Most data arrays which are "input file ordered" are therefore treated as holding arrays and play no further role in the calculation once the data in them has been mapped to corresponding arrays which are "data file ordered."

Most arrays in EQ3/6 are dimensioned using FORTRAN parameters. The value of a parameter is assigned once in a code (in a PARAMETER statement) and can not be changed elsewhere. Some FORTRAN compilers permit parameters to be passed through calling sequences, but others do not allow this, as a means of protecting the parameter's assigned value. A called module often requires the dimensions of passed arrays. This is handled in EQ3/6 by the use of "dimensioning variables," which are ordinary integer variables whose values have been set equal to the corresponding parameters. The names of the dimensioning parameters in EQ3/6 typically end in **par**, **pa**, or **pa1**. The names of the corresponding dimensioning variables end, respectively, in **max**, **mx**, and **mx1**. Thus, the dimension of the **aa** matrix is given by the pair **kpar/kmax**. The maximum number of aqueous species is given by **nstpar/nstmax**. The parameter suffixes are used exclusively by dimensioning parameters. However, the corresponding variable suffixes are not used exclusively by dimensioning variables. For example, ***itermx*** is the maximum number of Newton-Raphson iterations.

A number of variables and arrays in the EQ6 program are represented by two forms. The first contains data for the current value of reaction progress. The second contains corresponding data for the pervious point of reaction progress. This is necessary because EQ6 occasionally runs into situations which require it to return to the previous point. Also, in stepping to the new point, the code estimates certain variables at the new point using truncated Taylor's series expansions about

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the previous point. Variables that store values at the previous point typically end in **o**, **s**, or **0** (e.g. **km1** and **km10**).

$\underline{J}$	**aa**	The Jacobian matrix. Dimensioning: **aa(kpar,kpar)**. Usage: **aa(krow,kcol)** is the element corresponding to the **krow**-th row and the **kcol**-th column. Note: in EQ6, this is also used in module **jgibbs.f** to test for violations of the mineralogic phase rule. In EQ3NR, it is s also used as the matrix that is required for simultaneous solutions in pre-Newton-Raphson optimization.
A, A_{-}	**aff**	(1) Affinity of a pure mineral to precipitate, kcal. Dimensioning: **aff(nmtpar)**. Usage: **aff(nm)** refers to the affinity of the **nm**-th pure mineral (this is the same usage as in EQ3NR). (2) This is used as a holding array in **readz.f** to read in data to be stored in the **mprmn** and **mprmx** arrays.
A_{+}	**affrct**	Array containing the affinities (kcal) of irreversible reactions. Dimensioning: **affrct(nrctpa)**. Usage: **affrct(nrc)** is the affinity corresponding to the forward direction of the **nrc**-th irreversible reaction.
A_{+}	**afftot**	The total affinity of overall irreversible reaction, kcal.
	aftarg	The target affinity used to find a phase boundary at which a new phase appears in the equilibrium system. This is assigned a value midway between those of the supersaturation tolerance parameters **tolsst** and **tolsat**. If **iopt4t** = 0, **aftarg** defaults to 0.00075 kcal; if **iopt4** = 1, to 0.0075 kcal.
$\underline{D}$	**akm**	A two-dimensional array containing a matrix that relates finite differences of ascending order to corresponding derivatives. Dimensioning: **akm(nordpa,nordpa)**. Usage: **dzvec0(i) = akm(i,j)*fdz0(j)**, **drel0(i) = akm(i,j)*fdrr0(j)**, and **drirc0(i) = akm(i,j)*fdri0(j)**.
	binm	A two-dimensional array that contains the binomial coefficients up to order **nordpa**, where each index starts at 1 instead of zero. Dimensioning: **binm(nordp1,nordp1)**. All peculiar values default to 1. Thus, $$\mathbf{binm}(n+1, k+1) = \binom{n}{k} = \frac{n!\,k!}{(n-k)!}$$
$-N_{+,ij}$	**cdac**	A three-dimensional array containing exponents that are part of transition state theory or activity product term rate laws for irreversible reactions proceeding in the forward direction (e.g., dissolution). Dimensioning: **cdac(ndctpa,imchpa,nrctpa)**. Usage: **cdac(n,i,nrc)** is the exponent of the activity of the **ns**-th aqueous species (where **ns = ndac(n,i,nrc)**) in the **i**-th mechanism of the rate law for the disappearance of the **nrc**-th irreversible reaction. The data in this array are read from the **input** file.
b_g^T	**cdrgt**	Array containing the sums of the coefficients of aqueous solute species other than water and aqueous oxygen gas appearing in the reactions for the dissolution of gas species. Dimensioning: **cdrgt(ngtpar)**. Usage: **cdrgt(ng)** is this sum for the reaction for the **ng**-th gas.

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b_{ϕ}^{T}	**cdrmt**	Array containing the sums of the coefficients of aqueous solute species other than water and aqueous oxygen gas appearing in the reactions for the dissolution of pure minerals. Dimensioning: **cdrmt(nmtpar)**. Usage: **cdrmt(nm)** is this sum for the reaction for the **nm**-th pure mineral.
	cdrst	Array containing the sums of the coefficients of aqueous solute species other than water and aqueous oxygen gas appearing in the reactions for the dissociation of an *auxiliary basis* or a *non-basis aqueous species*. Dimensioning: **cdrst(nrstpa)**. Usage: **cdrst(nrs)** is this sum for the **nrs**-th such reaction.
$c_{\varepsilon g}$	**cegs**	Array containing the elemental composition coefficients of gas species. Dimensioning: **cegs(nctpar,ngtpar)**. Usage: **cegs(nc,ng)** is the coefficient of the **nc**-th chemical element for the **ng**-th gas.
$c_{\varepsilon\phi}$	**cemn**	Array containing the elemental composition coefficients of pure minerals. Dimensioning: **cemn(nctpar,nmtpar)**. Usage: **cemn(nc,nm)** is the coefficient of the **nc**-th chemical element for the **nm**-th pure mineral.
	cesr	Array containing the elemental composition coefficients of special reactants. Dimensioning: **cesr(nctpar,nsrtpa)**. Usage: **cesr(nc,nsr)** is the coefficient of the **nc**-th chemical element for the **nrs**-th special reactant.
	cesrb	Holding array giving the elemental composition of a special reactant. Dimensioning: **cesrb(nctpar,nsrtpa)**. It is read from the input file and is therefore input file ordered. The data are mapped into the **cesr** array, which is data file ordered.
$c_{\varepsilon s}$	**cess**	Array containing the elemental composition coefficients of aqueous species. Dimensioning: **cess(nctpar,nstpar)**. Usage: **cess(nc,ns)** is the coefficient of the **nc**-th chemical element for the **ns**-th aqueous species.
$-N_{-,ij}$	**cpdac**	Array containing exponents that are part of transition state theory or activity product term rate laws for irreversible reactions proceeding in the reverse direction (e.g., precipitation). Dimensioning: **cpdac(ndctpa,imchpa,nrctpa)**. Usage: **cpdac(n,i,nrc)** is the exponent of the activity of the **ns**-th aqueous species (where **ns** = **npdac(n,i,nrc)**) in the **i**-th mechanism of the rate law for the formation of the **nrc**-th irreversible reaction. The data in this array are read from the **input** file.
	cplim	The maximum number of computing units to be used in a run. It is read from the **input** file. Local modifications to the code must be made to implement this feature.
$\sigma_{-,ij}$	**cpsigm**	Array containing the "sigma" parameters appearing in transition state theory rate laws for irreversible reactions proceeding in the reverse direction (e.g., precipitation). Dimensioning: **cpsigm(imchpa,nrctpa)**. Usage: **cpsigm(i,nrc)** is the "sigma" parameter for the **i**-th mechanism in the rate law for the **nrc**-th irreversible reaction. It is read from the input file. The "sigma" parameter is the ratio of the affinity of a macroscopic reaction to the affinity of the corresponding microscopic reaction.
$b_{\phi,scale}$	**cscale**	Array containing the affinity scaling factors for pure minerals. Dimensioning: **cscale(nmtpar)**. Usage: **cscale(nm)** is the scaling factor the **nm**-th pure mineral. These scaling factors are used to determine which of a number of supersaturated minerals is to be precipitated in an attempt to find an equilibrium phase assemblage.

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$\sigma_{+,ij}$	**csigma**	Array containing the #sigma" parameters appearing in transition state theory rate laws for irreversible reactions proceeding in the forward direction (e.g., dissolution). Dimensioning: **csigma(imchpa,nrctpa)**. Usage: **csigma(i,nrc)** is the "sigma" parameter for the **i**-th mechanism in the rate law for the **nrc**-th irreversible reaction. It is read from the **input** file. The "sigma" parameter is the ratio of the affinity of a macroscopic reaction to the affinity of the corresponding microscopic reaction.
$\Delta\xi$	**delzi**	The step size of the reaction progress.
$\bar{\underline{W}}$	**dlogxw**	Array of partial derivatives of the log mole fraction of water with respect to the log number of moles of the aqueous basis species. Dimensioning: **dlogxw(nsqpar)**. Usage: **dlogxw(ns)** is the partial derivative with respect to the **ns**-th basis species. Note that **dxlogw** is defined differently in EQ6 than in EQ3NR, where it is the related array of partial derivatives with respect to the log molalities of the solute basis species.
Δt	**dltime**	The time step (seconds) corresponding to a step of reaction progress.
	dlzidp	The "dump" interval for the flow-through open system mode. It is a user-specified interval of reaction progress between transfers of product minerals to the physically removed system. It is read from the **input** file.
	dlzimn	The true minimum step size that the program will use. It is typically two orders of magnitude less than **dlzmx1**, the step size for zero order.
	dlzmx1	The maximum step size for order zero. It is specified on the input file.
	dlzmx2	The maximum step size for orders greater than zero. It is specified on the **input** file.
$\frac{dv_j^{rel}}{d\xi}$	**drelr0**	Array containing derivatives of ascending order for the relative rates of reaction of irreversible reactions. Dimensioning: **drelr0(nordpa,nrctpa)**. Usage: **drelr0(j,nrc)** is the **j**-th order derivative of the relative rate for the **nrc**-th irreversible reaction. These derivatives are estimates based on finite differences. They provide the means for representing the relative rates by truncated Taylor's series.
$\frac{dv_{1/t}}{d\xi}$	**drirc0**	Array containing derivatives of ascending order for the inverse rate function. Dimensioning: **drirc0(nordpa)**. Usage: **drirc0(j)** is the **j**-th order derivative of the inverse rate. These derivatives are estimates based on finite differences. They provide the means for representing the inverse rate by a truncated Taylor's series.
$\underline{w}$	**dsum**	Array containing the vector of sums of succeeding reaction progress increments. Dimensioning: **dsum(nordpa)**. Usage: **dsum(n)** is the sum accumulated to order **n**.
	dzplg	The logarithmic plot interval in terms of **c** (reaction progress). It triggers writing a description of the modeled system to the plot file. This value is specified by the user on the **input** file.
	dzplot	The linear plot increment, in terms of reaction progress. It triggers writing a description of the modeled system to the plot file. This value is specified by the user on the **input** file.

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dzprlg The logarithmic print interval, in terms of reaction progress. It triggers the writing of a description of the modeled system to the **output** file. This value is specified on the **input** file.

dzprnt The linear print interval, in terms of reaction progress. It triggers the writing of a description of the modeled system to the **output** file. This value is specified on the **input** file.

dzvcnp Array containing the predicted values of the first derivatives with respect to reaction progress of the master iteration variables at a new point of reaction progress. Dimensioning: **dzvcnp(kpar)**. Usage: **dzvcpn(kcol)** is the predicted value for the **kcol**-th master iteration variable. These values are obtained by evaluating truncated Taylor's series which are based on backward finite differences.

dzvec0 Array containing the estimated values of the first derivatives with respect to reaction progress of the master iteration variables at the previous point of reaction progress. Dimensioning: **dzvec0(nordpa,kpar)**. Usage: **dzvec(n,kcol)** is the estimated value corresponding to an **n**-th order fit for the **kcol**-th master iteration value. These values are obtained by evaluating truncated Taylor's series which are based on backward finite differences.

$\Delta(nz)$ **electr** The fixed electrical imbalance carried in the calculations.

fctrl Array of factorials up to order **nordp1**. Dimensioning: **fctrl(nordp1)**. Usage: **fctrl(n)** = $n!$.

fdri0 Array of backward finite differences of ascending order, describing the inverse rate as a function of reaction progress. Dimensioning: **fdri0(nordpa)**. Usage: **fdri0(n)** is the **n**-th order difference function. This array used to compute the array of corresponding derivatives, **drirc0**.

fdrr0 Array of backward finite differences of ascending order, describing the relative rates of irreversible reactions as functions of reaction progress. Dimensioning: **fdrr0(nordpa,nrctpa)**. Usage: **fdrr0(n)** is the **n**-th order difference function. This array is used to compute the array of corresponding derivatives, **drelr0**.

fdz0 Array of backward finite differences of ascending order, describing the rates of change in the master iteration variables as functions of reaction progress. Dimensioning: **fdz0(nordpa,kpar)**. Usage: **fdz0(n,kcol)** is the **n**-th order difference function for the **kcol**-th master iteration variable. It is used to compute the array of corresponding derivatives, **dzvec0**.

f_j **fk** Array containing the ratios of effective surface area to total surface area of the reactants associated with irreversible reactions. Dimensioning: **fk(nrctpa)**. Usage: **fk(nrc)** is ration for the **nrc**-th irreversible reaction. This array can also be used as an array of generalized correction factors for the corresponding array of rate constants for all irreversible reactions.

gtr Array containing the elemental composition of the theoretical rock (g/kg). Dimensioning: **gtr(nctpar)**. Usage: **gtr(nc)** is the number of grams of the **nc**-th element per kg of rock.

ibetmx The index of the element of the **beta** array having the largest magnitude.

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iexr Array containing the indices of reactants associated with irreversible reactions that have become exhausted (reduced to zero mass) at the current value of reaction progress. Dimensioning: **iexr(nrctpa)**. Usage: **iexr(i)** is the index of the **i**-th exhausted reactant

iexrt The number of reactants associated with irreversible reactions that have become exhausted at the current value of reaction progress.

ifile A flag variable read from the **input** file. It instructs the code which from which to read the last half of the #input" for a problem. The normal value is 60, indicating that the **input** file is to be used. If a value of 9 is given, the **pickup** file is to be used instead.

iindx0 Copy of the **iindx1** array at the previous point of reaction progress. Dimensioning: **iindx0(kpar)**. Usage: **iindx0(kcol)** is the index at the previous point of the **kcol**-th master iteration variable.

iindx1 Array containing the indices of species whose masses are used as master iteration variables. Dimensioning: iindx1(**kpar**). Usage: for **kcol** between 1 and **ksq**, **iindx1(kcol)** gives the index of an aqueous species; for **kcol** between **km1** and **kmt**, **iindx1(kcol)** gives the index of a pure mineral; for **kcol** between **kx1** and **kxt**, **iindx1(kcol)** gives an index of the form 50000 + 100***nx** + **ik**, where **nx** is the index of a solid solution and **ik** is the index of an end member component.

imchmx Maximum number of terms in a transition-state theory or activity product term rate law. This is the variable equivalent to the parameter **imchpa**.

imchpa Dimensioning parameter: the maximum number of terms in a transition state theory or activity product term kinetic rate law. See **imchmx**.

$i_{T,+j}$ **imech** Array giving the number of parallel mechanisms in transition state theory or activity product term rate laws for irreversible reactions proceeding in the forward direction (e.g., dissolution). Dimensioning: **imech(nrctpa)**. Usage: **imech(nrc)** is the number of mechanisms for the **nrc**-th irreversible reaction. It is read from the **input** file.

iodb1, etc. Debugging print option switches; see Chapter 5. Some of these switches differ from those used in EQ3NR.

iopg1, etc. Activity coefficient option switches; see Chapter 5. These switches are all identical to those used in EQ3NR.

iopr1, etc., Print option switches; see Chapter 5.Some of these switches differ from those used in EQ3NR.

iopt1, etc. Model option switches; see Chapter 5.Some of these switches differ from those used in EQ3NR.

ioscan Flag switch to control scanning on the oxygen fugacity variable; setting it to -1 on the **input** file turns off scanning.

$i_{T,-j}$ **ipmech** Array giving the number of parallel mechanisms in transition state theory or activity product term rate laws for irreversible reactions proceeding in the reverse direction (e.g., precipitation). Dimensioning: **ipmech(nrctpa)**. Usage: **ipmech(nrc)** is the

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number of mechanisms for the **nrc**-th irreversible reaction. It is read from the **input** file.

jcode Array specifying the types of the reactants associated with irreversible reactions. Dimensioning: **jcode(nrctpa)**. Usage: **jcode(nrc)** is the type flag for the **nrc**-th irreversible reaction. It is read from the **input** file and has the following meanings:

= 0 Pure mineral
= 1 Solid solution
= 2 Special reactant
= 3 Aqueous species
= 4 Gas

jflag A flag that determines whether an auxiliary basis species is treated as a basis species (**jflag(ns)** = 0), or a dependent species (**jflag(ns)** = 30). Dimensioning: **jflag(nstpar)**. Usage: **jflag(ns)** is the flag for the **ns**-th aqueous basis species read from the data file. In the present version of EQ6, **jflag** is required to have a value of 30 for all auxiliary basis species.

jgflag Array of status flags for gas species. Dimensioning: **jgflag(ngtpar)**. Usage: **jgflag(ng)** is the flag for the **ng**-th gas species:

= 0 Normal status
= 2 Thermodynamically suppressed
= 3 Not in the current model

jkflag Array of status flags for solid solution end member components. Dimensioning: **jkflag(iktpar,nxtpar)**. Usage: **jkflag(ik,nx)** is the flag for the **ik**-th component of the **nx**-th solid solution:

= -10 Saturated, not present as a matrix variable
= -2 Supersaturated
= -1 Saturated, present as a matrix variable
= 0 Normal status
= 2 Thermodynamically suppressed
= 3 Not in the current model

jmflag Array of status flags for pure minerals. Dimensioning: **jmflag(nmtpar)**. Usage: **jmflag(nm)** is the flag for the **nm**-th pure mineral:

= -10 Saturated, not present as a matrix variable
= -2 Supersaturated
= -1 Saturated, present as a matrix variable
= 0 Normal status
= 2 Thermodynamically suppressed
= 3 Not in the current model

jreac Array of status flags for irreversible reactions. Dimensioniug: **jreac(nrctpa)**. Usage: **jreac(nrc)** is the flag for th **nrc**-th irreversible reaction:

= -1 Saturated, remaining reactant mass continues to react irreversibly
= 0 Normal status
= 1 Exhausted
= 2 Saturated, remaining reactant mass is converted to correspondiug product mineral mass

jsflag Status switch array for aqueous species. Dimensioning: **jsflag(nstpar)**. Usage: **jsflag(ns)** is the flag for the **ns**-th aqueous species:

= 0 A mineral appears in the current model

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= 2 It is thermodynamically suppressed
= 3 It does not appear in the current model

jtemp Temperature tracking flag, read from the **input** file:
= 0 Taylor's series in reaction progress (**iopt1** = 0) or time,(**iopt1** = 1)
= 1 Fluid mixing tracking

jxflag Array of status flags for solid solutions. Dimensioning: **jxflag(nxtpar)**. Usage: **jxflag(nx)** is the flag for the **nx**-th solid solution:
= -10 Saturated, not present as a matrix variable
= -2 Supersaturated
= -1 Saturated, present as a matrix variable
= 0 Normal status
= 2 Thermodynamically suppressed
= 3 Not in the current model

kct The number of chemical elements present in the Jacobian matrix.

kdim The dimension of the Jacobian matrix.

kdim0 The value of **kdim** at the previous point of reaction progress.

km1 The first position in the Jacobian matrix corresponding to a pure mineral.

km10 The value of **km1** at the previous point of reaction progress.

kmax The maximum number of master variables. This is the variable corresponding to the parameter **kpar**.

kpar Dimensioning parameter: the maximum number of master variables. See **kmax**.

kmt The last position in the Jacobian matrix corresponding to a pure mineral.

kmt0 The value of **kmt** at the previous point of reaction progress.

kord The maximum allowable order of the finite differences for a given step of reaction progress.

kprs A flag on the **input** file which marks the presence on that file of data for the masses of phases and components in the physically removed system.

ksat The number of supersaturated pure minerals, ignoring minerals which are suppressed or for which a precipitation rate law is given.

kspimx The maximum number of steps between writes to the plot file. This is specified on the **input** file.

ksppmx The maximum number of steps between writes of a detailed description of the modeled system to the **output** file. This is specified on the **input** file.

kstep The number of reaction progress steps that have been made.

kstpmx The maximum number of steps for a problem. This is specified on the **input** file.

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	kstppr	The number of steps since the last print point.
	kx1	The first position in the Jacobian matrix corresponding to a solid solution end member component.
	kx10	The value of **kx1** at the previous point of reaction progress.
	kxsat	The number of supersaturated solid-solution phases, ignoring phases which are suppressed or for which a precipitation rate law is given.
	kxt	The last position in the Jacobian matrix corresponding to a solid solution end member component.
	kxt0	The value of **kxt** at the previous point of reaction progress.
$log\ n_\phi$	**lomn**	Array containing the logarithms of the number of moles of the pure minerals. Dimensioning: **lomn(nmtpar)**. Usage: **lomn(nm)** is the logarithm of the number of moles of the **nm**-th pure mineral.
$log\ n_{\chi\psi}$	**lomx**	Array containing the logarithms of the number of moles of the solid solution end member components. Dimensioning: **lomx(iktpar,nxtpar)**. Usage: **lomx(ik,nx)** is the logarithm of the number of moles of the **ik**-th component of the **nx**-th solid solution.
$log\ n_s$	**loss**	Array containing the logarithms of the number of moles of the aqueous species. Dimensioning: **loss(nstpar)**. Usage: **loss(ns)** is the logarithm of the number of moles of the **ns-th** aqueous species.
$log\ n_\psi$	**lotx**	Array containing the logarithms of the number of moles of the solid solutions. Dimensioning: **lotx(nxtpar)**. Usage: **lotx(nx)** is the logarithm of the number of moles of the **nx**-th solid solution.
	lscanh	The thermodynamic lower limit on the oxygen fugacity (the same as the standard lower stability limit of liquid water as represented on *Eh-pH* diagrams).
	lscano	The thermodynamic upper limit on the oxygen fugacity. (the same as the standard upper stability limit of liquid water as represented on *Eh-pH* diagrams)
	mipm	Array containing the rates of formation of product minerals forming in partial equilibrium with a moving aqueous fluid. Dimensioning: **mipm(kpar)**. Usage: **mipm(kcol)** is the value for the mineral component (pure mineral or solid solution component) which is associated with the **kcol**-th master iteration variable. This array is used only in connection with the fluid-centered flow-through system model (specified by **nmodl1** = 3). The quantity is defined as $\frac{dn_i}{d\xi}$, where n_i is the number of moles of the i-th mineral component.
	modr	Array containing the number of moles of destroyed reactants. Dimensioniug: **modr(nrctpa)**. Usage: **modr(nrc)** is the number of moles of the **nrc**-th reactant that have been destroyed.

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	modrs	Array containing the number of moles of destroyed reactants at the previous point of reaction progress. Dimensioning: **modrs(nrctpa)**. Usage: **modrs(nrc)** is the number of moles of the **nrc**-th reactant that were destroyed at the previous point.
	moffg	Array containing the number of moles of fictive fugacity-fixing phases to add to the system. This is specified on the **input** file. Dimensioning: **moffg(nffgpa)**. Usage: **moffg(nf)** is the number of moles for the **nf**-th such gas.
n_ϕ	**momn**	Array containing the number of moles of minerals. Dimensioning: **momn(nmtpar)**. Usage: **momn(nm)** is the number of moles of the **nm**-th mineral present in the equilibrium system.
$n_{\xi\psi}$	**momx**	Array containing the number of moles of solid solution end member components. Dimensioning: **momx(iktpar,nxtpar)**. Usage: **momx(ik,nx)** is the number of moles of the **ik**-th end-member of the **nx**-th solid solution.
	morr	Array containing the number of remaining moles of reactants. Dimensioning: **morr(nrctpa)**. Usage: **morr(nrc)** is the number of remaining moles of the **nrc**-th reactant. It appears on the **input** file. When a problem is initially defined, the user uses this to specify the initial number of moles of the reactants.
	morrs	Array containing the number of remaining moles of reactants at the previous point of reaction progress. Dimensioning: **morrs(nrctpa)**. Usage: **morrs(nrc)** is the number of remaining moles of the **nrc**-th reactant at the previous point.
n_s	**moss**	Array containing the number of moles of aqueous species. Dimensioning: **moss(nstpar)**. Usage: **moss(ns)** is the number of moles of the **ns**-th aqueous species present in the equilibrium system.
n_ψ	**motx**	Array containing the number of moles of solid solutions. Dimensioning: **motx(nxtpar)**. Usage: **motx(nx)** is the number of moles of the **nx**-th solid solution present in the equilibrium system.
	mprmn	Array containing the number of moles of pure minerals present in the physically removed system. Dimensioning: **mprmn(nmtpar)**. Usage: **mprmn(nm)** is the number of moles of the **nm**-th pure mineral present in this system.
	mprmx	Array containing the number of moles of end member components of solid solutions present in the physically removed system. Dimensioning: **mprmx(iktpar,nxtpar)**. Usage: **mprmx(ik,nx)** is the number of moles of the **ik**-th component in the **nx**-th solid solution present in this system.
	msort	Array containing the number of moles of the aqueous species, in order of increasing value. Dimensioning: **msort(nstpar)**. Usage: primarily as a storage array required for the sorting; **msort(n) = moss(jsort(n)**.
$n_{T,\varepsilon}$	**mte**	Array containing the total number of moles of the chemical elements. Dimensioning: **mte(nctpar)**. Usage: **mte(nc)** is the total number of moles of the **nc**-th element in the equilibrium system. This array is data file ordered.
	mteaq	Array containing the total number of moles of the chemical elements present in the aqueous phase. Dimensioning: **mteaq(nctpar)**. Usage: **mteaq(nc)** is the number of moles of the **nc**-th element in this phase. This array is data file ordered.

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	mteaqb	Array containing the same information as in the **mteaq** array, but input file ordered. Dimensioning: **mteaqb(nctpar)**. Usage: **mteaqb(ncb)** is the number of moles of the **ncb-th** element in the aqueous phase read from the **input** file.
	mteb	Array containing the same information as in the **mte** array, but input file ordered. Dimensioning: **mteb(nctpar)**. Usage: **mte(ncb)** is the number of moles of the **ncb-th** element read from the **input** file.
$n_{T,\varepsilon}$	**mtes**	Array containing the contents of the **mte** array at the previous value of reaction progress. Dimensioning: **mtes(nctpar)**. Usage: **mtes(nc)** is the total number of moles of the **nc**-th element at the previous point.
M_g	**mwtgs**	Array containing the molecular weights of gas species. Dimensioning: **mwtgs(ngtpar)**. Usage: **mwtgs(ng)** is the molecular weight of the **ng**-th gas.
M_ϕ	**mwtmn**	Array containing the molecular weights of pure minerals. Dimensioning: **mwtmn(nmtpar)**. Usage: **mwtmn(nm)** is the molecular weight of the **nm**-th pure mineral.
	mwtrc	Array containing the molecular weights of reactants. Dimensioning: **mwtrc(nrctpa)**. Usage: **mwtrc(nrc)** is the molecular weight of the **nrc**-th reactant.
M_i	**mwtss**	Array of molecular weights of aqueous species. Dimensioning: **mwtss(nstpar)**. Usage: **mwtss(ns)** is the molecular weight of the **ns**-th aqueous species.
	nart	The number of aqueous species reactants associated with irreversible reactions.
	ncorr	The number of corrector cycles, including step size cuts, to achieve desired accuracy in the integration of kinetic rate laws.
	ndac	Array giving the index of an aqueous species whose thermodynamic activity appears as a factor in a transition theory rate law for an irreversible reaction proceeding in the forward direction (e.g., dissolution). Dimensioning: **ndac(ndctpa,imchpa,nrctpa)**. Usage: **ndac(n,i,nrc)** is the species index for the **n**-th such species appearing in the **i**-th mechanism for the **nrc**-th irreversible reaction.
$N_{T,+,ij}$	**ndact**	The number of aqueous species whose thermodynamic activities appear in factors for a transition state theory or activity product term rate law for an irreversible reaction proceeding in the forward direction (e.g., dissolution). Dimensioning: ndact(imchpa,nrctpa). Usage: **ndact(i,nrc)** is the number of such species for the **i**-th mechanism for the **nrc**-th irreversible reaction.
	ndctmx	Maximum number of species whose activities can appear in a transition state theory or activity product term rate law term. This is the variable equivalent to **ndctpa**.
	ndctpa	Dimensioning parameter: the maximum number of species whose activities can appear in a transition state theory or activity product term rate law term. See **ndctmx**.
	newsat	The number of newly saturated phases (pure minerals plus solid solution end member components), excluding suppressed phases.
	nffg	The number of gases whose fugacities are to be fixed in a problem. This is read from the **input** file.

Information Only

nffgmx The maximum number of gas species whose fugacities have been fixed. This is the variable equivalent to **nffgpa**.

nffgpa Dimensioning parameter: the maximum number of gas species whose fugacities have been fixed.

ngrt The number of gas species reactants associated with irreversible reactions.

nh2g The index of the species hydrogen gas.

nmchk Array used to mark pure minerals which are used as reactants associated with irreversible reactions. Dimensioning: **nmchk(nmtpar)**. Usage: if **nmchk(nm)** = 1, then the **nm**-th pure mineral is used as a reactant. If **nmchk(nm)** = 0, it is not so used.

nmodl1 Physical model option switch, read from the **input** file:
= 0 Defaults to 2
= 1 Titration
= 2 Closed system
= 3 Fluid-centered flow-through system.

nmodl2 Path tracing option switch, read from the **input** file:
= 0 Normal path tracing
= 1 Permits selection of economy mode
= 2 Permits selection of super economy mode
Economy mode forces larger step sizes, but still finds phase boundaries and other points of interest. Super economy model does not bother to find such points of interest. Economy mode and super economy model do not work if kinetic mode is selected. Economy mode and super economy mode do not work well in version 7.0 of EQ6 due to present limitations of the performance of the pre-Newton-Raphson optimization algorithm.

nmrt The number of pure mineral reactants associated with irreversible reactions.

no2g The index of the aqueous oxygen gas species.

nord The actual order of the finite differences, and hence also that of the truncated Taylor's series.

nordlm The maximum value of **nord** permitted by the user. It is specified on the **input** file.

nordmx The maximum order of the finite differences and truncated Taylor's series. This is the variable equivalent to **nordpa**.

nordpa Dimensioning parameter: the maximum order of the finite differences and truncated Taylor's series. See **nordmx**.

nordsv The saved value of **nord**.

npdac Array giving the index of an aqueous species whose thermodynamic activity appears as a factor in a transition theory or activity product term rate law for an irreversible reaction proceeding in the reverse direction (e.g., precipitation). Dimensioning: **npdac(ndctpa,imchpa,nrctpa)**. Usage: **npdac(n,i,nrc)** is the species index for the **n**-th such species appearing in the **i**-th mechanism for the **nrc**-th irreversible reaction.

Information Only

$N_{T,-,ij}$

npdact The number of aqueous species whose thermodynamic activities appear in factors for a transition state theory or activity product term rate law for an irreversible reaction proceeding in the reverse direction (e.g., precipitation). Dimensioning: **npdact(imchpa,nrctpa)**. Usage **npdact(i,nrc)** is the number of such species for the i-th mechanism for the nrc-th irreversible reaction.

nprmn The number of pure minerals in the physically removed system. This is read from the **input** file.

nprmx The number of solid solution end member components in the physically removed system. This is read from the **input** file.

nprsmx The maximum number of species in the physically removed system. This is the variable equivalent to **nprspa**.

nprspa Dimensioning parameter: the maximum number of species in the physically removed system. See **nprsmx**.

npslmx The maximum number of attempts sliding forward in reaction progress to get over a critical region around a phase boundary. This is specified on the **input** file (A zero defaults to 3, and a value of -1 inhibits such sliding).

nrct The total number of irreversible reactions.

nrctmx The maximum number of irreversible reactions. This is the variable equivalent to **nrctpa**.

nrctpa Dimensioning parameter: the maximum number of irreversible reactions. See **nrctmx**.

nrk Array specifying the rate law type to use for an irreversible reaction proceeding in the forward direction (e.g., dissolution). This is read from the **input** file. Dimensioning: **nrk(nrctpa)**. Usage: **nrk(nrc)** is the flag for the **nrc**-th irreversible reaction:

= -1 Use the specified reverse rate law
= 0 Illegal value
= 1 Relative rate expression
= 2 Transition state theory
= 3 Specified (fixed) rate
= 4 Activity product term rate law

nrndex Array giving the species indices of the reactants associated with irreversible reactions. Dimensioning: **nrndex(nrctpa)**. Usage: **nrndex(nrc)** is the species index of the **nrc**-th reactant.

nrpk Array specifying the rate law type to use for an irreversible reaction proceeding in the reverse direction (e.g., precipitation). This is read from the **input** file. Dimensioning: **nrpk(nrctpa)**. Usage: **nrpk(nrc)** is the flag for the **nrc**-th irreversible reaction:

= -1 Use the specified forward rate law
= 0 Instantaneous partial equilibrium
= 1 Relative rate expression
= 2 Transition state theory
= 3 Specified (fixed) rate
= 4 Activity product term rate law

Information Only

nsk Array of flags for treating the surface areas of the reactants associated with irreversible reactions. Dimensioning: **nsk(nrctpa)**. Usage: **nsk(nrc)** is the flag for the **nrc**-th irreversible reaction:
= 0 Fixed surface area
= 1 Fixed specific surface area.

nsrt The number of special reactants.

nsrtmx The maximum number of special reactant species. This is the variable equivalent to **nsrtpa**.

nsrtpa Dimensioning parameter: the maximum number of special reactant species. See **nsrtmx**.

nsslmx The maximum number of steps sliding forward to get over a critical region of redox instability (A zero defaults to 3, and a -1 inhibits sliding). It is read from the **input** file.

ntab Device number for the **tab** file.

ntabs Device number for the **tabs** file.

ntabx Device number for the **tabx** file.

ntitl1 The number of lines in the problem title given on the **input** file.

ntitl2 The number of lines in the title on the **input** file carried forward from a previous run.

nxchk Array used to mark solid solutions which are used as reactants associated with irreversible reactions. Dimensioning: **nxchk(nxtpar)**. Usage: if **nxchk(nx)** = 1, then the **nx**-th solid solution is used as a reactant. If **nxchk(nx)** = 0, it is not so used.

nxopex The number of exceptions to a pure mineral subset-selection suppression option. This is read from the **input** file. The names of the exceptions are read into the **uxopex** array.

nxopmx The maximum number of subset-selection options for suppressing pure minerals. This is the variable equivalent to the parameter **nxoppa**.

nxoppa Dimensioning parameter: the maximum number of subset-selection options for suppressing pure minerals. See **nxopmx**.

nxopt The number of mineral subset-selection suppression options to be executed. This is read from the input file.

nxpemx The maximum number of specified exceptions to a pure mineral subset-selection suppression option. This is the variable equivalent to the parameter **nxpepa**.

nxpepa Dimensioning parameter: the maximum number of specified exceptions to a pure mineral subset-selection suppression option. See **nxpemx**

nxridx Array giving the solid solution index of a solid solution reactant associated with an irreversible reaction. Dimensioning: **nxridx(nxrtpa)**. Usage: **nxridx(nxrt)** is the normal solid solution index of the **nxrt**-th solid solution reactant.

Information Only

nxrt The number of solid solution reactants associated with irreversible reactions.

nxrtmx The maximum number of solid solution reactants associated with irreversible reactions. This is the variable equivalent to the parameter **nxrtpa**.

nxrtpa Dimensioning parameter: the maximum number of solid solution reactants associated with irreversible reactions. See **nxrtmx**.

qcorr Logical flag which is true if the corrector tolerance is satisfied.

qdump Logical flag which is true if product mineral mass is to be transferred to the physically removed system.

qecon Logical flag which is true if the code is operating in economy mode.

qfcp2 Logical flag which is true if assumed phase assemblage in the equilibrium system violates the apparent phase rule.

qflag Logical flag which is true if the temperature is changing with reaction progress and has just crossed 100°C.

qmod Logical flag which is true if the equilibrium phase assemblage has just been changed.

qnochb Logical flag which is true if the charge balance constraint is not active.

qnocor Logical flag which is true when no corrector cycles are to be done, even if the corrector tolerance is not satisfied (**qnocor = qqmode .or. qsmode .or. qpmode**).

qnocut Logical flag which is true if no step size cuts are to be made to satisfy the corrector tolerance (**qnocut = qsmode.or. qpmode**).

qphasl Logical flag which is true if eqcalc.f just slid forward in reaction progress avoid numerical instability associated with a phase entering or leaving the equilibrium phase assemblage.

qpmode Logical flag which is true if **qphasl** was set to true in the most recent call to module **eqcalc.f.**

qprint Logical flag which is true if a detailed description of the state of the reacting system is to be written to the **output** file at the current point of reaction progress.

qqmode Logical flag which is true if Newton-Raphson iteration has failed and cannot be made to work at the current point of reaction progress.

qriinf Logical flag which is true if time has reached infinity.

qscon Logical flag which is true if the code is running in super economy mode.

qsmode Logical flag which is true if the code is in redox scanning mode.

qtayli Logical flag which is true if "linear" instead of "logarithmic" Taylor's series are to be employed to represent the change in master iteration variables with increase in reaction progress.

Information Only

	qtime	Logical flag which is true if the limit on computing units is close to being exceeded.
	rirec0	The inverse rate (seconds/mole) at the previous point of reaction progress.
	rirec1	The inverse rate at the current point of reaction progress.
	rirecp	The predicted value of the inverse rate at a new point of reaction progress, based on backward finite differences expressed as a truncated Taylor's series.
$k_{+,ij}$	**rk**	Array of rate constants for irreversible reactions proceeding in the forward direction (e.g., dissolution). This is read form the **input** file. Dimensioning: **rk(imchpa,nrctpa)**. Usage: **rk(i,nrc)** is the forward rate constant for the **i**-th mechanism of the **nrc**-th irreversible reaction. The exact meaning of the values depends on the actual rate laws used. See **nrk**.
$k_{-,ij}$	**rpk**	Array of rate constants for irreversible reactions proceeding in the reverse direction (e.g., precipitation). This is read form the **input** file. Dimensioning: **rpk(imchpa,nrctpa)**. Usage: **rpk(i,nrc)** is the reverse rate constant for the **i**-th mechanism of the **nrc**-th irreversible reaction. The exact meaning of the values depends on the actual rate laws used. See **nrpk**.
v_j	**rreac0**	Array of reaction rates of the irreversible reactions at the previous point of reaction progress. Dimensioning: **rreac0(nrctpa)**. Usage: **rreac0(nrc)** is the rate at that point of the **nrc**-th irreversible reaction.
v_j	**rreac1**	Array of reaction rates of the irreversible reactions at the current point of reaction progress. Dimensioning: **rreac1(nrctpa)**. Usage: **rreac1(nrc)** is the rate of the **nrc**-th irreversible reaction.
v_j^{rel}	**rrelr0**	Array of relative rates of the irreversible reactions at the previous point of reaction progress. Dimensioning: **rrelr0(nrctpa)**. Usage: **rrelr0(nrc)** is the relative rate at that point of the **nrc**-th irreversible reaction.
v_j^{rel}	**rrelr1**	Array of relative rates of the irreversible reactions at the current point of reaction progress. Dimensioning: **rrelr1(nrctpa)**. Usage: **rrelr1(nrc)** is the relative rate of the **nrc**-th irreversible reaction.
v_j^{rel}	**rrelrp**	Array of predicted values of relative rates of irreversible reactions at a new point of reaction progress. Dimensioning: **rrelrp(nrctpa)**.Usage: **rrelrp(nrc)** is the predicted relative rate of the **nrc**-th irreversible reaction.
	rxbar	Array of mole fractions of end member components in solid solution reactants associated with irreversible reactions. Dimensioning: **rxbar(iktpar,nxrtpa)**. Usage: **rxbar(ikb,nxr)** is the mole fraction of the **ikb**-th end-member of the **nxr**-th solid solution reactant. The first dimension of this array is data file ordered.
	rxbarb	Array of mole fractions of end member components in solid solution reactants associated with irreversible reactions. Dimensioning: **rxbarb(iktpar,nxrtpa)**. This is read from the **input** file. Usage: **rxbar(ikb,nxr)** is the mole fraction of the **ikb**-th end-member of the **nxr**-th solid solution reactant. The first dimension of this array is input file ordered. This array is used to set up the **rxbar** array.

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	scmax	Array of step size scaling factors corresponding to different possible orders of predictor functions based on finite differences. Dimensioning: **scmax(nordp1)**. Usage: **scmax(n)** is the factor for the **n**-th order.
	screw1	Setscrew variable used to determine the order and step size. It bounds the absolute value of the highest order term in any truncated Taylor's series used to describe a master iteration variable. This variable is read from the **input** file. It has a default value of 0.0001.
	screw2	Not currently used.
	screw3	Setscrew variable used to determine the order and step size. It bounds the absolute value of the highest order term in any truncated Taylor's series used to describe a kinetic rate function. This variable is read from the **input** file. It has a default value of 0.0001. It also serves a function similar to that of **screw4** in testing the estimated error in the absolute time or the reaction progress variable of any individual irreversible reaction after a step has been made to see if corrective action is required. If either of the **screw3** or **screw4** tests are satisfied, no corrective action (corrector iteration or step size cuts) is taken.
	screw4	The tolerance parameter for corrective action (corrector iteration or step size cut) used to insure accurate integration of kinetic rate functions. It bounds the magnitudes of the differences between rate functions estimated at the new point of reaction progress from the actual rate expressions and corresponding values predicted by using finite differences. It is read from the **input** file. It has a default value of 4.0.
δ'	**screw5**	An under-relaxation control parameter which bounds the magnitude of the largest applied Newton-Raphson correction term on any given iteration. It is read from the **input** file.It has a default value of 4.0.
	screw6	Setscrew variable used to control the step size in economy mode. It bounds the predicted change in a master iteration variable. It is read from the **input** file. It has a default value of 4.0
	sk	Array of surface areas (cm^3) of reactants associated with irreversible reactions. Dimensioning: **sk(nrctpa)**. Usage: **sk(nrc)** is read from the **input** file if **nsk(nrc)** = 0; otherwise, it is calculated from **ssk(nrc)**.
	ssk	Array of specific surface areas (cm^3/g) of the reactants associated with irreversible reactions. Dimensioning: **ssk(nrctpa)**. Usage: **ssk(nrc)** is read from the **input** file if **nsk(nrc)** = 1; otherwise, it is calculated from **sk(nrc)**.
H_{sr}, H_{zr}	**stor1**	The H_{sr} or H_{zr} factors defiued in Chapter 8. Dimensioning: **stor1(nrstpa)**. Usage: **stor1(nrs)** is the factor for the **nrs**-th reaction. Note that these are defined in terms of moles in EQ6, whereas they are defined in terms of molalities in EQ3NR
$\Lambda_{\sigma j}$	**sx**	Array containing partial derivatives of expressions for the logarithms of the activity coefficient of solid solutions end member components with respect to mole fractions appearing in the expressions. Dimensioning: **sx(iktpar,iktpar)**. Usage: **sx(ik,ikk)** is the derivative of **lamlg(ik,nx)** with respect to **xbar(ikk,nx)**, where **nx** denotes the current solid solution.
	tcnst1	The number of secouds per day (86,400).

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	tcnst2	The number of days per year (365.25).
	tdays	The time (days).
	tempc	Temperature, °C.
	tempc0	The temperature (°C) at $\xi = 0$ in non-kinetic mode, at $t = 0$ in kinetic mode. This variable is read from the **input** file.
	tempci	The temperature (°C) at the end of the previous EQ3NR or EQ6 run. It is used to detect temperature jumps. This variable is read from the **input** file.
T	**tempk**	The absolute temperature (°K).
t	**time**	The time (seconds) at the current point of reaction progress.
	timemx	The desired maximum value of time (seconds).
t	**times**	The time (seconds) at the previous point of reaction progress.
k_{T1}	**tk1**	The first temperature tracking coefficient. Its meaning is determined by the values of **iopt1** and **jtemp** flag. If **jtemp** = 1, the temperature changes according to a fluid mixing model and **tk1** is the ratio of the mass of the starting aqueous solution to that of the aqueous solution being treated as a reactant. Usually both masses are close to 1 kilogram, so the value of **tk1** is close to unity. If **jtemp** = 0, then **tk1** is a first-order polynomial coefficient. If **iopt1** = 0, the polynomial is one in reaction progress; if **iopt1** = 1, it is one in time (seconds).
k_{T2}	**tk2**	The second temperature tracking coefficient. Its meaning is determined by the values of **iopt1** and **jtemp** flag. If **jtemp** = 1, the temperature changes according to a fluid mixing model and tk2 is the temperature of the fluid which is being treated as a reactant (and **tempc0** is the temperature of the other fluid prior to mixing). If **jtemp** = 0, then **tk2** is a second-order polynomial coefficient. If **iopt1** = 0, the polynomial is one in reaction progress; if **iopt1** = 1, it is one in time (seconds).
k_{T3}	**tk3**	The third temperature tracking coefficient. Its meaning is determined by the values of **iopt1** and **jtemp** flag. If **jtemp** = 1, the temperature changes according to a fluid mixing model and **tk3** is not used. If **jtemp** = 0, then **tk3** is a third-order polynomial coefficient. If **iopt1** = 0, the polynomial is one in reaction progress; if **iopt1** = 1, it is one in time (seconds).
	tlogd	The logarithm of the time (days).
$\log t$	**tlogs**	The logarithm of the time (seconds).
	tlogyr	The logarithm of the time (years).
	tolaft	The tolerance about the target affinity (**aftarg**), used in finding the step size, according to finite differences, corresponding to a phase boundary at which a new phase appears in the equilibrium system. This variable is set to **tolsst - aftarg**, so the corresponding range in which the affinity is desired to fall runs from **tolsat** to **tolsst**.
	told	The temperature (°C) at the previous point of reaction progress.

Information Only

tolbt Convergence bound on **betamx**.

toldl Convergence bound on **delmax**.

tolsat The value of the affinity (kcal) to precipitate, below which EQ6 will not attempt to actually form the phase as part of the equilibrium system. This is read from the **input** file. If **iopt4** = 0, the default value for this is 0.0005 kcal. If **iopt4** = 1, the default is 0.005 kcal.

tolsst The value of the affinity (kcal) to precipitate, above which EQ6 will cut the step size in order to accurately locate a phase boundary at which a phase appears in the equilibrium system. This is read from the **input** file. Its value must exceed that of **tolsat**. Its default value is twice **tolsat**.

tolx A generalized search/find tolerance parameter, used for a variety of specific purposes. It is read from the **input** file. Its default value is set equal to **tolbt**.

tstrt The time (seconds) at the start of execution of a problem.

tyears The time (years) at the current point of reaction progress.

tzero The last temperature (°C) at which temperature dependent data were evaluated.

uall The string 'all'.

ualwth The string 'alwith'.

uaq The string "aqueous species".

ubas The string "basis variable".

ublank A blank string.

udac Array of names of species whose activities appear as factors in certain kinetic rate laws for irreversible reactions proceeding in the forward direction (e.g., dissolution). Dimensioning: **udac(ndctpa,imchpa,nrctpa)**. Usage: **udac(n,i,nrc)** is the name of the **n**-th species appearing in the **i**-th mechanism or term in the rate law for the **nrc**-th irreversible reaction. Note that the first dimension is input file ordered. The actual species index is given by **ndac(n,i,nrc)**. This is read from the **inpnt** file. The **udac** array is used to set up the **ndac** array.

uelect The string 'electr'.

uelemb Array containing the names (symbols) of chemical elements, as read from the **input** file. Dimensioning: **uelemb(nctpar)**. Usage: **uelemb(ncb)** is the **ncb**-th element read from the data file. Note that this array is input file ordered.

uendb Array containing the names of end member components of solid solution reactants associated with irreversible reaetions. Dimensioning: **uendb(iktpar,nxrtpa)**. Usage: **nendb(ikb,nxr)** is the **ikb**-th component of the **nxr**-th solid solution reactant. This is read from the **input** file. Note that both dimensions are input file ordered.

uendit The string 'endit.'.

Information Only

uerror The string 'error'.

uesrb Array containing the names (symbols) of chemical elements of which are composed special reactants. Dimensioning: **uesrb(nctpar,nsrtpa)**. Usage: **uesrb(ncb,nsr)** is the name of the **ncb**-th element making up the **nsr**-th reactant. It is read from the **input** file. Note that the first dimension is input file ordered.

uffg Array containing the names of the gases whose fugacities are to be fixed. Dimensioning: **uffg(nffgpa)**. Usage: **uffg(nf)** is the **nf**-th such gas. This is read from the **input** file.

ufix The string 'fix'.

ugs The string 'gases'.

uh2g The string 'h2(g)'.

uinv The string 'inverse rate'.

umn The string 'minerals'.

unone The string 'none'.

uo2g The string 'o2(g)'.

updac Array of names of species whose activities appear as factors in certain kinetic rate laws for irreversible reactions proceeding in the reverse direction (e.g., precipitation). Dimensioning: **updac(ndctpa,imchpa,nrctpa)**. Usage: **updac(n,i,nrc)** is the name of the **n**-th species appearing in the **i**-th mechanism or term in the rate law for the **nrc**-th irreversible reaction. This is read from the **input** file. Note that the first dimension is input file ordered. The actual species index is given by **npdac(n,i,nrc)**.The **updac** array is used to set up the **npdac** array.

uprs Array of names of pure minerals and solid solution end member components in the physically removed system. Dimensioning: **uprs(nprspa)**. Usage: **uprs(nprmx)** is the name of the **nprmx**-th such entity. This is read from the **input** file. If the entity is a pure mineral, its name appears in the first twelve characters. If it is an end member component of a solid solution, the component name appears in the first twelve characters and the solid solution name in the second twelve characters.

ureac Array of names of the reactants associated with irreversible reactions. Dimensioning: **ureac(nrctpa)**. Usage: **ureac(nrc)** is the name of the **nrc**-th such reactant.

urel The string 'relative rate'.

usr The string 'special reactants'.

uss The string 'solid solutions'.

utitl1 An array which is the main title of the problem. Dimensioning: **utitl1(ntitpa)**. Usage: **utitl1(n)** is the **n**-th line of the title. This is read from the **input** file.

Information Only

utitl2 An array which is the title from the previous EQ3NR or EQ6 run. Dimensioning: **utitl2(ntitpa)**. Usage: **utitl2(n)** is the **n**-th line of this title. This is read from the **input** file.

uxcat Array of character strings containing the names of chemical elements used to complete the definition of pure mineral subset-selection suppression options. Dimensioning: **uxcat(nxoppa)**. Usage: **uxcat(n)** is the **n**-th such element. This is read from the **input** file.

uxopex Array of names of pure minerals which are to be exceptions to pure mineral subset-selection suppression options. Dimensioning: **uxopex(nxpepa)**. Usage: **uxopex(n)** is the **n**-th such exception. This is read from the **input** file.

uxopt Array of character strings defining pure mineral subset-selection suppression options. Dimensioning: **uxopt(nxoppa)**. Usage: **uxopt(n)** is the **n**-th such option.

uxtype Array containing strings which describe models for the activity coefficients of solid solution end member components. Dimensioning: **uxtype(10)**. Usage: **uxtype(n)** is the **n**-th such model. Such models are specified by the **jsol** flag array (see Appendix C of the EQ3NR User's Manual, Wolery, 1992b).

uzvec0 Array of names of the master iteration variables at the previous point of reaction progress. Dimensioning: **uzvec0(kpar)**. Usage: **uzvec0(kcol)** is the name of the **kcol**-th such variable at that point.

uzvec1 Array of names of the master iteration variables at the current point of reaction progress. Dimensioning: **uzvec1(kpar)**. Usage: **uzvec1(kcol)** is the name of the **kcol**-th such variable.

volmn Array of the volumes (cm^3) of pure minerals in the equilibrium system. Dimensioning: **volmn(nmtpar)**. Usage: **volmn(nm)** is this volume for the **nm**-th pure mineral.

volxx Array of the volumes (cm^3) of solid solutions in the equilibrium system. Dimensioning: **volxx(nxtpar)**. Usage: **volxx(nx)** is this volume for the **nx**-th solid solution.

vreac Array of the molar volumes (cm^3/mol) of the solid reactants associated with irreversible reactions. Dimensioning: **vreac(mrctpa)**. Usage: **vreac(nrc)** is the molar volume of the **nrc**-th reactant, if it is a solid. If it is not a solid, **vreac(nrc)** is set to zero.

xlkffg Array of logarithms of the desired fixed fugacities of specified gases. Dimensioning: **xlkffg(nffgpa)**. Usage: **xlkffg(nf)** is the desired log fugacity of the **nf**-th such gas. This is read from the **input** file.

ξ **zi1** The value of reaction progress at the current point.

ξ **zi2** The value of reaction progress at the previous point.

ξ **zi3** The value of reaction progress at the point preceding the previous point.

zidump The next value of reaction progress at which mass belonging to solid phases in the equilibrium system is to be transferred to the physically removed system.

zimax The maximum desired value of reaction progress. This is read from the **input** file.

Information Only

	zipr1	The next value of reaction progress at which the linear print interval (**dzprnt**) requires the writing to the **output** file of a detailed description of the state of the modeled system.
	zipr2	The next value of reaction progress at which the logarithmic print interval (**dzprlg**) requires the writing to the **output** file of a detailed description of the state of the modeled system.
ξ_j	**zirct**	Array of reaction progress variables for individual irreversible reactions at the current point of reaction progress. Dimensioning: **zirct(nrctpa)**. Usage: **zirct(nrc)** is the progress variable for the **nrc**-th irreversible reaction.
ξ_j	**zircts**	Array of reaction progress variables for individual irreversible reactions at the previous point of reaction progress. Dimensioning: **zircts(nrctpa)**. Usage: **zircts(nrc)** is the progress variable at the previous point for the **nrc**-th irreversible reaction.
	zistrt	The value of the reaction progress variable at the start of a problem.
	zkfac	A control parameter used in connection with the fluid-centered flow-through open system mode. It is read from the **input** file. It determines the minimum number of moles of a mineral that will be left in the equilibrium system after a partial shift to the physically removed system. The minimum number of moles is $10^{\mathbf{zklgmn}}$ (where **zklgmn = alog10(zkfac) + zklogu**). If the number of moles of a phase is less than this to start with, none of it is removed from the equilibrium system.
	zklgmn	The minimum logarithm of the number of moles of a solid phase in the equilibrium system after a partial shift to the physically removed system. This value is calculated from **zkfac** and **zklogu**, which are both read from the **input** file. See **zkfac**.
	zklogl	A variable which controls the extent of partial transfers of solid phases from the equilibrium system to the physically removed system. It is read from the **input** file. The number of moles of a solid phase in the equilibrium system is reduced by a factor of $10^{-zklogl}$. Thus, setting **zklogl** = 2 transfers 99% of the mass, and setting it to 3 transfers 99.9%. Values between 2.0 and 4.0 are recommended.
	zklogu	A threshold/target value for the logarithm of the number of moles of solid phases. Usage: (1) when the log mass of a phase exceeds this value, EQ6 limits the step size to keep the corresponding truncated Taylor's series accurate according to the criterion using the **screw1** variable; (2) this variable is the target value of the logarithm of the number of moles of a solid phase wheu trying to use truncated Taylor's series to locate a phase disappearance boundary; (3) in the fluid-centered flow-through open system mode, **zklogu** also defines the maximum number of moles of a solid phase that may be redissolved. Reasonable values range from -6. to -I0.
z	**zvclg0**	Array of logarithmic master iteration variables at the previous point of reaction progress. Dimensioning: **zvclg0(kpar)**. Usage: **zvclg0(kcol)** is the value for the **kcol**-th master iteration variable.
z	**zvclg1**	Array of logarithmic master iteration variables at the current point of reaction progress.Dimensioning: **zvclg1(kpar)**. Usage: **zvclg1(kcol)** is the value of the **kcol**-th logarithmic master iteratiou variable.

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z

zvclgi Array of values of logarithmic master iteration variables as read from the **input** file. Dimensioning: **zvclgi(kpar)**. Usage: **zvclgi(kcol)** is the value of the **kcol**-th logarithmic master iteration variable.

zvec0 Array of values of linear master iteration variables at the previous point of reaction progress. Dimensioning: **zvec0(kpar)**. Usage: **zvec0(kcol)** is the value of the **kcol**-th such linear master iteration variable.

zvec1 Array of values of linear master iteration variables at the current point of reaction progress. Dimensioning: **zvec1(kpar)**. Usage: **zvec1(kcol)** is the value of the **kcol**-th linear master iteration variable.Note: **zvec1(kcol)** = $10^{zvclg1(kcol)}$.

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Appendix B. Glossary of EQ6 Modules

EQ6 is a fairly large code. The source code consists of the main program and a number of subroutines. In addition, EQ6 uses a number of modules from the EQLIB library. These are described in the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a). The modules are described as "**.f**" files, as this is how they are normally worked with under a UNIX operating system. For a description of the code architecture, see Chapter 9.

affunc.f This module is a function called by **betaz.f**, **satchk.f**, and **sfncaf.f**. It computes the affinity (kcal/mol), defined as 2.303 *RT log Q/K)*, for a given mineral. The activity product *Q* and the equilibrium constant *K* are defined for the dissolution reaction, but the affinity as calculated is for the precipitation reaction. The logarithm of the equilibrium constant is given by **xlkm(nm)**, where **nm** is the index of the mineral. If its value of greater than or equal to 500, a "no data" condition is defined and the value of **affunc** is returned as -999.

akmatr.f This module is called by **path.f**. It computes the **akm** matrix, which relates finite differences to derivatives.

balcmz.f This module is called by **matrxz.f**. It builds a pure mineral mass action row for the Jacobian matrix.

balcnz.f This module is called by **matrxz.f**. It builds either a mass balance or a charge balance row for the Jacobian matrix. It is analogous to the EQ3NR module **balcon.f**.

balcsz.f This module is called by **matrxz.f**. It builds a solid solution end member component mass action row for the Jacobian matrix.

betaz.f This module is called by **eqcalc.f**, **optmzr.f**, **path.f**, and the EQLIB modules **newton.f** and **nrstep.f** (these latter two modules call it as **betae**). It computes the residual functions ($\underline{\alpha}$, $\underline{\beta}$, and β_{max}). The calling sequence of this routine must be identical in form to that of the EQ3NR module **betas.f**.

comp1.f This module is called by **scripz.f**. It calculates the values of many secondary parameters for subsequent output by **scripz.f**.

deriv.f This module is called by **path.f**. It calculates finite-difference estimates of the derivatives of master iteration variables from finite differences.

derspc.f This module is called by **ncmpz.f**. It calculates the number of moles of dependent aqueous species, using the corresponding mass action expressions. It also calculates the equilibrium fugacities of relevant gas species.

echoz.f This module is called by **eq6.f**. It writes a description of the input problem on the **output** file. Unlike the "instant echo" of the **input** file, this description includes data file statistics, any default values that were chosen by EQ6, and any changes in the **input** constraint options made by the code to resolve inconsistencies among these constraints or with truncation limits imposed on certain run parameters. It is analogous to the EQ3NR module **echox.f**.

eq6.f This is the main program of EQ6. It connects the necessary files except **input** (**data1**, **output**, **pickup**, **tab**, and **tabx**). It sets up a run by initializing arrays to appropriate initial values. It performs certain checks on the input, sets up default values as necessary for run parameters, and directly oversees the calculation of the state of the modeled system at the initial point of reaction progress. If calculations are to be made at succeeding points (i.e., a reaction path is to be computed), it calls **path.f** to oversee the rest of the calculations. Then **eq6.f** makes a call to write the **pickup** file, which is an **input** file for restarting the calculation.

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eqcalc.f This module is called by **eq6.f** and **path.f**. It finds the state of a system at full or restricted chemical equilibrium. The system is defined by elemental composition (determined by the **mte** array), temperature and pressure. This module calls the EQLIB module **newton.f**, which uses a hybrid Newton-Raphson method to solve the relevant equations for a given phase assemblage.

escalc.f This module is called by **path.f** and **shftz.f**. It recomputes the component totals (**mte** array) for the equilibrium system.

evratc.f This module is called by **eq6.f** and **tstep.f**. It evaluates rate constants as functions of temperature, assuming either a constant activation energy or a constant activation enthalpy for each rate constant.

fittst.f This module is called by **path.f**. It executes the **iodb10** and **iodb11** debugging options if they were set on the **input** file. It compares the results of truncated Taylor's series expansions with equivalent finite difference expansions.

flgstz.f This module is called by **indat1.f**. It sets up the species status switch arrays **jsflag**, **jmflag**, **jkflag**, **jxflag**, and **jgflag**. It is analogous to the EQ3NR module **flgstx.f**.

glxrn.f This module is called by **indat1.f**. It matches names read from the **input** file with those read from the **data1** file. The **data1** indices of the reactants read from the **input** file are stored in the **nrndex** array.

gmte.f This module is called by **indatz.f**. It matches the element names read from the **input** file with those read from the **data1** file. When a match is found, the two corresponding element mass balance totals (**mteb(ncb)** and **mteaqb(ncb)**)read from the **input** file are respectively stored in **mte(nc)** and **mteaq(nc)**, where **nc** is the **data1** index corresponding to **nch**.

ibswch.f This module is called by **indat1.f**. It matches the basis species names read from the **input** file into the **undms** and **unrms** arrays with the names read from the **data1** file. The **undms** array contains the names of data file basis species. The **unrms** array contains the names of corresponding species to be used as basis species in the run. If corresponding names are not the same, and the string read into the **undms** array is not blank, then the data specify a basis switch to be made.

indat1.f This module is called by **indatz.f**. It carries out various setup functions after the **input** and **data1** files have been read. These functions include: carrying out the **nxmod** alter/suppress options; finding the **data1** indices of basis species names read from the **input** file; finding the **data1** indices of reactants listed on the **input** file; finding the **data1** indices of chemical elements listed on the **input** file as composing special reactants; finding the **data1** indices of end member components specified on the **input** file as making up solid solution reactants;carrying out initial basis switching, if any; setting up species status flags; creating fictive pure minerals for gases whose fugacities are to be fixed, and setting these up in the equilibrium system; recalculating the initially specified mass balance totals, if needed; reading the Pitzer parameters, if Pitzer's equations are to be used, and building the ${}^{S}\lambda_{ij}$ and μ_{ijk} index arrays; calculating the array of values of one-half the charge squared for aqueous species; and initializing the values of ${}^{E}\lambda$ sums for the different charge types to zero.

indatz.f This module is called by **eq6.f**. It reads the data file **data1**. It is analogous to the EQ3NR module **indatx.f**.

init6v.f This module is called by **rd6new.f**. It initializes values for **input** file parameters before the input on a "D" format **input** file is read. It is analogous to the EQ3NR module **init3v.f**.

inndx.f This module is called by **indat1.f**. It matches the names of basis species read from the **input** file (**undms** array) with names read from the **data1** file. The array of corresponding **data1** indices is stored in the **iindx1** array. Values of associated parameters are stored in the **zvclg1** array.

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integr.f This module is called by **path.f**, **reacts.f**, and **sfncre.f**. It integrates a relative rate in order to calculate the advancement of the irreversible reaction corresponding to a given reactant.

jgibbs.f This module is called by **eqcalc.f**. It is called when the equilibrium phase assemblage violates the apparent or mineralogic phase rule. This module determines which phase should be dropped from the current assemblage. It has not been extended to handle solid solutions.

killt.f This module is called by **eqcalc.f**. This is an interactive routine that "kills" a matrix variable by treating it as a known constant. This is used strictly for debugging by code developers.

matrxz.f This module is called by the EQLIB routine **nrstep.f** (which calls it by the name of **matrxe**). It computes the Jacobian matrix (*J*). It is analogous to the EQ3NR module **matrix.f**.

modexz.f This module is called by **eqcalc.f**, **indat1.f**, and **path.f**. It modifies the matrix indexing as required to satisfy basis switching or changes in the equilibrium phase assemblage.

mshift.f This module is called by **path.f** and **shftz.f**. It shifts the mass of a pure mineral in the equilibrium system to the physically removed system. This shift can be total or partial. This module does not recalculate the component total masses for the equilibrium system. To do this, **escalc.f** must be called after one or more mineral phases have been shifted.

ncmpz.f This module is called by **eq6.f**, **eqcalc.f**, **optmzr.f**, **path.f**, **sfncaf.f** and the EQLIB modules **ngcadv.f** and **nrstep.f** (which call it by the name of **ncmpe**). It computes all parameters that derive from the primary iteration variables and are necessary to write the Jacobian matrix (e.g., the number of moles, concentrations, and activities of the species present in the equilibrium system). This is analogous to the EQ3NR module **ncmpx.f**.

ncmpz2.f This module is called by **ncmpz.f**. It computes from the basis set data in the **zvclg1** array various secondary variables describing the solid phases in the equilibrium system.

nlkffg.f This module is called by **indat1.f**. It sets up a fictive pure mineral for fixing the fugacity of a specified gas. The fugacity is actually fixed only if the fictive mineral is in equilibrium with the aqueous system. Otherwise, the fugacity may be less than the specified fugacity value.

ophelp.f This module is called by **optmzr.f**. It prints various optional debugging information and calls the EQLIB modnle **gbfac.f** to obtain some of the parameters required for pre-Newton-Raphson optimization.

optmzr.f This module is called by **eqcalc.f**. It carries out pre-Newton-Raphson iteration optimization to eliminate excessively positive or negative mass balance residuals. It does not optimize matrix variables for water, the aqueous hydrogen ion, or aqueous oxygen gas. It is fairly analogous to the EQ3NR module **arrset.f**.

pabssw.f This module is called by **eq6.f** and **path.f**. It oversees the selection and execution of automatic basis switching.

path.f This module is called by **eq6.f**. It supervises the tracing of a reaction path. The mathematical method for dealing with matrix variables is analogous to the predictor-corrector method of integrating differential equations. Finite difference expressions are transformed into equivalent truncated Taylor's series and used as predictor functions. The routine **eqcalc.f**, which computes the equilibrium state of a system, is used as the corrector. Thus, it corrects to satisfy algebraic, not differential, equations. In kinetic mode (**iopt1** = 1), the integration of the rate equations is handled by a true predictor-corrector algorithm, which is similar in format to the predictor for matrix variables. This routine has three cal-

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culation modes which pertain to step size and resolution:

Normal mode - The step size is constrained to keep the predictor functions fairly accurate. This causes less burden on the Newton-Raphson algebraic calculations and gives high resolution along the reaction path. Some types of calculations can only be done in this mode (e.g., kinetic mode, the fluid-centered flow-through open system).

Economy mode- The step size is allowed to become larger more quickly than in normal mode.The predictor functions are limited to first order. There is no attempt to constrain the step size to keep these functions accurate. The useful information density along the reaction path is close to that obtained using normal mode. Phase boundaries, for example, are still accurately located, provided the code detects their presence. The code in this mode could miss the appearance of a product phase if its appearance is followed closely by its disappearance. A small region in which a product phase disappears and reappears could similarly be missed.

Super economy mode - Here the step size is typically large (defaults to **dzprnt**). Phase boundaries are ignored. The order of the finite differences is restricted to zero. This mode provides the least information density along the reaction path.

phsdrp.f This module is called by **eqcalc.f**. It picks a phase to drop from the equilibrium system. Four independent algorithms are used to find candidates, and a final choice is made from these.

raff.f This module is called by **eq6.f** and **path.f**. It calculates the affinities of the irreversible reactions.

ratinv.f This module is presently not used. It converts the truncated Taylor's series representation of a rate function into the corresponding truncated Taylor's series of its inverse.

rd6ff.f This module is called by **rd6new.f**. It reads the part of the "D" format input for fixed fugacity options.

rd6inp.f This module is called by **rd6inp.f**. It reads the **input** file in "D" format. It writes an "instant echo" of each problem on this **input** data on the **output** file. It contains full internal documentation. This is analogous to the EQ3NR module **rdninp.f**.

rd6log.f This module is called by **rd6new.f**. It reads the part of the "D" format input for the basis species and associated master variables.

rd6new.f This module is called by **rd6inp.f**. It reads a problem file in "W" format, and **rd6new.f** to read one in "D" format. This is analogous to the EQ3NR module **rdinp.f**.

rd6prs.f This module is called by **rd6new.f**. It reads the part of the "D" format input which describes the contents of the physically removed system.

rd6rea.f This module is called by **rd6new.f**. It reads the part of the "D" format input which describes the irreversible reactants and associated parameters. It calls **rdrate.f** to read the rate law parameters.

rd6sup.f This module is called by **rd6new.f**. It reads the part of the "D" format input which describes the subset-selection mineral suppression options.

rd6tol.f This module is called by **rd6new.f**. It reads the part of the "D" format input which consists of numerical run parameters, such as tolerance and setscrew variables.

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rderiv.f This module is called by **path.f**. It transforms finite differences of the rates of irreversible reactions into corresponding derivatives. This module is analogous to **deriv.f**.

rdmole.f This module is called by **rd6new.f**. It reads the part of the "D" format input which specifies the total number of moles of the components (chemical elements) in the equilibrium system and in the aqueous solution.

rdrate.f This module is called by **rd6rea.f**. It reads from the **input** file in "D" format the surface area information, rate law codes, and rate law parameters for the dissolution and precipitation of the reactants. This is analogous in function to **readrt.f**, which reads the same information from **input** files in "W" format.

reacts.f This module is called by **path.f** and **eqcalc.f**. It computes the destroyed and current masses of the reactants, and calculates the current element totals in the equilibrium system.

readrt.f This module is called by **readz.f**. It reads from the **input** file in "W" format the surface area information, rate law codes, and rate law parameters for the dissolution and precipitation of the reactants. This is analogous in function to **rdrate.f**, which reads the same information from **input** files in "D" format.

readz.f This module is called by **rd6inp.f**. It reads the **input** file in "W" format. It writes an "instant echo" of each problem on this **input** data on the **output** file. It contains full internal documentation. This is analogous to the EQ3NR module **readx.f**.

redatz.f This module is called by **tstep.f**. It recomputes temperature dependent thermodynamic data if the temperature changes along the reaction path.

rfdiff.f This module is called by **fittst.f**. It evaluates finite difference expressions for reaction rates as functions of reaction progress. It is roughly analogous to **zfdiff.f**.

rsatch.f This module is called by **eq6.f** and **path.f**. It tests whether the equilibrium system has become saturated with any of the reactants.

rsetup.f This module is called by **eq6.f**. It sets up the molecular weights and partial molar volumes of the reactants.

rtaylr.f This module is called by **fittst.f** and **path.f**. It evaluates truncated Taylor's series for reaction rates as functions of reaction progress. It is roughly analogous to **taylor.f**.

rtcalc.f This module is called by **eq6.f** and **path.f**. It calculates the relative rates of irreversible reactions. In non-kinetic mode, these rates are evaluated directly from specified expressions. In kinetic mode, absolute rates are first calculated, and the overall rate of reaction progress is computed as the sum of the absolute values of the individual rates. The relative rates are then calculated as the ratio of the corresponding absolute rates to this overall rate.

satchk.f This module is called by **eqcalc.f** and **path.f**. It carries out saturation testing of non-aqueous phases. Affinity functions are directly computed for pure minerals. They are also directly computed for solid solutions and their end members, if the solid solutions are present in the equilibrium system. If they are not present, values are computed for the compositions which maximize the affinity functions.

scribe.f Directs the writing of the EQ6 **pickup** file. It calls either **scribo.f** to write this file in "W" format or the combination **writ6x.f** and the EQLIB module **scribn.f** to write it in "D" format. It is analogous to the EQ3NR module **scribx.f**.

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scribo.f This module is called by **scribe.f**. It writes the **pickup** file in "W" format. It is analogous to the EQ3NR module of the same name (note: having two modules in the software package with the same name is a violation of the usual policy).

scripz.f This module is called by **eq6.f** and **path.f**. It writes a detailed description on the **output** file of the state of the system at a point of reaction progress. The scope of these prints can be controlled by the use of the **iopr1**, **iopr2**, etc., print options. It is analogous to the EQ3NR module **scripx.f**.

search.f This module is called by **eq6.f** and **path.f**. It finds the value of reaction progress at which certain kinds of events occur. These include points at which a mineral supersaturates at the target affinity (**aftarg**), a product phase disappears, the number of moles of a product mineral is maximized (**nmodl1** = 3 only), the inverse rate changes sign, and the number of moles of a reactant becomes exhausted.

sfncaf.f This module is called by **search.f**. It is a function subroutine which computes the affinity of a potential product mineral as a function of step size ($\Delta\xi$), based upon the results of truncated Taylor's series. It support search.f in find the location of a phase boundary at which a new phase appears in the equilibrium system.

sfncpd.f This module is called by **search.f**. It is a function subroutine which computes the remaining mass of a product mineral as a function of step size($\Delta\xi$), based upon truncated Taylor's series. It supports **search.f** in finding the location of a phase boundary at which a phase in the equilibrium system disappears. A phase boundary is defined here as the point at which the remaining mass = -**eps100**, not zero (**eps100** is 100 times the machine epsilon).

sfncpm.f This module is called by **search.f**. It is a function subroutine which computes the first derivative of the mass of a mineral with respect to reaction progress as a function of step size ($\Delta\xi$), based upon the results of truncated Taylor's series. It supports **search.f** in finding the location of the maximum in the mass of a product phase. The maximum is defined here as the point at which the derivative = -**eps100**, not zero.

sfncre.f This module is called by **search.f**. It is a function subroutine which computes the remaining mass of a reactant as a function of step size ($\Delta\xi$). It supports **search.f** in finding the point at which the reactant is exhausted. This point is defined as that at which the remaining mass = -**eps100**, not zero.

sfncri.f This module is called by **search.f**. It is a function subroutine which computes the inverse rate as a function of step size ($\Delta\xi$). It supports **search.f** in finding the point at which the inverse rate goes to zero. The target value is actually 2***eps100**, not zero.

sfncrr.f This module is called by **search.f**. It is a function subroutine which computes the relative rate of a reactant as a function of step size ($\Delta\xi$). It supports **search.f** in finding the point at which the relative rate goes to zero.

shftz.f This module is called by **eq6.f** and **path.f**. It oversees the transfer of solid phases from the equilibrium system to the physically removed system. Shifts may be total or partial. This routine calls **mshift.f** and **sshift.f**.

sshift.f This module is called by **shftz.f**. It shifts the mass of a solid solution in the equilibrium system, to the physically removed system. The shift can be total or partial. This module is analogous to **mshift.f**. It does not recalculate the mass balance totals for the equilibrium system. Because of this, module **escalc.f** must be called after one or more mineral phases have been shifted.

sxterm.f This module is called by **balcsz.f**. It computes the array **sx**, which contains partial derivatives with respect to mole fractions of expressions for the activity coefficients of solid solution components. These derivatives are used in writing solid solution component mass action rows in the Jacobian matrix.

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taylor.f This module is called by **eqcalc.f**, **fittst.f**, **path.f**, **sfncaf.f**, and **sfncpd.f**. It evaluates truncated Taylor's series for matrix variables. It is roughly analogous to **rtaylr.f**.

taylr2.f This module is called by **eq6.f** and **path.f**. It evaluates truncated Taylor's series for the first derivatives with respect to reaction progress of matrix variables.

timer.f This module is called by **eqcalc.f** and **path.f**. It calculates the time step (Δt, seconds) corresponding to the step size ($\Delta \xi$).

tstep.f This module is called by **eq6.f**, **path.f**, and **sfncaf.f**. It recalculates the temperature and all temperature dependent thermodynamic data.

writ6x.f This module is called by **scribe.f**. It writes the bottom half of the **pickup** file in "D" format.

wrtabx.f This module is called by **scripz.f**. It writes summary table information to the **tabx** file. The lines belonging to different tables are interleaved, but carry a table identifier in column one.

zfdiff.f This module is called by **fittst.f**. It directly evaluates finite difference expressions of matrix variables as functions of reaction progress. It is roughly analogous to **rfdiff.f**.

zvecpr.f This module is called by **path.f**. It writes on the **output** file the components of the truncated Taylor's series representing the matrix variables.

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Appendix C. EQ6 Error Messages

All EQ3/6 error messages fit into one of three categories: *error*, *warning*, and *note*. An *error* implies a fatal error. Execution of the current input problem will cease without completion, immediately in some cases, later in others. Which is the case depends on whether it makes more sense to stop immediately or to continue checking for other errors before ceasing execution. A *warning* indicates a condition which may or may not represent a real error. A *note* indicates a condition knowledge of which may assist the user in determining or tracking down the cause of an error. An *error* message may be preceded or followed by one or more other *error*, *warning*, or *note* messages. These messages are written to both the screen file and the **output** file.

Each EQ3/6 error message has the following format:

* *msgtype* - (*source/module*) *Message.*

where *msgtype* = *error*, *warning*, or *note*, *source* is the root name of the source file (e.g., *eqlib*, *eqpt*, *eq3nr*, or *eq6*) containing the *module*, *module* is the name of the module (main program or subroutine) which writes the message, and *Message* is the message itself. The messages are designed to be as self-explanatory as possible. The messages are reproduced here using *AAAA* to stand for a character variable, *IIII* for an integer, and *RRRR* for a floating point number.

Most of the error messages that users are likely to encounter deal with problems regarding the input file, the data file, or both of these. In most instances, the meaning of these messages should be immediately clear to the user. In other instances, it may be necessary to search out other information. In such cases, there are three principal actions that users should take. The first is to check the **output** file for additional diagnostic messages (*warnings* and *notes*) which may bear on the matter. If this does not suffice to identify corrective action, compare the instant echo of the **input** file on the **output** file with the original **input** file. You may find that certain data were not entered in the correct fields, that certain inputs fail to correspond with the necessary lines to follow, or that a line is missing or you have an extra line. In addition, it may help to re-run the problem with the debugging option switch **iodb1** set to 1 or 2. This will trigger the printing of additional information which should help to identify the problem. A small number of messages deal with installation errors. These should also be quite clear.

Some messages deal with programming errors. The user should see these rarely if ever. These are likely to appear somewhat more cryptic to users. Problems of this type must be dealt with by diagnosing the problem (probably with the help of a symbolic debugger) and modifying the code. Most users should probably not attempt corrective action of this sort. The code custodian should be notified of suspected programming errors and may be able to provide fixes.

Some of the messages displayed in this appendix are followed by *Comments* that may help to explain them. Users of EQ6 may also encounter error messages from EQLIB modules. These messages are listed in similar format in the EQ3/6 Package Overview and Installation Guide (Wolery, 1992). The *errors* are listed first, then the *warnings* and finally the *notes*.

Message: * error - (eq6/echoz) Programming error: Have encountered unknown value of the temperature function flag "jtemp."

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Comment: This is a programming error.

Message: * error - (eq6/eq6) Can not match "AAAA", which appears in the rate law for "AAAA", with any species name read from the data file.

Comment: Any species appearing in a rate law must appear on the data file. If you are sure that the species is on the data file, check to see that the name is exactly the same. Remember that blanks are significant, so blank-shifting will cause a name mismatch.

Message: * error - (eq6/eq6) Have a mineral named "AAAA" in the physically removed system described on the input file, but this does not match any mineral name read from the data file.

Comment: Check to see that you haven't switched data files, or switched to a newer version of the "same" data file.

Message: * error - (eq6/eq6) The Newton-Raphson algorithm has failed at the start of the run- betamx = RRRR

Comment: Look for preceding error, warning, or note messages. To obtain more diagnostic information, set **iodb1** = 1, **iodb2** = 1, and **iodb4** = 1 *and run again. If you are executing a temperature jump, it may be necessary to change the temperature in small increments instead of one large increment.If you are not executing a temperature jump, the problem is likely connected to the oxygen fugacity. If the system at the start is very ill-posed, the code will not be able to compute this. If so, the basic problem may be that the problem itself has no real redox aspect. In that case, you should set* **iopt11** = 1 *and try again.*

Message: * error - (eq6/eqcalc) Scanning for fO2 is inhibited by the setting of the flag variable "ioscan". This variable is set on the input file.

Comment: Set **ioscan** = 0 *on the* **input** *file and try again.*

Message: * error - (eq6/eqcalc) The species "h2(g)" is not present. Scanning for log fO2 is inhibited.

Comment: The species 'h2(g)' *is not on the data file. Use a data file that has it, or add it to the current data file.*

Message: * error - (eq6/eqcalc) The species "o2(g)" is not present. Scanning for log fO2 is inhibited.

Comment: The species 'o2(g)' *is not on the data file. Use a data file that has it, or add it to the current data file.*

Message: * error - (eq6/eqcalc) Caught in a region of critical redox instability. Have done the maximum number of tries (nsslmx) to slide over it.

Comment: The basic problem may be that the problem itself has no real redox aspect. In that case, you should set **iopt11** = 1 *and try again. Otherwise, try restarting the code using the* **pickup** *file.*

Message: * error - (eq6/eqcalc) Caught in a region of critical phase instability. Trying to get a new product phase in the system, but can not get iteration to converge with it present.

Comment: Try restarting the code using the **pickup** *file.*

Message: * error - (eq6/eqcalc) Caught in a region of critical phase instability. Have done the maximum number of tries (npslmx) to slide over it.

Comment: Try restarting the code using the **pickup** *file.*

Message: * error - (eq6/flgstz) The species "AAAA" is in the strict basis set after basis switching, but it has a status flag value (jsflag= IIII) that is incompatible with a member of this set.

Information Only

Comment: This is really a programming error, as any attempt to switch such a species should have been caught prior to the switching.

Message: * error - (eq6/flgstz) Do not recognize the option type "AAAA" input with category "AAAA" in a mineral subset-selection suppression option.

Message: * error - (eq6/flgstz) The mineral "AAAA" is suppressed illegally, because it is currently present in the equilibrium system.

Message: * error - (eq6/flgstz) The component "AAAA" in solid solution "AAAA" is suppressed illegally because it is currently present in the equilibrium system.

Message: * error - (eq6/flgstz) Do not recognize "AAAA" as an argument to an "alwith" mineral subset-selection suppression option.

Message: * error - (eq6/glxrn) The reactant "AAAA" is not among the AAAA read from the data file.

Message: * error - (eq6/glxrn) The component "AAAA" of solid solution reactant "AAAA" is not among the minerals read from the data file.

Message: * error - (eq6/glxrn) The element "AAAA" used to specify the composition of the special reactant "AAAA" does not match any element read from the data file.

Message: * error - (eq6/gmte) The total number of moles of "AAAA" in the equilibrium system was specified more than once on the input file.

Message: * error - (eq6/ibswch) The species "AAAA" is specified on the input file to be switched into the basis set, but it does not match any species read from the data file.

Comment: If you are sure that the species is on the data file, check to see that the name is exactly the same. Remember that blanks are significant, so blank-shifting will cause a name mismatch.

Message: * error - (eq6/ibswch) The following basis switch directed on the input file failed- "AAAA" for "AAAA".

Comment: A preceding message should say why.

Message: * error - (eq6/indat1) The fictive fixed fugacity phase "AAAA" is specified on the input file to have RRRR moles of mass added at the start of this run. Negative values are not permitted.

Message: * error - (eq6/indatz) Have wrong file header = "AAAA" on the data file. The first five characters must be "data1".

Comment: You appear to have specified a non-data1 file as the **data1** *file.*

Message: * error - (eq6/indatz) The number of chemical elements on the data file is IIII. This exceeds the dimensioned limit (nctpar) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/indatz) The number of basis species on the data file is IIII. This exceeds the dimeusioned limit (nsqpar) of IIII.

Information Only

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/indatz) The composition of species "AAAA" on the data file is described in terms of an unrecognized chemical element called "AAAA". If this is an actual element, it is not in the list of chemical elements on this data file.

Message: * error - (eq6/indatz) The maximum number of aqueous species (nstpar) is IIII. This has been exceeded while trying to read the data file.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/indatz) The reaction for the destruction of the species "AAAA" is written is written on the data file in terms of an unrecognized basis species called "AAAA". If this is an actual species, it is not among the basis species on this data file

Message: * error - (eq6/indatz) The maximum number of pure minerals (nmtpar) is IIII. This has been exceeded while trying to read the data file.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/indatz) The maximum number of gas species (ngtpar) is IIII. This has been exceeded while trying to read the data file.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/indatz) The chemical element "AAAA" was referenced on the input file but was not read from the data file.

Comment: Is the element name valid? If so, check the **slist** *file to see which elements are on the current data file. It may be necessary to use a different data file.*

Message: * error - (eq6/indatz) The maximum number of solid solutions (nxtpar) is IIII. This has been exceeded while trying to read the data file.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/inndx) The basis species "AAAA" specified on the input file is not defined on the data file as a strict basis species. It is defined instead as a dependent species.

Comment: Direct a basis switch on the **input** *file.*

Message: * error - (eq6/inndx) The basis species "AAAA" specified on the input file is not defined on the data file as a strict basis species. It is defined instead as an auxiliary basis species.

Comment: Direct a basis switch on the **input** *file.*

Message: * error - (eq6/inndx) The basis species "AAAA" specified on the inpnt file does not match any of the aqueous species read from the data file.

Information Only

Message: * error - (eq6/inndx) The mineral "AAAA" specified on the input file to be in the initial equilibrium system does not match any of the minerals read from the data file.

Comment: You have probably switched data files, or used a different version of a given data file.

Message: * error - (eq6/inndx) The solid solution "AAAA" specified on the input file to be in the initial equilibrium system does not match any of the minerals read from the data file.

Comment: You have probably switched data files, or used a different version of a given data file.

Message: * error - (eq6/inndx) The component "AAAA" of solid solution "AAAA" specified on the input file to be in the initial equilibrium system does not match any of the components read from the data file.

Comment: You have probably switched data files, or used a different version of a given data file.

Message: * error - (eq6/modexz) Have exceeded the Jacobian matrix dimension (kpar) trying to put "AAAA" in the equilibrium system.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/mshift) The current matrix index (kcol= IIII) is out of range for the function of this routine.

Comment: This is a programming error.

Message: * error - (eq6/nlkffg) Have an input file directive to fix the fugacity of "AAAA", but this does not match any of the gas species read from the data file.

Comment: Is the gas species name valid? If so, check the **slist** *file to see which such species are on the current data file. It may be necessary to use a different data file.*

Message: * error - (eq6/nlkffg) The maximum IIII number of pure minerals (nmtpar) would be exceeded by creating a fictive fixed fugacity mineral for "AAAA".

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/pabssw) Automatic basis switching failed.

Comment: This is a programming error.

Message: * error - (eq6/path) The step size (delzi) has been zero IIII times in a row.

Comment: This is a trap designed to keep the code from wasting time when the reaction path calculation has gotten stuck for some reason. Try restarting using the **pickup** *file.*

Message: * error - (eq6/path) The step size (delzi) has not exceeded the minimum value IIII times in a row.

Comment: This is a trap designed to keep the code from wasting time when the reaction path calculation has gotten stuck for some reason. Try restarting using the **pickup** *file.*

Message: * error - (eq6/path) Reaction path tracing has failed. The pickup file if written corresponds to the last solved point of reaction progress. If it is written, try restarting the run with it.

Information Only

Message: * error - (eq6/rd6ff) Have blank input for name of gas whose fugacity is to be fixed. Check INPUT file line IIII.

Message: * error - (eq6/rd6ff) Can only fix the fugacity of IIII gas species. Exceeded this value on INPUT file line IIII. Increase the dimensioning parameter nffgpa.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6log) Have exceeded the dimensioned limit on matrix variables (kpar) of IIII on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6log) A log mass variable can not be less than or equal to -999. Check INPUT file line IIII.

Message: * error - (eq6/rd6new) Looking for heading: "AAAA" Found string: "AAAA" See INPUT file line: IIII

Message: * error - (eq6/rd6new) EOF encountered. See INPUT file line IIII.

Message: * error - (eq6/rd6new) AAAA must be >= 0. Value read: AAAA Check INPUT file line IIII.

Message: * error - (eq6/rd6prs) Solid solution name field is blank. Check INPUT file line IIII.

Message: * error - (eq6/rd6prs) Have exceeded the dimensioned limit on species in the physically removed system (nprspa) of IIII on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6rea) Have exceeded the dimensioned limit on number of reactants (nrctpa) of IIII on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6rea) Found unexpected string "AAAA" on INPUT file line IIII.

Message: * error - (eq6/rd6rea) Have invalid reactant type "AAAA" referenced on INPUT file line IIII.

Message: * error - (eq6/rd6rea) Specify end-member and mole fraction for solid solution reactants only. Check INPUT file line IIII.

Message: * error - (eq6/rd6rea) Have exceeded the dimensioned limit of IIII for this type reactant on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6rea) Maximum number of end-members of a solid solution reactant is IIII. Exceeded this value on INPUT file line IIII.

Information Only

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6rea) Specify volume for special reactants only. Check INPUT file line IIII.

Message: * error - (eq6/rd6rea) Specify element and moles of element per mole of reactant for special reactants only. Check INPUT file line: IIII.

Message: * error - (eq6/rd6rea) Maximum number of elements in a special reactant is IIII. Exceeded this value on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6rea) Valid dissolution rate law codes are -1, 1, 2, 3, and 4- Value read: IIII Check INPUT file line: IIII

Message: * error - (eq6/rd6rea) Valid precipitation rate laws codes are -1 through 4- Value read: IIII Check INPUT file line: IIII

Message: * error - (eq6/rd6rea) Found blank input where the name of a chemical element was expected. See INPUT file line IIII.

Message: * error - (eq6/rd6rea) Found blank input where the name of a solid solution component was expected. Check INPUT file line IIII.

Message: * error - (eq6/rd6rea) If nrk= -1, nrpk must equal 1, 2,or 4. if nrpk= -1, nrk must equal 2 or 4. Check above INPUT file line IIII.

Message: * error - (eq6/rd6rea) The following reactant category must be specified once: AAAA Check above INPUT file line IIII

Message: * error - (eq6/rd6rea) The following reactant category must be specified: AAAA. Check above INPUT file line IIII

Message: * error - (eq6/rd6rea) nrk= 1 and nrpk= 3 is not allowed unless the reactant is a mineral or solid. solution. Check above INPUT file line IIII.

Message: * error - (eq6/rd6sup) Valid suppress options are "phases w/ elements" or "phases except". Value read: "AAAA" See INPUT file line: IIII

Message: * error - (eq6/rd6sup) The maximum number of suppress phases is IIII. Exceeded this value on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6sup) The maximum number of suppress exceptions is IIII. Exceeded this value on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rd6tol) Programmer error: unknown tolerance parameter code.

Information Only

Message: * error - (eq6/rd6tol) Invalid tolerance string. Check INPUT file line IIII.

Message: * error - (eq6/rd6tol) AAAA must be >= zero. Check INPUT file line IIII.

Message: * error - (eq6/rdmole) The maximum number of elements is IIII. Exceeded this value on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rdmole) Element name can not be blank. Check INPUT file line IIII.

Message: * error - (eq6/rdrate) Have rate specified more than once: "AAAA" Check INPUT file line IIII.

Message: * error - (eq6/rdrate) Valid rate law mechanism or term indices are 1 through IIII- Illegal value read: AAAA Check INPUT file line: IIII

Message: * error - (eq6/rdrate) Entry must follow a valid rate constant entry. Check INPUT file line IIII.

Message: * error - (eq6/rdrate) The maximum number of species in the kinetic activity product of any single mechanism is IIII. Exceeded this value on INPUT file line IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/rdrate) You must specify at least 1 rate constant. Check above INPUT file line IIII.

Message: * error - (eq6/rdrate) You may not specify negative rate constants with the above rate law. Check above INPUT file line IIII.

Message: * error - (eq6/rdrate) You must specify a value in either column 2 or column 4, but not both. Check above INPUT file line IIII.

Message: * error - (eq6/rdrate) Rate laws 2 and 4 can only be used with a mineral or solid solution reactant. Check above INPUT file line IIII.

Message: * error - (eq6/reacts) The total equilibrium system mass of "AAAA" is RRRR moles. This was the base point value.

Comment: This is probably due to a corrupted **pickup** *file.*

Message: * error - (eq6/reacts) Have encountered bad value of IIII for the status flag of reactant "AAAA".

Comment: This is probably due to a corrupted **pickup** *file.*

Message: * error - (eq6/reacts) The total equilibrium system mass of "AAAA" is RRRR moles after incrementing by RRRR moles of reactant "AAAA".

Comment: This is probably due to a corrupted **pickup** *file.*

Message: * error - (eq6/readrt) The forward direction rate law code nrk may not be IIII if iopt1 = 0.

Message: * error - (eq6/readrt) The backward direction rate law code nrkp may not be IIII if iopt1 = 0.

Information Only

Message: * error - (eq6/readrt) The forward direction rate code nrk can not be -1 unless nrpk = 2 or 4.

Message: * error - (eq6/readrt) The forward direction rate code nrk can not be 0.

Message: * error - The number of mechanisms or terms in a forward rate law may not exceed IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readrt) Actual forward rate constants may not be negative.

Message: * error - (eq6/readrt) The number of species in a forward rate law kinetic activity product may not exceed IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readrt) Can not use an affinity dependent rate law for a reactant type other than a mineral or solid solution.

Message: * error - (eq6/readrt) The forward direction rate law code has a bad value of IIII for "AAAA".

Message: * error - (eq6/readrt) The backward rate law code nrpk can not be -1 unless nrk = 2 or 4.

Message: * error - The number of mechanisms or terms in a backward rate law may not exceed IIII.

Message: * error - (eq6/readrt) Actual backward rate constants may not be negative.

Message: * error - (eq6/readrt) The number of species in a backward rate law kinetic activity product may not exceed IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readrt) Can not have nrpk= 3 if nrk= IIII for a reactant which is not a mineral or solid solution.

Message: * error - (eq6/readrt) The backward direction rate law code has a bad value of IIII for "AAAA".

Message: * error - (eq6/readz) The input file has no title.

Message: * error - (eq6/readz) The IIII subset-selection suppression options exceed the dimensioned limit (nxoppa) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error -(eq6/readz) The IIII exceptions to the mineral subset-selection suppressions options exceed the dimensioned limit (nxpepa) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The IIII fixed fugacity species exceed the dimensioned limit (nffgpa) of IIII.

Information Only

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The IIII reactants exceed the dimensioned limit (nrctpa) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The IIII solid solution reactants exceed the dimensioned limit (nxrtpa) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The number of components for the solid solution reactant "AAAA" exceeds the dimensioned limit (iktpar) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The IIII special reactants exceed the dimensioned limit (nsrtpa) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The number of elements composing special reactant "AAAA" exceeds the dimensioned limit (nctpar) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The bottom part of the input file is missing.

Message: * error - (eq6/readz) The input file has no title from the previons run.

Message: * error - (eq6/readz) The IIII nxmod options exceed the dimensioned limit (nxmdpa) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The IIII matrix variables on the input file exceed the dimensioned limit (kpar) of IIII.

Comment: Increase the dimensioned limit. See the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

Message: * error - (eq6/readz) The basis species "AAAA" has a log mass of -999 on the input file.

Comment: Possibly a corrupted or badly written **pickup** *file.*

Message: * error - (eq6/rsatch) Can not find "AAAA" among the matrix variables.

Message: * error - (eq6/rsetup) In setting up for reactant "AAAA", can not find the matrix index for component "AAAA".

Message: * error - (eq6/rtcalc) The surface area code nsk has an unrecognized value of IIII for "AAAA".

Information Only

Message: * error - (eq6/rtcalc) The forward rate law code (nrk) can not be zero.

Message: * error - (eq6/rtcalc) Reactant "AAAA" has bad forward rate law code of IIII.

Message: * error - (eq6/rtcalc) Reactant "AAAA" has bad backward rate law code of IIII.

Message: * error- (eq6/rtcalc) Calculated rate is .gt. 0, but affinity is .lt. 0 --- (reactant is dissolving, but it should precipitate).

Comment: The associated kinetic rate law specified on the **input** *file is producing an unrealistic result.*

Message: * error- (eq6/rtcalc) Calculated rate is .lt. 0, but affinity is .gt. 0 --- (reactant is precipitating, but it should dissolve).

Comment: The associated kinetic rate law specified on the **input** *file is producing an unrealistic result.*

Message: * error - (eq6/taylr2) Erroneous call, as the order is zero.

Comment: This is a programmer error.

Message: * error - (eq6/zvecpr) Order is zero, but value of basis variable has changed.

Comment: This is a programmer error.

Message: * warning - (eq6/eq6) Have solid solutions in the initial physically removed system described on the input file, but do not presently have the coding to initialize that system with these phases present. The code will continue, but it will be as though these phases have been cleared from that system at the start of this run.

Message: * warning - (eq6/eqcalc) Have quasi-underflow of a log mass variable: zvclg1(AAAA) = RRRR

Comment: The mass when obtained by exponentiation will underflow. If this is for an aqueous species, it may be necessary to switch a more prominent species into the basis set in its place.

Message: * warning - (eq6/path) The current time increment is only RRRR seconds.

Message: * warning - (eq6/timer) Bad dltime= RRRR seconds calculated for nord= IIII.

Comment: This is a programmer error.

Message: * warning - (eq6/writ6x) Illegal value for "AAAA". Variable not set.

Comment: This is a programmer error.

Message: * warning - (eq6/writ6x) Programmer error: illegal value of "udv6vr (IIII)".

Comment: This is a programmer error.

Message: * warning - (eq6/writ6x) Illegal value for suppress option- Value read: "AAAA"

Message: * note - (eq6/eq6) Have detected a temperature jump from the previous run- Initial temperature = RRRR Celsius Previous run temperature = RRRR Celsius

Information Only

Message: * note - (eq6/eq6) The option switch iopt4 is set to, 1, turning on the treatment of solid solutions, but there were no relevant solid solutions on the data file. Have switched iopt4 to 0.

Message: * note - (eq6/eq6) The exponent range of this machine is only +/- IIII. Will use logarithmic variables for Taylor's series representations of masses of basis species in order to avoid potentially catastrophic underflows. A good machine these days has an exponent range of +/- 308.

Message: * note - (eq6/eq6) IIII basis switches have been executed.

Message: * note - (eq6/eq6) Have hit the user-specified computing limit.

Message: * note - (eq6/eqcalc) Have a violation of the mineralogic phase rule. Must drop a phase from the equilibrium system.

Message: * note - (eq6/eqcalc) Have encountered critical redox instability.

Message: * note - (eq6/eqcalc) Setting up to scan for log fO2.

Message: * note - (eq6/eqcalc) Have not been able to establish the correct phase assemblage in the maximum number of tries (ntrymx).

Message: * note - (eq6/eqcalc) The run may be attempting to cross a univariant curve at zi= RRRR.

Message: * note - (eq6/eqcalc) Have not been able to eliminate all "unexcused" supersaturations in the maximum allowed number of tries.

Message: * note - (eq6/flgstz) This run involves at least one redox reaction. The code will therefore use a redox parameter and the charge balance constraint.

Message: * note - (eq6/flgstz) This run does not involve any redox reactions. The code will therefore not use a redox parameter or the charge balance constraint.

Message: * note - (eq6/flgstz) The species "AAAA" is suppressed because its associated reaction is a redox reaction.

Message: * note - (eq6/flgstz) Executing the "all" mineral subset-selection suppression option.

Message: * note - (eq6/flgstz) Executing the "alwith AAAA" mineral subset-selection suppression option.

Message: * note - (eq6/indat1) The adjusted mass of the fictive fixed fugacity phase "AAAA" is computed to be RRRR moles. It will be set to zero.

Message: * note - (eq6/indat1) The value of the print option switch iopr10 is inconsistent with the value of the aqueous species activity coefficient option switch iopg1. Therefore, the former has been reset to 0.

Message: * note (eq6/indatz) The gas species "h2(g)" is not on the data file.

Message: * note (eq6/indatz) The gas species "o2(g)" is not on the data file.

Message: * note - (eq6/inndx) Have a left over fictive fixed fugacity phase for "AAAA" in the initial equilibrium system. Will purge it.

Message: * note - (eq6/jgibbs) This routine find the phases which are involved in a violation of the apparent or mineralogic phase rule, but it presently treats only pure minerals.

Information Only

Message: * note (eq6/jgibbs) Can not consider dropping "AAAA" from the equilibrium system because the calculation of its hypothetical affinity in the presence of the other phases present failed.

Message: * note - (eq6/path) The inverse rate at the base point is RRRR, which is less than or equal to 100 times the machine epsilon. Therefore, the code will not make a search for the point at which the where the predicted inverse rate hits the target value for

Message: * note - (eq6/path) Have made an infinite time step.

Message: * note - (eq6/rd6rea) The effective surface ratio factor (fk) must be > 0. It has been reset to 1.0. See INPUT file line IIII.

Message: * note - (eq6/rd6rea) The surface area parameter (sk) must be >= 0. It has been reset to 0. See INPUT file line IIII.

Message: * note - (eq6/rd6rea) Found blank input where the, name of a reactant was expected. Skipping to the next reactant. See INPUT file line IIII.

Message: * note - (eq6/rd6tol) AAAA must be >= zero. Have reset it to a default value. Check INPUT file line IIII.

Message: * note - (eq6/rdrate) Only the first rate constant is used with rate law 3 (specified rate). Check above INPUT file line IIII.

Message: * note - (eq6/rdrate) Only first three rate constants are used with rate law 1. Check above INPUT file line IIII.

Message: * note - (eq6/rdrate) The activation energy or enthalpy was not specified, so temperature correction will not be made. Note that temperature of run does not match the temperature corresponding to the input rate constant value. Check above INPUT file line

Message: * note - (eq6/rdrate) Have csigma(IIII) <= 0. Have reset this to 1.0. Check above INPUT file line IIII.

Message: * note - (eq6/rdrate) The "csigma" input will be ignored because the rate law selected does not use it. See INPUT file line IIII.

Message: * note - (eq6/rdrate) The specified values will be ignored because of the rate law selected. See INPUT file line: IIII.

Message: * note - (eq6/rdrate) Normally only the first rate constant is set when using rate law 1 (arbitrary kinetics). Check above INPUT file line IIII.

Message: * note - (eq6/rdrate) In the case of rate constant IIII, a corresponding temperature was not specified, or it was <= 0. Will use a temperature of 25.0 Celsius. Check above INPUT file line IIII.

Message: * note - (eq6/rsatch) The reactant "AAAA" has saturated but differs in composition from the corresponding product form. Therefore, it must remain in the reactant system instead of being transferred to the equilibrium system.

Message: * note - (eq6/rsetup) The strict basis species corresponding to an element may be not represented on the input file. Check to see if the identity of the appropriate strict basis species has been changed on the data file (e.g., "fe+++" for "fe++", "h3bo3(aq)" for "b(oh)3(aq)").

Message: * note - (eq6/satchk) The hypothetical affinity calculation failed to converge for solid solution "AAAA".

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Message: * note - (eq6/search) Bad value of ntype = IIII hit during search for where a AAAA- the phase is "AAAA" delzi will be set to RRRR

Message: * note - (eq6/search) The supporting function call did not work during a search for where a AAAA- the phase is "AAAA" delzi will be set to RRRR

Message: * note - (eq6/search) A search for where a AAAA indicates that the event has been stepped over. the phase is "AAAA" delzi will be set to dlzimn.

Message: * note - (eq6/search) A search for where a AAAA indicates that the event being searched for does not take place in the interval being examined. the phase is "AAAA" delzi will not be decreased.

Message: * note - (eq6/search) A search for where a AAAA has hit the maximum number of iterations without succeeding- the phase is "AAAA" delzi will be set to a safe value of RRRR

Message: * note - (eq6/sfncaf) A required hypothetical affinity calculation failed to converge.

Message: * note - (eq6/sfncpd) The matrix position index (indx) is IIII. This is out of range.

Message: * note - (eq6/sfncpm) The matrix position index (indx) is IIII. This is out of range.

Message: * note - (eq6/sfncre) The matrix position index (indx) is IIII. This is out of range.

Message: * note - (eq6/sfncrr) The matrix position index (indx) is IIII. This is out of range.

Message: * note - (eq6/sshift) The matrix position index (kcol) is IIII. This is out of range.

Message: * note - (eq6/sshift) The end-member index (ik) is IIII for "AAAA". This is out of range.

Message: * note - (eq6/tstep) Stopping because the temperature is RRRR Celsius at zi= RRRR.

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Appendix D. Notes on Known Bugs and Such

This appendix presents notes on known bugs and other known unusual phenomena.

1. The differential equation integration algorithm in EQ6 will not handle "stiff systems" of ordinary differential equations (ODEs). A system of ODEs *per se* is not inherently stiff or non-stiff; rather, stiffness is a condition that appears under certain circumstances. This is a problem only in kinetic mode; the actual rate laws comprise the set of ODEs. Stiffness can occur only if there are two or more such rate laws. The condition of stiffness occurs when the magnitude of one of these rates is much greater than that of the other or others, and it begins to rapidly change. Typically, this happens when the reaction in question begins to closely approach a state of partial equilibrium. When stiffness is encountered, the step size is decreased and soon becomes stuck at the minimum value. The code now stops if the step size is stuck at this value, instead of running on. The only solution to this is to add a stiff-system integration algorithm to the code. There are currently no active plans to do this.

2. Another problem in EQ6 exhibits much the same symptoms. It also requires more than one reactant, and may occur in kinetic or reaction progress mode. If one chooses to set **nrk** = 1 (specified relative rate) to control the dissolution of a reactant and **nrpk** = 0 (follow partial equilibrium) to control its precipitation, the **nrpk** = 0 option can not be followed if one has also suppressed the formation of the reactant in question as a product mineral. The **nrpk** = 0 option requires the formation of such product mineral in order to hold the reactant affinity at zero. Without this, the dissolution rate goes to zero, but continued advancement in overall reaction progress may cause undersaturation, returning the relative rate of dissolution to the specified value. After another small advancement in reaction progress, the dissolution rate again goes to zero, and the pattern repeats itself. The step size is decreased and usually soon becomes stuck at the minimum value. The code then notes this and stops. Mathematically, the problem has become ill-posed. The solution is to not suppress a phase if **nrpk** is set to 0. When this problem has been seen to manifest itself, the phase has suppressed unintentionally by a subset-selection (**nxopt**) option and not specified as an exception to that option.

3. EQ6 periodically exhibits trouble when it encounters mineral assemblages which fix the activity of water (e.g., gypsum plus anhydrite, or epsomite plus hexahydrite). The step size may drop to and become stuck at the minimum value, leading to early termination of the run. The cause of this is presently unknown.

4. The code tends to converge slowly or not at all in dealing with extremely concentrated electrolyte solutions. Roughly speaking, these are solutions whose ionic strengths are greater than about 12 molal. However, there is no simple way to accurately categorize the code's performance envelope.

5. The EQ6 module **jgibbs.f** tests the mineral assemblage in the equilibrium system for violations of the mineralogical phase rule. The module as presently written only tests pure minerals. It does not look at any solid solutions. This condition forces the code to rely on other phase deletion algorithms.

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6. When EQ6 operates without a redox variable, the log oxygen fugacity variable is assigned a value of -999. The saturation indices and affinities for certain solid phases such as *al*, *graphite*, *k*, and *si* are calculated and reported using this value. These phases are irrelevant to the computed model and the reported *SI* and affinity data for them should be ignored. These phases are technically suppressed when there is no redox variable. Thus, they can not be precipitated.

7. The maximum time parameter **timemx** which appears in the EQ6 **input** file may be exceeded when the code is running in time mode. The code does not find the value of reaction progress corresponding to the desired maximum time. Instead, it simply stops the reaction path calculation when this is exceeded. Note also that the code does not provide for the use of print intervals defined in terms of time.

For a complete list of known bugs and such for EQ3/6, see Appendix D of the EQ3/6 Package Overview and Installation Guide (Wolery, 1992a).

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Appendix E. Examples of More Complex EQ6 Input files

This appendix presents a few more complex EQ6 **input** files. The first is for kinetic modeling of groundwater interacting with devitrified tuff in a hydrothermal experiment. The second deals with the reaction of groundwater with spent nuclear fuel. Refer to the internal titles for further information. The third is similar to that last example in Chapter 6. It models the precipitation of quartz according to a different rate law, and illustrates the use of activation energies on the EQ6 **input** file. There is however a problem with the way the rate law for net dissolution is extrapolated to the case of net precipitation (see the title of the **input** file and also comments for the last example in Chapter 6).

<u>The EQ6 **input** file (**j13wwtuff.6i**), groundwater-tuff hydrothermal reaction ("W" format):</u>

```
EQ6 input file name= j13wwtuff.6i
Description= "Reaction of J-13 water with devitrified tuff at 150 C"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  React devitrified Topopah Springs tuff with J-13 well water at
150 C. This simulates a hydrothermal experiment in a closed
autoclave, so the CO2 fugacity is allowed to drift. The tuff is
represented by six minerals: (Na-K)-sanidine, plagioclase, biotite,
cristobalite, quartz, and Mg-beidellite. The first three of these
are solid solution minerals. The option switch iopt1 is set to 1
to direct the code to compute the simulation in a time frame. A
kinetic rate law of transition state theory form describes the
dissolution rate of each of the mineral reactants. No precipitation
rate laws are specified. This test case is adapted from Appendix C
of Delany (1985).

  Purpose: to test the ability of the code to model rock-water
interaction in a time frame in the case of system whose complexity
is representative of a real geologic system. The scenario
corresponds to an actual hydrothermal experiment (cf. Delany, 1985).
The J-13 well water composition used here is taken from Harrer et
al. (1990) and differs slightly from that used by Delany (1985).
The results from this test case may be compared with those reported
by her. Semi-quantitative agreement is expected.

  Six minerals (quartz, chalcedony, tridymite, pyrophyllite, maximum
microcline, and illite) should be suppressed (see Delany, 1985).
This is done by means of "nxmod" options specified on the EQ3NR
test case input file j13wwA.3i, which initializes the present
input file. These options are passed on to the present file.

  The option switch iopt4 is set to 1 to direct the code to permit
the use of solid solutions. The print option switch iopr8 is set
to 1 to direct the code to print a table of equilibrium gas
fugacities at each print point.

                          References

Delany, J. M., 1985, Reaction of Topopah Spring Tuff with J-13 water:
  A geochemical modeling approach using the EQ3/6 Reaction Path Code:
  UCRL-53631, Lawrence Livermore National Laboratory, Livermore,
  California, 46 p.

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990,
  Report of the Committee to Review the Use of J-13 Well Water in
  Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence
  Livermore National Laboratory, Livermore, California.

endit.
    nmodl1=  2              nmodl2=  0
    tempc0=  150.00E+00      jtemp=  0
       tk1=  0.00000E+00       tk2=  0.00000E+00       tk3=  0.00000E+00
    zistrt=  0.00000E+00     zimax=  1.00000E+00
     tstrt=  0.00000E+00    timemx=  6.05000E+06
    kstpmx=           200     cplim=  0.00000E+00
    dzprnt=  1.00000E+38    dzprlg=  1.00000E+00    ksppmx=   100
    dzplot=  1.00000E+38    dzpllg=  1.00000E+38    ksplmx= 10000
     ifile= 60
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=    1    0    0    1    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    1    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
```

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```
* nxopex = number of exceptions
     nxopt=  0
* nffg = number of gas species with fixed fugacities
     nffg =  0
* nrct = number of reactants
      nrct=  6
*-----------------------------------------------------------------------
  reactant= sanidine-ss
     jcode=  1              jreac=  0
      morr=  1.69400E-02     modr=  0.00000E+00
   sanidine high             0.58000E+00
   albite high               0.41000E+00
   anorthite                 0.01000E+00
   endit.
       nsk=  0                 sk=  16822.0E+00        fk=  0.20000E+00
       nrk=  2               nrpk=  0
     imech=  1
       rk0=  2.88000E-16     trk0=  150.000E+00      iact=  0
      eact=  0.00000E+00     hact=  0.00000E+00
     ndact=  0             csigma=  1.00000E+00
*-----------------------------------------------------------------------
  reactant= plagioclase
     jcode=  1              jreac=  0
      morr=  4.53300E-04     modr=  0.00000E+00
   albite high               0.76000E+00
   anorthite                 0.17000E+00
   sanidine high             0.07000E+00
   endit.
       nsk=  0                 sk=  432.000E+00        fk=  0.20000E+00
       nrk=  2               nrpk=  0
     imech=  1
       rk0=  3.90000E-14     trk0=  150.000E+00      iact=  0
      eact=  0.00000E+00     hact=  0.00000E+00
     ndact=  0             csigma=  1.00000E+00
*-----------------------------------------------------------------------
  reactant= biotite
     jcode=  1              jreac=  0
      morr=  2.94600E-05     modr=  0.00000E+00
   phlogopite                0.43000E+00
   annite                    0.57000E+00
   endit.
       nsk=  0                 sk=  40.5000E+00        fk=  0.20000E+00
       nrk=  2               nrpk=  0
     imech=  1
       rk0=  4.09000E-14     trk0=  150.000E+00      iact=  0
      eact=  14.0000E+00     hact=  0.00000E+00
     ndact=  0             csigma=  1.00000E+00
*-----------------------------------------------------------------------
  reactant= cristobalite
     jcode=  0              jreac=  0
      morr=  6.66300E-02     modr=  0.00000E+00
       nsk=  0                 sk=  16178.0E+00        fk=  0.20000E+00
       nrk=  2               nrpk=  0
     imech=  1
       rk0=  3.55000E-13     trk0=  150.000E+00      iact=  0
      eact=  0.00000E+00     hact=  0.00000E+00
     ndact=  0             csigma=  1.00000E+00
*-----------------------------------------------------------------------
  reactant= quartz
     jcode=  0              jreac=  0
      morr=  3.00300E-02     modr=  0.00000E+00
       nsk=  0                 sk=  6429.00E+00        fk=  0.20000E+00
       nrk=  2               nrpk=  0
     imech=  1
       rk0=  1.20000E-13     trk0=  150.000E+00      iact=  0
      eact=  0.00000E+00     hact=  0.00000E+00
     ndact=  0             csigma=  1.00000E+00
*-----------------------------------------------------------------------
  reactant= beidellite-mg
     jcode=  0              jreac=  0
      morr=  3.52200E-04     modr=  0.00000E+00
       nsk=  0                 sk=  432.000E+00        fk=  0.20000E+00
       nrk=  2               nrpk=  0
     imech=  1
       rk0=  7.50000E-14     trk0=  150.000E+00      iact=  0
      eact=  0.00000E+00     hact=  0.00000E+00
     ndact=  0             csigma=  1.00000E+00
*-----------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00     told1=  0.00000E+00      tolx=  0.00000E+00
    tolsat=  0.00000E+00    tolsst=  0.00000E+00
    screw1=  0.00000E+00    screw2=  0.00000E+00    screw3=  0.00000E+00
    screw4=  0.00000E+00    screw5=  0.00000E+00    screw6=  0.00000E+00
    zklogu=        0.000    zklogl=        0.000     zkfac=        0.000
    dlzmx1=  0.00000E+00    dlzmx2=  0.00000E+00    nordlm=  0
    itermx=  0              ntrymx=  0
    npslmx=  0              nsslmx=  0              ioscan=  0
*-----------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= j13wwA.3i
Description= "J-13 well water, six minerals suppressed"
Version number= 3245   Stage number= 01
```

Information Only

```
Created 10/07/90     Creator= T.J. Wolery
Revised 10/07/90     Revisor= T.J. Wolery

  Water from well J-13 at the Nevada Test Site. The composition
is identical to that in the EQ3NR test case input file j13ww.3i,
which is based on data reported by Harrer et al. (1990). Water
from this well is commonly used to represent the groundwater
at the proposed high-level nuclear waste repository at Yucca
Mountain, Nevada.

  Purpose: to initialize the EQ6 test case input file j13wwtuff.6i,
in which this water is reacted with devitrified tuff at 150 C.
Six minerals (quartz, chalcedony, tridymite, pyrophyllite,
maximum microcline, and illite) are suppressed by means of
"nxmod" options. These suppressions have no effect on the EQ3NR
calculation, but will be passed on to j13wwtuff.6i.

                              References

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990,
  Report of the Committee to Review the Use of J-13 Well Water in
  Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence
  Livermore National Laboratory, Livermore, California.

endit.
    tempci=  0.25000E+02
     nxmod=  6
   species= quartz
      type=  1                 option= -1                xlkmod=  0.00000E+00
   species= chalcedony
      type=  1                 option= -1                xlkmod=  0.00000E+00
   species= tridymite
      type=  1                 option= -1                xlkmod=  0.00000E+00
   species= pyrophyllite
      type=  1                 option= -1                xlkmod=  0.00000E+00
   species= maximum microcline
      type=  1                 option= -1                xlkmod=  0.00000E+00
   species= illite
      type=  1                 option= -1                xlkmod=  0.00000E+00
     iopg1=  0                  iopg2=  0                 iopg3=  0
     iopg4=  0                  iopg5=  0                 iopg6=  0
     iopg7=  0                  iopg8=  0                 iopg9=  0
    iopg10=  0
       kct= 19                    ksq= 20                   kmt= 20
       kxt= 20                   kdim= 20                  kprs=  0
   o                  0.555183619996184E+02
   al                 0.296499013987773E-06
   b                  0.123882029374571E-04
   ca                 0.324367483418525E-03
   cl                 0.201395098257713E-03
   f                  0.114746504969044E-03
   fe                 0.716242591683072E-06
   h                  0.111019041364482E+03
   c                  0.230099280306266E-02
   p                  0.125027141351693E-05
   k                  0.128905860357201E-03
   li                 0.691543005331060E-05
   mg                 0.826990331249453E-04
   mn                 0.218456477571116E-06
   na                 0.199219043949006E-02
   n                  0.141601620864581E-03
   si                 0.101474095562313E-02
   s                  0.191539771578739E-03
   sr                 0.456516777005975E-06
   electr             0.103370768598040E-03
   h2o                h2o                     0.174435898352698E+01
   al+++              al+++                  -0.138327589967153E+02
   b(oh)3(aq)         b(oh)3(aq)             -0.491386263393695E+01
   ca++               ca++                   -0.350490382237190E+01
   cl-                cl-                    -0.369612063671960E+01
   f-                 f-                     -0.394148547298545E+01
   fe++               fe++                   -0.888881411500307E+01
   h+                 h+                     -0.738394246929729E+01
   hco3-              hco3-                  -0.267503530048784E+01
   hpo4--             hpo4--                 -0.613006179481343E+01
   k+                 k+                     -0.389019626762259E+01
   li+                li+                    -0.516054511756232E+01
   mg++               mg++                   -0.410420281907220E+01
   mn++               mn++                   -0.670367598253854E+01
   na+                na+                    -0.270232246215246E+01
   no3-               no3-                   -0.324846174258599E+02
   sio2(aq)           sio2(aq)               -0.299512354313566E+01
   so4--              so4--                  -0.373802108388307E+01
   sr++               sr++                   -0.635066503949193E+01
   o2(g)              o2(g)                  -0.304751407267451E+02
```

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The EQ6 input file (j13wwtuff.6i), groundwater-tuff hydrothermal reaction ("D" format):

```
EQ6 input file name= j13wwtuff.6i
Description= "Reaction of J-13 water with devitrified tuff at 150 C"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  React devitrified Topopah Springs tuff with J-13 well water at
150 C. This simulates a hydrothermal experiment in a closed
autoclave, so the CO2 fugacity is allowed to drift. The tuff is
represented by six minerals: (Na-K)-sanidine, plagioclase, biotite,
cristobalite, quartz, and Mg-beidellite. The first three of these
are solid solution minerals. The option switch iopt1 is set to 1
to direct the code to compute the simulation in a time frame. A
kinetic rate law of transition state theory form describes the
dissolution rate of each of the mineral reactants. No precipitation
rate laws are specified. This test case is adapted from Appendix C
of Delany (1985).

  Purpose: to test the ability of the code to model rock-water
interaction in a time frame in the case of system whose complexity
is representative of a real geologic system. The scenario
corresponds to an actual hydrothermal experiment (cf. Delany, 1985).
The J-13 well water composition used here is taken from Harrer et
al. (1990) and differs slightly from that used by Delany (1985).
The results from this test case may be compared with those reported
by her. Semi-quantitative agreement is expected.

  Six minerals (quartz, chalcedony, tridymite, pyrophyllite, maximum
microcline, and illite) should be suppressed (see Delany, 1985).
This is done by means of "nxmod" options specified on the EQ3NR
test case input file j13wwA.3i, which initializes the present
input file. These options are passed on to the present file.

  The option switch iopt4 is set to 1 to direct the code to permit
the use of solid solutions. The print option switch iopr8 is set
to 1 to direct the code to print a table of equilibrium gas
fugacities at each print point.

                          References

Delany, J. M., 1985, Reaction of Topopah Spring Tuff with J-13 water:
  A geochemical modeling approach using the EQ3/6 Reaction Path Code:
  UCRL-53631, Lawrence Livermore National Laboratory, Livermore,
  California, 46 p.

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990,
  Report of the Committee to Review the Use of J-13 Well Water in
  Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence
  Livermore National Laboratory, Livermore, California.

 calculational mode    |*normal      | economy            | super economy
 model type            | titration   |*closed             | open
 temperature model     |*power       | fluid mixing
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c
 tstart(c)|  150.0    |tk1|     0.    |tk2|     0.    |tk3|     0.
 starting value of zi |      0.     |max. value of zi     |  1.0000
 starting time (sec)  |      0.     |max. time (sec)      | 6.05000E+06
 max. steps           |       200   |max. steps w/o print|       100
 linear print interval| 1.00000E+38|log print interval   |  1.0000
 suppress mineral phases
 phases w/ elements|                          |                          n
 phases except     |                          |                          n
 fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
 none                                |                |                n
```

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```
c                    R A T E     L A W S
c 1 = relative                    rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory     rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate          rate = CHECK DOCUMENTATION

c                    R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                    S U R F A C E     T Y P E
c 0 = fixed surface area     1 = fixed specific surface area
c
c                    N O T E S
c status and jreac are normally not set by the user
reactants   (ss) solid solution only     (sp) special reactant only

REACTANT            sanidine-ss          status      0
moles remaining     1.69400E-02          destroyed       0.
reactant type       solid solution       sk          16822.
surface type        0                    fk          0.20000
end-member          sanidine high        mole fr       0.580000      ss,n
end-member          albite high          mole fr       0.410000      ss,n
end-member          anorthite            mole fr       0.100000E-01  ss,n
volume                                                               sp
element                                  moles                       sp,n
DISSOLUTION LAW     2
rate constant rk1   2.88000E-16          csigma1       1.00000
temperature (c)     150.00                                           234
PRECIPITATION LAW   0
c
REACTANT            plagioclase          status      0
moles remaining     4.53300E-04          destroyed       0.
reactant type       solid solution       sk          432.00
surface type        0                    fk          0.20000
end-member          albite high          mole fr       0.760000      ss,n
end-member          anorthite            mole fr       0.170000      ss,n
end-member          sanidine high        mole fr       0.700000E-01  ss,n
volume                                                               sp
element                                  moles                       sp,n
DISSOLUTION LAW     2
rate constant rk1   3.90000E-14          csigma1       1.00000
temperature (c)     150.00                                           234
PRECIPITATION LAW   0
c
REACTANT            biotite              status      0
moles remaining     2.94600E-05          destroyed       0.
reactant type       solid solution       sk          40.500
surface type        0                    fk          0.20000
end-member          phlogopite           mole fr       0.430000      ss,n
end-member          annite               mole fr       0.570000      ss,n
volume                                                               sp
element                                  moles                       sp,n
DISSOLUTION LAW     2
rate constant rk1   4.09000E-14          csigma1       1.00000
temperature (c)     150.00                                           234
PRECIPITATION LAW   0
c
REACTANT            cristobalite         status      0
moles remaining     6.66300E-02          destroyed       0.
reactant type       mineral              sk          16178.
surface type        0                    fk          0.20000
end-member                               mole fr                     ss,n
volume                                                               sp
element                                  moles                       sp,n
DISSOLUTION LAW     2
rate constant rk1   3.55000E-13          csigma1       1.00000
temperature (c)     150.00                                           234
PRECIPITATION LAW   0
c
REACTANT            quartz               status      0
moles remaining     3.00300E-02          destroyed       0.
reactant type       mineral              sk          6429.0
surface type        0                    fk          0.20000
end-member                               mole fr                     ss,n
volume                                                               sp
element                                  moles                       sp,n
DISSOLUTION LAW     2
rate constant rk1   1.20000E-13          csigma1       1.00000
temperature (c)     150.00                                           234
PRECIPITATION LAW   0
c
REACTANT            beidellite-mg        status      0
moles remaining     3.52200E-04          destroyed       0.
reactant type       mineral              sk          432.00
surface type        0                    fk          0.20000
end-member                               mole fr                     ss,n
volume                                                               sp
element                                  moles                       sp,n
DISSOLUTION LAW     2
rate constant rk1   7.50000E-14          csigma1       1.00000
temperature (c)     150.00                                           234
PRECIPITATION LAW   0
```

Information Only

```
-----------------------------------------------------------------------
options
-----------------------------------------------------------------------
 - SOLID SOLUTIONS -
     ignore solid solutions
   * process solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * don't print
     lists species loaded into memory
 - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
   * don't print
     print
 - LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
   * don't print
     print
 - LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
   * only species > 10**-12 molal
     all species
     don't print
 - LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
   * don't print
     print
 - LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
   * don't print
     print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
     don't print
   * print
 - PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
   * don't print
     print
 - TAB FILES -
   * write
     append to previous tabx file
     don't write
 - WRITE PICKUP FILE -
   * write pickup file at end of run
     don't write pickup file
     write pickup file for each print point
 - PHYSICALLY REMOVED SUBSYSTEM -
   * does nothing
     transfer minerals but leave trivial mass in the system
     transfer minerals
 - CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
   * does nothing
     clear p.r.s. before first reaction progress advance
 - PHASE BOUNDARY SEARCH -
   * step size constrained by predicted phase boundaries
     phase boundaries estimated from Taylor's series and printed
     locations of phase boundaries ignored
 - AUTO BASIS SWITCHING -
   * off
     on
 - SUPPRESS REDOX REACTIONS -
   * does nothing
     suppress all redox reactions
 - LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
   * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
     logarithmic for kcol = 1,kbt
     linear for kcol = 1,kdim
 - AZERO AND HYDRATION NUMBERS -
   * no change
     read in new azero and hydration numbers
 - PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
   * does nothing
     print
 - PITZER DATABASE INFORMATION -
   * print only warnings
     print species in model and number of Pitzer coefficients
     print species in model and names of Pitzer coefficients
 - PRINT DIAGNOSTIC MESSAGES -
   * don't print
     print level 1 messages
     print level 2 messages
 - PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
   * don't print
     print summary information
     print detailed information
 - PRINT STEP SIZE AND ORDER -
   * don't print
     print scale factor
     print orders and step size scaling factors
 - CONTROL STEP SIZE AND ORDER PRINT -
   * does nothing
     print step size and order when delzi .le. dlzmxl
 - NEWTON ITERATIONS -
   * don't print
     print summary of newton iterations
     print summary, residual functions and correction terms
```

Information Only

```
    print summary, residual functions, correction terms and matrix
 - PRINT SEARCH ITERATIONS -
   * don't print
     print
 - PRINT HPSAT ITERATIONS -
   * don't print
     print
 - PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
   * don't print
     print computations from RDERIV, and RTAYLR
     print computations from RDERIV, RTAYLR, DERIV and TAYLOR
 - PRINT KINETICS DIAGNOSTIC MESSAGES -
   * don't print
     print level 1 diagnostics
     print level 1 and level 2 diagnostics
 - PRINT AKMATR -
   * don't print
     print level 1 diagnostics
 - KILL ITERATION VARIABLES -
   * does nothing
     allow selection of variables to remove
-------------------------------------------------------------------------
 development options  (used for code development)
-------------------------------------------------------------------------
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
-------------------------------------------------------------------------
 tolerances                        desired values - defaults info-only
-------------------------------------------------------------------------
 number of N-R iterations          |                  | 40      itermx
 p.r.s. transfer interval          |                  | varies  dlzidp
 residual magnitude                |                  | 1.0e-06 tolbt
 correction magnitude              |                  | 1.0e-06 toldl
 search/find tolerance             |                  | varies  tolx
 supersaturation                   |                  | varies  tolsat
 supersaturation set size          |                  | varies  tolsst
 max. size Taylor's series term    |                  | 1.0e-04 screw1
 max. initial value betamx         |                  | n/a     screw2
 max. Taylor's series term (kin.)  |                  | 1.0e-04 screw3
 corrector iteration               |                  | 1.0e-04 screw4
 max. size of N-R correction term  |                  | 4.0     screw5
 step size (economy mode)          |                  | 4.0     screw6
 log mass of phases                |                  | varies  zklogu
 decrement mass (p.r.s.)           |                  | 2.0     zklogl
 min. left after p.r.s.            |                  | .98     zkfac
 initial step size                 |                  | varies  dlzmx1
 upper limit step size             |                  | varies  dlzmx2
 maximum order                     |                  | 6       nordlm
 num. attempted assemblages        |                  | 25      ntrymx
 slide -> over phase bound.        |                  | 8       npslmx
 slide -> over redox insta.        |                  | 3       nsslmx
 fo2 scan control                  |                  | none    ioscan
-------------------------------------------------------------------------
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= j13wwA.3i
Description= "J-13 well water, six minerals suppressed"
Version number= 3245   Stage number= 01
Created 10/07/90    Creator= T.J. Wolery
Revised 10/07/90    Revisor= T.J. Wolery

  Water from well J-13 at the Nevada Test Site. The composition
is identical to that in the EQ3NR test case input file j13ww.3i,
which is based on data reported by Harrer et al. (1990). Water
from this well is commonly used to represent the groundwater
at the proposed high-level nuclear waste repository at Yucca
Mountain, Nevada.

  Purpose: to initialize the EQ6 test case input file j13wwtuff.6i,
in which this water is reacted with devitrified tuff at 150 C.
Six minerals (quartz, chalcedony, tridymite, pyrophyllite,
maximum microcline, and illite) are suppressed by means of
"nxmod" options. These suppressions have no effect on the EQ3NR
calculation, but will be passed on to j13wwtuff.6i.

                          References

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990,
  Report of the Committee to Review the Use of J-13 Well Water in
  Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence
  Livermore National Laboratory, Livermore, California.

-------------------------------------------------------------------------
 temperature (C)                    |     25.000
-------------------------------------------------------------------------
 electrical imbalance               |      1.033707685980400E-04
-------------------------------------------------------------------------
 number of aqueous master species   |     20
-------------------------------------------------------------------------
 position of last pure mineral      |     20
-------------------------------------------------------------------------
 position of last solid solution    |     20
-------------------------------------------------------------------------
```

Information Only

suppressed species	(suppress,replace,augmentk,augmentg)		value
quartz	mineral	suppress	0.
chalcedony	mineral	suppress	0.
tridymite	mineral	suppress	0.
pyrophyllite	mineral	suppress	0.
maximum microcline	mineral	suppress	0.
illite	mineral	suppress	0.

iopg options

- pH SCALE CONVENTION -
  - * modified NBS
    internal
    rational
- ACTIVITY COEFFICIENT OPTIONS -
  - * use B-dot equation
    Davies' equation
    Pitzer's equations

elements, moles and moles aqueous

o	5.551836199961840E+01	0.000000000000000E+00
al	2.964990139877730E-07	0.000000000000000E+00
b	1.238820293745710E-05	0.000000000000000E+00
ca	3.243674834185250E-04	0.000000000000000E+00
cl	2.013950982577130E-04	0.000000000000000E+00
f	1.147465049690440E-04	0.000000000000000E+00
fe	7.162425916830720E-07	0.000000000000000E+00
h	1.110190413644820E+02	0.000000000000000E+00
c	2.300992803062660E-03	0.000000000000000E+00
p	1.250271413516930E-06	0.000000000000000E+00
k	1.289058603572010E-04	0.000000000000000E+00
li	6.915430053310600E-06	0.000000000000000E+00
mg	8.269903312494529E-05	0.000000000000000E+00
mn	2.184564775711160E-07	0.000000000000000E+00
na	1.992190439490060E-03	0.000000000000000E+00
n	1.416016208645810E-04	0.000000000000000E+00
si	1.014740955623130E-03	0.000000000000000E+00
s	1.915397715787390E-04	0.000000000000000E+00
sr	4.565167770059750E-07	0.000000000000000E+00

master species and logarithmic basis variables

h2o	h2o	1.744358983526980E+00
al+++	al+++	-1.383275899671530E+01
b(oh)3(aq)	b(oh)3(aq)	-4.913862633936950E+00
ca++	ca++	-3.504903822371900E+00
cl-	cl-	-3.696120636719600E+00
f-	f-	-3.941485472985450E+00
fe++	fe++	-8.888814115003070E+00
h+	h+	-7.383942469297290E+00
hco3-	hco3-	-2.675035300487840E+00
hpo4--	hpo4--	-6.130061794813430E+00
k+	k+	-3.890196267622590E+00
li+	li+	-5.160545117562320E+00
mg++	mg++	-4.104202819072200E+00
mn++	mn++	-6.703675982538540E+00
na+	na+	-2.702322462152460E+00
no3-	no3-	-3.248461742585990E+01
sio2(aq)	sio2(aq)	-2.995123543135660E+00
so4--	so4--	-3.738021083883070E+00
sr++	sr++	-6.350665039491930E+00
o2(g)	o2(g)	-3.047514072674510E+01

physically removed subsystem (solid solution, mineral, moles)

none

The EQ6 input file (j13wwsf.6i), groundwater-spent nuclear fuel reaction ("W" format):

```
EQ6 input file name= j13wwsf.6i
Description= "Reaction of J-13 well water with spent nuclear fuel"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  React spent nuclear fuel with J-13 well water. The O2 and CO2
fugacities are fixed at atmospheric values. The spent nuclear
fuel is treated as a special reactant. One "mole" is equivalent
to 100 grams. The spent fuel composition corresponds to average
PWR spent fuel with burnup of 33,000 MWd/MTIHM at 1,000 years
This was computed by Henry Shaw (LLNL, 1/12/89) as a correction to
the data published in Table 2 of Bruton and Shaw (1988).

  Purpose: to test the ability of the code to model reaction in a
```

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very complex system, whose components exhibit a variety of chemical behaviors. Results may be roughly compared with those reported by Bruton and Shaw (1988).

References

Bruton, C. J., and Shaw, H. F., 1988, Geochemical simulation of reaction between spent fuel waste form and J-13 water at 25 C and 90 C: In Apted, M. J., and Westerman, R. E., editors, Scientific Basis for Nuclear Waste Management XI, Materials Research Society Symposium Proceedings, v. 112, Materials Research Society, Pittsburgh, Pennsylvania, p. 485-494.


```
endit.
    nmodl1=  2                nmodl2=  0
    tempc0=  2.50000E+01       jtemp=  0
       tk1=  0.00000E+00         tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.00000E+00      zimax=  1.00000E+00
     tstrt=  0.00000E+00     timemx=  1.00000E+38
    kstpmx=           10      cplim=  0.00000E+00
    dzprnt=  1.00000E-01     dzprlg=  1.00000E+38     ksppmx=   100
    dzplot=  1.00000E+38     dzpllg=  1.00000E+38     ksplmx= 10000
     ifile= 60
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    1    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
     nxopt=  0
* nffg = number of gas species with fixed fugacities
      nffg=  2
   species= o2(g)            moffg=  5.00000E-01    xlkffg= -0.70000E+00
   species= co2(g)           moffg=  5.00000E-01    xlkffg= -3.50000E+00
* nrct = number of reactants
      nrct=  1
*-----------------------------------------------------------------------
  reactant= spent fuel
     jcode=  2                jreac=  0
      morr=  1.00000E+00       modr=  0.00000E+00
     vreac=  0.00000E+00
   c        1.3122e-03
   ca       4.2800e-09
   ni       2.0940e-02
   se       2.4150e-05
   tc       7.7500e-04
   sn       3.1736e-03
   i        1.5000e-04
   cs       1.1400e-03
   pb       1.8300e-11
   ra       1.4000e-09
   th       3.7100e-07
   u        4.0543e-01
   np       5.9800e-04
   pu       3.1420e-03
   am       1.4020e-04
   o        8.5186e-01
   endit.
       nsk=  0                   sk=  0.00000E+00         fk=  0.00000E+00
       nrk=  1                 nrpk=  0
       rk1=  1.00000E+00        rk2=  0.00000E+00        rk3=  0.00000E+00
*-----------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00      toldl=  0.00000E+00       tolx=  0.00000E+00
    tolsat=  0.00000E+00     tolsst=  0.00000E+00
    screw1=  0.00000E+00     screw2=  0.00000E+00     screw3=  0.00000E+00
    screw4=  0.00000E+00     screw5=  0.00000E+00     screw6=  0.00000E+00
    zklogu=        0.000     zklogl=        0.000      zkfac=        0.000
    dlzmx1=  0.00000E+00     dlzmx2=  0.00000E+00     nordlm=  0
    itermx=  0               ntrymx=  0
    npslmx=  0               nsslmx=  0               ioscan=  0
*-----------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= j13wwsf.3i
Description= "J-13 well water, with traces of spent fuel components"
Version number= 3245   Stage number= 01
Created 10/29/90     Creator= T.J. Wolery
Revised 11/30/90     Revisor= T.J. Wolery

  Water from well J-13 at the Nevada Test Site, spiked with
trace amounts of spent nuclear fuel components. The composition
is otherwise identical to that in the EQ3NR test case input file
j13ww.3i, which is based on data reported by Harrer et al. (1990).
Water from this well is commonly used to represent the groundwater
at the proposed high-level nuclear waste repository at Yucca
Mountain, Nevada.

  Purpose: to initialize the EQ6 test case input file j13wwsf.6i,
```

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which simulates the interaction of J-13 well water with spent nuclear fuel. This test case also tests the ability of EQ3NR to handle a system containing many components.

References

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990, Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence Livermore National Laboratory, Livermore, California.


```
endit.
    tempci=  0.25000E+02
     nxmod=  0
     iopg1=  0              iopg2=  0              iopg3=  0
     iopg4=  0              iopg5=  0              iopg6=  0
     iopg7=  0              iopg8=  0              iopg9=  0
    iopg10=  0
       kct= 33                ksq= 34                kmt= 34
       kxt= 34               kdim= 34               kprs=  0
   o                  0.555183619996426E+02
   al                 0.296499013903087E-06
   am                 0.100000000074117E-11
   b                  0.123882029374860E-04
   ca                 0.324367483413227E-03
   cl                 0.201395098257697E-03
   cs                 0.100000000000002E-11
   cu                 0.100000000033842E-11
   f                  0.114746504968947E-03
   fe                 0.716242591559603E-06
   h                  0.111019041364491E+03
   c                  0.230099280303300E-02
   p                  0.125027141331246E-05
   i                  0.100000000000001E-11
   k                  0.128905860357153E-03
   li                 0.691543005330863E-05
   mg                 0.826990331229586E-04
   mn                 0.218456477562591E-06
   na                 0.199219043948851E-02
   ni                 0.100000000001087E-11
   n                  0.141601620819403E-03
   np                 0.100000000116054E-11
   pb                 0.100000000000221E-11
   pu                 0.100000000111923E-11
   ra                 0.100000000000000E-11
   se                 0.100000000013940E-11
   si                 0.101474095562361E-02
   sn                 0.100000000029450E-11
   s                  0.191539771573646E-03
   sr                 0.456516776999134E-06
   tc                 0.100000000000000E-11
   th                 0.100000000131883E-11
   u                  0.999999999854155E-12
   electr             0.103370774446833E-03
   h2o                h2o                     0.174435898352698E+01
   al+++              al+++                  -0.138327589966763E+02
   am+++              am+++                  -0.145308311774254E+02
   b(oh)3(aq)         b(oh)3(aq)             -0.491386263393704E+01
   ca++               ca++                   -0.350490382233382E+01
   cl-                cl-                    -0.369612063672929E+01
   cs+                cs+                    -0.120000558761336E+02
   cu++               cu++                   -0.132790717879252E+02
   f-                 f-                     -0.394148547301295E+01
   fe++               fe++                   -0.888881411498135E+01
   h+                 h+                     -0.738394246929239E+01
   hco3-              hco3-                  -0.267503530128449E+01
   hpo4--             hpo4--                 -0.613006186896716E+01
   i-                 i-                     -0.120000230937543E+02
   k+                 k+                     -0.389019626762229E+01
   li+                li+                    -0.516054511756228E+01
   mg++               mg++                   -0.410420281902607E+01
   mn++               mn++                   -0.670367598236572E+01
   na+                na+                    -0.270232246214992E+01
   ni++               ni++                   -0.120063306585993E+02
   no3-               no3-                   -0.324846174258542E+02
   np++++             np++++                 -0.361319387966242E+02
   pb++               pb++                   -0.120023581739487E+02
   pu++++             pu++++                 -0.336651221721892E+02
   ra++               ra++                   -0.120000000000000E+02
   seo3--             seo3--                 -0.122103640108786E+02
   sio2(aq)           sio2(aq)               -0.299512354313568E+01
   sn++               sn++                   -0.485760129923613E+02
   so4--              so4--                  -0.373802108391864E+01
   sr++               sr++                   -0.635066503948517E+01
   tco4-              tco4-                  -0.120000000000000E+02
   th++++             th++++                 -0.253326654106689E+02
   uo2++              uo2++                  -0.178343803749574E+02
   o2(g)              o2(g)                  -0.304751407267449E+02
```

Information Only

The EQ6 input file (j13wwsf.6i), groundwater-spent nuclear fuel reaction ("D" format):

```
|-----------------------------------------------------------------------|
EQ6 input file name= j13wwsf.6i
Description= "Reaction of J-13 well water with spent nuclear fuel"
Version number= 3245    Stage number= 01
Created 10/29/90     Creator= T.J. Wolery
Revised 10/29/90     Revisor= T.J. Wolery

  React spent nuclear fuel with J-13 well water. The O2 and CO2
fugacities are fixed at atmospheric values. The spent nuclear
fuel is treated as a special reactant. One "mole" is equivalent
to 100 grams. The spent fuel composition corresponds to average
PWR spent fuel with burnup of 33,000 MWd/MTIHM at 1,000 years
This was computed by Henry Shaw (LLNL, 1/12/89) as a correction to
the data published in Table 2 of Bruton and Shaw (1988).

  Purpose: to test the ability of the code to model reaction in a
very complex system, whose components exhibit a variety of chemical
behaviors. Results may be roughly compared with those reported by
Bruton and Shaw (1988).

                          References

Bruton, C. J., and Shaw, H. F., 1988, Geochemical simulation of
  reaction between spent fuel waste form and J-13 water at 25 C
  and 90 C: In Apted, M. J., and Westerman, R. E., editors,
  Scientific Basis for Nuclear Waste Management XI, Materials
  Research Society Symposium Proceedings, v. 112, Materials
  Research Society, Pittsburgh, Pennsylvania, p. 485-494.


|-----------------------------------------------------------------------|
| calculational mode   |*normal     | economy            | super economy |
|-----------------------------------------------------------------------|
| model type           | titration  |*closed             | open          |
|-----------------------------------------------------------------------|
| temperature model    |*power      | fluid mixing                       |
|-----------------------------------------------------------------------|
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c-----------------------------------------------------------------------|
| tstart(c)| 25.00    |tk1|     0.    |tk2|     0.    |tk3|     0.      |
|-----------------------------------------------------------------------|
| starting value of zi |      0.    |max. value of zi    |  1.0000       |
|-----------------------------------------------------------------------|
| starting time (sec)  |      0.    |max. time (sec)     | 1.00000E+38   |
|-----------------------------------------------------------------------|
| max. steps           |        10  |max. steps w/o print|       100     |
|-----------------------------------------------------------------------|
| linear print interval| 0.10000    |log print interval  | 1.00000E+38   |
|-----------------------------------------------------------------------|
| suppress mineral phases                                                |
|-----------------------------------------------------------------------|
| phases w/ elements|                        |                          n
| phases except     |                        |                          n
|-----------------------------------------------------------------------|
| fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)
|-----------------------------------------------------------------------|
| o2(g)                              | 0.50000        |-0.70000         n
| co2(g)                             | 0.50000        | -3.5000         n
|-----------------------------------------------------------------------|
c                    R A T E     L A W S
c 1 = relative                    rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory     rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate          rate = CHECK DOCUMENTATION

c                    R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                    S U R F A C E    T Y P E
c 0 = fixed surface area     1 = fixed specific surface area
c
c                    N O T E S
c status and jreac are normally not set by the user
|-----------------------------------------------------------------------|
| reactants   (ss) solid solution only     (sp) special reactant only   |
|-----------------------------------------------------------------------|
| REACTANT         |  spent fuel            |status    | 0              |
```

Information Only

```
| moles remaining   | 1.0000                  | destroyed |      0.                  |
| reactant type     | special                 | sk        |      0.                  |
| surface type      | 0                       | fk        |   1.0000                 |
| end-member        |                         | mole fr   |                          | ss,n
| volume            |      0.                 |           |                          | sp
| element           | c          | moles      |  1.312200000000000E-03   | sp,n
| element           | ca         | moles      |  4.280000000000000E-09   | sp,n
| element           | ni         | moles      |  2.094000000000000E-02   | sp,n
| element           | se         | moles      |  2.415000000000000E-05   | sp,n
| element           | tc         | moles      |  7.750000000000000E-04   | sp,n
| element           | sn         | moles      |  3.173600000000000E-03   | sp,n
| element           | i          | moles      |  1.500000000000000E-04   | sp,n
| element           | cs         | moles      |  1.140000000000000E-03   | sp,n
| element           | pb         | moles      |  1.830000000000000E-11   | sp,n
| element           | ra         | moles      |  1.400000000000000E-09   | sp,n
| element           | th         | moles      |  3.710000000000000E-07   | sp,n
| element           | u          | moles      |  4.054300000000000E-01   | sp,n
| element           | np         | moles      |  5.980000000000000E-04   | sp,n
| element           | pu         | moles      |  3.142000000000000E-03   | sp,n
| element           | am         | moles      |  1.402000000000000E-04   | sp,n
| element           | o          | moles      |  8.518600000000000E-01   | sp,n
| DISSOLUTION LAW   |   1                     |
| rate constant rk1 | 1.0000                  | csigma1
| rate constant rk2 |      0.                 | csigma2
| rate constant rk3 |      0.                 | csigma3
| PRECIPITATION LAW |   0                     |
-------------------------------------------------------------------------
options
-------------------------------------------------------------------------
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * don't print
     lists species loaded into memory
 - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
   * don't print
     print
 - LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
   * don't print
     print
 - LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
   * only species > 10**-12 molal
     all species
     don't print
 - LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
   * don't print
     print
 - LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
   * don't print
     print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
     don't print
   * print
 - PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
   * don't print
     print
 - TAB FILES -
   * write
     append to previous tabx file
     don't write
 - WRITE PICKUP FILE -
   * write pickup file at end of run
     don't write pickup file
     write pickup file for each print point
 - PHYSICALLY REMOVED SUBSYSTEM -
   * does nothing
     transfer minerals but leave trivial mass in the system
     transfer minerals
 - CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
   * does nothing
     clear p.r.s. before first reaction progress advance
 - PHASE BOUNDARY SEARCH -
   * step size constrained by predicted phase boundaries
     phase boundaries estimated from Taylor's series and printed
     locations of phase boundaries ignored
 - AUTO BASIS SWITCHING -
   * off
     on
 - SUPPRESS REDOX REACTIONS -
   * does nothing
     suppress all redox reactions
 - LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
   * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
     logarithmic for kcol = 1,kbt
     linear for kcol = 1,kdim
 - AZERO AND HYDRATION NUMBERS -
   * no change
     read in new azero and hydration numbers
```

Information Only

```
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
  * does nothing
    print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
    print summary information
    print detailed information
- PRINT STEP SIZE AND ORDER -
  * don't print
    print scale factor
    print orders and step size scaling factors
- CONTROL STEP SIZE AND ORDER PRINT -
  * does nothing
    print step size and order when delzi .le. dlzmx1
- NEWTON ITERATIONS -
  * don't print
    print summary of newton iterations
    print summary, residual functions and correction terms
    print summary, residual functions, correction terms and matrix
- PRINT SEARCH ITERATIONS -
  * don't print
    print
- PRINT HPSAT ITERATIONS -
  * don't print
    print
- PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
  * don't print
    print computations from RDERIV, and RTAYLR
    print computations from RDERIV, RTAYLR, DERIV and TAYLOR
- PRINT KINETICS DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 diagnostics
    print level 1 and level 2 diagnostics
- PRINT AKMATR -
  * don't print
    print level 1 diagnostics
- KILL ITERATION VARIABLES -
  * does nothing
    allow selection of variables to remove
-----------------------------------------------------------------------
development options  (used for code development)
-----------------------------------------------------------------------
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
-----------------------------------------------------------------------
tolerances                          desired values - defaults info-only
-----------------------------------------------------------------------
number of N-R iterations                              40       itermx
p.r.s. transfer interval                              varies   dlzidp
residual magnitude                                    1.0e-06  tolbt
correction magnitude                                  1.0e-06  toldl
search/find tolerance                                 varies   tolx
supersaturation                                       varies   tolsat
supersaturation set size                              varies   tolsst
max. size Taylor's series term                        1.0e-04  screw1
max. initial value betamx                             n/a      screw2
max. Taylor's series term (kin.)                      1.0e-04  screw3
corrector iteration                                   1.0e-04  screw4
max. size of N-R correction term                      4.0      screw5
step size (economy mode)                              4.0      screw6
log mass of phases                                    varies   zklogu
decrement mass (p.r.s.)                               2.0      zklogl
min. left after p.r.s.                                .98      zkfac
initial step size                                     varies   dlzmx1
upper limit step size                                 varies   dlzmx2
maximum order                                         6        nordlm
num. attempted assemblages                            25       ntrymx
slide -> over phase bound.                            8        npslmx
slide -> over redox insta.                            3        nsslmx
fo2 scan control                                      none     ioscan
-----------------------------------------------------------------------
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= j13wwsf.3i
Description= "J-13 Well water, with traces of spent fuel components"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 11/30/90    Revisor= T.J. Wolery

  Water from well J-13 at the Nevada Test Site, spiked with
trace amounts of spent nuclear fuel components. The composition
is otherwise identical to that in the EQ3NR test case input file
j13ww.3i, which is based on data reported by Harrer et al. (1990).
Water from this well is commonly used to represent the groundwater
at the proposed high-level nuclear waste repository at Yucca
```

Information Only

Mountain, Nevada.

Purpose: to initialize the EQ6 test case input file jl3wwsf.6i, which simulates the interaction of J-13 well water with spent nuclear fuel. This test case also tests the ability of EQ3NR to handle a system containing many components.

References

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990, Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence Livermore National Laboratory, Livermore, California.

temperature (C)	25.000
electrical imbalance	1.033707744468330E-04
number of aqueous master species	34
position of last pure mineral	34
position of last solid solution	34

suppressed species	(suppress,replace,augmentk,augmentg) value
none	

iopg options

- pH SCALE CONVENTION -
  * modified NBS
  internal
  rational
- ACTIVITY COEFFICIENT OPTIONS -
  * use B-dot equation
  Davies' equation
  Pitzer's equations

elements, moles and moles aqueous

o	5.551836199964260E+01	0.000000000000000E+00
al	2.964990139030870E-07	0.000000000000000E+00
am	1.000000000741170E-12	0.000000000000000E+00
b	1.238820293748600E-05	0.000000000000000E+00
ca	3.243674834132270E-04	0.000000000000000E+00
cl	2.013950982576970E-04	0.000000000000000E+00
cs	1.000000000000020E-12	0.000000000000000E+00
cu	1.000000000338420E-12	0.000000000000000E+00
f	1.147465049689470E-04	0.000000000000000E+00
fe	7.162425915596031E-07	0.000000000000000E+00
h	1.110190413644910E+02	0.000000000000000E+00
c	2.300992803033000E-03	0.000000000000000E+00
p	1.250271413312460E-06	0.000000000000000E+00
i	1.000000000000010E-12	0.000000000000000E+00
k	1.289058603571530E-04	0.000000000000000E+00
li	6.915430053308630E-06	0.000000000000000E+00
mg	8.269903312295860E-05	0.000000000000000E+00
mn	2.184564775625910E-07	0.000000000000000E+00
na	1.992190439488510E-03	0.000000000000000E+00
ni	1.000000000010870E-12	0.000000000000000E+00
n	1.416016208194030E-04	0.000000000000000E+00
np	1.000000001160540E-12	0.000000000000000E+00
pb	1.000000000002210E-12	0.000000000000000E+00
pu	1.000000001119230E-12	0.000000000000000E+00
ra	1.000000000000000E-12	0.000000000000000E+00
se	1.000000000139400E-12	0.000000000000000E+00
si	1.014740955623610E-03	0.000000000000000E+00
sn	1.000000000294500E-12	0.000000000000000E+00
s	1.915397715736460E-04	0.000000000000000E+00
sr	4.565167769991340E-07	0.000000000000000E+00
tc	1.000000000000000E-12	0.000000000000000E+00
th	1.000000001318830E-12	0.000000000000000E+00
u	9.999999998541551E-13	0.000000000000000E+00

master species and logarithmic basis variables

h2o	h2o	1.744358983526980E+00
al+++	al+++	-1.383275899667630E+01
am+++	am+++	-1.453083117742540E+01
b(oh)3(aq)	b(oh)3(aq)	-4.913862633937040E+00
ca++	ca++	-3.504903822333820E+00
cl-	cl-	-3.696120636729290E+00
cs+	cs+	-1.200005587613360E+01
cu++	cu++	-1.327907178792520E+01
f-	f-	-3.941485473012950E+00
fe++	fe++	-8.888814114981351E+00
h+	h+	-7.383942469292390E+00
hco3-	hco3-	-2.675035301284490E+00
hpo4--	hpo4--	-6.130061868967160E+00
i-	i-	-1.200002309375430E+01
k+	k+	-3.890196267622290E+00

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li+	li+	-5.160545117562280E+00
mg++	mg++	-4.104202819026070E+00
mn++	mn++	-6.703675982365720E+00
na+	na+	-2.702322462149920E+00
ni++	ni++	-1.200633065859930E+01
no3-	no3-	-3.248461742585420E+01
np++++	np++++	-3.613193879662420E+01
pb++	pb++	-1.200235817394870E+01
pu++++	pu++++	-3.366512217218920E+01
ra++	ra++	-1.200000000000000E+01
seo3--	seo3--	-1.221036401087860E+01
sio2(aq)	sio2(aq)	-2.995123543135680E+00
sn++	sn++	-4.857601299236130E+01
so4--	so4--	-3.738021083918640E+00
sr++	sr++	-6.350665039485170E+00
tco4-	tco4-	-1.200000000000000E+01
th++++	th++++	-2.533266541066890E+01
uo2++	uo2++	-1.783448037495740E+01
o2(g)	o2(g)	-3.047514072674490E+01

physically removed subsystem (solid solution, mineral, moles)		
none		

The EQ6 **input** file (**pquartzA.6i**), precipitation of quartz ("W" format):

```
EQ6 input file name= pquartzA.6i
Description= "Precipitate quartz using Knauss and Wolery rate law"
Version number= 3245   Stage number= 01
Created 10/31/90    Creator= T.J. Wolery
Revised 10/31/90    Revisor= T.J. Wolery

  Precipitate quartz from supersaturated solution at 105 C, using
the rate law of Knauss and Wolery (1988). This is adapted from test
problem 1 of Delany, Puigdomenech, and Wolery (1986, p. 19-21, 31-33),
which simulates an experiment (Run 2E) reported by Rimstidt and Barnes
(1980, p. 1687-1688, Figure 2). Another EQ6 test case input file,
pquartz.6i, runs the same problem, but uses the Rimstidt and Barnes
rate model.

  Purpose: to test the kinetics mode of EQ6 in the case of a rate
law that depends on pH, and to illustrate the extrapolation of rate
constants to different temperatures using activation energies.
Results may be compared with Figure 2 of Rimstidt and Barnes (1980)
and Figure 1 of Delany, Puigdomenech, and Wolery (1986). They do not
match. See the warning below.

  The precipitation rate law is expressed in terms of a reversal of
the net rate form for dissolution, as the precipitation rate law code
"nprk" is set to -1. Thus, the specified rate constant is k(+)
(the dissolution rate constant) instead of k(-) (the precipitation
rate constant). Note that this is a two-term rate law, requiring
two rate constants. The second term depends on pH. The rate constants
pertain to 70 C and are extrapolated to 105 C using the activation
energy formalism. In addition to activation energies, activation
enthalpies are entered on the "W" format version of this input
file. They are not used, as the "iact" flags are set to 0 (use
activation energy) instead of 1 (use activation enthalpy). The data
are taken from Table 5 of Knauss and Wolery (1988).

  Warning- the second term of the two-term rate model improperly
extrapolates to the case of precipitation. It accelerates the
precipitation rate at low to moderate pH. The computed results are
not in accord with the modeled experiment. A much better match
can be obtained by simply by dropping the second term.

  The option switch ioptl1 is set to 1 to indicate that this problem
has no redox aspect.

  Note that the silica polymorphs tridymite, chalcedony, sio2(am),
and cristobalite have been suppressed by means of "nxmod" options.
These were set on the EQ3NR test case input file sio2.3i, which was
used to initialize this EQ6 test case.

                          References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986,
  Precipitation Kinetics Option for the EQ6 Geochemical Reaction
  Path Code: UCRL-53642, Lawrence Livermore National Laboratory,
  Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of
  quartz as a function of pH and time at 70 C: Geochimica et
  Cosmochimica Acta, v. 52, p. 43-53.

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water
```

Information Only

```
  reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

endit.
    nmodl1=  2                 nmodl2=  0
    tempc0=  105.000E+00        jtemp=  0
       tk1=  0.00000E+00          tk2=  0.00000E+00        tk3=  0.00000E+00
    zistrt=  0.00000E+00        zimax=  1.00000E+00
     tstrt=  0.00000E+00       timemx=  6.92000E+05
    kstpmx=          500.        cplim=  0.00000E+00
    dzprnt=  1.00000E-04       dzprlg=  10.0000E+00     ksppmx=    10
    dzplot=  1.00000E+38       dzpllg=  1.00000E+38     ksplmx= 10000
     ifile= 60
*              1    2    3    4    5    6    7    8    9   10
  ioptl-10=    1    0    0    0    0    0    0    0    0    0
     11-20=    1    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     11-20=    0    0    0    0    0    0    0    0    0    0
* nxopt = number of mineral subset-selection suppression options
* nxopex = number of exceptions
    nxopt=  0
* nffg = number of gas species with fixed fugacities
    nffg =  0
* nrct = number of reactants
     nrct=  1
*-----------------------------------------------------------------------------
  reactant= quartz
    jcode=  0                  jreac=  0
     morr=  4.72000E+02         modr=  0.00000E+00
      nsk=  0                     sk=  2.61280E+06        fk=  1.00000E+00
      nrk=  2                    nrpk= -1
    imech=  2
      rk0=  5.01000E-16          trk0=  70.0000E+00      iact=  1
     eact=  21.8000E+00          hact=  21.2000E+00
    ndact=  0                  csigma=  1.00000E+00
      rk0=  1.58000E-18          trk0=  70.0000E+00      iact=  1
     eact=  25.9000E+00          hact=  25.3000E+00
    ndact=  1                  csigma=  1.00000E+00
     udac= h+                    cdac= -0.50000E+00
*-----------------------------------------------------------------------------
    dlzidp=  0.00000E+00
     tolbt=  0.00000E+00        toldl=  0.00000E+00      tolx=  0.00000E+00
    tolsat=  0.00000E+00       tolsst=  0.00000E+00
    screw1=  0.00000E+00       screw2=  0.00000E+00    screw3=  0.00000E+00
    screw4=  0.00000E+00       screw5=  0.00000E+00    screw6=  0.00000E+00
    zklogu=          0.000      zklogl=          0.000    zkfac=          0.000
    dlzmx1=  0.00000E+00       dlzmx2=  0.00000E+00    nordlm=  0
    itermx=  0                 ntrymx=  0
    nps1mx=  0                 nss1mx=  0              ioscan=  0
*-----------------------------------------------------------------------------
* pickup file written by eq3nr.3245R124x
*  supported by eqlib.3245R153
EQ3NR input file name= sio2.3i
Description= "Solution containing 101.0 mg/L SiO2"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery
```

Solution containing 101.0 mg/L of dissolved SiO2. This test case is otherwise nearly identical to that in the EQ3NR test case input file deionw.3i.

Purpose: to initialize the EQ6 test case input files pquartz.6i and pquartzA.6i, both of which simulate the precipitation of quartz from supersaturated solution at 105 C. The former EQ6 test case is test problem 1 from Delany, Puigdomenech, and Wolery (1986, p. 19-21, 31-33), which simulates an experiment (Run 2E) reported by Rimstidt and Barnes (1980, p. 1687-1688, Figure 2) and uses their rate law model, which is independent of pH. The latter is the same problem, but uses a rate law model from Knauss and Wolery (1988) that does include a dependence on pH.

Note that the dissolved gases O2 and H2 have been suppressed. This is because this problem has no redox aspect. The EQ6 option switch ioptl1 should be set to 1 in the EQ6 test case input files so that EQ6 knows this.

Note also that the silica polymorphs tridymite, chalcedony, sio2(am), and cristobalite have been suppressed by means of "nxmod" options.

References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986, Precipitation Kinetics Option for the EQ6 Geochemical Reaction Path Code: UCRL-53642, Lawrence Livermore National Laboratory, Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of quartz as a function of pH and time at 70 C: Geochimica et Cosmochimica Acta, v. 52, p. 43-53.

Information Only

```
Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water
  reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

endit.
    tempci=  0.25000E+02
     nxmod=  4
   species= tridymite
      type=  1                 option= -1                 xlkmod=  0.00000E+00
   species= chalcedony
      type=  1                 option= -1                 xlkmod=  0.00000E+00
   species= sio2(am)
      type=  1                 option= -1                 xlkmod=  0.00000E+00
   species= cristobalite
      type=  1                 option= -1                 xlkmod=  0.00000E+00
     iopg1=  0                  iopg2=  0                  iopg3=  0
     iopg4=  0                  iopg5=  0                  iopg6=  0
     iopg7=  0                  iopg8=  0                  iopg9=  0
    iopg10=  0
       kct=  4                    ksq=  5                    kmt=  5
       kxt=  5                   kdim=  5                   kprs=  0
   o                   0.555118250703269E+02
   h                   0.111016874628103E+03
   c                   0.129065694976057E-04
   si                  0.168097156827988E-02
   electr              0.196977511883988E-16
   h2o                 h2o                      0.174435898352698E+01
   h+                  h+                      -0.564737292052235E+01
   hco3-               hco3-                   -0.566471043900596E+01
   sio2(aq)            sio2(aq)                -0.277446121770296E+01
   o2(g)               o2(g)                    0.000000000000000E+00
```

The EQ6 input file (pquartzA.6i), precipitation of quartz ("D" format):

```
-----------------------------------------------------------------------
EQ6 input file name= pquartzA.6i
Description= "Precipitate quartz using Knauss and Wolery rate law"
Version number= 3245    Stage number= 01
Created 10/31/90     Creator= T.J. Wolery
Revised 10/31/90     Revisor= T.J. Wolery

  Precipitate quartz from supersaturated solution at 105 C, using
the rate law of Knauss and Wolery (1988). This is adapted from test
problem 1 of Delany, Puigdomenech, and Wolery (1986, p. 19-21, 31-33),
which simulates an experiment (Run 2E) reported by Rimstidt and Barnes
(1980, p. 1687-1688, Figure 2). Another EQ6 test case input file,
pquartz.6i, runs the same problem, but uses the Rimstidt and Barnes
rate model.

  Purpose: to test the kinetics mode of EQ6 in the case of a rate
law that depends on pH, and to illustrate the extrapolation of rate
constants to different temperatures using activation energies.
Results may be compared with Figure 2 of Rimstidt and Barnes (1980)
and Figure 1 of Delany, Puigdomenech, and Wolery (1986). They do not
match. See the warning below.

  The precipitation rate law is expressed in terms of a reversal of
the net rate form for dissolution, as the precipitation rate law code
"nprk" is set to -1. Thus, the specified rate constant is k(+)
(the dissolution rate constant) instead of k(-) (the precipitation
rate constant). Note that this is a two-term rate law, requiring
two rate constants. The second term depends on pH. The rate constants
pertain to 70 C and are extrapolated to 105 C using the activation
energy formalism. In addition to activation energies, activation
enthalpies are entered on the "W" format version of this input
file. They are not used, as the "iact" flags are set to 0 (use
activation energy) instead of 1 (use activation enthalpy). The data
are taken from Table 5 of Knauss and Wolery (1988).

  Warning- the second term of the two-term rate model improperly
extrapolates to the case of precipitation. It accelerates the
precipitation rate at low to moderate pH. The computed results are
not in accord with the modeled experiment. A much better match
can be obtained by simply by dropping the second term.

  The option switch ioptl1 is set to 1 to indicate that this problem
has no redox aspect.

  Note that the silica polymorphs tridymite, chalcedony, sio2(am),
and cristobalite have been suppressed by means of "nxmod" options.
These were set on the EQ3NR test case input file sio2.3i, which was
used to initialize this EQ6 test case.

                              References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986,
  Precipitation Kinetics Option for the EQ6 Geochemical Reaction
  Path Code: UCRL-53642, Lawrence Livermore National Laboratory,
```

Information Only

Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of quartz as a function of pH and time at 70 C: Geochimica et Cosmochimica Acta, v. 52, p. 43-53.

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

calculational mode	*normal	economy	super economy
model type	titration	*closed	open
temperature model	*power	fluid mixing	

```
c power model  -->   temp = tstart + tk1*zi + tk2*zi**2 + tk3*zi**3
c mixing model -->   temp = (tstart * tk1 + zi*tk2) / (zi + tk1)
c
```

tstart(c)	105.0	tk1	0.	tk2	0.	tk3	0.
starting value of zi	0.	max. value of zi	1.0000				
starting time (sec)	0.	max. time (sec)	6.92000E+05				
max. steps	500	max. steps w/o print	10				
linear print interval	1.00000E-04	log print interval	10.000				
suppress mineral phases							
phases w/ elements							n
phases except							n
fixed fugacity phases- species, moles(per kg h2o), log fugacity(bars)							
none							n

```
c                    R A T E     L A W S
c 1 = relative                    rate = rk1 + rk2*zi + (1/2)rk3*zi*zi
c 2 = transition state theory     rate = CHECK DOCUMENTATIONc 3 = specified rate
c 4 = activity term rate          rate = CHECK DOCUMENTATION

c                    R E A C T A N T     T Y P E S
c mineral     solid solution     special    aqueous    gas
c
c                    S U R F A C E     T Y P E
c 0 = fixed surface area      1 = fixed specific surface area
c
c                    N O T E S
c status and jreac are normally not set by the user
```

reactants (ss) solid solution only (sp) special reactant only

REACTANT	quartz	status	0	
moles remaining	472.00	destroyed	0.	
reactant type	mineral	sk	2.61280E+06	
surface type	0	fk	1.0000	
end-member		mole fr		ss,n
volume				sp
element		moles		sp,n
DISSOLUTION LAW	2			
rate constant rk1	5.01000E-16	csigma1	1.00000	
temperature (c)	70.000			234
act. energy-kcal	21.800	enthalpy		234
rate constant rk2	1.58000E-18	csigma2	1.00000	
aqueous species	h+	cdac	-0.50000	n
temperature (c)	70.000			234
act. energy-kcal	25.900	enthalpy		234
PRECIPITATION LAW	-1			

options

```
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * don't print
     lists species loaded into memory
 - LIST DERIVATIVES OF BASIS ELEMENTS AT EACH PRINT POINT -
   * don't print
     print
 - LIST ALL SPECIES LOADED INTO MEMORY AND THEIR LOG K VALUES -
   * don't print
     print
 - LIST DISTRIBUTION OF AQUEOUS SPECIES AT EACH PRINT POINT -
   * only species > 10**-12 molal
     all species
     don't print
 - LIST CATION/H+ ACTIVITY RATIOS AT EACH PRINT POINT -
   * don't print
     print
 - LIST BULK ELEMENT AND OXIDE COMPOSITION AT EACH PRINT POINT -
```

Information Only

```
  * don't print
    print
- MINERAL SATURATION STATES -
  * print if affinity > -10 kcals
    print all
    don't print
- LIST GAS SPECIES SUMMARY AT EACH PRINT POINT -
  * don't print
    print
- PRINT AQUEOUS MASS AND CONCENTRATION TOTALS -
  * don't print
    print
- TAB FILES -
  * write
    append to previous tabx file
    don't write
- WRITE PICKUP FILE -
  * write pickup file at end of run
    don't write pickup file
    write pickup file for each print point
- PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    transfer minerals but leave trivial mass in the system
    transfer minerals
- CLEAR INITIAL PHYSICALLY REMOVED SUBSYSTEM -
  * does nothing
    clear p.r.s. before first reaction progress advance
- PHASE BOUNDARY SEARCH -
  * step size constrained by predicted phase boundaries
    phase boundaries estimated from Taylor's series and printed
    locations of phase boundaries ignored
- AUTO BASIS SWITCHING -
  * off
    on
- SUPPRESS REDOX REACTIONS -
    does nothing
  * suppress all redox reactions
- LINEAR OR LOGARITHMIC TAYLOR'S SERIES -
  * linear for kcol = 1,kdim, logarithmic for kcol = 1,kbt
    logarithmic for kcol = 1,kbt
    linear for kcol = 1,kdim
- AZERO AND HYDRATION NUMBERS -
  * no change
    read in new azero and hydration numbers
- PRINT MEAN MOLAL ACTIVITY COEFFICIENTS FOR DISSOLVED SPECIES -
  * does nothing
    print
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PRINT DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 messages
    print level 2 messages
- PRINT PRE-NEWTON-RAPHSON OPTIMIZATION -
  * don't print
    print summary information
    print detailed information
- PRINT STEP SIZE AND ORDER -
  * don't print
    print scale factor
    print orders and step size scaling factors
- CONTROL STEP SIZE AND ORDER PRINT -
  * does nothing
    print step size and order when delzi .le. dlzmx1
- NEWTON ITERATIONS -
  * don't print
    print summary of newton iterations
    print summary, residual functions and correction terms
    print summary, residual functions, correction terms and matrix
- PRINT SEARCH ITERATIONS -
  * don't print
    print
- PRINT HPSAT ITERATIONS -
  * don't print
    print
- PRINT FINITE DIFFERENCE AND DERIVATIVE DATA -
  * don't print
    print computations from RDERIV, and RTAYLR
    print computations from RDERIV, RTAYLR, DERIV and TAYLOR
- PRINT KINETICS DIAGNOSTIC MESSAGES -
  * don't print
    print level 1 diagnostics
    print level 1 and level 2 diagnostics
- PRINT AKMATR -
  * don't print
    print level 1 diagnostics
- KILL ITERATION VARIABLES -
  * does nothing
    allow selection of variables to remove
-----------------------------------------------------------------------
development options  (used for code development)
```

Information Only

```
    0 check finite difference and Taylor series expression
    0 check reaction rate finite difference and Taylor series
```

tolerances	desired values	defaults	info-only
number of N-R iterations		40	itermx
p.r.s. transfer interval		varies	dlzidp
residual magnitude		1.0e-06	tolbt
correction magnitude		1.0e-06	toldl
search/find tolerance		varies	tolx
supersaturation		varies	tolsat
supersaturation set size		varies	tolsst
max. size Taylor's series term		1.0e-04	screw1
max. initial value betamx		n/a	screw2
max. Taylor's series term (kin.)		1.0e-04	screw3
corrector iteration		1.0e-04	screw4
max. size of N-R correction term		4.0	screw5
step size (economy mode)		4.0	screw6
log mass of phases		varies	zklogu
decrement mass (p.r.s.)		2.0	zklogl
min. left after p.r.s.		.98	zkfac
initial step size		varies	dlzmx1
upper limit step size		varies	dlzmx2
maximum order		6	nordlm
num. attempted assemblages		25	ntrymx
slide -> over phase bound.		8	npslmx
slide -> over redox insta.		3	nsslmx
fo2 scan control		none	ioscan

```
c pickup file written by eq3nr.3245R124
c supported by eqlib.3245R153
EQ3NR input file name= sio2.3i
Description= "Solution containing 101.0 mg/L SiO2"
version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery
```

Solution containing 101.0 mg/L of dissolved SiO2. This test case is otherwise nearly identical to that in the EQ3NR test case input file deionw.3i.

Purpose: to initialize the EQ6 test case input files pquartz.6i and pquartzA.6i, both of which simulate the precipitation of quartz from supersaturated solution at 105 C. The former EQ6 test case is test problem 1 from Delany, Puigdomenech, and Wolery (1986, p. 19-21, 31-33), which simulates an experiment (Run 2E) reported by Rimstidt and Barnes (1980, p. 1687-1688, Figure 2) and uses their rate law model, which is independent of pH. The latter is the same problem, but uses a rate law model from Knauss and Wolery (1988) that does include a dependence on pH.

Note that the dissolved gases O2 and H2 have been suppressed. This is because this problem has no redox aspect. The EQ6 option switch iopt11 should be set to 1 in the EQ6 test case input files so that EQ6 knows this.

Note also that the silica polymorphs tridymite, chalcedony, sio2(am), and cristobalite have been suppressed by means of "nxmod" options.

References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986, Precipitation Kinetics Option for the EQ6 Geochemical Reaction Path Code: UCRL-53642, Lawrence Livermore National Laboratory, Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of quartz as a function of pH and time at 70 C: Geochimica et Cosmochimica Acta, v. 52, p. 43-53.

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

temperature (C)	25.000
electrical imbalance	1.969775118839880E-17
number of aqueous master species	5
position of last pure mineral	5
position of last solid solution	5

suppressed species	(suppress,replace,augmentk,augmentg)		value
tridymite	mineral	suppress	0.
chalcedony	mineral	suppress	0.
sio2(am)	mineral	suppress	0.
cristobalite	mineral	suppress	0.

Information Only

```
iopg options
-----------------------------------------------------------------------
 - pH SCALE CONVENTION -
    * modified NBS
      internal
      rational
 - ACTIVITY COEFFICIENT OPTIONS -
    * use B-dot equation
      Davies' equation
      Pitzer's equations
-----------------------------------------------------------------------
 elements, moles and moles aqueous
-----------------------------------------------------------------------
          o        |    5.551182507032690E+01|    0.000000000000000E+00|
          h        |    1.110168746281030E+02|    0.000000000000000E+00|
          c        |    1.290656949760570E-05|    0.000000000000000E+00|
          si       |    1.680971568279880E-03|    0.000000000000000E+00|
-----------------------------------------------------------------------
 master species and logarithmic basis variables
-----------------------------------------------------------------------
h2o                |h2o                      |    1.744358983526980E+00|
h+                 |h+                       |   -5.647372920522350E+00|
hco3-              |hco3-                    |   -5.664710439005960E+00|
sio2(aq)           |sio2(aq)                 |   -2.774461217702960E+00|
o2(g)              |o2(g)                    |    0.000000000000000E+00|
-----------------------------------------------------------------------
 physically removed subsystem  (solid solution, mineral, moles)
-----------------------------------------------------------------------
 none              |                         |
-----------------------------------------------------------------------
```

Information Only

Appendix F. EQ3NR Input Files Used to Initialize EQ6 Sample Problems

This appendix presents the EQ3NR **input** files used to initialize the EQ6 sample problems presented in Chapter 6 and in Appendix E. The **input** files are here given in both "W" and "D" format.

The following is the EQ3NR **input** file for the sea water used in the first example EQ6 calculation (precipitate supersaturated minerals) in Chapter 6.

The EQ3NR **input** file (**swpar.3i**), the sea water partial benchmark test case ("W" format):

```
EQ3NR input file name= swpar.3i
Description= "Sea water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  Sea water, including all solute components present above 1 mg/kg,
plus phosphate, iodide, iron, and aluminum. This is a moderately
pared-down version of swtst.3i, which contains the full benchmark
sea water test case of Nordstrom et al. (1979, Table III). An even
more pared-down version of that benchmark sea water test case is
in swmaj.3i.

  Purpose: to test the code on an intermediate-sized problem
involving a moderately concentrated solution and to initialize the
EQ6 test case input files swtitr.6i and pptminssw.6i. The first of
these two test cases simulates an alkalinity titration. The second
is calculation of the precipitation of an equilibrium mineral
assemblage so as to eliminate any remaining supersaturations. The
activity coefficients of the aqueous species are calculated from
the B-dot equation and related equations.

  The original test problem permits specification of the total
alkalinity instead of total HCO3-. This was expressed in the
following equivalent units:

    141.682 mg/L HCO3- (total alkalinity expressed as HCO3-;
                        not the conventional HCO3 alkalinity)
    0.00240659 eq/kg
    0.00237625 eq/L

This is equivalent to:

    116.208 mg/L CaCO3 (total alkalinity)

This is the more standard way of reporting alkalinity (see Standard
Methods, 1976).

                          References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical
  models for equilibrium calculations in aqueous systems, in Jenne,
  E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium
  Series, v. 93, American Chemical Society, Washington, D.C.,
  p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976,
  Prepared and jointly published by the American Public Health
  Association, the American Water Works Association, and the Water
  Pollution Control Federation: American Public Health Association,
  1015 Eighteenth Street NW, Washington, D.C.

endit.
     tempc=          25.
       rho=      1.02336    tdspkg=          0.     tdspl=          0.
       fep=        0.500    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=  0
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=   -1    0    0    0    0    0    0    0    0    0
  iopg1-10=    0    0    0    0    0    0    0    0    0    0
  icpr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     uebal= none
     nxmod=  0
*
data file master species= ca++
   switch with species=
   jflag=  3   csp= 412.3
```

Information Only

```
data file master species= mg++
   switch with species=
   jflag=  3   csp= 1291.8
data file master species= na+
   switch with species=
   jflag=  3   csp= 10768.
data file master species= k+
   switch with species=
   jflag=  3   csp= 399.1
data file master species= cl-
   switch with species=
   jflag=  3   csp= 19353.
data file master species= so4--
   switch with species=
   jflag=  3   csp= 2712.
data file master species= hco3-
   switch with species=
   jflag=  0   csp= .002022
data file master species= br-
   switch with species=
   jflag=  3   csp= 67.3
data file master species= sr++
   switch with species=
   jflag=  3   csp= 8.14
data file master species= b(oh)3(aq)
   switch with species=
   jflag=  0   csp= 0.00042665
data file master species= sio2(aq)
   switch with species=
   jflag=  3   csp= 4.28
data file master species= f-
   switch with species=
   jflag=  3   csp= 1.39
data file master species= hpo4--
   switch with species=
   jflag=  0   csp= 0.000000655
data file master species= i-
   switch with species=
   jflag=  3   csp= 0.062
data file master species= fe++
   switch with species=
   jflag=  3   csp= 0.002
data file master species= al+++
   switch with species=
   jflag=  3   csp= 0.002
data file master species= h+
   switch with species=
   jflag= 16   csp= -8.22
data file master species= o2(aq)
   switch with species=
   jflag=  2   csp= 6.6
endit.
```

The EQ3NR **input** file (**swpar.3i**), the sea water partial benchmark test case ("D" format):

```
-----------------------------------------------------------------------
EQ3NR input file name= swpar.3i
Description= "Sea water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  Sea water, including all solute components present above 1 mg/kg,
plus phosphate, iodide, iron, and aluminum. This is a moderately
pared-down version of swtst.3i, which contains the full benchmark
sea water test case of Nordstrom et al. (1979, Table III). An even
more pared-down version of that benchmark sea water test case is
in swmaj.3i.

  Purpose: to test the code on an intermediate-sized problem
involving a moderately concentrated solution and to initialize the
EQ6 test case input files swtitr.6i and pptminssw.6i. The first of
these two test cases simulates an alkalinity titration. The second
is calculation of the precipitation of an equilibrium mineral
assemblage so as to eliminate any remaining supersaturations. The
activity coefficients of the aqueous species are calculated from
the B-dot equation and related equations.

  The original test problem permits specification of the total
alkalinity instead of total HCO3-. This was expressed in the
following equivalent units:

    141.682 mg/L HCO3- (total alkalinity expressed as HCO3-;
                        not the conventional HCO3 alkalinity)
    0.00240659 eq/kg
    0.00237625 eq/L
```

Information Only

This is equivalent to:

116.208 mg/L CaCO3 (total alkalinity)

This is the more standard way of reporting alkalinity (see Standard Methods, 1976).

References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical models for equilibrium calculations in aqueous systems, in Jenne, E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium Series, v. 93, American Chemical Society, Washington, D.C., p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.

Temperature (C)	25.00	Density(gm/cm3)	1.02336
Total Dissolved Salts		mg/kg | mg/l	*not used
Electrical Balancing on		code selects	*not performed

SPECIES	BASIS SWITCH/CONSTRAINT	CONCENTRATION	UNITS OR TYPE
redox		0.5000	eh
ca++		412.30	mg/kg
mg++		1291.8	mg/kg
na+		10768.	mg/kg
k+		399.10	mg/kg
cl-		19353.	mg/kg
so4--		2712.0	mg/kg
hco3-		0.20220E-02	molality
br-		67.300	mg/kg
sr++		8.1400	mg/kg
b(oh)3(aq)		0.42665E-03	molality
sio2(aq)		4.2800	mg/kg
f-		1.3900	mg/kg
hpo4--		0.65500E-06	molality
i-		0.62000E-01	mg/kg
fe++		0.20000E-02	mg/kg
al+++		0.20000E-02	mg/kg
h+		8.2200	ph
o2(aq)		6.6000	mg/l

Input Solid Solutions

none

SUPPRESSED SPECIES	(suppress,replace,augmentk,augmentg)	value
none		

OPTIONS

```
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * does nothing
     lists species loaded into memory
 - ECHO DATABASE INFORMATION -
   * does nothing
     lists all reactions
     lists reactions and log K values
     lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
   * in order of decreasing concentration
     in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
   * all species
     only species > 10**-20 molal
     only species > 10**-12 molal
     not printed
 - LIST OF AQUEOUS SPECIES (by element) -
   * print major species
     print all species
     don't print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - pH SCALE CONVENTION -
   * modified NBS
     internal
     rational
 - ACTIVITY COEFFICIENT OPTIONS -
```

Information Only

```
    * use B-dot equation
      Davies' equation
      Pitzer's equations
  - AUTO BASIS SWITCHING -
    * off
      on
  - PITZER DATABASE INFORMATION -
    * print only warnings
      print species in model and number of Pitzer coefficients
      print species in model and names of Pitzer coefficients
  - PICKUP FILE -
    * write pickup file
      don't write pickup file
  - LIST MEAN IONIC PROPERTIES -
    * don't print
      print
  - LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
    * print
      don't print
  - CONVERGENCE CRITERIA -
    * test both residual functions and correction terms
      test only residual functions
-----------------------------------------------------------------
DEBUGGING SWITCHES (0-off, 1,2-on, default is off)
-----------------------------------------------------------------
0  generic debugging information                                2
0  print details of pre-Newton-Raphson iteration                2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                      2
0  print details of stoichiometric factors calculation
0  write reactions on RLIST
0  list stoichiometric concentrations of master species
0  request iteration variables to be killed
-----------------------------------------------------------------
DEVELOPMENT OPTIONS  (used for code development)
-----------------------------------------------------------------
 none
-----------------------------------------------------------------
TOLERANCES                  (desired values)        (defaults)
-----------------------------------------------------------------
      residual functions  |                        |1.e-10
        correction terms  |                        |1.e-10
        saturation state  |                        |0.5
number of N-R iterations  |                        |30
-----------------------------------------------------------------
```

The following is the EQ3NR **input** file for the quenched fluid used in the second example EQ6 calculation (heat quenched fluid) in Chapter 6.

<u>The EQ3NR **input** file (**quenchfl.3i**), the quenched fluid example ("W" format):</u>

```
EQ3NR input file name= quenchfl.3i
Description= "Quenched fluid from a hydrothermal experiment"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Quenched fluid from a hydrothermal experiment involving the
reaction of water with vitric tuff. This fluid is for day 16
of the 150 C experiment reported by Knauss and Peifer (1986,
Appendix B2, p. 31).

  Purpose: to test the ability of the code to compute the high
temperature, in situ pH of a fluid from the measured quench pH.
This test case produces a model of the quenched solution, which
is used to initialize the EQ6 test case input file heatqf.6i,
which takes the fluid up to the in situ temperature and gives
the in situ pH.

  Data for the following was originally specified as:

    SiO2(aq) :   Si          = 156 mg/L

                             References

Knauss, K. G., and Peifer, D. W., 1986, Reaction of Vitric Topopah
  Spring Tuff and J-13 Ground Water under Hydrothermal Conditions
  Using Dickson-Type, Gold-Bag Rocking Autoclaves: UCRL-53795,
  Lawrence Livermore National Laboratory, Livermore, California,
  39 p.

endit.
     tempc=          25.
       rho=          1.0    tdspkg=          0.     tdspl=          0.
```

Information Only

```
      fep=        -0.700     uredox=
     tolbt=           0.      toldl=            0.     tolsat=            0.
    itermx=  0
*                1    2    3    4    5    6    7    8    9   10
  iopt1-10=      0    0    0    0    0    0    0    0    0    0
  iopg1-10=      0    0    0    0    0    0    0    0    0    0
  iopr1-10=      0    0    0    0    0    0    0    0    0    0
 iopr11-20=      0    0    0    0    0    0    0    0    0    0
  iodb1-10=      0    0    0    0    0    0    0    0    0    0
     uebal= none
     nxmod=  0
*
data file master species= al+++
   switch with species=
   jflag=  2   csp= 1.40
data file master species= sio2(aq)
   switch with species=
   jflag=  2   csp= 333.7
data file master species= ca++
   switch with species=
   jflag=  2   csp= 5.4
data file master species= k+
   switch with species=
   jflag=  2   csp= 16.0
data file master species= mg++
   switch with species=
   jflag=  2   csp= 0.15
data file master species= na+
   switch with species=
   jflag=  2   csp= 58.44
data file master species= f-
   switch with species=
   jflag=  2   csp= 2.3
data file master species= cl-
   switch with species=
   jflag=  2   csp= 7.5
data file master species= no3-
   switch with species=
   jflag=  2   csp= 6.6
data file master species= so4--
   switch with species=
   jflag=  2   csp= 22.9
data file master species= hco3-
   switch with species=
   jflag=  2   csp= 142.2
data file master species= h+
   switch with species=
   jflag= 16   csp= -6.17
endit.
```

The EQ3NR **input** file (**quenchfl.3i**), the quenched fluid example ("D" format):

```
-----------------------------------------------------------------------
EQ3NR input file name= quenchfl.3i
Description= "Quenched fluid from a hydrothermal experiment"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Quenched fluid from a hydrothermal experiment involving the
reaction of water with vitric tuff. This fluid is for day 16
of the 150 C experiment reported by Knauss and Peifer (1986,
Appendix B2, p. 31).

  Purpose: to test the ability of the code to compute the high
temperature, in situ pH of a fluid from the measured quench pH.
This test case produces a model of the quenched solution, which
is used to initialize the EQ6 test case input file heatqf.6i,
which takes the fluid up to the in situ temperature and gives
the in situ pH.

  Data for the following was originally specified as:

    SiO2(aq) :   Si          = 156 mg/L

                           References

Knauss, K. G., and Peifer, D. W., 1986, Reaction of Vitric Topopah
  Spring Tuff and J-13 Ground Water under Hydrothermal Conditions
  Using Dickson-Type, Gold-Bag Rocking Autoclaves: UCRL-53795,
  Lawrence Livermore National Laboratory, Livermore, California,
  39 p.

-----------------------------------------------------------------------
Temperature (C)          | 25.00        |Density(gm/cm3)|  1.00000
-----------------------------------------------------------------------
Total Dissolved Salts    |              | mg/kg | mg/l  |*not used
```

Information Only

```
-----------------------------------------------------------------------
Electrical Balancing on |                | code selects  |*not performed
-----------------------------------------------------------------------
SPECIES    | BASIS SWITCH/CONSTRAINT | CONCENTRATION| UNITS OR TYPE
-----------------------------------------------------------------------
redox      |                         | -.7000       |logfo2
al+++      |                         | 1.4000       |mg/l
sio2(aq)   |                         | 333.70       |mg/l
ca++       |                         | 5.4000       |mg/l
k+         |                         | 16.000       |mg/l
mg++       |                         |0.15000       |mg/l
na+        |                         | 58.440       |mg/l
f-         |                         | 2.3000       |mg/l
cl-        |                         | 7.5000       |mg/l
no3-       |                         | 6.6000       |mg/l
so4--      |                         | 22.900       |mg/l
hco3-      |                         | 142.20       |mg/l
h+         |                         | 6.1700       |ph
-----------------------------------------------------------------------
Input Solid Solutions
-----------------------------------------------------------------------
 none      |                         |              |
-----------------------------------------------------------------------
SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value
-----------------------------------------------------------------------
 none                    |              |
-----------------------------------------------------------------------
OPTIONS
-----------------------------------------------------------------------
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * does nothing
     lists species loaded into memory
 - ECHO DATABASE INFORMATION -
   * does nothing
     lists all reactions
     lists reactions and log K values
     lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
   * in order of decreasing concentration
     in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
   * all species
     only species > 10**-20 molal
     only species > 10**-12 molal
     not printed
 - LIST OF AQUEOUS SPECIES (by element) -
   * print major species
     print all species
     don't print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - pH SCALE CONVENTION -
   * modified NBS
     internal
     rational
 - ACTIVITY COEFFICIENT OPTIONS -
   * use B-dot equation
     Davies' equation
     Pitzer's equations
 - AUTO BASIS SWITCHING -
   * off
     on
 - PITZER DATABASE INFORMATION -
   * print only warnings
     print species in model and number of Pitzer coefficients
     print species in model and names of Pitzer coefficients
 - PICKUP FILE -
   * write pickup file
     don't write pickup file
 - LIST MEAN IONIC PROPERTIES -
   * don't print
     print
 - LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
   * print
     don't print
 - CONVERGENCE CRITERIA -
   * test both residual functions and correction terms
     test only residual functions
-----------------------------------------------------------------------
DEBUGGING SWITCHES (o-off, 1,2-on, default is off)
-----------------------------------------------------------------------
0  generic debugging information                                      2
0  print details of pre-Newton-Raphson iteration                     2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                           2
0  print details of stoichiometric factors calculation
0  write reactions on RLIST
```

Information Only

```
0  list stoichiometric concentrations of master species
0  request iteration variables to be killed
-----------------------------------------------------------------------
DEVELOPMENT OPTIONS  (used for code development)
-----------------------------------------------------------------------
 none
-----------------------------------------------------------------------
TOLERANCES                    (desired values)        (defaults)
-----------------------------------------------------------------------
      residual functions                              1.e-10
        correction terms                              1.e-10
        saturation state                              0.5
number of N-R iterations                              30
-----------------------------------------------------------------------
```

The following is the EQ3NR **input** file for the sea water used in the third and fourth example EQ6 calculations (dissolution of microcline is dilute *HCl* in closed system and fluid-centered flow-through open system, respectively) in Chapter 6.

The EQ3NR **input** file (**ph4hcl.3i**), pH 4 HCl solution ("W" format):

```
EQ3NR input file name= ph4hcl.3i
Description= "A pH 4 HCl solution, with traces of K, Al, and Si"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  Dilute HCl solution, pH 4.00, with traces of potassium, aluminum,
and silica. This problem is part of test problem 3 of INTERA
(1983), who report a comparison study of EQ3/6 with PHREEQE
(Parkhurst, Thorstenson, and Plummer, 1980). Note that quartz,
chalcedony, and tridymite are suppressed by means of "nxmod"
options. This has no effect on the EQ3NR calculation. It is simply
needed for the subsequent EQ6 problem. EQ3NR passes this on to
EQ6 on the pickup file.

  Purpose: to provide a pickup file for construction of the EQ6 test
cases microhcl.6i and microhclft.6i. It also tests the "nxmod"
suppress option.

  This problem is actually redox-indifferent. The auxiliary basis
species O2(aq) and H2(aq) have therefore been suppressed. The EQ6
option switch iopt11 should be set to 1.

                          References

INTERA Environmental Consultants, Inc., 1983, Geochemical Models
  Suitable for Performance Assessment of Nuclear Waste Storage:
  Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste
  Isolation, Battelle Project Management Division, Columbus, Ohio,
  ONWI-473, 114 p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980,
  PHREEQE- A Computer Program for Geochemical Calculations: Water
  Resources Investigations Report 80-96, U.S. Geological Survey,
  Reston, Virginia, 210 p.

endit.
     tempc=          25.
       rho=           1.    tdspkg=          0.     tdspl=          0.
       fep=        -0.70    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=  0
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=    0    0    0    0    0    0    0    0    0    0
  iopg1-10=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     uebal= cl-
     nxmod=  3
   species= quartz
      type=  1              option= -1              xlkmod=          0.
   species= chalcedony
      type=  1              option= -1              xlkmod=          0.
   species= tridymite
      type=  1              option= -1              xlkmod=          0.
*
data file master species= h+
   switch with species=
   jflag= 16   csp= -4.00
```

Information Only

```
data file master species= cl-
   switch with species=
   jflag=  0   csp= 1.e-4
data file master species= k+
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= al+++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= sio2(aq)
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= o2(aq)
   switch with species=
   jflag= -1   csp= 0.
data file master species= h2(aq)
   switch with species=
   jflag= -1   csp= 0.
endit.
```

The EQ3NR input file (ph4hcl.3i), pH 4 HCl solution ("D" format):

```
EQ3NR input file name= ph4hcl.3i
Description= "A pH 4 HCl solution, with traces of K, Al, and Si"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  Dilute HCl solution, pH 4.00, with traces of potassium, aluminum,
and silica. This problem is part of test problem 3 of INTERA
(1983), who report a comparison study of EQ3/6 with PHREEQE
(Parkhurst, Thorstenson, and Plummer, 1980). Note that quartz,
chalcedony, and tridymite are suppressed by means of "nxmod"
options. This has no effect on the EQ3NR calculation. It is simply
needed for the subsequent EQ6 problem. EQ3NR passes this on to
EQ6 on the pickup file.

  Purpose: to provide a pickup file for construction of the EQ6 test
cases microhcl.6i and microhclft.6i. It also tests the "nxmod"
suppress option.

  This problem is actually redox-indifferent. The auxiliary basis
species O2(aq) and H2(aq) have therefore been suppressed. The EQ6
option switch ioptl1 should be set to 1.

                          References

INTERA Environmental Consultants, Inc., 1983, Geochemical Models
  Suitable for Performance Assessment of Nuclear Waste Storage:
  Comparison of PHREEQE and EQ3/EQ6: Office of Nuclear Waste
  Isolation, Battelle Project Management Division, Columbus, Ohio,
  ONWI-473, 114 p.

Parkhurst, D. L., Thorstenson, D. C., and Plummer, L. N., 1980,
  PHREEQE- A Computer Program for Geochemical Calculations: Water
  Resources Investigations Report 80-96, U.S. Geological Survey,
  Reston, Virginia, 210 p.
```

Temperature (C)	25.00	Density(gm/cm3)	1.00000
Total Dissolved Salts		mg/kg | mg/l	*not used
Electrical Balancing on	cl-	code selects	not performed

SPECIES	BASIS SWITCH/CONSTRAINT	CONCENTRATION	UNITS OR TYPE
redox		-.7000	logfo2
h+		4.0000	ph
cl-		0.10000E-03	molality
k+		0.10000E-11	molality
al+++		0.10000E-11	molality
sio2(aq)		0.10000E-11	molality
o2(aq)		0.	suppress
h2(aq)		0.	suppress

Input Solid Solutions

none			

SUPPRESSED SPECIES	(suppress,replace,augmentk,augmentg)		value
quartz	mineral	suppress	0.00000E+00
chalcedony	mineral	suppress	0.00000E+00
tridymite	mineral	suppress	0.00000E+00

Information Only

```
OPTIONS
-----------------------------------------------------------------------
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * does nothing
     lists species loaded into memory
 - ECHO DATABASE INFORMATION -
   * does nothing
     lists all reactions
     lists reactions and log K values
     lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
   * in order of decreasing concentration
     in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
   * all species
     only species > 10**-20 molal
     only species > 10**-12 molal
     not printed
 - LIST OF AQUEOUS SPECIES (by element) -
   * print major species
     print all species
     don't print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - pH SCALE CONVENTION -
   * modified NBS
     internal
     rational
 - ACTIVITY COEFFICIENT OPTIONS -
   * use B-dot equation
     Davies' equation
     Pitzer's equations
 - AUTO BASIS SWITCHING -
   * off
     on
 - PITZER DATABASE INFORMATION -
   * print only warnings
     print species in model and number of Pitzer coefficients
     print species in model and names of Pitzer coefficients
 - PICKUP FILE -
   * write pickup file
     don't write pickup file
 - LIST MEAN IONIC PROPERTIES -
   * don't print
     print
 - LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
   * print
     don't print
 - CONVERGENCE CRITERIA -
   * test both residual functions and correction terms
     test only residual functions
-----------------------------------------------------------------------
DEBUGGING SWITCHES (0-off, 1,2-on, default is off)
-----------------------------------------------------------------------
0  generic debugging information                                      2
0  print details of pre-Newton-Raphson iteration                      2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                            2
0  print details of stoichiometric factors calculation
0  write reactions on RLIST
0  list stoichiometric concentrations of master species
0  request iteration variables to be killed
-----------------------------------------------------------------------
DEVELOPMENT OPTIONS  (used for code development)
-----------------------------------------------------------------------
 none
-----------------------------------------------------------------------
TOLERANCES                    (desired values)        (defaults)
-----------------------------------------------------------------------
      residual functions |                        |1.e-10
        correction terms |                        |1.e-10
        saturation state |                        |0.5
number of N-R iterations |                        |30
-----------------------------------------------------------------------
```

Information Only

The following is the EQ3NR **input** file for the dilute *$CaSO_4$-NaCl* solution used in the fifth example EQ6 calculation (solubility of gypsum in the system in *$CaSO_4$-NaCl-H_2O*) in Chapter 6.

The EQ3NR **input** file (**caso4naclB.3i**), dilute *$CaSO_4$-NaCl* solution ("W" format):

```
EQ3NR input file name= caso4naclB.3i
Description= "Trace CaSO4-NaCl solution, anhydrite suppressed"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Nearly pure water, with traces of calcium sulfate and sodium
chloride.

  Purpose: to initialize the EQ6 test case input file gypsumB.6i,
which in turn initializes the EQ6 test case input file gypnacl.6i.
This test case is identical to that in the EQ3NR test case input
file caso4nacl.3i, except that anhydrite is suppressed by an "nxmod"
option. This test case uses Pitzer's equations to calculate the
activity of water and the activity coefficients of the aqueous
solute species. The Harvie- Moller-Weare (hmw) data file (after
Harvie, Moller, and Weare, 1984) should be employed.

                              References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction
  of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-
  OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C:
  Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

endit.
     tempc=          25.
       rho=           1.    tdspkg=          0.     tdspl=          0.
       fep=           0.    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=  0
*              1    2    3    4    5    6    7    8    9   10
  ioptl-10=    0    0    0    0    0    0    0    0    0    0
  iopgl-10=    1    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     uebal= h+
     nxmod=  1
   species= anhydrite
      type=  1              option= -1              xlkmod=          0.
*
data file master species= h+
   switch with species=
   jflag=  0   csp= 1.e-7
data file master species= ca++
   switch with species=
   jflag=  0   csp= 1.e-10
data file master species= so4--
   switch with species=
   jflag=  0   csp= 1.e-10
data file master species= na+
   switch with species=
   jflag=  0   csp= 1.e-10
data file master species= cl-
   switch with species=
   jflag=  0   csp= 1.e-10
endit.
```

The EQ3NR **input** file (**caso4naclB.3i**), dilute *$CaSO_4$-NaCl* solution ("D" format):

```
-----------------------------------------------------------------------
EQ3NR input file name= caso4naclB.3i
Description= "Trace CaSO4-NaCl solution, anhydrite suppressed"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Nearly pure water, with traces of calcium sulfate and sodium
chloride.

  Purpose: to initialize the EQ6 test case input file gypsumB.6i,
which in turn initializes the EQ6 test case input file gypnacl.6i.
This test case is identical to that in the EQ3NR test case input
```

Information Only

file caso4nacl.3i, except that anhydrite is suppressed by an "nxmod" option. This test case uses Pitzer's equations to calculate the activity of water and the activity coefficients of the aqueous solute species. The Harvie- Moller-Weare (hmw) data file (after Harvie, Moller, and Weare, 1984) should be employed.

References

Harvie, C. E., Moller, N., and Weare, J. H., 1984, The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO4-OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25 C: Geochimica et Cosmochimica Acta, v. 48, p. 723-751.

Temperature (C)	25.00	Density(gm/cm3)	1.00000

Total Dissolved Salts		mg/kg	mg/l	*not used
Electrical Balancing on	h+	code selects		not performed

SPECIES	BASIS SWITCH/CONSTRAINT	CONCENTRATION	UNITS OR TYPE
redox		0.	logfo2
h+		0.10000E-06	molality
ca++		0.10000E-09	molality
so4--		0.10000E-09	molality
na+		0.10000E-09	molality
cl-		0.10000E-09	molality

Input Solid Solutions

none			

SUPPRESSED SPECIES	(suppress,replace,augmentk,augmentg)	value
anhydrite	mineral	suppress	0.00000E+00

OPTIONS

```
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * does nothing
     lists species loaded into memory
 - ECHO DATABASE INFORMATION -
   * does nothing
     lists all reactions
     lists reactions and log K values
     lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
   * in order of decreasing concentration
     in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
   * all species
     only species > 10**-20 molal
     only species > 10**-12 molal
     not printed
 - LIST OF AQUEOUS SPECIES (by element) -
   * print major species
     print all species
     don't print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - pH SCALE CONVENTION -
   * modified NBS
     internal
     rational
 - ACTIVITY COEFFICIENT OPTIONS -
     use B-dot equation
     Davies' equation
   * Pitzer's equations
 - AUTO BASIS SWITCHING -
   * off
     on
 - PITZER DATABASE INFORMATION -
   * print only warnings
     print species in model and number of Pitzer coefficients
     print species in model and names of Pitzer coefficients
 - PICKUP FILE -
   * write pickup file
     don't write pickup file
 - LIST MEAN IONIC PROPERTIES -
   * don't print
     print
 - LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
   * print
     don't print
 - CONVERGENCE CRITERIA -
   * test both residual functions and correction terms
```

Information Only

```
     test only residual functions
-----------------------------------------------------------------
DEBUGGING SWITCHES (o-off, 1,2-on, default is off)
-----------------------------------------------------------------
0  generic debugging information                                 2
0  print details of pre-Newton-Raphson iteration                 2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                       2
0  print details of stoichiometric factors calculation
0  write reactions on RLIST
0  list stoichiometric concentrations of master species
0  request iteration variables to be killed
-----------------------------------------------------------------
DEVELOPMENT OPTIONS  (used for code development)
-----------------------------------------------------------------
 none
-----------------------------------------------------------------
TOLERANCES                  (desired values)        (defaults)
-----------------------------------------------------------------
      residual functions  |                      |1.e-10
        correction terms  |                      |1.e-10
        saturation state  |                      |0.5
number of N-R iterations  |                      |30
-----------------------------------------------------------------
```

The following is the EQ3NR **input** file for the river water used in the sixth example EQ6 calculation (alkalinity titration) in Chapter 6.

<u>The EQ3NR **input** file (**rwpar.3i**), the river water partial benchmark test case ("W" format):</u>

```
EQ3NR input file name= rwpar.3i
Description= "River water, partial benchmark test case"
Version number= 3245   Stage number= 01
Created 06/08/90    Creator= T.J. Wolery
Revised 06/08/90    Revisor= T.J. Wolery

  River water, including all solute components present above 0.05
mg/L, plus nitrite, sulfide, iron, and aluminum. This is a
moderately pared-down version of rwtst.3i, which contains the full
benchmark river water test case of Nordstrom et al. (1979, Table
III).

  Purpose: to test the code on an intermediate-sized problem
involving a dilute solution, and to initialize the EQ6 test case
input file rwtitr.6i (which simulates an alkalinity titration of
this water). The activity coefficients of the aqueous species are
calculated from the B-dot equation and related equations.

  Data for the following were originally specified as:

    HCO3-     :   alkalinity = 75.2  mg/L HCO3- (total alkalinity,
                                                not the conventional
                                                HCO3 alkalinity)
    SiO2(aq) :   Si          = 8.52  mg/L
    H3BO3(aq):   B           = 0.050 mg/L
    HPO4-     :   PO4---     = 0.210 mg/L
    HS-       :   H2S(aq)    = 0.002 mg/L

The pH (8.01) lies well in between the pKa values of carbonic
acid (~6.3 and ~10.3), so equating the total molality of HCO3-
to the reported alkalinity is not likely to cause a problem.
This can be confirmed by simulating the alkalinity titration.
This is the purpose of the EQ6 test case represented by the
EQ6 input file rwtitr.6i.

  The total alkalinity of 75.2 mg/L HCO3- noted above is equivalent
to 61.7 mg/L CaCO3 (total alkalinity). This is the more standard
way of reporting alkalinity (see Standard Methods, 1976).

                          References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical
  models for equilibrium calculations in aqueous systems, in Jenne,
  E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium
  Series, v. 93, American Chemical Society, Washington, D.C.,
  p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976,
  Prepared and jointly published by the American Public Health
  Association, the American Water Works Association, and the Water
  Pollution Control Federation: American Public Health Association,
  1015 Eighteenth Street NW, Washington, D.C.
```

Information Only

```
endit.
     tempc=          9.5
       rho=         1.00    tdspkg=          0.     tdspl=          0.
       fep=        0.440    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=  0
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=   -1    0    0    0    0    0    0    0    0    0
  iopg1-10=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     uebal= none
     nxmod=  0
*
data file master species= na+
   switch with species=
   jflag=  2   csp= 12.
data file master species= k+
   switch with species=
   jflag=  2   csp= 1.4
data file master species= ca++
   switch with species=
   jflag=  2   csp= 12.2
data file master species= mg++
   switch with species=
   jflag=  2   csp= 7.5
data file master species= sio2(aq)
   switch with species=
   jflag=  2   csp= 18.227
data file master species= hco3-
   switch with species=
   jflag=  2   csp= 75.2
data file master species= cl-
   switch with species=
   jflag=  2   csp= 9.9
data file master species= so4--
   switch with species=
   jflag=  2   csp= 7.7
data file master species= b(oh)3(aq)
   switch with species=
   jflag=  2   csp= 0.28597
data file master species= f-
   switch with species=
   jflag=  2   csp= 0.10
data file master species= hpo4--
   switch with species=
   jflag=  2   csp= 0.21223
data file master species= no3-
   switch with species=
   jflag=  2   csp= 0.898
data file master species= no2-
   switch with species=
   jflag=  2   csp= 0.019
data file master species= nh4+
   switch with species=
   jflag=  2   csp= 0.144
data file master species= fe++
   switch with species=
   jflag=  2   csp= 0.015
data file master species= fe+++
   switch with species=
   jflag=  2   csp= 0.0007
data file master species= al+++
   switch with species=
   jflag=  2   csp= 0.005
data file master species= hs-
   switch with species=
   jflag=  2   csp= 0.0019408
data file master species= h+
   switch with species=
   jflag= 16   csp= -8.01
data file master species= o2(aq)
   switch with species=
   jflag=  2   csp= 10.94
endit.
```

Information Only

The EQ3NR **input** file (**rwpar.3i**), the river water partial benchmark test case ("D" format):

```
-----------------------------------------------------------------------
EQ3NR input file name= rwpar.3i
Description= "River water, partial benchmark test case"
Version number= 3245    Stage number= 01
Created 06/08/90     Creator= T.J. Wolery
Revised 06/08/90     Revisor= T.J. Wolery

  River water, including all solute components present above 0.05
mg/L, plus nitrite, sulfide, iron, and aluminum. This is a
moderately pared-down version of rwtst.3i, which contains the full
benchmark river water test case of Nordstrom et al. (1979, Table
III).

  Purpose: to test the code on an intermediate-sized problem
involving a dilute solution, and to initialize the EQ6 test case
input file rwtitr.6i (which simulates an alkalinity titration of
this water). The activity coefficients of the aqueous species are
calculated from the B-dot equation and related equations.

  Data for the following were originally specified as-

    HCO3-     :   alkalinity = 75.2  mg/L HCO3- (total alkalinity,
                                                 not the conventional
                                                 HCO3 alkalinity)
    SiO2(aq) :   Si          = 8.52  mg/L
    H3BO3(aq):   B           = 0.050 mg/L
    HPO4-    :   PO4---      = 0.210 mg/L
    HS-      :   H2S(aq)     = 0.002 mg/L

The pH (8.01) lies well in between the pKa values of carbonic
acid (~6.3 and ~10.3), so equating the total molality of HCO3-
to the reported alkalinity is not likely to cause a problem.
This can be confirmed by simulating the alkalinity titration.
This is the purpose of the EQ6 test case represented by the
EQ6 input file rwtitr.6i.

  The total alkalinity of 75.2 mg/L HCO3- noted above is equivalent
to 61.7 mg/L CaCO3 (total alkalinity). This is the more standard
way of reporting alkalinity (see Standard Methods, 1976).

                          References

Nordstrom, D. K., et al., 1979, A comparison of computerized chemical
  models for equilibrium calculations in aqueous systems, in Jenne,
  E. A., editor, Chemical Modeling in Aqueous Systems, ACS Symposium
  Series, v. 93, American Chemical Society, Washington, D.C.,
  p. 857-892.

Standard Methods for the Examination of Water and Wastewater, 1976,
  Prepared and jointly published by the American Public Health
  Association, the American Water Works Association, and the Water
  Pollution Control Federation: American Public Health Association,
  1015 Eighteenth Street NW, Washington, D.C.

-----------------------------------------------------------------------
Temperature (C)          |  9.50        |Density(gm/cm3)|  1.00000
-----------------------------------------------------------------------
Total Dissolved Salts    |              | mg/kg | mg/l  |*not used
-----------------------------------------------------------------------
Electrical Balancing on  |              | code selects  |*not performed
-----------------------------------------------------------------------
SPECIES    | BASIS SWITCH/CONSTRAINT | CONCENTRATION| UNITS OR TYPE
-----------------------------------------------------------------------
redox      |                         | 0.4400       |eh
na+        |                         | 12.000       |mg/l
k+         |                         | 1.4000       |mg/l
ca++       |                         | 12.200       |mg/l
mg++       |                         | 7.5000       |mg/l
sio2(aq)   |                         | 18.227       |mg/l
hco3-      |                         | 75.200       |mg/l
cl-        |                         | 9.9000       |mg/l
so4--      |                         | 7.7000       |mg/l
b(oh)3(aq) |                         | 0.28597      |mg/l
f-         |                         | 0.10000      |mg/l
hpo4--     |                         | 0.21223      |mg/l
no3-       |                         | 0.89800      |mg/l
no2-       |                         | 0.19000E-01  |mg/l
nh4+       |                         | 0.14400      |mg/l
fe++       |                         | 0.15000E-01  |mg/l
fe+++      |                         | 0.70000E-03  |mg/l
al+++      |                         | 0.50000E-02  |mg/l
hs-        |                         | 0.19408E-02  |mg/l
h+         |                         | 8.0100       |ph
o2(aq)     |                         | 10.940       |mg/l
-----------------------------------------------------------------------
Input Solid Solutions
-----------------------------------------------------------------------
 none      |                         |              |
-----------------------------------------------------------------------
```

Information Only

```
SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value
-----------------------------------------------------------------------
 none                    |              |
-----------------------------------------------------------------------
OPTIONS
-----------------------------------------------------------------------
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * does nothing
     lists species loaded into memory
 - ECHO DATABASE INFORMATION -
   * does nothing
     lists all reactions
     lists reactions and log K values
     lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
   * in order of decreasing concentration
     in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
   * all species
     only species > 10**-20 molal
     only species > 10**-12 molal
     not printed
 - LIST OF AQUEOUS SPECIES (by element) -
   * print major species
     print all species
     don't print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - pH SCALE CONVENTION -
   * modified NBS
     internal
     rational
 - ACTIVITY COEFFICIENT OPTIONS -
   * use B-dot equation
     Davies' equation
     Pitzer's equations
 - AUTO BASIS SWITCHING -
   * off
     on
 - PITZER DATABASE INFORMATION -
   * print only warnings
     print species in model and number of Pitzer coefficients
     print species in model and names of Pitzer coefficients
 - PICKUP FILE -
   * write pickup file
     don't write pickup file
 - LIST MEAN IONIC PROPERTIES -
   * don't print
     print
 - LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
   * print
     don't print
 - CONVERGENCE CRITERIA -
   * test both residual functions and correction terms
     test only residual functions
-----------------------------------------------------------------------
DEBUGGING SWITCHES (o-off, 1,2-on, default is off)
-----------------------------------------------------------------------
0  generic debugging information                                      2
0  print details of pre-Newton-Raphson iteration                     2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                           2
0  print details of stoichiometric factors calculation
0  write reactions on RLIST
0  list stoichiometric concentrations of master species
0  request iteration variables to be killed
-----------------------------------------------------------------------
DEVELOPMENT OPTIONS  (used for code development)
-----------------------------------------------------------------------
 none
-----------------------------------------------------------------------
TOLERANCES                    (desired values)        (defaults)
-----------------------------------------------------------------------
      residual functions  |                        |1.e-10
        correction terms  |                        |1.e-10
        saturation state  |                        |0.5
number of N-R iterations  |                        |30
-----------------------------------------------------------------------
```

Information Only

The following is the EQ3NR **input** file for the 0.1 N H_2SO_4 solution used to calculate the composition of the special reactant in the sixth example EQ6 calculation (alkalinity titration) in Chapter 6.

The EQ3NR **input** file (**h2so4p1N.3i**), 0.1 N H_2SO_4 solution ("W" format):

```
EQ3NR input file name= h2so4p1N.3i
Description= "H2SO4, 0.1 N"
Version number= 3245   Stage number= 01
Created 11/30/91    Creator= T.J. Wolery
Revised 11/30/91    Revisor= T.J. Wolery

  Aqueous H2SO4, 0.1 N.

  Purpose: to use in simulating alkalinity titrations for samples
of moderate to high alkalinity (> 20 mg/L CaCO3 or 0.60 meq/L).
See Standard Methods, Section 403, "Alkalinity," p. 278-282. 0.1 N
HCl is also acceptable. For samples of low alkalinity, 0.02 N H2SO4
or 0.02 N HCl should be used.

  Two end points (measures of alkalinity) are required for the
reporting procedure recommended by Standard Methods. One is the
phenolphthalein alkalinity (P), the other the total alkalinity (T).
The former corresponds to an end point pH of 8.3. The end point
for the latter is not any one fixed value, but generally falls in
the range of pH 3.7-5.1. It may be defined by an inflection point,
the pK of one of several indicator dyes, or chosen based on the
recommendation of the following table:

    Alkalinity      End Point
    mg/L CaCO3        pH

        30            5.1
       150            4.8
       500            4.5

    silicates,
    phosphates
    known or
    suspected         4.5

    industrial
    waste or
    complex
    system            3.7
       500            4.5
       500            4.5


Alkalinity is not reported as T and P, but as hydroxide, carbonate,
and bicarbonate alkalinities. Their values are determined from T
and P as follows:

    Result of       OH Alkalinity     CO3 Alkalinity     HCO3 Alkalinity
    Titration        mg/L CaCO3         mg/L CaCO3         mg/L CaCO3

      P = 0              0                  0                  T
      P < 1/2 T          0                 2P                T - 2P
      P = 1/2 T          0                 2P                  0
      P > 1/2 T       2P - T            2(T - P)               0
      P = T              T                  0                  0


  Note that what most geochemical modeling codes expect in terms of
alkalinity is the total alkalinity, expressed in eq/L or meq/L. Be
warned that CO2(aq) (also known as H2CO3(aq)) is not measured by
the alkalinity. Thus, total HCO3- (mol/L) is greater than the HCO3
alkalinity (eq/L) plus twice the CO3 alkalinity (eq/L). If the
pH is greater than 8.3 at 25 C, the contribution to total HCO3-
from CO2(aq) is negligible. At about pH 6.3, CO2(aq) makes up about
half of total HCO3-. At lower pH values, it makes up more than
half, and the use of alkalinity measurements becomes increasingly
unsuitable.

  Dissolved oxygen and CO2 are assumed to be in equilibrium with the
atmosphere.

                          References

Standard Methods for the Examination of Water and Wastewater, 1976,
  Prepared and jointly published by the American Public Health
  Association, the American Water Works Association, and the Water
  Pollution Control Federation: American Public Health Association,
  1015 Eighteenth Street NW, Washington, D.C.
```

Information Only

P = T	T	0	0

Note that what most geochemical modeling codes expect in terms of alkalinity is the total alkalinity, expressed in eq/L or meq/L. Be warned that CO2(aq) (also known as H2CO3(aq)) is not measured by the alkalinity. Thus, total HCO3- (mol/L) is greater than the HCO3 alkalinity (eq/L) plus twice the CO3 alkalinity (eq/L). If the pH is greater than 8.3 at 25 C, the contribution to total HCO3- from CO2(aq) is negligible. At about pH 6.3, CO2(aq) makes up about half of total HCO3-. At lower pH values, it makes up more than half, and the use of alkalinity measurements becomes increasingly unsuitable.

Dissolved oxygen and CO2 are assumed to be in equilibrium with the atmosphere.

References

Standard Methods for the Examination of Water and Wastewater, 1976, Prepared and jointly published by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation: American Public Health Association, 1015 Eighteenth Street NW, Washington, D.C.

Temperature (C)	25.00	Density(gm/cm3)	1.00000
Total Dissolved Salts		mg/kg | mg/l	*not used
Electrical Balancing on	h+	code selects	not performed

SPECIES	BASIS SWITCH/CONSTRAINT	CONCENTRATION	UNITS OR TYPE
redox		-.7000	logfo2
so4--		0.50000E-01	molality
hco3-	co2(g)	-3.5000	log fugacity
h+		1.0000	ph
o2(aq)		0.	eliminated

Input Solid Solutions

none			

SUPPRESSED SPECIES	(suppress,replace,augmentk,augmentg)	value
none		

OPTIONS

- SOLID SOLUTIONS -
  * ignore solid solutions
    process hypothetical solid solutions
    process input and hypothetical solid solutions
- LOADING OF SPECIES INTO MEMORY -
  * does nothing
    lists species loaded into memory
- ECHO DATABASE INFORMATION -
  * does nothing
    lists all reactions
    lists reactions and log K values
    lists reactions, log K values and polynomial coef.
- LIST OF AQUEOUS SPECIES (ordering) -
  * in order of decreasing concentration
    in same order as input file
- LIST OF AQUEOUS SPECIES (concentration limit) -
  * all species
    only species > 10**-20 molal
    only species > 10**-12 molal
    not printed
- LIST OF AQUEOUS SPECIES (by element) -
  * print major species
    print all species
    don't print
- MINERAL SATURATION STATES -
  * print if affinity > -10 kcals
    print all
    don't print
- pH SCALE CONVENTION -
  * modified NBS
    internal
    rational
- ACTIVITY COEFFICIENT OPTIONS -
  * use B-dot equation
    Davies' equation
    Pitzer's equations
- AUTO BASIS SWITCHING -
  * off
    on
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients

Information Only

```
endit.
     tempc=          25.
       rho=      1.00000    tdspkg=          0.     tdspl=          0.
       fep=       -0.700    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=  0
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=    0    0    0    0    0    0    0    0    0    0
  iopg1-10=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     uebal= h+
     nxmod=  0
*
data file master species= so4--
   switch with species=
   jflag=  0   csp= 0.05
data file master species= hco3-
   switch with species=
   jflag= 21   csp= -3.5
     gas= co2(g)
data file master species= h+
   switch with species=
   jflag= 16   csp= -1.0
data file master species= o2(aq)
   switch with species=
   jflag= 30   csp= 0.
endit.
```

The EQ3NR input file (h2so4p1N.3i), 0.1 N H_2SO_4 solution ("D" format):

```
-----------------------------------------------------------------------
EQ3NR input file name= h2so4p1N.3i
Description= "H2SO4, 0.1 N"
Version number= 3245   Stage number= 01
Created 11/30/91    Creator= T.J. Wolery
Revised 11/30/91    Revisor= T.J. Wolery

  Aqueous H2SO4, 0.1 N.

  Purpose: to use in simulating alkalinity titrations for samples
of moderate to high alkalinity (> 20 mg/L CaCO3 or 0.60 meq/L).
See Standard Methods, Section 403, "Alkalinity," p. 278-282. 0.1 N
HCl is also acceptable. For samples of low alkalinity, 0.02 N H2SO4
or 0.02 N HCl should be used.

  Two end points (measures of alkalinity) are required for the
reporting procedure recommended by Standard Methods. One is the
phenolphthalein alkalinity (P), the other the total alkalinity (T).
The former corresponds to an end point pH of 8.3. The end point
for the latter is not any one fixed value, but generally falls in
the range of pH 3.7-5.1. It may be defined by an inflection point,
the pK of one of several indicator dyes, or chosen based on the
recommendation of the following table:

    Alkalinity      End Point
    mg/L CaCO3        pH

        30            5.1
       150            4.8
       500            4.5

    silicates,
    phosphates
    known or
    suspected         4.5

    industrial
    waste or
    complex
    system            3.7
       500            4.5
       500            4.5


Alkalinity is not reported as T and P, but as hydroxide, carbonate,
and bicarbonate alkalinities. Their values are determined from T
and P as follows:

    Result of       OH Alkalinity     CO3 Alkalinity     HCO3 Alkalinity
    Titration        mg/L CaCO3         mg/L CaCO3         mg/L CaCO3

      P = 0              0                  0                  T
      P < 1/2 T          0                 2P                T - 2P
      P = 1/2 T          0                 2P                  0
      P > 1/2 T       2P - T            2(T - P)               0
```

Information Only

```
- PICKUP FILE -
  * write pickup file
    don't write pickup file
- LIST MEAN IONIC PROPERTIES -
  * don't print
    print
- LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
  * print
    don't print
- CONVERGENCE CRITERIA -
  * test both residual functions and correction terms
    test only residual functions
-----------------------------------------------------------------
DEBUGGING SWITCHES (0-off, 1,2-on, default is off)
-----------------------------------------------------------------
0  generic debugging information                                  2
0  print details of pre-Newton-Raphson iteration                  2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                        2
0  print details of stoichiometric factors calculation
0  write reactions on RLIST
0  list stoichiometric concentrations of master species
0  request iteration variables to be killed
-----------------------------------------------------------------
DEVELOPMENT OPTIONS  (used for code development)
-----------------------------------------------------------------
 none
-----------------------------------------------------------------
TOLERANCES                    (desired values)        (defaults)
-----------------------------------------------------------------
      residual functions  |                        |1.e-10
        correction terms  |                        |1.e-10
        saturation state  |                        |0.5
number of N-R iterations  |                        |30
-----------------------------------------------------------------
```

The following is the EQ3NR **input** file for the SiO_2 solution used in the seventh example EQ6 calculation (kinetic modeling of quartz precipitation) in Chapter 6.

<u>The EQ3NR **input** file (**sio2.3i**), SiO_2 solution ("W" format):</u>

```
EQ3NR input file name= sio2.3i
Description= "Solution containing 101.0 mg/L SiO2"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Solution containing 101.0 mg/L of dissolved SiO2. This test
case is otherwise nearly identical to that in the EQ3NR test case
input file deionw.3i.

  Purpose: to initialize the EQ6 test case input files pquartz.6i
and pquartzA.6i, both of which simulate the precipitation of
quartz from supersaturated solution at 105 C. The former EQ6
test case is test problem 1 from Delany, Puigdomenech, and Wolery
(1986, p. 19-21, 31-33), which simulates an experiment (Run 2E)
reported by Rimstidt and Barnes (1980, p. 1687-1688, Figure 2)
and uses their rate law model, which is independent of pH. The
latter is the same problem, but uses a rate law model from Knauss
and Wolery (1988) that does include a dependence on pH.

  Note that the dissolved gases O2 and H2 have been suppressed.
This is because this problem has no redox aspect. The EQ6 option
switch ioptl1 should be set to 1 in the EQ6 test case input files
so that EQ6 knows this.

  Note also that the silica polymorphs tridymite, chalcedony,
sio2(am), and cristobalite have been suppressed by means of "nxmod"
options.

                          References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986,
  Precipitation Kinetics Option for the EQ6 Geochemical Reaction
  Path Code: UCRL-53642, Lawrence Livermore National Laboratory,
  Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of
  quartz as a function of pH and time at 70 C: Geochimica et
  Cosmochimica Acta, v. 52, p. 43-53.

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water
```

Information Only

```
  reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

endit.
     tempc=          25.
       rho=           1.    tdspkg=          0.     tdspl=          0.
       fep=           0.    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=  0
*            1    2    3    4    5    6    7    8    9   10
  iopt1-10=     0    0    0    0    0    0    0    0    0    0
  iopg1-10=     0    0    0    0    0    0    0    0    0    0
  iopr1-10=     0    0    0    0    0    0    0    0    0    0
 iopr11-20=     0    0    0    0    0    0    0    0    0    0
  iodb1-10=     0    0    0    0    0    0    0    0    0    0
     uebal= h+
     nxmod=  4
   species= tridymite
      type=  1              option= -1              xlkmod=          0.
   species= chalcedony
      type=  1              option= -1              xlkmod=          0.
   species= sio2(am)
      type=  1              option= -1              xlkmod=          0.
   species= cristobalite
      type=  1              option= -1              xlkmod=          0.
*
data file master species= h+
   switch with species=
   jflag= 16   csp= -5.5
data file master species= sio2(aq)
   switch with species=
   jflag=  2   csp= 101.0
data file master species= hco3-
   switch with species=
   jflag= 21   csp= -3.5
     gas= co2(g)
data file master species= o2(aq)
   switch with species=
   jflag= -1   csp= 0.
data file master species= h2(aq)
   switch with species=
   jflag= -1   csp= 0.
endit.
```

The EQ3NR **input** file (**sio2.3i**), SiO_2 solution ("D" format):

```
-----------------------------------------------------------------------
EQ3NR input file name= sio2.3i
Description= "Solution containing 101.0 mg/L SiO2"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 10/29/90    Revisor= T.J. Wolery

  Solution containing 101.0 mg/L of dissolved SiO2. This test
case is otherwise nearly identical to that in the EQ3NR test case
input file deionw.3i.

  Purpose: to initialize the EQ6 test case input files pquartz.6i
and pquartzA.6i, both of which simulate the precipitation of
quartz from supersaturated solution at 105 C. The former EQ6
test case is test problem 1 from Delany, Puigdomenech, and Wolery
(1986, p. 19-21, 31-33), which simulates an experiment (Run 2E)
reported by Rimstidt and Barnes (1980, p. 1687-1688, Figure 2)
and uses their rate law model, which is independent of pH. The
latter is the same problem, but uses a rate law model from Knauss
and Wolery (1988) that does include a dependence on pH.

  Note that the dissolved gases O2 and H2 have been suppressed.
This is because this problem has no redox aspect. The EQ6 option
switch iopt11 should be set to 1 in the EQ6 test case input files
so that EQ6 knows this.

  Note also that the silica polymorphs tridymite, chalcedony,
sio2(am), and cristobalite have been suppressed by means of "nxmod"
options.

                          References

Delany, J. M., Puigdomenech, I., and Wolery, T. J., 1986,
  Precipitation Kinetics Option for the EQ6 Geochemical Reaction
  Path Code: UCRL-53642, Lawrence Livermore National Laboratory,
  Livermore, California, 44 p.

Knauss, K. G., and Wolery, T. J., 1988, The dissolution kinetic of
  quartz as a function of pH and time at 70 C: Geochimica et
  Cosmochimica Acta, v. 52, p. 43-53.

Rimstidt, J. D., and Barnes, H. L., 1980, The kinetics of silica-water
```

Information Only

```
reactions: Geochimica et Cosmochimica Acta, v. 44, p. 1683-1699.

Temperature (C)          | 25.00        |Density(gm/cm3)|  1.00000
Total Dissolved Salts    |              | mg/kg | mg/l  |*not used
Electrical Balancing on |h+              | code selects  | not performed

SPECIES    | BASIS SWITCH/CONSTRAINT | CONCENTRATION| UNITS OR TYPE
redox      |                         |     0.       |logfo2
h+         |                         | 5.5000       |ph
sio2(aq)   |                         | 101.00       |mg/l
hco3-      |co2(g)                   |-3.5000       |log fugacity
o2(aq)     |                         |     0.       |suppress
h2(aq)     |                         |     0.       |suppress

Input Solid Solutions
 none      |                         |              |

SUPPRESSED SPECIES   (suppress,replace,augmentk,augmentg)    value
tridymite                | mineral        | suppress | 0.00000E+00
chalcedony               | mineral        | suppress | 0.00000E+00
sio2(am)                 | mineral        | suppress | 0.00000E+00
cristobalite             | mineral        | suppress | 0.00000E+00

OPTIONS
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * does nothing
     lists species loaded into memory
 - ECHO DATABASE INFORMATION -
   * does nothing
     lists all reactions
     lists reactions and log K values
     lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
   * in order of decreasing concentration
     in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
   * all species
     only species > 10**-20 molal
     only species > 10**-12 molal
     not printed
 - LIST OF AQUEOUS SPECIES (by element) -
   * print major species
     print all species
     don't print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
   pH SCALE CONVENTION -
   * modified NBS
     internal
     rational
 - ACTIVITY COEFFICIENT OPTIONS -
   * use B-dot equation
     Davies' equation
     Pitzer's equations
 - AUTO BASIS SWITCHING -
   * off
     on
 - PITZER DATABASE INFORMATION -
   * print only warnings
     print species in model and number of Pitzer coefficients
     print species in model and names of Pitzer coefficients
 - PICKUP FILE -
   * write pickup file
     don't write pickup file
 - LIST MEAN IONIC PROPERTIES -
   * don't print
     print
 - LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
   * print
     don't print
 - CONVERGENCE CRITERIA -
   * test both residual functions and correction terms
     test only residual functions

DEBUGGING SWITCHES (0-off, 1,2-on, default is off)
0  generic debugging information                                  2
0  print details of pre-Newton-Raphson iteration                  2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                        2
```

Information Only

```
|0  print details of stoichiometric factors calculation                |
|0  write reactions on RLIST                                            |
|0  list stoichiometric concentrations of master species                |
|0  request iteration variables to be killed                            |
|-----------------------------------------------------------------------|
|DEVELOPMENT OPTIONS  (used for code development)                       |
|-----------------------------------------------------------------------|
| none                                                                  |
|-----------------------------------------------------------------------|
|TOLERANCES                    (desired values)        (defaults)       |
|-----------------------------------------------------------------------|
|      residual functions  |                        |1.e-10            |
|        correction terms  |                        |1.e-10            |
|        saturation state  |                        |0.5               |
|number of N-R iterations  |                        |30                |
|-----------------------------------------------------------------------|
```

The following is the EQ3NR **input** file for the J-13 well water used in the first EQ6 **input** file (hydrothermal reaction of groundwater with devitrified tuff) presented in Appendix E.

The EQ3NR **input** file (**j13wwA.3i**), J-13 well water ("W" format):

```
EQ3NR input file name= j13wwA.3i
Description= "J-13 well water, six minerals suppressed"
Version number= 3245   Stage number= 01
Created 10/07/90    Creator= T.J. Wolery
Revised 10/07/90    Revisor= T.J. Wolery

  Water from well J-13 at the Nevada Test Site. The composition
is identical to that in the EQ3NR test case input file j13ww.3i,
which is based on data reported by Harrer et al. (1990). Water
from this well is commonly used to represent the groundwater
at the proposed high-level nuclear waste repository at Yucca
Mountain, Nevada.

  Purpose: to initialize the EQ6 test case input file j13wwtuff.6i,
in which this water is reacted with devitrified tuff at 150 C.
Six minerals (quartz, chalcedony, tridymite, pyrophyllite,
maximum microcline, and illite) are suppressed by means of
"nxmod" options. These suppressions have no effect on the EQ3NR
calculation, but will be passed on to j13wwtuff.6i.

                          References

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990,
  Report of the Committee to Review the Use of J-13 Well Water in
  Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence
  Livermore National Laboratory, Livermore, California.

endit.
     tempc=          25.
       rho=      1.00000    tdspkg=          0.     tdspl=          0.
       fep=        0.340    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=  0
*              1    2    3    4    5    6    7    8    9   10
  ioptl-10=   -1    0    0    0    0    0    0    0    0    0
  iopgl-10=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodbl-10=    0    0    0    0    0    0    0    0    0    0
     uebal= none
     nxmod=  6
   species= quartz
      type=  1              option= -1              xlkmod=          0.
   species= chalcedony
      type=  1              option= -1              xlkmod=          0.
   species= tridymite
      type=  1              option= -1              xlkmod=          0.
   species= pyrophyllite
      type=  1              option= -1              xlkmod=          0.
   species= maximum microcline
      type=  1              option= -1              xlkmod=          0.
   species= illite
      type=  1              option= -1              xlkmod=          0.
*
data file master species= na+
   switch with species=
   jflag=  2   csp= 45.8
data file master species= sio2(aq)
   switch with species=
   jflag=  2   csp= 60.970
```

Information Only

```
data file master species= ca++
   switch with species=
   jflag=  2   csp= 13.0
data file master species= k+
   switch with species=
   jflag=  2   csp= 5.04
data file master species= mg++
   switch with species=
   jflag=  2   csp= 2.01
data file master species= li+
   switch with species=
   jflag=  2   csp= 0.048
data file master species= h+
   switch with species=
   jflag= 16   csp= -7.41
data file master species= hco3-
   switch with species=
   jflag=  2   csp= 140.4
data file master species= o2(aq)
   switch with species=
   jflag=  2   csp= 5.6
data file master species= f-
   switch with species=
   jflag=  2   csp= 2.18
data file master species= cl-
   switch with species=
   jflag=  2   csp= 7.14
data file master species= no3-
   switch with species=
   jflag=  2   csp= 8.78
data file master species= so4--
   switch with species=
   jflag=  2   csp= 18.4
data file master species= b(oh)3(aq)
   switch with species=
   jflag=  2   csp= 0.766
data file master species= al+++
   switch with species=
   jflag=  2   csp= 0.008
data file master species= mn++
   switch with species=
   jflag=  2   csp= 0.012
data file master species= fe++
   switch with species=
   jflag=  2   csp= 0.040
data file master species= sr++
   switch with species=
   jflag=  2   csp= 0.040
data file master species= hpo4--
   switch with species=
   jflag=  2   csp= 0.120
endit.
```

The EQ3NR input file (j13wwA.3i), J-13 well water ("D" format):

```
-----------------------------------------------------------------------
EQ3NR input file name= j13wwA.3i
Description= "J-13 well water, six minerals suppressed"
Version number= 3245   Stage number= 01
Created 10/07/90    Creator= T.J. Wolery
Revised 10/07/90    Revisor= T.J. Wolery

  Water from well J-13 at the Nevada Test Site. The composition
is identical to that in the EQ3NR test case input file j13ww.3i,
which is based on data reported by Harrer et al. (1990). Water
from this well is commonly used to represent the groundwater
at the proposed high-level nuclear waste repository at Yucca
Mountain, Nevada.

  Purpose: to initialize the EQ6 test case input file j13wwtuff.6i,
in which this water is reacted with devitrified tuff at 150 C.
Six minerals (quartz, chalcedony, tridymite, pyrophyllite,
maximum microcline, and illite) are suppressed by means of
"nxmod" options. These suppressions have no effect on the EQ3NR
calculation, but will be passed on to j13wwtuff.6i.

                          References

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990,
  Report of the Committee to Review the Use of J-13 Well Water in
  Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence
  Livermore National Laboratory, Livermore, California.

-----------------------------------------------------------------------
Temperature (C)          | 25.00        |Density(gm/cm3)|  1.00000
-----------------------------------------------------------------------
Total Dissolved Salts    |              | mg/kg | mg/l  |*not used
```

Information Only

Electrical Balancing on | | code selects | *not performed

SPECIES	BASIS SWITCH/CONSTRAINT	CONCENTRATION	UNITS OR TYPE
redox		0.3400	eh
na+		45.800	mg/l
sio2(aq)		60.970	mg/l
ca++		13.000	mg/l
k+		5.0400	mg/l
mg++		2.0100	mg/l
li+		0.48000E-01	mg/l
h+		7.4100	ph
hco3-		140.40	mg/l
o2(aq)		5.6000	mg/l
f-		2.1800	mg/l
cl-		7.1400	mg/l
no3-		8.7800	mg/l
so4--		18.400	mg/l
b(oh)3(aq)		0.76600	mg/l
al+++		0.80000E-02	mg/l
mn++		0.12000E-01	mg/l
fe++		0.40000E-01	mg/l
sr++		0.40000E-01	mg/l
hpo4--		0.12000	mg/l

Input Solid Solutions

none			

SUPPRESSED SPECIES	(suppress,replace,augmentk,augmentg)		value
quartz	mineral	suppress	0.00000E+00
chalcedony	mineral	suppress	0.00000E+00
tridymite	mineral	suppress	0.00000E+00
pyrophyllite	mineral	suppress	0.00000E+00
maximum microcline	mineral	suppress	0.00000E+00
illite	mineral	suppress	0.00000E+00

OPTIONS

```
 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
 - LOADING OF SPECIES INTO MEMORY -
   * does nothing
     lists species loaded into memory
 - ECHO DATABASE INFORMATION -
   * does nothing
     lists all reactions
     lists reactions and log K values
     lists reactions, log K values and polynomial coef.
 - LIST OF AQUEOUS SPECIES (ordering) -
   * in order of decreasing concentration
     in same order as input file
 - LIST OF AQUEOUS SPECIES (concentration limit) -
   * all species
     only species > 10**-20 molal
     only species > 10**-12 molal
     not printed
 - LIST OF AQUEOUS SPECIES (by element) -
   * print major species
     print all species
     don't print
 - MINERAL SATURATION STATES -
   * print if affinity > -10 kcals
     print all
     don't print
 - pH SCALE CONVENTION -
   * modified NBS
     internal
     rational
 - ACTIVITY COEFFICIENT OPTIONS -
   * use B-dot equation
     Davies' equation
     Pitzer's equations
 - AUTO BASIS SWITCHING -
   * off
     on
 - PITZER DATABASE INFORMATION -
   * print only warnings
     print species in model and number of Pitzer coefficients
     print species in model and names of Pitzer coefficients
 - PICKUP FILE -
   * write pickup file
     don't write pickup file
 - LIST MEAN IONIC PROPERTIES -
   * don't print
     print
 - LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
   * print
     don't print
```

Information Only

```
 - CONVERGENCE CRITERIA -
   * test both residual functions and correction terms
     test only residual functions
-----------------------------------------------------------------------
DEBUGGING SWITCHES (o-off, 1,2-on, default is off)
-----------------------------------------------------------------------
0  generic debugging information                                        2
0  print details of pre-Newton-Raphson iteration                        2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                              2
0  print details of stoichiometric factors calculation
0  write reactions on RLIST
0  list stoichiometric concentrations of master species
0  request iteration variables to be killed
-----------------------------------------------------------------------
DEVELOPMENT OPTIONS  (used for code development)
-----------------------------------------------------------------------
 none
-----------------------------------------------------------------------
TOLERANCES                    (desired values)        (defaults)
-----------------------------------------------------------------------
      residual functions |                        |1.e-10
        correction terms |                        |1.e-10
        saturation state |                        |0.5
number of N-R iterations |                        |30
-----------------------------------------------------------------------
```

The following is the EQ3NR **input** file for the spiked J-13 well water used in the second EQ6 **input** file (reaction of groundwater with spent nuclear fuel) presented in Appendix E.

The EQ3NR **input** file (**j13wwsf.3i**), spiked J-13 well water ("W" format):

```
EQ3NR input file name= j13wwsf.3i
Description= "J-13 well water, with traces of spent fuel components"
Version number= 3245   Stage number= 01
Created 10/29/90    Creator= T.J. Wolery
Revised 11/30/90    Revisor= T.J. Wolery

  Water from well J-13 at the Nevada Test Site, spiked with
trace amounts of spent nuclear fuel components. The composition
is otherwise identical to that in the EQ3NR test case input file
j13ww.3i, which is based on data reported by Barrer et al. (1990).
Water from this well is commonly used to represent the groundwater
at the proposed high-level nuclear waste repository at Yucca
Mountain, Nevada.

  Purpose: to initialize the EQ6 test case input file j13wwsf.6i,
which simulates the interaction of J-13 well water with spent
nuclear fuel. This test case also tests the ability of EQ3NR to
handle a system containing many components.

                              References

Barrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990,
  Report of the Committee to Review the Use of J-13 Well Water in
  Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence
  Livermore National Laboratory, Livermore, California.

endit.
     tempc=          25.
       rho=      1.00000    tdspkg=          0.     tdspl=          0.
       fep=        0.340    uredox=
     tolbt=           0.     toldl=          0.    tolsat=          0.
    itermx=  0
*              1    2    3    4    5    6    7    8    9   10
  iopt1-10=   -1    0    0    0    0    0    0    0    0    0
  iopg1-10=    0    0    0    0    0    0    0    0    0    0
  iopr1-10=    0    0    0    0    0    0    0    0    0    0
 iopr11-20=    0    0    0    0    0    0    0    0    0    0
  iodb1-10=    0    0    0    0    0    0    0    0    0    0
     uebal= none
     nxmod=  0
*
data file master species= na+
   switch with species=
   jflag=  2   csp= 45.8
data file master species= sio2(aq)
   switch with species=
   jflag=  2   csp= 60.970
data file master species= ca++
   switch with species=
   jflag=  2   csp= 13.0
```

Information Only

```
data file master species= k+
   switch with species=
   jflag=  2   csp= 5.04
data file master species= mg++
   switch with species=
   jflag=  2   csp= 2.01
data file master species= li+
   switch with species=
   jflag=  2   csp= 0.048
data file master species= h+
   switch with species=
   jflag= 16   csp= -7.41
data file master species= hco3-
   switch with species=
   jflag=  2   csp= 140.4
data file master species= o2(aq)
   switch with species=
   jflag=  2   csp= 5.6
data file master species= f-
   switch with species=
   jflag=  2   csp= 2.18
data file master species= cl-
   switch with species=
   jflag=  2   csp= 7.14
data file master species= no3-
   switch with species=
   jflag=  2   csp= 8.78
data file master species= so4--
   switch with species=
   jflag=  2   csp= 18.4
data file master species= b(oh)3(aq)
   switch with species=
   jflag=  2   csp= 0.766
data file master species= al+++
   switch with species=
   jflag=  2   csp= 0.008
data file master species= mn++
   switch with species=
   jflag=  2   csp= 0.012
data file master species= fe++
   switch with species=
   jflag=  2   csp= 0.040
data file master species= sr++
   switch with species=
   jflag=  2   csp= 0.040
data file master species= hpo4--
   switch with species=
   jflag=  2   csp= 0.120
*
data file master species= am+++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= cs+
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= cu++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= i-
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= np++++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= ni++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= pb++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= pu++++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= ra++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= seo3--
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= sn++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= tco4-
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= th++++
   switch with species=
   jflag=  0   csp= 1.e-12
data file master species= uo2++
   switch with species=
   jflag=  0   csp= 1.e-12
endit.
```

Information Only

The EQ3NR input file (j13wwsf.3i), spiked J-13 well water ("D" format):

```
EQ3NR input file name= j13wwsf.3i
Description= "J-13 well water, with traces of spent fuel components"
Version number= 3245    Stage number= 01
Created 10/29/90     Creator= T.J. Wolery
Revised 11/30/90     Revisor= T.J. Wolery

  Water from well J-13 at the Nevada Test Site, spiked with
trace amounts of spent nuclear fuel components. The composition
is otherwise identical to that in the EQ3NR test case input file
j13ww.3i, which is based on data reported by Harrer et al. (1990).
Water from this well is commonly used to represent the groundwater
at the proposed high-level nuclear waste repository at Yucca
Mountain, Nevada.

  Purpose: to initialize the EQ6 test case input file j13wwsf.6i,
which simulates the interaction of J-13 well water with spent
nuclear fuel. This test case also tests the ability of EQ3NR to
handle a system containing many components.

                          References

Harrer, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., 1990,
  Report of the Committee to Review the Use of J-13 Well Water in
  Nevada Nuclear Waste Storage Investigations: UCID-21867, Lawrence
  Livermore National Laboratory, Livermore, California.
```

Temperature (C)	25.00	Density(gm/cm3)	1.00000
Total Dissolved Salts		mg/kg | mg/l	*not used
Electrical Balancing on		code selects	*not performed

SPECIES	BASIS SWITCH/CONSTRAINT	CONCENTRATION	UNITS OR TYPE
redox		0.3400	eh
na+		45.800	mg/l
sio2(aq)		60.970	mg/l
ca++		13.000	mg/l
k+		5.0400	mg/l
mg++		2.0100	mg/l
li+		0.48000E-01	mg/l
h+		7.4100	ph
hco3-		140.40	mg/l
o2(aq)		5.6000	mg/l
f-		2.1800	mg/l
cl-		7.1400	mg/l
no3-		8.7800	mg/l
so4--		18.400	mg/l
b(oh)3(aq)		0.76600	mg/l
al+++		0.80000E-02	mg/l
mn++		0.12000E-01	mg/l
fe++		0.40000E-01	mg/l
sr++		0.40000E-01	mg/l
hpo4--		0.12000	mg/l
am+++		0.10000E-11	molality
cs+		0.10000E-11	molality
cu++		0.10000E-11	molality
i-		0.10000E-11	molality
np++++		0.10000E-11	molality
ni++		0.10000E-11	molality
pb++		0.10000E-11	molality
pu++++		0.10000E-11	molality
ra++		0.10000E-11	molality
seo3--		0.10000E-11	molality
sn++		0.10000E-11	molality
tco4-		0.10000E-11	molality
th++++		0.10000E-11	molality
uo2++		0.10000E-11	molality

Input Solid Solutions

none		

SUPPRESSED SPECIES	(suppress,replace,augmentk,augmentg)	value
none		

```
OPTIONS

 - SOLID SOLUTIONS -
   * ignore solid solutions
     process hypothetical solid solutions
     process input and hypothetical solid solutions
```

Information Only

```
- LOADING OF SPECIES INTO MEMORY -
  * does nothing
    lists species loaded into memory
- ECHO DATABASE INFORMATION -
  * does nothing
    lists all reactions
    lists reactions and log K values
    lists reactions, log K values and polynomial coef.
- LIST OF AQUEOUS SPECIES (ordering) -
  * in order of decreasing concentration
    in same order as input file
- LIST OF AQUEOUS SPECIES (concentration limit) -
  * all species
    only species > 10**-20 molal
    only species > 10**-12 molal
    not printed
- LIST OF AQUEOUS SPECIES (by element) -
  * print major species
    print all species
    don't print
- MINERAL SATURATION STATES -
  * print if affinity > -10 kcals
    print all
    don't print
- pH SCALE CONVENTION -
  * modified NBS
    internal
    rational
- ACTIVITY COEFFICIENT OPTIONS -
  * use B-dot equation
    Davies' equation
    Pitzer's equations
- AUTO BASIS SWITCHING -
  * off
    on
- PITZER DATABASE INFORMATION -
  * print only warnings
    print species in model and number of Pitzer coefficients
    print species in model and names of Pitzer coefficients
- PICKUP FILE -
  * write pickup file
    don't write pickup file
- LIST MEAN IONIC PROPERTIES -
  * don't print
    print
- LIST AQUEOUS SPECIES, ION SIZES, AND HYDRATION NUMBERS -
  * print
    don't print
- CONVERGENCE CRITERIA -
  * test both residual functions and correction terms
    test only residual functions
-----------------------------------------------------------------
DEBUGGING SWITCHES (o-off, 1,2-on, default is off)
-----------------------------------------------------------------
0  generic debugging information                                 2
0  print details of pre-Newton-Raphson iteration                2
0  print details of Newton-Raphson iteration
0  print details of stoichiometric factors                      2
0  print details of stoichiometric factors calculation
0  write reactions on RLIST
0  list stoichiometric concentrations of master species
0  request iteration variables to be killed
-----------------------------------------------------------------
DEVELOPMENT OPTIONS  (used for code development)
-----------------------------------------------------------------
 none
-----------------------------------------------------------------
TOLERANCES                  (desired values)        (defaults)
-----------------------------------------------------------------
      residual functions |                        |1.e-10
        correction terms |                        |1.e-10
        saturation state |                        |0.5
number of N-R iterations |                        |30
-----------------------------------------------------------------
```

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