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Subject: Recommended Change in the FMT Thermodynamic Data Base:

After Giambalvo (2002) recommended updated parameters for the chemical equilibrium code FMT, Neck et al. (2002) reported a summary and critical analysis of the published data of several investigators from which they derived hydrolysis constants for thorium hydroxides (Neck et al., 2002, Table 1). At values of pH greater than approximately 6, the primary aqueous thorium species is $Th(OH)_4$. Their value for the logarithm of the hydrolysis constant for $Th(OH)_4$ ($\log {}^*\beta^0_{1,4}$) is -17.5 ± 1.0 for the following reaction:

$$Th^{4+} + 4H_2O = Th(OH)_4 + 4H^+ \qquad \log {}^*\beta^0_{1,4} = -17.5 \pm 1.0 \tag{1}$$

I recommend revising the value of μ^0/RT (dimensionless standard free energy of formation) for $Th(OH)_4$ in the FMT data base to a value derived from that hydrolysis constant using values of μ^0/RT now in the FMT data base for Th^{4+}, H_2O, and H^+. The new derived value of μ^0/RT for $Th(OH)_4$ ($(\mu^0/RT)_{Th(OH)_4(aq)}$) that I recommend was calculated as follows:

$$\ln {}^*\beta^0_{1,4} = -\mu_r^0/RT \tag{2}$$

and

$$\log {}^*\beta^0_{1,4} = \ln {}^*\beta^0_{1,4} (\log e) = (-\mu_r^0/RT)(\log e) \tag{3}$$

where

e = base of natural logarithm (ln)

μ_r^0 = the standard free energy change per mol for the reaction described by Equation (1).

R = ideal gas constant

T = absolute temperature

Solving Equation (3) for μ_r^0/RT and inserting values,

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$\mu_r^0/RT = -\log {}^*\beta^0_{1,4} / \log e = -(-17.5)/0.43429 = 40.2957$

For the reaction described in Equation (1),

$$\mu_r^0/RT = \left(\mu^0/RT\right)_{Th(OH)_4(aq)} + 4\left(\mu^0/RT\right)_{H^+} - \left(\mu^0/RT\right)_{Th^{4+}} - 4\left(\mu^0/RT\right)_{H_2O} \quad (4)$$

Solving Equation (4) for $(\mu^o/RT)_{Th(OH)4(aq)}$,

$$\left(\mu^0/RT\right)_{Th(OH)_4(aq)} = \mu_r^0/RT - 4\left(\mu^0/RT\right)_{H^+} + \left(\mu^0/RT\right)_{Th^{4+}} + 4\left(\mu^0/RT\right)_{H_2O} \quad (5)$$

The following values of μ^0/RT for Th^{4+}, H_2O, and H^+ are now in the FMT data base:

$\left(\mu^0/RT\right)_{H^+} = 0$

$\left(\mu^0/RT\right)_{Th^{4+}} = -284.227$

$\left(\mu^0/RT\right)_{H_2O} = -95.6635$

Substituting the above values into Equation (5),

$\left(\mu^0/RT\right)_{Th(OH)_4(aq)} = 40.2957 - 4(0) + (-284.227) + 4\,(-95.6635)$

$\left(\mu^0/RT\right)_{Th(OH)_4(aq)} = 40.2957 - 4(0) + (-284.227) + (-382.6540)$

$\left(\mu^0/RT\right)_{Th(OH)_4(aq)} = -626.5853$

I recommend a new value for $\left(\mu^0/RT\right)_{Th(OH)_4(aq)} = -626.5853$

Yongliang Xiong (SNL Org. 6822) also estimated a value for $\left(\mu^0/RT\right)_{Th(OH)_4(aq)}$ from a recommended range of 10^{-7} to 10^{-9} M by Hummel and Berner (2002, p. 7) for solubilities of ThO_2(am) in the pH region where $Th(OH)_4$(aq) dominates (pH = approximately 6 to greater than 12). They considered the solubility of 10^{-7} M as the conservative limit. Using this conservative limit, he set log K = 10^{-7} for the reaction:

$$ThO_2\,(am) + 2H_2O = Th(OH)_4\,(aq). \quad (6)$$

Therefore, by an analysis similar to that described above, the change of μ_r^0/RT for Reaction (6) is 16.121. Values of $\left(\mu^0/RT\right)_{H_2O}$ and $\left(\mu^0/RT\right)_{ThO_2(am)}$ in the FMT data base are –95.6635 and –451.408, respectively. Using those values, Yongliang calculated a value of $\left(\mu^0/RT\right)_{Th(OH)_4(aq)}$ as follows, in good agreement with my recommended value:

$\left(\mu^0/RT\right)_{Th(OH)_4(aq)} = 16.121 - 2 \times 95.6635 - 451.408 = -626.614.$

Giambalvo (2002) calculated the current value of $(\mu^0/RT)_{Th(OH)_4(aq)}$ in the FMT data base, which is –622.4700. She calculated that value as described in the following excerpt from Giambalvo (2002):

"2. The μ^0/RT value for $Th(OH)_4(aq)$ is derived from a traceable data set (Ryan and Rai, 1987) as follows. From the low pH (<7) data of Ryan and Rai (1987), Felmy et al. (1991) calculated log K_{sp} = –45.5 for the dissolution reaction:

$$ThO_2(am) + 2H_2O = Th^{4+} + 4H_2O \qquad \log K_{sp} = -45.5.$$

"In the pH range where $Th(OH)_4(aq)$ is the dominant Th species in solution (pH = 7-14), Ryan and Rai's (1987) data yield a Th solubility of $10^{-8.8}$ mol/L, or:

$$ThO_2(am) + 2H_2O = Th(OH)_4(aq) \qquad \log K_{sp} = -8.8.$$

"Differencing these equations yields the complexation constant for $Th(OH)_4$, which is easily converted to μ^o/RT:

$$Th^{4+} + 4\ OH^- = Th(OH)_4(aq) \qquad \log K = 36.7.$$

"This calculation assumes that all Pitzer parameters related to $Th(OH)_4(aq)$ are zero (i.e., the activity of $Th(OH)_4$ is independent of ionic strength). The complexation constant obtained in this way is similar to that used in the baseline An(IV) model and to that obtained from a similar analysis of the solubility data presented by Felmy et al. (1991) (log K = 36.9 and 37.0, respectively). The log K calculated from either the Ryan and Rai (1987) or the Felmy et al. (1991) data set results in a conservative prediction of Th solubility at neutral and alkaline pH, because, in both experiments, measured solubilities in the pH range 7-14 were at the detection limit of the measurement technique."

Neck et al. (2001) and Neck et al. (2002, Table 1) critically reviewed and analyzed data on the solubility of tetravalent actinides from several publications and selected log K_{sp} = –47.0 for the reaction:

$$ThO_2(am) + 2H_2O = Th^{4+} + 4H_2O \qquad \log K_{sp} = -47.0 \qquad (7)$$

Felmy et al. (1991) calculated log K_{sp} = -45.5 for the same reaction, and Giambalvo (2002) used that value as described above. Neck et al. (2001) state that the interpretation of Felmy et al. (1991), which neglects all hydrolysis species except $Th(OH)_4(aq)$ at low pH, is not consistent with the results of potentiometric titration and solvent extraction studies.

I recommend the following uncertainty analysis for solubility calculations with FMT using the recommended new value: Calculate thorium solubility values with FMT using the new recommended value for $(\mu^0/RT)_{Th(OH)_4(aq)}$ and compare them with data in the APPENDIX of Felmy et al. (1991) for thorium solubility in 3.0 M NaCl at values of pH(obs) above 3.6.

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