

# Thermodynamic model for the solubility of thorium dioxide in the Na<sup>+</sup>-Cl<sup>-</sup>-OH<sup>-</sup>-H<sub>2</sub>O system at 23 °C and 90 °C

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**Summary.** Data are extremely limited on the effects of temperature on crystallinity and the resulting changes in solubility products of thermally transformed thorium oxide phases. Such data are required to reliably predict thorium behavior in high-level waste repositories where higher than ambient temperatures are expected. Solubility studies were conducted as a function of pH and time and at 0.1 M NaCl for 1) ThO<sub>2</sub>(am) at 23 °C, 2) ThO<sub>2</sub>(am→c), a thermally transformed amorphous thorium hydrous oxide at 90 °C, and 3) ThO<sub>2</sub>(c) at 23 °C and 90 °C. Results show that when ThO<sub>2</sub>(am) is heated to 90 °C, it transforms to a relatively insoluble and crystalline solid [ThO<sub>2</sub>(am→c)]. At a fixed pH, the observed solubility of ThO<sub>2</sub>(am) at 23 °C is more than 11 orders of magnitude greater than those for ThO<sub>2</sub>(c) at 23 °C or of ThO<sub>2</sub>(am→c) and ThO<sub>2</sub>(c) at 90 °C. Solubility data were interpreted using the Pitzer ion-interaction model. The log of the solubility product for the thorium dioxide dissolution reaction [ThO<sub>2</sub>(s) + 2 H<sub>2</sub>O ⇌ Th<sup>4+</sup> + 4 OH<sup>-</sup>] was determined to be -44.9 for ThO<sub>2</sub>(am) at 23 °C, ≥ -56.9 for ThO<sub>2</sub>(c) at 23 °C, and -51.4 for ThO<sub>2</sub>(c) at 90 °C. At 90 °C, a relatively less crystalline phase, ThO<sub>2</sub>(am→c), showed slightly higher solubility (log K<sub>sp</sub> = -49.2) than crystalline ThO<sub>2</sub>(c).

## Introduction

Thorium hydrous oxide [ThO<sub>2</sub>(am)] is generally used to estimate leachable thorium concentrations under waste repository conditions (e.g., JNC [1]). The temperatures in high-level nuclear waste repositories are expected to be considerably higher than ambient and may reach 100 °C. Under these conditions, predictions of leachable thorium require a solubility model of the appropriate thorium oxide phase as a function of temperature. Data are extremely limited on the effects of temperature on crystallinity and resulting changes in the solubility products of thermally transformed phases. Prasad *et al.* [2] showed that the transformation of ThO<sub>2</sub>(am) to crystalline ThO<sub>2</sub> is slow at 25 °C (about 270 days) and much more rapid (about 12 days) at 100 °C. The solubility product (K<sub>sp</sub>) of crystalline ThO<sub>2</sub> [ThO<sub>2</sub>(c)] has been shown to be approximately eight orders of magnitude lower than that for the hydrous oxide [3, 4]

at room temperature. Therefore, potential thorium concentrations in aqueous solutions contacting failed repositories may be many orders of magnitude lower than indicated by measurements of ThO<sub>2</sub>(am) solubility at 25 °C.

At 25 °C, the precipitation/dissolution kinetics of ThO<sub>2</sub>(c) are not known, which makes it difficult to accurately ascertain the solubility product of ThO<sub>2</sub>(c) at this temperature. Fortunately, in addition to being relevant to expected repository conditions, a moderate increase in temperature accelerates the precipitation/dissolution kinetics such that the solubility of ThO<sub>2</sub>(c) can be approached from both the oversaturation and undersaturation directions. Therefore, it is possible to study the effect of temperature on the crystallinity of thorium hydrous oxides as well as the solubility products of these solid phases at elevated temperatures. While the solubility product of ThO<sub>2</sub>(c) can be calculated (see Appendix A), experimental verification is required due to uncertainties<sup>1</sup> in the thermodynamic quantities for ThO<sub>2</sub>(c), C<sub>p</sub><sup>o</sup> for Th<sup>4+</sup>, and the absence of C<sub>p</sub><sup>o</sup> values for aqueous Th<sup>4+</sup> at temperatures >55 °C. Thus, the primary objectives of this study were to demonstrate the effects of elevated temperature on the degree of crystallinity of ThO<sub>2</sub> and the consequent effects on the solubilities of the thermally transformed phases.

## Experimental procedure

### Preparation of materials

Stock solutions were prepared from reagent grade Th(NO<sub>3</sub>)<sub>4</sub> · 4 H<sub>2</sub>O(c), concentrated NaOH(aq) (Anachemia), concentrated reagent grade HCl(aq) (GFS), and reagent grade NaCl(c) (Alfa Products).

A 100 g per liter solution of thorium was prepared in 0.1 M HNO<sub>3</sub>(aq) using the reagent grade Th(NO<sub>3</sub>)<sub>4</sub> · 4 H<sub>2</sub>O. Stock solutions of 5.0 M NaOH and 1.0 M NaCl were prepared using the reagents mentioned above. Deionized distilled water was used in all solution preparations.

<sup>1</sup> For example, the reported C<sub>p</sub><sup>o</sup> values for Th<sup>4+</sup> vary considerably. Values at 298 K are -60 J · mol<sup>-1</sup> · K<sup>-1</sup> based on Morss and McCue's [5] data as recalculated by Hovey [6] and -224 J · mol<sup>-1</sup> · K<sup>-1</sup> reported by Hovey [6]; 111 and -228 J · mol<sup>-1</sup> · K<sup>-1</sup> at 303 K reported by Apelblat and Sahar [7] and Hovey [6], respectively. Hovey's data are most recent and appear more reliable and thus were selected for calculations reported here. However, Hovey's heat capacity measurements extend to only 55 °C; thus, extrapolation to higher temperatures is dependent upon the reliability of the extrapolation method.

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**Table 1.** Comparison of filtered and unfiltered aqueous thorium concentrations from solutions maintained at 90 °C.

pH	log ( $C_{Th}/\text{mol} \cdot \text{kg}^{-1}$ ) <sup>a</sup>	
	filtered	unfiltered
2.51	-5.52	-5.50
2.57	-5.25	-5.29
2.69	-5.46	-5.48
2.78	-5.48	-5.48

a: All solutions were centrifuged at 5000 rpm for 10 to 15 minutes. Amicon Centricon-30 filters (30,000 MW cutoff) were used.

ThO<sub>2</sub>(am) was precipitated from the nitrate solution by adding an aliquot to 10 mL of water and adjusting the pH to about 10.5 using the NaOH(aq) stock solution. The resulting suspensions were centrifuged and the supernatant discarded. Soluble nitrates, chlorides, and sodium were removed by washing twice with 10-mL aliquots of water.

ThO<sub>2</sub>(c) was prepared by initially dissolving a quantity of Th(NO<sub>3</sub>)<sub>4</sub> · 4 H<sub>2</sub>O(c) in hot 0.3 M HNO<sub>3</sub>(aq). Oxalic acid dihydrate was then vigorously stirred into the solution at 75 °C. The resulting precipitate and solution were then allowed to rest for 30 minutes between 50 and 75 °C and then filtered through a coarse sintered glass filter. ThO<sub>2</sub>(c) was then produced by firing the oxalate in air for 2 hours at 750 °C. X-ray diffraction (XRD) analysis confirmed the solid to be crystalline ThO<sub>2</sub>.

### Equilibration, sampling, and analysis

All experiments were conducted on a benchtop at room temperature (23 ± 2 °C)<sup>2</sup> or at 90 °C. A heating block was used for the experiments at 90 °C. For each experiment, several milligrams of ThO<sub>2</sub>(am) or ThO<sub>2</sub>(c) were loaded into a number of 50-mL polypropylene centrifuge tubes containing approximately 38 mL of 0.1 M NaCl(aq). The pH of the suspensions was adjusted using HCl, and the tubes were then sealed with Nalgene caps. The amount of HCl used in the pH adjustments was recorded and used in conjunction with the added NaCl to calculate the final chloride molality. The suspensions were shaken continuously over the course of the experiments.

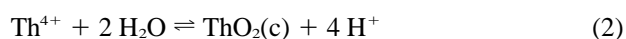
Aliquots of the suspensions were periodically extracted to determine the thorium concentration in the aqueous phase and to characterize the degree of solid phase crystallinity. Degree of crystallinity was assessed by XRD, and thorium concentrations were determined by inductively coupled plasma mass spectroscopy (ICP-MS). The analytical errors in thorium concentrations are estimated to be less than 10% in all cases. The pH of the suspensions was measured using a semi-micro Orion Ross combination electrode calibrated against standard buffers with pH values corresponding to the range in experimental pH values. Standardizations were carried out at the experimental temperatures with buffers and electrodes maintained at 23 or 90 °C. Specific procedures for the 90 °C experiments are detailed below.

<sup>2</sup> For data interpretations, 23 ± 2 °C was considered to be identical to 25 °C.

Aliquots of suspensions equilibrated at 23 or 90 °C were centrifuged at 5000 rpm for 10 to 15 minutes filtered through Amicon Centricon-30 filters (30,000 MW cutoff), acidified, and then analyzed for thorium. Thorium concentrations in unfiltered but centrifuged and filtered samples were similar, indicating that a significant amount of colloidal material was absent and that the results from the unfiltered samples are reliable (Table 1). This is particularly significant to the experiments at 90 °C where available filters may not be stable.

For the 90 °C experiments, all implements (e.g., pipette tips, sampling tubes, rinse water, pH buffers, centrifuge and centrifuge containers) that contacted or could change sample temperatures prior to pH measurement or sampling were maintained at 90 °C. For pH measurements, the electrode was rinsed with 90 °C water before being placed in samples. Maximum temperature decrease during pH measurements was about 5 °C. Subsequently, suspensions were centrifuged and small aliquots 1) from all suspensions were filtered through Amicon filters, equilibrated at 90 °C for 1 hour, and 2) a few selected samples were withdrawn for analysis. The filtered and unfiltered aliquots were then analyzed by ICP-MS. The analytical data obtained in this study are listed in Appendix Tables B.1 through B.4.

Three sets of experiments ranging in pH and amount of ThO<sub>2</sub>(am) were conducted at 23 °C (Table 2). All three sample sets were subsequently heated to 90 °C. Heating of ThO<sub>2</sub>(am) suspensions was expected [2] to result in increasing crystallinity and decreasing solubility [3] due to the formation of crystalline ThO<sub>2</sub>. For example, heating ThO<sub>2</sub>(am) suspensions in equilibrium with soluble Th<sup>4+</sup> or the samples in which the ThO<sub>2</sub>(am) dissolves completely, will result in the formation of crystalline ThO<sub>2</sub> either through solid-solid transformation (Eq. (1)) or by precipitation (Eq. (2)). The precipitation mechanism (Eq. (2)) will also be accompanied by an increase in H<sup>+</sup> concentration in proportion to the amount of precipitated thorium.



Therefore, to obtain a large range in pH values of heated suspensions, initial ThO<sub>2</sub>(am) suspensions for subsequent use in the 90 °C experiments were prepared such that the samples spanned a large pH range, even though the ThO<sub>2</sub>(am) precipitates were expected to completely solubilize in the low pH solutions at 23 °C. We also determined the solubility of ThO<sub>2</sub>(c) at 23 and 90 °C (see Sets IV and V, Table 2).

## Results and discussion

### Thorium dioxide solubility at 23 °C

The ThO<sub>2</sub>(am) solubility at 23 °C is highly dependent on pH (Fig. 1). For example, at pH values > 4, the solubility decreases several orders of magnitude for one unit increase in pH. The constant aqueous thorium concentrations at pH values < 4 are due to complete dissolution of the solid phase. Thorium concentrations at different equilibration periods are similar to each other at a given pH, indicating

**Table 2.** Listing of experiments conducted in this study.

Set number <sup>a</sup>	Solid phase	pH range	Equilibration periods (days)	Temperature (°C)
Set I	ThO <sub>2</sub> (am)	2.0 to 4.7	6, 21	23
	ThO <sub>2</sub> (am→c) <sup>b</sup>	1.5 to 2.2	76	90
Set II	ThO <sub>2</sub> (am)	4.2 to 5.1	5, 13	23
	ThO <sub>2</sub> (am→c) <sup>b</sup>	2.0 to 2.1	52	90
Set III	ThO <sub>2</sub> (am)	1.9 to 4.2	7, 22	23
	ThO <sub>2</sub> (am→c) <sup>b</sup>	1.9 to 3.0	76	90
Set IV	ThO <sub>2</sub> (c) <sup>c</sup>	1.3 to 3.6	11, 87, 687, 794 <sup>d</sup>	23
Set V	ThO <sub>2</sub> (c) <sup>c</sup>	1.4 to 3.5	12	90

a: The total approximate amounts of thorium solid phase used in each sample from different sets were 115 mg for Sets I and II, 5 mg in Set III, and 10 to 500 mg in Sets IV and V (the largest amounts of solid were used in low pH regions of Sets IV and V).

b: This solid phase resulted from heating the ThO<sub>2</sub>(am) to 90°C.

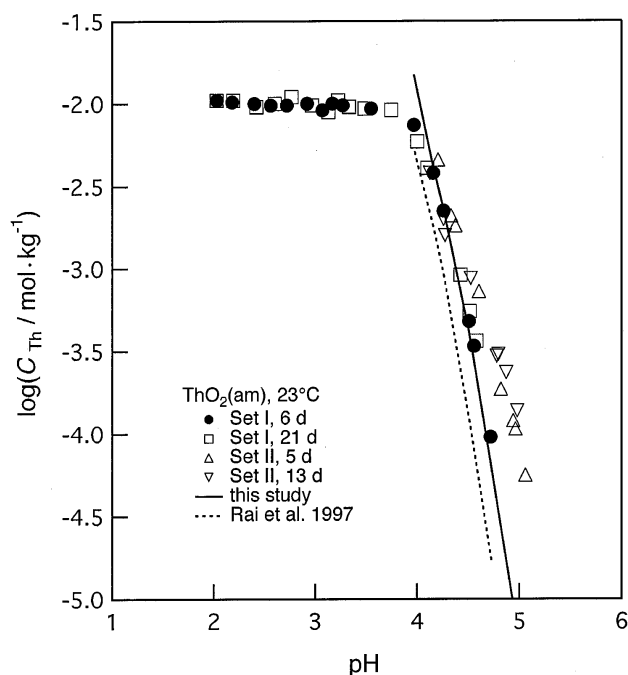
c: Produced by firing thorium oxalate at 750°C, see text for details.

d: The 794-day analyses correspond to samples that were equilibrated at 23°C for 779 days and maintained at 90°C for 14 days and then readjusted to 23°C for one day.

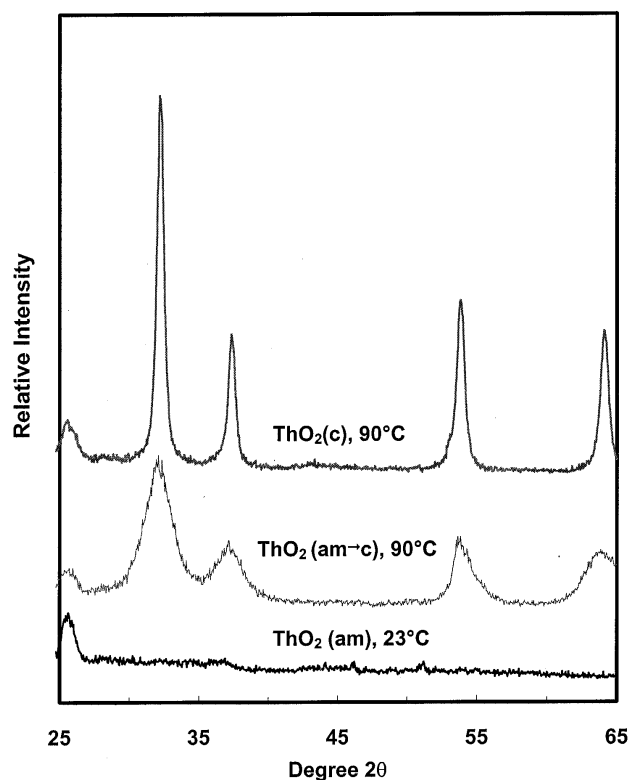
that steady-state concentrations are reached in <5 days. X-ray diffraction analyses indicate that the equilibrated solid phases are amorphous (Fig. 2). Previous studies [8–10] on the solubility of ThO<sub>2</sub>(am) have shown that equilibrium with these precipitates is reached within a few days. Therefore, the results obtained in this study, in conjunction with data available in the literature, can be used to interpret these data for equilibrium with ThO<sub>2</sub>(am).

The solubility of ThO<sub>2</sub>(c) as a function of pH at 23°C was found to be approximately 9 to 12 orders of magnitude lower than the solubility of ThO<sub>2</sub>(am) (Fig. 3). Aqueous thorium concentrations increased slightly with an increase in the equilibration period from 11 days to 687 days, but were similar to each other at longer equilibration periods,

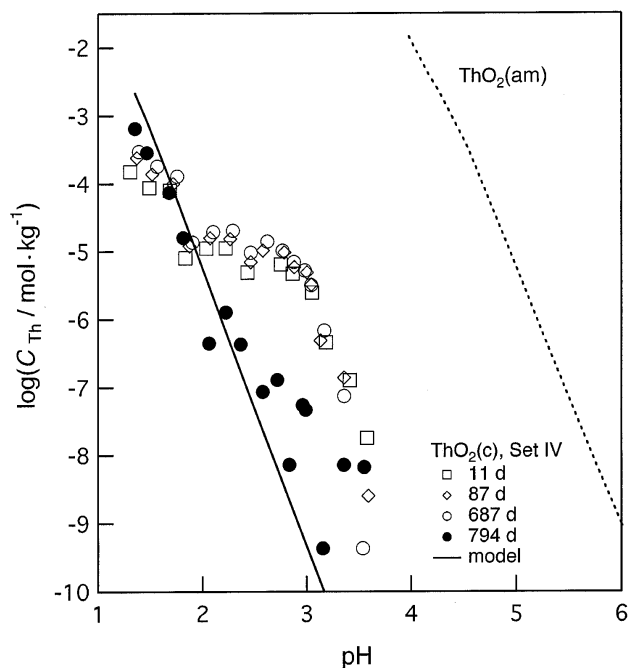
indicating that steady-state concentrations are reached by 687 days. At <687 days, aqueous thorium concentrations appear to be nearly independent of pH between pH values of 2 and 3. A continuous decrease in thorium concentrations is expected under these acidic conditions with increasing pH. The reasons are not known for the observed lack of dependence of thorium concentrations on pH in the middle pH range; however, this behavior may be due to the presence of a finite amount of a less crystalline material (estimated from these experiments to be about one percent).



**Fig. 1.** Experimental ThO<sub>2</sub>(am) solubilities in 0.1 M NaCl at 23°C plotted as the logarithm of total thorium versus measured pH. The dotted line represents predicted solubility of ThO<sub>2</sub>(am) using the modeling parameters reported in Tables 3 and 4.



**Fig. 2.** X-ray diffraction patterns for the solid ThO<sub>2</sub> phases examined in this study [(am) = amorphous, (am→c) = transformation of amorphous phase when heated to 90°C, (c) = fully crystalline phase prepared by firing thorium oxalate at 750°C].

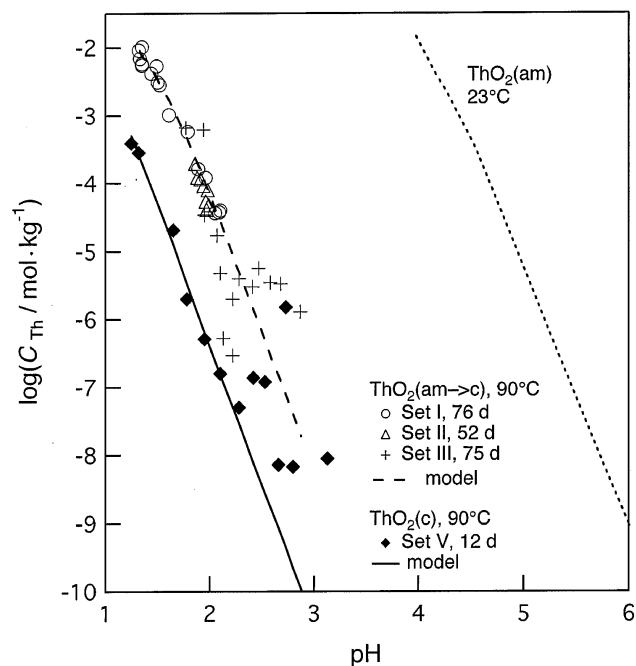


**Fig. 3.** Solubility of  $\text{ThO}_2(\text{c})$  at  $23^\circ\text{C}$  and different equilibration periods. The 794 day data represent data from  $\text{ThO}_2(\text{c})$  suspensions that were equilibrated for 779 days at  $23^\circ\text{C}$ , maintained at  $90^\circ\text{C}$  for 14 days, and then readjusted to  $23^\circ\text{C}$  for one day before sampling. Lines represent predicted solubilities of  $\text{ThO}_2(\text{am})$  and  $\text{ThO}_2(\text{c})$  using modeling parameters reported in Tables 3 and 4.

To confirm this hypothesis, we heated the  $\text{ThO}_2(\text{c})$  suspensions, which were previously equilibrated at  $23^\circ\text{C}$  for 779 days, at  $90^\circ\text{C}$  for 14 days; the suspensions were then maintained at  $23^\circ\text{C}$  for one day and sampled (data represented by 794-day equilibration period in Fig. 3; Table B.4) at pH values  $< 2$ . However, the observed thorium concentrations in the pH region 2 to 3 decreased by up to several orders of magnitude and indicated a more continuous decrease in thorium concentrations with the increase in pH. These results indicate that heating the suspensions may have crystallized the somewhat less crystalline  $\text{ThO}_2$  fraction. Although the aqueous thorium concentrations reached steady state at pH values  $< 2$  at longer equilibration periods, it is not known whether the samples reached equilibrium. We believe equilibrium may have been reached. This hypothesis is supported by the data of Prasad *et al.* [2], wherein  $\text{ThO}_2(\text{am})$  crystallized at  $> 270$  days, indicating that precipitation dissolution kinetics, although not rapid, are certainly achievable at longer equilibration periods. In addition, upon heating, a decrease in thorium concentrations from the 687-day steady-state concentrations between pH 2 and 3 suggests that for a given pH the  $\text{ThO}_2(\text{c})$  solubility cannot be higher than that observed at 687 days. Thus, these data can be used to set limits for the solubility of  $\text{ThO}_2(\text{c})$  at  $23^\circ\text{C}$ .

### Thorium dioxide solubility at $90^\circ\text{C}$

At  $90^\circ\text{C}$ , both the measured pH and thorium concentrations in the suspensions originally containing  $\text{ThO}_2(\text{am})$  are con-



**Fig. 4.** Experimental  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  and  $\text{ThO}_2(\text{c})$  solubilities in 0.1 M NaCl at  $90^\circ\text{C}$  plotted as the logarithm of total thorium versus measured pH.  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  data are for sample Sets I to III that were originally equilibrated at  $23^\circ\text{C}$  and then equilibrated at  $90^\circ\text{C}$  (for details see Appendix B). The lines represent predicted solubilities of various thorium solid phases using the modeling parameters reported in Tables 3 and 4. Although not plotted, the  $\text{ThO}_2(\text{c})$  solubility line at  $23^\circ\text{C}$  falls between the  $\text{ThO}_2(\text{am}(\text{C}))$  and  $\text{ThO}_2(\text{c})$  at  $90^\circ\text{C}$ .

siderably lower than those for identical samples equilibrated at  $23^\circ\text{C}$  (Fig. 4 and Appendix Tables B.1 through B.3). Thus, at a given pH, the thorium concentration is approximately 11 orders of magnitude lower at  $90^\circ\text{C}$  than at  $23^\circ\text{C}$ . However, it must be reiterated that upon heating each sample both pH and thorium concentration decreased. These decreases in pH and thorium concentration must result, as stated previously, from the transformation of  $\text{ThO}_2(\text{am})$  to a more crystalline form of  $\text{ThO}_2$ . This conclusion is consistent with XRD analyses of  $\text{ThO}_2(\text{am})$  samples equilibrated at  $23^\circ\text{C}$  and at  $90^\circ\text{C}$  (Fig. 2). Peaks corresponding to crystalline  $\text{ThO}_2$  are absent from  $\text{ThO}_2(\text{am})$  samples equilibrated at  $23^\circ\text{C}$ , but all of the peaks from  $\text{ThO}_2(\text{am})$  samples heated to  $90^\circ\text{C}$  [hereafter referred to as  $\text{ThO}_2(\text{am} \rightarrow \text{c})$ ] correspond to crystalline  $\text{ThO}_2$ .

At  $90^\circ\text{C}$  and any pH, the observed solubilities of the originally fully crystalline  $\text{ThO}_2$  are approximately two orders of magnitude lower than those for  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  (Fig. 4). Comparison of XRD patterns for  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  and  $\text{ThO}_2(\text{c})$  show that the  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  peaks are broader and considerably lower in intensity than those for  $\text{ThO}_2(\text{c})$  (Fig. 2). It is therefore not surprising to find that the solubility of  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  is greater than the solubility of  $\text{ThO}_2(\text{c})$ . Although the solubilities of  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  and  $\text{ThO}_2(\text{c})$  differ somewhat, both phases are many orders of magnitude ( $> 11$ ) less soluble than  $\text{ThO}_2(\text{am})$  at  $23^\circ\text{C}$ . It also should be noted that there is very little scatter in the data at pH values between 1.0 and 2.2, and that the observed thorium concentrations decrease by about four orders of magnitude with one unit increase in pH. Somewhat more scatter is observed in the data at pH values  $> 2.2$ . The

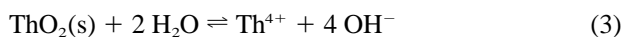
**Table 3.** Dimensionless standard molar Gibbs energies of formation of different species used in calculations.

Species	$\Delta G_f^0/RT$	Reference
For calculations at 25 °C		
Th <sup>4+</sup>	-284.227	[22]
ThO <sub>2</sub> (am)	-450.08	this study
ThO <sub>2</sub> (c)	$\geq -477.72$	this study
H <sub>2</sub> O	-95.663	[23]
OH <sup>-</sup>	-63.435	[23]
For calculations at 90 °C		
Th <sup>4+</sup>	-228.37	see Appendix A
ThO <sub>2</sub> (am → c)	-377.629	this study
ThO <sub>2</sub> (c)	-382.738	this study (experimental)
ThO <sub>2</sub> (c)	-383.27	this study (calculated; see Appendix A)
H <sub>2</sub> O	-75.21	see Appendix A
OH <sup>-</sup>	-46.60	see Appendix A

reason for this scatter is not known, but we surmise it may be related to the crystallinity of the solid phase.

### Thermodynamic model

Rai *et al.* [8] recently developed a model based on the Pitzer ion-interaction formalism [11, 12] to reproduce ThO<sub>2</sub>(am) solubilities in dilute to concentrated NaCl and MgCl<sub>2</sub> solutions at 25 °C. It is of interest to examine how closely that model [8] reproduces the results of this study. The equilibrium of solid thorium dioxide [ThO<sub>2</sub>(s)] with the aqueous solution is the primary reaction (Eq. (3)) investigated in this study.



To evaluate the equilibrium constant for Eq. (3), a coupled, nonlinear, least-squares and chemical equilibrium program INSIGHT [13] was used. In this program, the minimized quantity was the standard deviation,  $\sigma$ , defined as  $\sigma^2 = \sum_{i=1}^N f(x)^2/N$ , where N is the total number of data points, and  $f(x)$  is given by the phase rule equilibrium condition as  $f(x) = \Delta G_{\text{solid}} - \Delta G_{\text{solution}}$ . In the case of ThO<sub>2</sub>(s) solubility (Eq. (3)), this condition gives

$$f(x) = [(\Delta G_f^0/RT)_{\text{ThO}_2(\text{s})}] - [(\Delta G_f^0/RT)_{\text{Th}^{4+}} + 4 (\Delta G_f^0/RT)_{\text{OH}^-} - 2 (\Delta G_f^0/RT)_{\text{H}_2\text{O}}] + \ln [\text{Th}^{4+}] \gamma_{\text{Th}^{4+}} + 4 \ln [\text{OH}^-] \gamma_{\text{OH}^-} - 2 \ln [\text{H}_2\text{O}] \gamma_{\text{H}_2\text{O}} \quad (4)$$

where  $\Delta G_f^0/RT$  is the dimensionless molar Gibbs free energy of formation, quantities in brackets are concentrations, and  $\gamma_i$  is the activity coefficient of the species  $i$ .

Except for  $(\Delta G_f^0/RT)_{\text{ThO}_2(\text{s})}$ , all the values in Eq. (4) are known or are calculated from the aqueous phase thermodynamic model (see Tables 3 and 4) of Pitzer [11, 12] to evaluate  $\gamma_i$ . The value of  $\Delta G_f^0/RT$  for ThO<sub>2</sub>(s) needed to calculate the equilibrium constant for Eq. (3) was obtained by simultaneously fitting all of the appropriate experimental solubility data for the given ThO<sub>2</sub>(s) [in this case ThO<sub>2</sub>(am), ThO<sub>2</sub>(am → c), or ThO<sub>2</sub>(c)].

Predictions made using the Rai *et al.* [8] model are about 0.6 orders of magnitude lower than the observed ThO<sub>2</sub>(am)

**Table 4.** Pitzer ion-interaction parameters at 1 bar and at 23 and 90 °C.

	Binary parameters <sup>a</sup>				Reference
	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$10^3 \text{ C}^\phi$	
For calculations at 25 °C					
Na <sup>+</sup> , Cl <sup>-</sup>	0.0754	0.2770		0.700	[24]
Na <sup>+</sup> , OH <sup>-</sup>	0.0807	0.2982		5.050	[25]
H <sup>+</sup> , Cl <sup>-</sup>	0.1769	0.2973		0.362	[26]
Th <sup>4+</sup> , Cl <sup>-</sup>	1.0920	13.7	-160	-112	[18]
For calculations at 90 °C					
Na <sup>+</sup> , Cl <sup>-</sup>	0.0992	0.3253		-1.47	[24]
Na <sup>+</sup> , OH <sup>-</sup>	0.0868	0.3461		0.08	[25]
H <sup>+</sup> , Cl <sup>-</sup>	0.1536	0.3345		-1.61	[26]
Th <sup>4+</sup> , Cl <sup>-</sup>	1.0920	13.7	-160	-112	[18]
Ternary parameters <sup>b</sup>		Reference			
$^s\theta_{\text{H}^+, \text{Na}^+}$	0.036	[27]			
$^s\theta_{\text{H}^+, \text{Th}^{4+}}$	0.600	[18]			
$^s\theta_{\text{Na}^+, \text{Th}^{4+}}$	0.420	[8]			
$^s\theta_{\text{Cl}^-, \text{OH}^-}$	-0.050	[27]			
$\psi_{\text{H}^+, \text{Na}^+, \text{Cl}^-}$	-0.004	[27]			
$\psi_{\text{Na}^+, \text{OH}^-, \text{Cl}^-}$	-0.006	[27]			
$\psi_{\text{H}^+, \text{Th}^{4+}, \text{Cl}^-}$	0.080	[28]			
$\psi_{\text{Na}^+, \text{Th}^{4+}, \text{Cl}^-}$	0.210	[18]			

a: These values are for 23 °C and are assumed to apply to the 90 °C data (see text for details).

b: These values are of 23 °C and are assumed to apply to the 90 °C data. Because the experiments were conducted in relatively dilute NaCl solutions (0.1 M), the ternary parameters will not significantly affect the calculations.

solubility in 0.1 M NaCl at 23 °C (Fig. 1). However, the observed and predicted dependence of aqueous thorium concentrations on pH are very similar, indicating that the Rai *et al.* [8] model accounts for all the appropriate complexes and ion-interaction parameters expected in this system (Fig. 1). The Rai *et al.* [8] model does not include the hydrolysis reaction for thorium. However, when the hydrolysis reactions reported by Grenthe and Lagerman [14] are included, predicted thorium concentrations with and without the hydrolysis reactions do not differ significantly. It appears that for these solutions, hydrolysis species of thorium never dominate, and that a simpler model, which emphasizes interactions between Th<sup>4+</sup> and Cl<sup>-</sup>, is sufficient to reproduce the data at 23 °C (Fig. 1). A value of  $\Delta G_f^0/RT = -450.08$  for ThO<sub>2</sub>(am) at 23 °C was determined from a fit to the data using the Pitzer ion-interaction parameters reported in Tables 3 and 4 of this report. This value corresponds to a value of -44.9 for the log of the solubility product ( $K_{\text{sp}}$ ; Eq. (3)) of ThO<sub>2</sub>(am). The solubility product determined in this study is very close to the value (-45.5) reported by Felmy *et al.* [9] from a relatively limited data set.

Using the Pitzer ion-interaction parameters, other appropriate thermodynamic data (from Tables 3 and 4 of this report), and the 794-day solubility data, the  $\Delta G_f^0/RT$  value of ThO<sub>2</sub>(c) at 23 °C was calculated to be -477.72 (Fig. 3). While we can not conclusively demonstrate that equilibrium was achieved, these data certainly represent the lower solubility limit of ThO<sub>2</sub>(c) at 23 °C. Thus, the log  $K_{\text{sp}}$  value must be  $\geq -56.9$  for ThO<sub>2</sub>(c) at 23 °C.

**Table 5.** Solubility products ( $K_{sp}$ ) of different thorium dioxide solids [ $\text{ThO}_2(\text{s}) + 2 \text{H}_2\text{O} \rightleftharpoons \text{Th}^{4+} + 4 \text{OH}^-$ ].

Solid	Log $K_{sp}$	Ionic strength	Reference
Values at 25 °C			
$\text{ThO}_2(\text{am})$	$-44.9 \pm 0.5$	0	this study, experimental
	-44.8	< 0.02	[15]
	-45.5	0	[9]
	$-44.7^a$	0	[16]
	$-45.7^a$	$\leq 0.1$	[17]
	$-41.1^a$	0.1	[29]
	$-50.76^a$	0.1	[30]
$\text{ThO}_2(\text{act})^b$	-48.7	0	[20]
$\text{ThO}_2(\text{c})$	$\cong -56.9$	0	this study, experimental
	$-54.2 \pm 1.3^c$	0	calculated from Rai <i>et al.</i> [3]
	$-54.13^c$	0	calculated from Wagman <i>et al.</i> [4]
	$-54.2^c$	0	calculated <sup>d</sup> from Cox <i>et al.</i> [21], Wagman <i>et al.</i> [4], and CODATA [20]
Values at 90 °C			
$\text{ThO}_2(\text{am} \rightarrow \text{c})^e$	$-49.2 \pm 0.2$	0	this study, experimental
$\text{ThO}_2(\text{c})^f$	$-51.4 \pm 0.2$	0	this study, experimental
	-51.6	0	calculated <sup>d</sup> from Cox <i>et al.</i> [21], Wagman <i>et al.</i> [4], and CODATA [20]
	-50.8	0	Calculated <sup>d</sup> from Cox <i>et al.</i> [21], Wagman <i>et al.</i> [4] and CODATA [20] assuming that $\Delta C_{p,\text{rxn}}^0 = 0$ .

a: The authors designated the solid phase as  $\text{Th}(\text{OH})_4(\text{s})$ , and is more likely an amorphous phase.

b: act = a designation given by the authors to represent a microcrystalline phase.

c: These calculated  $K_{sp}$  values are similar because of similarities in the original source of the thermodynamic data.

d: For details see Appendix A.

e: This phase is expected to convert to fully crystalline  $\text{ThO}_2(\text{c})$  at longer equilibration periods and at higher temperatures. The standard deviation is for data Sets I and II.

f: The standard deviation in the data is higher at higher pH values, possibly due to the presence of finite amounts of more soluble phase as discussed in text. The reported value is for data at  $\text{pH} < 2.5$ .

To interpret the 90 °C data, values at 90 °C are required of  $\Delta G_f^0/RT$  for  $\text{Th}^{4+}$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ , and of ion-interaction parameters for chloride and hydroxide with the dominant cations ( $\text{Th}^{4+}$ ,  $\text{Na}^+$ ) in the system. With the exception of  $\text{Th}^{4+}-\text{Cl}^-$ , all of the appropriate ion-interaction parameters for this system are available or can be estimated (see Table 4 and Appendix A) for the temperature range between 23 and 90 °C. Making a reasonable<sup>3</sup> assumption that the ion-interaction parameters for  $\text{Th}^{4+}-\text{Cl}^-$  at 23 °C apply to the 90 °C data, the  $\Delta G_f^0/RT$  of the  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  was determined to be  $-377.629$ , which corresponds to the log  $K_{sp}$  of  $-49.2$  for  $\text{ThO}_2(\text{am} \rightarrow \text{c})$ . In a similar fashion, the log  $K_{sp}$  value for  $\text{ThO}_2(\text{c})$  at 90 °C was determined to be  $-51.4$  based on the experimental data (Fig. 3). The solubility of  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  is many orders of magnitude lower than the solubility for  $\text{ThO}_2(\text{am})$  and is only about 2.2 orders of magnitude higher than the value for  $\text{ThO}_2(\text{c})$ . The close agreement between the observed and predicted solubilities (Figs. 1, 3, and 4) shows that the modeling parameters re-

ported in this paper (Tables 3 and 4) will provide reliable predictions for these systems.

The solubility products obtained in this study for  $\text{ThO}_2(\text{am})$  and  $\text{ThO}_2(\text{c})$  at 25 °C and those reported in the literature are compared in Table 5. Although the primary objective of this study was not to determine the solubility product of  $\text{ThO}_2(\text{am})$ , the value obtained in this study agrees closely with our earlier studies [9, 15] and is similar to the values quoted by Kovalenko and Bagdasarov [16] and Bilinski *et al.* [17] (Table 5). The large differences in some of the reported values appear to be due to differences in experimental variables (e.g., the type and concentration of electrolyte), and the choice of aqueous species or modeling parameters used in calculations. For example, Felmy *et al.* [19] pointed out that differences between values reported in Östhols *et al.* [10] and those reported in Felmy *et al.* [9] are due to assumptions about the aqueous phase models rather than the absolute differences in solubilities. The fact that  $\text{ThO}_2(\text{am})$  solubility in very dilute to concentrated chloride and carbonate solutions [8, 9, 19] is consistent with the value reported in Felmy *et al.* [9], which is similar to the value obtained in this study, attests to the reliability of the recently determined values. No other experimental  $\text{ThO}(\text{c})$  solubility data at 25 or 90 °C are available for direct comparisons. However, comparisons can be made with calculated solubility products derived from calorimetric data.

<sup>3</sup> Values of ion-interaction parameters for  $\text{Th}^{4+}-\text{Cl}^-$  are not available at other than 25 °C. However, values of  $B_{\text{ThCl}}$  at 90 °C, the only parameter important in these relatively dilute solutions, can be estimated by analogy with  $\text{Th}[\text{ClO}_4]_4$  using Hovey's [6] heat capacity data (assuming  $(B_{\text{ThCl}}/T)_{\text{PI}}$  is similar to  $(B_{\text{ThClO}_4}/T)_{\text{PI}}$  and Roy *et al.* [18] value for  $B_{\text{ThCl}}$  at 25 °C. On this basis and at an ionic strength of 0.1 M,  $B_{\text{ThCl}}$  changes from  $-9.6$  at 25 °C to  $-9.7$  at 90 °C, which is not significant.

The log  $K_{sp}$  value of  $\geq -56.9$  for  $\text{ThO}_2(\text{c})$  at  $25^\circ\text{C}$  obtained in this study compares very favorably with previously calculated values ( $-54.2 \pm 1.3$ , Rai *et al.* [3];  $-54.13$ , Wagman *et al.* [4]) and with the calculated value ( $-54.2$ ) in this study using tabulated values from Wagman *et al.* [4], CODATA [20], and Cox *et al.* [21]. The experimental log  $K_{sp}$  value of  $-51.4$  for  $\text{ThO}_2(\text{c})$  at  $90^\circ\text{C}$  is almost identical to our calculated value ( $-51.6$ ) derived from the selected data cited above and the heat capacity function for  $\text{Th}^{4+}$  given by Hovey [6]. The slightly larger log  $K_{sp}$  value of  $-49.2$  for  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  at  $90^\circ\text{C}$  is consistent with the fact that this material is not fully crystalline.

## Conclusions

The data presented in this paper show that  $\text{ThO}_2(\text{am})$  converts upon heating at  $90^\circ\text{C}$  to a crystalline thorium dioxide [ $\text{ThO}_2(\text{am} \rightarrow \text{c})$ ] and that the  $K_{sp}$  for  $\text{ThO}_2(\text{am} \rightarrow \text{c})$  is many orders of magnitude lower than that for  $\text{ThO}_2(\text{am})$  at  $25^\circ\text{C}$ . The measured  $\text{ThO}_2(\text{c})$  solubility product at  $90^\circ\text{C}$  is in close agreement with the value calculated using selected calorimetric data and the Born model for  $\text{Th}^{4+}$  given by Hovey [6]. These thermodynamic data and models will provide reliable predictions for thorium behavior at temperatures reaching  $90^\circ\text{C}$ .

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## References

- JNC, Japan Nuclear Cycle Development Institute. May 1999. *H12 Project to Establish Technical Basis for HLW Disposal in Japan*. The draft second progress report on Research and Development for the Geological Disposal of HLW in Japan. JNC TN1400 99-013.
- Prasad, R., Beasley, M. L., Milligan, W. O.: Aging of Hydrous Thoria Gels. *J. Electron Microscopy* **16**(2), 101–119 (1967).
- Rai, D., Swanson, J. L., Ryan, J. L.: Solubility of  $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$  in the Presence of  $\text{Cu}(\text{I})/\text{Cu}(\text{II})$  Redox Buffer. *Radiochim. Acta* **42**, 35–41 (1987).
- Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttal, R. L.: The NBS Tables of Chemical Thermodynamic Properties, Selected Values for Inorganic and  $\text{C}_2$  and  $\text{C}_2$  Organic Substances in SI Units. *J. Phys. Chem. Ref. Data* Vol. **11**, Suppl. 2 (1982).
- Morss, L. R., McCue, M. C.: Partial Molal Entropy and Heat Capacity of the Aqueous Thorium(IV) Ion. *Thermochemistry of Thorium Nitrate Pentahydrate*. *J. Chem. Eng. Data*, **21**, 337–341 (1976).
- Hovey, J. K.: Thermodynamics of Hydration of a  $4+$  Aqueous Ion: Partial Molar Heat Capacities and Volumes of Aqueous Thorium(IV) from 10 to  $55^\circ\text{C}$ . *J. Phys. Chem. B* **101**, 4321–4334 (1997).
- Apelblat, A., Sahar, A.: Properties of Aqueous Thorium Nitrate Solutions. Part 3. Partial Molar Heat Capacities and Heats of Dilution at  $30^\circ\text{C}$ . *J. Chem. Soc. Faraday Trans. I*, **71**, 1667–1670 (1975).
- Rai, D., Felmy, A. R., Sterner, S. M., Moore, D. A., Mason, M. J., Novak, C. F.: The Solubility of  $\text{Th}(\text{IV})$  and  $\text{U}(\text{IV})$  Hydrated Oxides in Concentrated  $\text{NaCl}$  and  $\text{MgCl}_2$  Solutions. *Radiochim. Acta* **79**, 239–247 (1997).
- Felmy, A. R., Rai, D., Mason, M. J.: The Solubility of Hydrated Thorium (IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model. *Radiochim. Acta* **55**, 177–185 (1991).
- Östholts, E., Bruno, J., Grenthe, I.: On the Influence of Carbonate on Mineral Dissolution: III. The Solubility of Microcrystalline  $\text{ThO}_2$  in  $\text{CO}_2$ - $\text{H}_2\text{O}$  Media. *Geochim. Cosmochim. Acta* **58**, 613–623 (1994).
- Pitzer, K. S.: Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **77**, 268–277 (1973).
- Pitzer, K. S.: Ion Interaction Approach: Theory and Data Correlation: In *Activity Coefficients in Electrolyte Solutions*, 2<sup>nd</sup> ed., CRC Press, Boca Raton, p. 75–153 (1991).
- Sterner, S. M., Felmy, A. R., Rustad, J. R., Pitzer, K. S.: Thermodynamic Analysis of Aqueous Solutions Using INSIGHT. PNWD-SA-4436, Pacific Northwest National Laboratory, Richland, Washington (1997).
- Grenthe, I., Lagerman, B.: Studies of Metal Carbonate Equilibria. 23. Complex Formation in the  $\text{Th}(\text{IV})$ - $\text{H}_2\text{O}$ - $\text{CO}_2(\text{g})$  System. *Acta Chem. Scand.* **45**, 231–238 (1991).
- Ryan, J. L., Rai, D.: Thorium(IV) Hydrated Oxide Solubility. *Inorg. Chem.* **26**, 4140–4142 (1987).
- Kovalenko, P. N., Bagdasarov, K. N.: Use of the Photocolorimeter for Determination of the Solubility Product of Thorium Hydroxide. *J. Applied Chem. USSR* **34**, 759–763 (1961).
- Bilinski, H., Fűredi, H., Branica, M., Tezak, B.: Precipitation and Hydrolysis of Thorium(IV) in Aqueous Solution: Thorium Nitrate-Potassium Hydroxide. I. Determination of Solubility Constants of  $\text{Th}(\text{OH})_4$ . *Croat. Chem. Acta* **35**, 19–30 (1963).
- Roy, R. N., Vogel, K. M., Good, C. E., Davis, W. B., Roy, L. N., Johnson, D. A., Felmy, A. R., Pitzer, K. S.: Activity Coefficients in Electrolyte Mixtures:  $\text{HCl} + \text{ThCl}_4 + \text{H}_2\text{O}$  for  $5$ – $55^\circ\text{C}$ . *J. Phys. Chem.* **96**, 11065–11072 (1992).
- Felmy, A. R., Rai, D., Sterner, S. M., Mason, M. J., Hess, N. J., Conradson, S. D.: Thermodynamic Models of Highly Charged Aqueous Species: Solubility of  $\text{Th}(\text{IV})$  Hydrated Oxide in Concentrated  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  Solutions. *J. of Soln. Chem.* **26**, 233–248 (1997).
- CODATA 1978: Recommended Key Values for Thermodynamics. *J. Chem. Thermodyn.* **10**, 903–906 (1978).
- Cox, J. D., Wagman, D. D., Medvedev, V. A.: *CODATA Key Values for Thermodynamics*. Hemisphere Pub. Corp., 271 pages (1989).
- Fuger, J., Oetting, F. L.: The Chemical Thermodynamics of Actinide Elements and Compounds: Part 2, The Actinide Aqueous Ions. IAEA, Vienna (1976).
- Harvie, C. E., Müller, N., Weare, J. H.: The Prediction of Mineral Solubilities in Natural Waters: The  $\text{Na-K-Mg-Ca-H-Cl-SO}_4\text{-OH-HCO}_3\text{-CO}_2\text{-H}_2\text{O}$  System to High Ionic Strengths at  $25^\circ\text{C}$ . *Geochim. Cosmochim. Acta* **48**, 723 (1984).
- Pitzer, K. S., Peiper, J. C., Busey, R. H.: Thermodynamic Properties of aqueous Sodium Chloride Solutions. *J. Phys. Chem. Ref. Data* **13**, 1–102 (1984).
- Holmes, H. F., Mesmer, R. E.: Isopiestic Molalities for Aqueous Solutions of the Alkali Metal Hydroxides at Elevated Temperatures. *J. Chem. Thermodyn.* **30**, 311–326 (1998).
- Holmes, H. F., Busey, R. H., Simonson, J. M., Mesmer, R. E., Archer, D. G., Wood, R. H.: The Enthalpy of Dilution of  $\text{HCl}(\text{aq})$  to 648 K and 40 MPa. *J. Chem. Thermodyn.* **19**, 863–890 (1987).
- Pitzer, K. S., Kim, J.: Thermodynamics of Electrolytes. IV. Activity and Osmotic Coefficients for Mixed Electrolytes. *J. Amer. Chem. Soc.* **96**, 5701–5707 (1974).
- Felmy, A. R., Rai, D.: An Aqueous Thermodynamic Model for a High-Valence  $4:2$  Electrolyte  $\text{Th}^{4+}\text{-SO}_4^{2-}$  in the System  $\text{Na}^+\text{-K}^+\text{-Li}^+\text{-NH}_4^+\text{-Th}^{4+}\text{-SO}_4^{2-}\text{-HSO}_4^-\text{-H}_2\text{O}$  to High Concentration. *J. Sol. Chem.* **21**, 407–423 (1992).
- Nabivanets, B.I., Kudritskaya, L. N.: Hydro Complexes of  $\text{Th}(\text{IV})$ . *Ukr. Khim. Zh.* **30**, 891–895 (1964, in Russian).
- Moon, H.: Equilibrium Ultrafiltration of Hydrolyzed Thorium(IV) Solutions. *Bull. Korean Chem. Soc.* **10**, 270–272 (1989).

31. Haas, J. L. Jr., Fisher, J. R.: Simultaneous Evaluations and Correlation of Thermodynamic Data. *Amer. J. Sci.* **276**, 525–545 (1966).
32. Tanger, J. C., Helgeson, H. C.: Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Revised Equations of State for the Standard Partial Molal Properties of Ion and Electrolytes. *Amer. J. Sci.* **288**, 19–98 (1988).
33. Victor, A. C., Douglas, T. B.: Thermodynamic Properties of Thorium Dioxide from 298 to 1200 K. *Natl. Bur. Stds. J. Res. A.* **65**, 105–111 (1961).
34. Shock, E. L., Sassani, D. C., Willis, M., Sverjensky, D. A.: Inorganic Species in Geologic Fluids: Correlations Among Standard Molal Thermodynamic Properties of Aqueous Ions and Hydroxide Complexes. *Geochim. Cosmochim. Acta* **61**, 907–950 (1997).

## Appendix A: Literature sources of thermodynamic quantities used to calculate $K_{sp}$ for $\text{ThO}_2(\text{c})$ dissolution reaction $[\text{ThO}_2(\text{c}) + 2 \text{H}_2\text{O} (\text{Th}^{4+} + 4 \text{OH}^-)]$

The value of  $K_{sp}$  can be calculated from the thermodynamic relationships

$$\ln K_{sp} = \Delta G_{f,rxn}^0 / RT \quad (\text{A.1})$$

and

$$\Delta G_{f,rxn}^0 = \Delta H_{f,rxn}^0 - T \Delta S_{f,rxn}^0 \quad (\text{A.2})$$

where  $K_{sp}$  is solubility product;  $\Delta G_{f,rxn}^0$ ,  $\Delta H_{f,rxn}^0$ ,  $\Delta S_{f,rxn}^0$  are standard Gibbs free energy, enthalpy, and entropy, of formation, respectively, of reaction (rxn); R is the gas constant; and T is the temperature in Kelvin.

At elevated temperatures, these calculations are most accurate if heat capacity ( $C_p^0$ ) data are available for the temperature range of interest (e.g., and  $\int_{298\text{K}}^T d\Delta H_{f,rxn}^0 = \int_{298\text{K}}^T \Delta C_{p,rxn}^0 dT$  and  $\int_{298\text{K}}^T d\Delta S_{f,rxn}^0 = \int_{298\text{K}}^T (\Delta C_{p,rxn}^0 / T) dT$ ). Values of  $\Delta H_{f,rxn}^0(T)$  and  $\Delta S_{f,rxn}^0(T)$  were obtained by integration

of fits to the heat capacities for the individual species using the function

$$C_p^0 = q_0 + q_1 T + q_2 T^{-2} + q_3 T^2 + q_4 T^{-1/2} \quad (\text{A.3})$$

reported by Haas and Fisher [31], where the  $q_i$  terms are fitting constants. The following sources were used for the heat capacities of the species required for  $K_{sp}$  calculations: Hovey [6] for  $\text{Th}^{4+}(\text{aq})^1$ ; Tanger and Helgeson [32] for  $\text{OH}^-(\text{aq})$ ; Victor and Douglas [3] for  $\text{ThO}_2(\text{c})$ ; and Cox *et al.* [21] for  $\text{H}_2\text{O}(\text{l})$ . Values of  $\Delta H_f^0$  (298 K) and  $\Delta S_f^0$  (298 K) for the individual species were obtained from Shock *et al.* [34], which in turn were taken from Wagman *et al.* [4] and CODATA [20] for  $\text{Th}^{4+}(\text{aq})$ , Tanger and Helgeson [32] for  $\text{OH}^-(\text{aq})$ , and from Cox *et al.* [21] for  $\text{ThO}_2(\text{c})$  and  $\text{H}_2\text{O}(\text{l})$ . Hovey's experimental heat capacities were only measured to 55 °C. Consequently, his Born model was used to produce  $C_p^0(\text{Th}^{4+})$  values to higher temperatures. Values of the fitting constants in Eq. (A.3) for each species are listed in Table A.1. Values of  $\Delta H_f^0$  and  $\Delta S_f^0$  for each species and calculated values of  $\ln K$  at 298.15 K and 363.15 K are listed in Table A.2. Note that the 363.15 K  $\ln K_{sp} = -117$  if the van't Hoff relationship ( $\Delta C_p^0 = 0$ ) is assumed versus  $\ln K_{sp} = -119$  for the case where heat capacities were taken into account.

**Table A.1.** Parameters for Eq. (A.3) and temperature range (degrees Kelvin, K) over which heat capacities were fit.

Fitting constant	$\text{Th}^{4+}$	$\text{OH}^-$	$\text{ThO}_2(\text{c})$	$\text{H}_2\text{O}$
$10^{-3} q_0$	-22.204	-281.236	0.159053	-0.0187226
$q_1$	12.90903	346.775	-0.051403	0.099873
$10^{-8} q_2$	-3.12312	-20.5431		
$q_3$		-0.217902		
$10^{-3} q_4$	373.811	3801.96	-1.41471	1.11031
Temp. range (K)	273–373	273–423	263–373	293–373

**Table A.2.** Thermodynamic quantities of species taking part in  $K_{sp}$  calculation for  $\text{ThO}_2(\text{c})$  at 298 K and at 363 K.

Units	$\text{Th}^{4+}$ Shock <i>et al.</i> [34]	$\text{OH}^-$ Tanger and Helgeson [32]	$\text{ThO}_2(\text{c})^a$ Cox <i>et al.</i> [21]	$\text{H}_2\text{O}^a$ Cox <i>et al.</i> [21]	
Values at 298 K					
$\text{J} \cdot \text{mol}^{-1}$	$\Delta H_f^0$	-769 019	-230 024	-1 226 400	-285 830
$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta S_f^0$	-215	-243.93	-191.61	-163.14
$\text{J} \cdot \text{mol}^{-1}$	$\Delta G_f^0$	-705 004	-157 297	-1 169 271	-237 190
	$\Delta G_f^0/RT$	-284.40	-63.45	-471.68	-95.68
Values at 363 K					
$\text{J} \cdot \text{mol}^{-1}$	$\Delta H_f^0$	-784 500	-237 100	-1 222 000	-280 900
$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\Delta S_f^0$	-261.4	-265.6	-179.0	-148.3
$\text{J} \cdot \text{mol}^{-1}$	$\Delta G_f^0$	-689 500	-140 700	-1 157 000	-227 100
	$\Delta G_f^0/RT$	-228.37	-46.60	-383.27	-75.21

a: Values of  $\Delta S_f^0$  (298 K,  $\text{ThO}_2$ ) and  $\Delta S_f^0$  (298 K,  $\text{H}_2\text{O}$ ) were calculated from the following values:  $S^0(\text{Th})$  51.8;  $S^0(\text{O}_2, \text{g})$  205.043;  $S^0(\text{ThO}_2, \text{c})$ , 65.23;  $S^0(\text{H}_2, \text{gas})$ , 130.57; and  $S^0(\text{H}_2\text{O}, \text{l})$ , 69.95 reported by Cox *et al.* [21].



## Appendix B: Experimental data tables

**Table B.1.** Measured ThO<sub>2</sub> solubilities in 0.1 mol · kg<sup>-1</sup> NaCl(aq) at 23 and 90 °C (Set I).

ThO <sub>2</sub> (am) 23 ± 2 °C				ThO <sub>2</sub> (am → c) 23 ± 2 °C	
6 days		21 days		76 days	
pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )
2.030	-1.978	2.027	-1.985	1.466	-2.156
2.182	-1.995	2.191	-1.981	1.469	-2.039
2.397	-1.999	2.419	-2.023	1.479	-2.262
2.564	-2.007	2.599	-2.003	1.480	-2.239
2.721	-2.007	2.764	-1.959	1.509	-1.986
2.915	-1.998	2.968	-2.010	1.620	-2.271
3.074	-2.036	3.130	-2.047	1.567	-2.380
3.170	-1.996	3.224	-1.977	1.615	-2.515
3.270	-2.011	3.332	-2.018	1.634	-2.551
3.546	-2.034	3.485	-2.035	1.722	-2.988
3.970	-2.134	3.748	-2.037	1.901	-3.240
4.157	-2.423	4.002	-2.234	2.000	-3.788
4.256	-2.650	4.105	-2.389	2.060	-3.916
4.506	-3.318	4.427	-3.039	2.192	-4.435
4.555	-3.469	4.517	-3.258	2.150	-4.441
4.718	-4.024	4.581	-3.436	2.206	-4.398

**Table B.2.** Measured ThO<sub>2</sub> solubilities in 0.1 mol · kg<sup>-1</sup> NaCl(aq) at 23 and 90 °C (Set II).

ThO <sub>2</sub> (am) 23 ± 2 °C				ThO <sub>2</sub> (am → c) 90 ± 2 °C	
5 days		13 days		52 days	
pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )
4.207	-2.340	4.128	-2.417	1.970	-3.707
4.336	-2.681	4.277	-2.701	2.011	-3.939
4.377	-2.738	4.260	-2.804	1.983	-3.917
4.608	-3.138	4.527	-3.056	2.048	-4.044
4.823	-3.732	4.796	-3.520	2.081	-4.099
4.943	-3.918	4.782	-3.527	2.065	-4.267
4.964	-3.967	4.873	-3.625	2.076	-4.385
5.060	-4.252	4.982	-3.860	2.090	-4.320

**Table B.3.** Measured ThO<sub>2</sub> solubilities in 0.1 mol · kg<sup>-1</sup> NaCl(aq) at 23 and 90 °C (Set III). Note that the log thorium values for most of the 23 °C samples are essentially constant due to complete solubilization of the solid phase.

ThO <sub>2</sub> (am) 23 ± 2 °C				ThO <sub>2</sub> (am → c) 90 ± 2 °C	
7 days		22 days		76 days	
pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )
1.809	-3.368	1.794	-3.406	ND <sup>a</sup>	ND <sup>a</sup>
1.992	-3.347	1.984	-3.402	1.881	-3.179
2.124	-3.319	2.109	-3.374	2.047	-3.210
2.281	-3.308	2.280	-3.374	2.055	-4.474
2.408	-3.341	2.415	-3.388	2.176	-4.775
2.587	-3.369	2.595	-3.421	2.202	-5.323
2.744	-3.360	2.759	-3.441	2.233	-6.278
2.832	-3.475	2.848	-3.530	2.320	-6.532
3.019	-3.344	3.047	-3.397	2.327	-5.697
3.174	-3.373	3.200	-3.426	2.381	-5.400
3.337	-3.375	3.360	-3.421	2.514	-5.521
3.594	-3.355	3.620	-3.402	2.568	-5.248
3.750	-3.371	3.791	-3.416	2.687	-5.458
3.876	-3.455	3.927	-3.490	2.778	-5.479
4.106	-3.777	4.133	-3.763	2.975	-5.894
4.218	-4.008	4.229	-4.004	ND <sup>a</sup>	ND <sup>a</sup>

a: ND = no data.

**Table B.4.** Measured ThO<sub>2</sub>(c) solubilities at 23 and 90 °C.

23 °C (Set IV) <sup>a</sup>								90 °C (set V) <sup>a</sup>	
11 days		87 days		687 days		794 <sup>b</sup> days		12 days	
pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )	pH	log (C <sub>Th</sub> /mol · kg <sup>-1</sup> )
1.308	-3.824	1.372	-3.616	1.391	-3.528	1.353	-3.187	1.367	-3.413
1.491	-4.059	1.518	-3.860	1.568	-3.743	1.466	-3.542	1.432	-3.548
1.688	-4.101	1.719	-4.000	1.757	-3.892	1.682	-4.131	1.753	-4.688
1.835	-5.098	1.876	-4.925	1.904	-4.870	1.816	-4.801	1.886	-5.700
2.037	-4.957	2.074	ND <sup>c</sup>	2.103	-4.713	2.063	-6.350	2.058	-6.288
2.223	-4.954	2.267	-4.816	2.292	-4.694	2.225	-5.896	2.207	-6.798
2.431	-5.311	2.463	-5.160	2.463	-5.021	2.367	-6.366	2.381	-7.296
2.597	ND <sup>c</sup>	2.581	-4.988	2.623	-4.856	2.579	-7.063	2.525	-6.863
2.751	-5.191	2.786	-5.019	2.768	-4.991	2.718	-6.889	2.632	-6.926
2.865	-5.329	2.881	-5.235	2.878	-5.159	2.834	-8.142	2.758	-8.143
2.983	ND <sup>c</sup>	3.003	-5.312	2.981	-5.282	2.962	-7.261	2.830	-5.822
3.051	-5.609	3.045	-5.493	3.043	-5.498	2.991	-7.331	2.906	-8.172
3.185	-6.338	3.133	-6.311	3.168	-6.166	3.155	-9.369	3.232	-8.054
3.413	-6.894	3.358	-6.857	3.359	-7.127	3.357	-8.144	3.489	ND <sup>c</sup>
3.578	-7.747	3.591	-8.598	3.538	-9.367	3.551	-8.178	ND <sup>c</sup>	ND <sup>c</sup>

a: Different set of samples were used in Sets IV and V.

b: ThO<sub>2</sub>(c) suspensions, previously equilibrated at 23 °C for 779 days, were then equilibrated at 90 °C for 14 days and then maintained at 23 °C for 1 day before sampling.

c: ND = no data.