Thermodynamic properties of soddyite from solubility and calorimetry measurements

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Received 27 July 2006; received in revised form 6 September 2006; accepted 7 September 2006
Available online 14 September 2006

Abstract

The release of uranium from geologic nuclear waste repositories under oxidizing conditions can only be modeled if the thermodynamic properties of the secondary uranyl minerals that form in the repository setting are known. Toward this end, we synthesized soddyite ((UO2)2(SiO4)(H2O)2), and performed solubility measurements from both undersaturation and supersaturation. The solubility measurements rigorously constrain the value of the solubility product of synthetic soddyite, and consequently its standard-state Gibbs free energy of formation. The log solubility product ($\log K_{sp}$) with its error ($1\sigma$) is $6.43 \pm 0.20 / 0.37$, and the standard-state Gibbs free energy of formation is $43652.2 \pm 4.2 \text{ (}2\sigma\text{) kJ mol}^{-1}$. High-temperature drop solution calorimetry was conducted, yielding a calculated standard-state enthalpy of formation of soddyite of $-4045.4 \pm 4.9 \text{ (}2\sigma\text{) kJ mol}^{-1}$. The standard-state Gibbs free energy and enthalpy of formation yield a calculated standard-state entropy of formation of soddyite of $1318.7 \pm 21.7 \text{ (}2\sigma\text{) J} \text{ mol}^{-1} \text{ K}^{-1}$. The measurements and associated thermodynamic calculations not only describe the $T=298$ K stability and solubility of soddyite, but they also can be used in predictions of repository performance through extrapolation of these properties to repository temperatures.

Keywords: Soddyite; Uranyl silicate; Gibbs free energy; Enthalpy; Entropy; Solubility; Supersaturation; Solubility product; Calorimetry

1. Introduction

Uranyl silicates are common constituents of the altered portions of U deposits, and are important for understanding the genesis of such deposits as well as the mobility of uranium in the environment [1]. Uranyl silicate minerals consist of three structurally and chemically distinct groups [2,3]. The uranophane group is the most abundant, and each of its structures contains sheets of uranyl polyhedra and silicate tetrahedra, with lower-valence cations and H2O groups located in the interlayer regions. The weeksite group also corresponds to minerals with sheet structures, but the sheets contain more silicate that those of the uranophane group. In contrast, soddyite, the chemically simplest uranyl silicate with formula $(\text{UO}_2)_2\text{SiO}_4(\text{H}_2\text{O})_2$, has a framework structure composed of uranyl polyhedra and silicate tetrahedra that share vertices.

The performance of geologic nuclear waste repositories will be influenced by interactions between the spent nuclear fuel and the environment in which it is placed. Oxidative weathering of commercial spent nuclear fuel under oxidizing conditions, such as those expected at the proposed repository at Yucca Mountain, will likely result in the formation of U(VI) mineral phases [1,2,4]; consequently, the formation and stability of U(VI) minerals will impact the release of U(VI) from the waste package, and potentially also from the repository. Uranyl minerals that form in a
geological repository may also incorporate radionuclides such as Np into their structures, potentially having a profound impact on the release of such radionuclides [5–7].

Finch et al. [4] examined the alteration products that formed after groundwater dripped onto the spent nuclear fuel in a laboratory setting for six years at $T = 363$ K. The experiments used two pressurized-water-reactor fuels, ATM103 and ATM106, with corresponding burn-up histories of $\sim 30$ MWd $\cdot$ kg$^{-1}$ U and $\sim 45$ MWd $\cdot$ kg$^{-1}$ U, respectively. The groundwater used was from well J-13 at the Yucca Mountain site, and was reacted with crushed Tonopah Springs tuff at $T = 363$ K for 80 days prior to use (designated EJ-13 water). Alteration of the spent fuel in four experiments with different water injection rates resulted in mostly uranyl compounds. These included several uran oxide hydrates as well as the uranyl silicates soddyite, $\beta$-uranophane, Ca(UO$_2$)$_2$(SiO$_2$)(OH)$_2$(H$_2$O)$_3$, and Na-boltwoodite, (Na,K)(UO$_2$)(SiO$_2$)(OH)(H$_2$O)$_{1.5}$. In similar experiments, Wronkiewicz et al. [8,9] examined non-irradiated UO$_2$ placed under dripping EJ-13 water at $T = 363$ K for more than 10 years. Wronkiewicz et al. [9] found that the alteration phases that formed initially were uran oxide hydrates, followed by uranyl silicates, a paragenetic sequence which is generally consistent with natural analogues.

Despite the potential importance of U(VI) silicate minerals in the performance of a geologic nuclear waste repository under oxidizing conditions, reliable thermodynamic data are lacking for most of these minerals. In order to predict the stability and solubility of U(VI) silicate minerals as a function of solution composition (pH, ionic strength, etc.) and temperature, it is necessary to know the standard-state Gibbs free energy, enthalpy, and entropy of formation for each phase of interest. These thermodynamic parameters are crucial for predicting repository performance.

Soddyite is a common uranyl silicate in nature, and has been found as an alteration product of spent nuclear fuel under moist oxidizing conditions [4]. Previous studies of the solubility of soddyite have produced a wide range of solubility product values. Nguyen et al. [10] and Moll et al. [11] reported $\log K_{\text{sp}}$ (solubility product) values of $(5.74 \pm 0.21)$ and $(6.15 \pm 0.53)$, respectively, for batch dissolution experiments. Perez et al. [12] reported a wide range of values for the $\log K_{\text{sp}}$ with values from 2.58 to 6.36, for experiments conducted in the presence of dissolved Na and Si. Despite three separate studies measuring the solubility of soddyite, there is a lack of an accepted value for the solubility product. Part of the problem stems from deficiencies in the previous studies. Reliable thermodynamic parameters can be derived from solubility studies only when the following conditions are met: (1) the mineral of interest is stable under the experimental conditions, (2) a true equilibrium state is attained during the experiments, and (3) the pH and metal concentrations present in the equilibrium state are measured. The first condition should be established by characterizing the mineral phase both before and after the solubility experiment using X-ray diffractometry (XRD) and/or other spectrometry approaches. The attainment of equilibrium can only be demonstrated via reversibility experiments; that is, approaching the equilibrium state from supersaturated as well as from under saturated conditions with respect to the dissolved species of interest. All previous studies of the solubility of soddyite have neglected to demonstrate at least one of the above three conditions.

The Gibbs free energy of formation of a phase, coupled with the enthalpy of formation of that phase, can be used to calculate the standard entropy of formation. With these thermodynamic parameters, the stability and solubility of the phase can be calculated as a function of temperature. High-temperature oxide-melt solution calorimetry has been applied successfully in order to determine the standard enthalpies of formation of some uranyl minerals [13–15]. In this study, we synthesized soddyte using mild hydrothermal conditions and thoroughly characterized the mineral using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, thermogravimetry, and chemical analysis. Using batch experiments, we measured the solubility of soddyite from undersaturation and supersaturation between pH 3.0 and 3.6, and we characterized the post-experimental mineral residue. High-temperature oxide-melt solution calorimetry was used to obtain the heat of drop solution of soddyite in molten sodium molybdate. Although the early studies of uranyl minerals by high-temperature calorimetry were successful, the same method cannot be applied to uranyl silicates because of the lack of solubility of SiO$_2$ in sodium molybdate. Thus, a slightly modified calorimetric method, in which the solvent is saturated with SiO$_2$ prior to the experiment, was developed. Using the calorimetric and solubility measurements, we calculate the $T = 298$ K standard-state Gibbs free energy, enthalpy, and entropy of formation from the elements of soddyite.

2. Experimental materials and methods

2.1. Syntheses

Soddyte for the solubility experiments was synthesized by placing 0.42 g UO$_2$(CH$_3$COO)$_2$(H$_2$O)$_2$ (prepared from heating $\sim 0.5$ g UO$_2$ (Strem Chemicals) with $\sim 600$ cm$^3$ glacial acetic acid (Fisher ACS grade)), $0.25$ cm$^3$ of 1 M Na$_2$SiO$_2$(H$_2$O)$_5$ (Fisher Chemicals ACS grade), and 4.75 cm$^3$ of 18 MΩ H$_2$O in a 23 cm$^3$ Teflon-lined Parr reaction vessel. This method yielded a run product that included both soddyite and amorphous silica, so a second approach was used to produce solids for the drop solution calorimetry in order to eliminate as much amorphous silica from the run product as possible. The calorimetry solids were synthesized by placing 0.21 g UO$_2$(CH$_3$COO)$_2$(H$_2$O)$_2$, 0.25 cm$^3$ of 1 M Na$_2$SiO$_2$(H$_2$O)$_5$, and 4.75 cm$^3$ of 18 MΩ H$_2$O in a 23 cm$^3$ Teflon-lined Parr reaction vessel. For both types of syntheses, the reactants were heated to $T = 389$ K.
for 7 days. The products were recovered by filtration and rinsed 4 times with boiling 18 MΩ H2O. The syntheses were repeated multiple times to produce enough powder for the experiments. Soddyite containing amorphous silica was used to determine the final state of soddyite in the calorimetric solvent sodium molybdate. The pure soddyite sample was used for calorimetric measurements without additional treatment.

Cristobalite used in high-temperature calorimetry was synthesized by heating quartz (Fluka, 0.999 mass fraction purity of metal basis) at T = 1773 K for 60 h. XRD showed complete conversion to cristobalite.

2.2. Characterization

The X-ray powder diffraction patterns were collected for each batch of soddyite by finely grinding ~5 mg of powder and depositing the paste onto a zero-background orientated quartz slide. Diffraction patters were collected using a Bruker D8 Discovery diffractometer equipped with Cu Kα radiation and a solid-state detector. All powder diffraction patterns exhibited sharp profiles and no extraneous peaks, and they confirmed the presence of soddyite as the only crystalline phase in the syntheses. FT-IR analyses were performed using an IlluminaIR FT-IR micro-spectrometer with a diamond total attenuated reflectance (ATR) objective in an open atmosphere, background spectra taken prior to measurement, over a frequency range of (400 to 4000) cm⁻¹ using ~(5 to 10) mg of powder placed on a glass slide. The IR spectra were in good agreement with previously published spectra for soddyite by Cjeka and Urbanec [16] and amorphous silica (determined from FT-IR analysis of silica gel). Thermogravimetry (t.g.a.) and differential scanning calorimetry (d.s.c.) analyses were carried out by heating the powder to T = 983 K at 10 K · min⁻¹ under flowing argon at 50 cm³ · min⁻¹. Two consecutive runs were performed with the sample mass between 12 mg and 14 mg. Water content was calculated from the weight loss. Soddyite dehydrates at approximately T = 673 K. The water content calculated from the weight loss upon heating was (5.52 ± 0.15) wt%, which represents (2.05 ± 0.06) H₂O molecules per mole of soddyite, consistent within experimental error with the ideal stoichiometry for soddyite of (UO₂)₂SiO₄ · 2H₂O. The molecular weight corresponding to the ideal stoichiometry is used for further calculations. Chemical analyses were performed by dissolving ~(50 to 100) mg of powder in ~17 cm³ of 2 M HCl and analyzing for U and Si concentrations by inductively coupled plasma-optical emission spectrometry (ICP-OES) with an analytical uncertainty of 3.5%. The chemical analysis of the soddyte that was synthesized for the solubility experiments indicated a slight excess (~7.1%) of Si that we attribute to the presence of an amorphous silica phase. The parallel ICP-OES analysis of the soddyte that was synthesized for the drop solution calorimetry did not exhibit excess Si.

2.3. Solubility experiments

All solubility measurements were batch experiments conducted in Teflon reaction vessels. An Orion combination pH electrode that was calibrated daily with 4 NIST standards was used for pH measurements. Although the ionic strength of the buffers was not perfectly matched to the ionic strength of the experiments the additional error associated with pH measurements as a result of the difference in ionic strength and liquid-junction error is likely much smaller than experimental error which dominates the stated uncertainties for the calculated thermodynamic parameters. All the experiments were conducted at pH values less than 3.9 in order to increase dissolution reaction kinetics. The low pH conditions also enabled us to operate under conditions where UO₂⁺ is the dominant uranium species in solution [17,18], thereby eliminating the complexities in aqueous uranium speciation that occur under higher pH conditions. In order to further decrease the time necessary to reach equilibrium, we started the experiments in solutions containing dissolved U and Si. The initial experimental solutions were prepared by taking aliquots of silica atomic absorption spectroscopy standard and uranyl nitrate stock solution, prepared from adding uranyl nitrate hexahydrate to 18 MΩ · cm⁻³ H₂O, and diluting to the desired concentrations. Approximately ~350 mg of soddyte were added to ~7 cm³ of the prepared U and Si starting solution. The pH of the batch experiments was adjusted using minute quantities of 15 M HNO₃ (0.999 mass fraction purity of metal basis), and was continuously monitored throughout each experiment. Reaction vessels were sealed and agitated slowly end over end. Aliquots of the experimental solution were taken at various intervals, filtered with 0.1 μm nylon filters, and diluted for ICP-OES analysis of U and Si concentrations with an analytical uncertainty of 3.5%. In order to verify the composition of the mineral residue after 7 days of reaction, and at the end of the experiment, ~10 mg of residue was taken for XRD and FT-IR analyses. Control experiments, performed without mineral phases present, indicated that the loss of U and Si due to adsorption or precipitation reactions under the experimental conditions was negligible. Initial experimental results indicated that soddyte was stable under the experimental conditions, but that amorphous silica was also forming in the reactors. Consequently, we prepared subsequent experiments as described above and added (200 to 300) mg of amorphous silica gel in order to increase the kinetics of the amorphous silica precipitation reaction. The co-existence of two phases (soddyte and amorphous silica) in the experimental systems is consistent with the Gibbs phase rule for a two-component system such as these. As long as both phases are stable under the experimental conditions and we measure all dissolved element concentrations, the experimental measurements rigorously constrain the value of the solubility products for each phase present.
TABLE 1  
Calorimetric cycle for calculation of enthalpy of formation of soddyite

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Heat effect (values are in table 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{UO}_2\text{J}_2\text{SiO}_4)\cdot 2\text{H}<em>2\text{O}</em>{\text{dil,298}}\cdot k = 2\text{UO}_2\text{SiO}_2\cdot k + \text{SiO}_2\text{O}_2\cdot k + 2\text{H}_2\text{O}_2\cdot k)</td>
<td>(\Delta H_f^\circ = \Delta H_f^\circ(\text{soddyite}))</td>
</tr>
<tr>
<td>(\text{UO}_2\text{SiO}_2\cdot k = \text{UO}_2\text{SiO}_2\cdot k)</td>
<td>(\Delta H_f^\circ = \Delta H_f^\circ(\text{UO}_2\text{J}_2))</td>
</tr>
<tr>
<td>(\text{SiO}_2\cdot k + \text{O}_2\cdot k = \text{SiO}_2\cdot k)</td>
<td>(\Delta H_f^\circ = \Delta H_f^\circ(\text{SiO}_2\text{O}_2\cdot k))</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}_2\cdot k = \text{H}_2\text{O}_2\cdot k)</td>
<td>(\Delta H_f^\circ = \Delta H_f^\circ(\text{H}_2\text{O}_2))</td>
</tr>
<tr>
<td>(2\text{UO}_2\text{SiO}_2\cdot k + \text{SiO}_2\cdot k + 2\text{H}_2\text{O}_2\cdot k = (\text{UO}_2\text{J}_2\text{SiO}_4)\cdot 2\text{H}<em>2\text{O}</em>{\text{dil,298}}\cdot k)</td>
<td>(\Delta H_f^\circ = \Delta H_f^\circ(\text{soddyite})) - (\Delta H_f^\circ + 2\Delta H_f^\circ + \Delta H_f^\circ + 2\Delta H_f^\circ)</td>
</tr>
</tbody>
</table>

2.4. High-temperature oxide-melt solution calorimetry

The calorimetry of soddyite was performed using a custom-built Tian-Calvet high-temperature micro-calorimeter [19,20]. Pellets were dropped into a Pt crucible containing a melt of composition 3NaO·4MoO3 at \(T = 976\) K. To provide stirring, prevent local saturation, speed the dissolution, and to maintain an oxidizing atmosphere, oxygen was flushed over the solvent (30 \(\text{cm}^3\cdot \text{min}^{-1}\)) and bubbled through the solvent (3 to 3.5 \(\text{cm}^3\cdot \text{min}^{-1}\)) to accelerate precipitation of SiO2 (see discussion below) and to obtain consistent values of \(\Delta H_f\); 50 mg of cristobalite were added to the solvent prior to dropping the samples. The measured enthalpies of drop solution, \(\Delta H_f\), were used to calculate enthalpies of formation using the calorimetric cycle depicted in table 1. References phases were cristobalite (dropped into sodium molybdate at the same conditions as described above for soddyite), H2O [21] and UO3 [30].

We have observed previously that silica does not dissolve readily in sodium molybdate, and that the oxidative dissolution of silicon nitride precipitates as cristobalite. To further constrain the final state of SiO2 in sodium molybdate (necessary for writing a well-defined thermodynamic cycle for the heat of formation of soddyite), a series of experiments was performed. In these experiments, amorphous silica (SiO2 · xH2O with \(x = 1.2\) to 1.6, Alfa Aesar, 0.995 mass fraction purity on metals basis), quartz, cristobalite (synthesized as described above) and soddyite (containing ~7 wt% amorphous SiO2) were dissolved into molten sodium molybdate. The solvent was then quenched and dissolved in an abundance of water. The collected precipitates were then checked by XRD to determine the phase(s) present.

3. Results and discussion

3.1. High-temperature oxide-melt solution calorimetry

Recovery of a silicate-rich precipitate from the sodium molybdate indicated the presence of cristobalite under experimental conditions, demonstrating the instability of amorphous silica under these conditions. After quartz reaction, the run sediment contained quartz as a major phase and cristobalite as a minor admixture, indicating a slow transition of quartz to cristobalite during the experiment. Measured values of \(\Delta H_f\) for cristobalite (see figure 1) and quartz gradually decreased, indicating that the apparent value of \(\Delta H_f\) strongly depends on SiO2 concentration in the solvent and that the solvent is saturated when approximately (25 to 30) mg of SiO2 are dropped. The heat effect after the solvent was saturated showed values close to the heat content of SiO2, indicating that no silica dissolved. Calorimetry of cristobalite in sodium molybdate that was initially saturated with amorphous silica (~500 mg in 20.0 g of sodium molybdate) exhibited nearly constant values with an average for six drops of \((40.7 \pm 0.6)\) kJ·mol\(^{-1}\), which is close to the heat content of cristobalite at \(T = 976\) K \((43.0\) kJ·mol\(^{-1}\), [21]).

The XRD analysis of the precipitate after recovery of soddyite dissolved in sodium molybdate soddyite showed that SiO2 from soddyte also precipitates as cristobalite, indicating that the final state of SiO2 from soddyte dissolution is cristobalite. Thus, cristobalite was used as the reference phase in the calorimetric cycle (table 1) to calculate the enthalpy of formation of soddyite from elements, \(\Delta H_f^\circ\).
and oxides, $\Delta H_{\text{ox}}^\circ$. We used the enthalpy of drop solution of cristobalite obtained from our work (40.7 ± 0.6 kJ·mol⁻¹) in these calculations.

The calculated enthalpy of formation from the binary oxides is (117.8 ± 4.3) kJ·mol⁻¹ (table 2). Soddyite is more stable than the mechanical mixture of its constituent oxides by 117.8 kJ·mol⁻¹. Previously published values for the enthalpies of formation from the binary oxides for rutherfordine and metaschoepite are 99.1 kJ·mol⁻¹ and 4.4 kJ·mol⁻¹ [13,14], respectively. Soddyite is more stable than rutherfordine and metaschoepite with respect to the enthalpy of formation from the binary oxides. The standard-state enthalpy of formation from the elements of soddyite is (4045.4 ± 4.9) kJ·mol⁻¹.

3.2. Solubility experiments

Equilibrium was achieved within 20 days in all experiments as shown in figure 2. Our initial experiment (figure 2a, diamond symbols) contained only soddyite added to a solution containing aqueous U and Si. The equilibrium Si concentration was $10^{2.63±0.08}$, suggesting that Si was buffered in solution by amorphous silica, which has reported solubility values varying from $10^{2.38}$ to $10^{2.71}$ molal [22,23]. Subsequent XRD analysis of the mineral residue from this initial experiment indicated that soddyite was the only crystalline phase present. However, FT-IR results demonstrated the presence of amorphous silica. In light of these results, we chose to add silica gel, in addition to aqueous Si, to all subsequent experiments to ensure that the amorphous silica precipitation/dissolution reaction reached equilibrium within ~20 days. Figure 2 illustrates that the Si concentrations in all subsequent experiments were in the range reported for the solubility of amorphous silica. As the pH of the experiments decreased, the U concentrations in solution increased and the Si concentrations remained constant at a value within the range of reported amorphous silica solubility values. The XRD and FT-IR analyses of all subsequent experimental mineral residues verified that soddyite was the only crystalline phase present and that amorphous silica remained present and stable as well.

We based our solubility calculations on the following stoichiometry for the soddyite dissolution reaction:
For each solubility measurement on the equilibrium concentration plateau (compiled in Table 3), we calculated the ionic strength of the solution from the concentration of U and Si, the pH measurement for each sample, and the known amount of acid added for pH adjustments.

We used the extended Debye–Hückel equation to calculate the activity coefficients, $\gamma_i$, for each experimental condition:

$$\log \gamma_i = \frac{-A_i z_i^2 I^{1/2}}{1 + a B I^{1/2}} + b I,$$

(2)

where $I$ and $z_i$ represent the ionic strength and ionic charge, respectively, $A_i$ and $B$ are constants with values of 0.5105 and 0.3285, respectively, and $a$ and $b$ are values for RbNO$_3$ from Helgeson et al. [24] of 5.22 and 0.062, respectively. Parameters $a$ and $b$ take unique values for a particular electrolyte. Because we did not buffer ionic strength in these experiments with such an electrolyte, and because values of $a$ and $b$ have not been determined for uranyl-dominated systems, RbNO$_3$ was chosen as the most reasonable approximation to the experimental solutions, based on cation size, of those for which extended Debye–Hückel parameters are calculated [24]. The standard-states employed in this study for solid phases and for H$_2$O are the pure mineral or fluid, respectively. The standard-state for aqueous species is defined as a hypothetical one molal solution whose behavior is that of infinite H$_2$O dilution. Molal activity coefficients of neutral aqueous species are assumed to be unity. Using these standard-states, and assuming that the solid phase is pure and that the activity of water is unity under the experimental conditions, the solubility product for each data point was calculated based on the following mass action equation:

$$K_{sp} = \frac{a_{UO_2}^2 a_{SiO_2} a_{aq}}{a_{H_2O}^4}.$$

(3)

When calculating the solubility product, the aqueous complexation reactions listed in Table 4 were taken into consideration in order to calculate the activity of the aqueous uranyl cation under each experimental condition from our measurement of total aqueous uranium concentration. The calculated solubility product, averaged for all of the equilibrium measurements (Table 3), with its 1σ error is $(6.43 \pm 0.20)/0.37)$. Our solubility product is within error of some of the previously published values; however, our study is the first to rigorously demonstrate attainment of equilibrium from both supersaturation and undersaturation and to measure equilibrium pH and fully characterize the final run product identification. With our calculated solubility product value, in conjunction with the aqueous complexation reactions and $K$ values listed in Table 4, we extrapolate our results to calculate uranium concentrations in equilibrium with (soddyite + amorphous silica) at higher pH values of environmental interest (Figure 3).
concentrations would be correspondingly higher throughout the pH range if we considered the aqueous phase to equilibrate with (soddyite + quartz) due to the lower activities of silica in equilibrium with quartz. These calculations demonstrate that soddyite is less soluble than metaschoepite and rutherfordine in the circumneutral pH range, but considerably more soluble than uranyl phosphate phases [25–27].

The standard-state Gibbs free energy of formation of soddyite was calculated for each equilibrium measurement from the following equation:

\[
\Delta G_f^\circ = 2 \cdot \Delta G_f^\circ(UO_2^{2+}) + \Delta G_f^\circ(H_2SiO_3) + 4 \cdot \Delta G_f^\circ(H_2O) - \Delta G_f^\circ(soddyite),
\]

(4)

All other stability constants from reference [36].

<table>
<thead>
<tr>
<th>UO_2^{2+} + H_2O = UO_2(OH)^{+} + H^+</th>
<th>574</th>
</tr>
</thead>
<tbody>
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<td>UO_2^{2+} + 2H_2O = UO_2(OH)^{2+} + 2H^+</td>
<td>-12.0b</td>
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<td>-5.62b</td>
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<td>3UO_2^{2+} + 5H_2O = (UO_2)(OH)^{3+} + 5H^+</td>
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<td>3UO_2^{2+} + 7H_2O = (UO_2)(OH)^{4+} + 7H^+</td>
<td>-31.0</td>
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<td>4UO_2^{2+} + 7H_2O = (UO_2)(OH)^{5+} + 7H^+</td>
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<td>UO_2^{+} + CO_3^{2-} = UO_2CO_3</td>
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<td>UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_{2}^{2-}</td>
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<tr>
<td>UO_2^{3+} + 3CO_3^{2-} = UO_2(CO_3)_{3}^{3-}</td>
<td>23.63</td>
</tr>
<tr>
<td>2UO_2^{2+} + CO_3^{2-} + 3OH^- = (UO_2)<em>{2}(CO_3)(OH)</em>{3}</td>
<td>40.82c</td>
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<tr>
<td>H_2SiO_3(aq) = H_2SiO_3 + H^+</td>
<td>-9.83d</td>
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<tr>
<td>H_2SiO_4(aq) = H_2SiO_4^{2-} + 2H^+</td>
<td>-23.07</td>
</tr>
<tr>
<td>UO_2^{2+} + H_2SiO_4(aq) = UO_2H_2SiO_4^{2-} + H^+</td>
<td>-2.57</td>
</tr>
</tbody>
</table>

All other stability constants from reference [36].

\[\Delta G_f^\circ = -2.303RT \cdot \lg K_{sp},\]

(5)

where \(R\) is the universal gas constant and \(T\) is absolute temperature. The average standard-state Gibbs free energy of formation with its 2σ error is \((-3652.2 \pm 4.2)\) kJ·mol\(^{-1}\). Chen et al. [30] predicted the standard-state Gibbs free energy of formation of soddyite from an empirical method that derives the molar contributions of the structural components to \(\Delta G_f^\circ\) and \(\Delta H_f^\circ\) from thermodynamic data of phases for which the crystal structures are known. Their value, \(-3653.0\) kJ·mol\(^{-1}\), agrees with our value based on our solubility measurements.

3.3. Entropy calculations

The standard-state entropy of formation of soddyite, \(\Delta S_f^\circ\), can be calculated from the standard-state Gibbs free energy and enthalpy of formation:

\[\Delta S_f^\circ = \Delta H_f^\circ - T \Delta S_f^\circ,\]

(6)

where \(\Delta G_f^\circ\) is the standard-state Gibbs free energy of formation of soddyite, as determined from the solubility measurements, and \(\Delta H_f^\circ\) is the standard-state enthalpy of formation of soddyite, as determined from the calorimetry measurements. The calculated standard-state entropy of formation of soddyite, with propagated 2σ uncertainty, is \((-1318.7 \pm 21.7)\) J·mol\(^{-1}\)·K\(^{-1}\).

Alteration of spent nuclear fuel in a geological repository under oxidizing conditions is expected to result in the formation of a variety of uranyl minerals, and the solubilities of these minerals will impact the release of uranium and other radionuclides that they incorporate. Therefore, it is crucial to augment the sparse thermodynamic dataset that exists for uranyl minerals in order to predict repository performance. Standard-state Gibbs free energies, enthalpies, and entropies of formation for environmentally important uranyl minerals can be used to estimate mineral stabilities and solubilities under the elevated temperatures of a repository setting. In this study, we calculated the standard-state enthalpy of formation of soddyite from drop solution calorimetric measurements. We measured the solubility of soddyte as well, using solubility reversals to rigorously demonstrate that equilibrium was attained during the experiments. The solubility measurements were used to calculate the standard-state Gibbs free energy of formation of soddyte, and together with the enthalpy value, we calculated the standard-state entropy of formation of soddyte. This study demonstrates the power of combining solubility and calorimetry measurements to produce reliable and internally consistent thermodynamic data for uranyl minerals. The results of this and future similar studies of other environmentally relevant uranyl phases will enable predictions of uranyl mineral configurations.
stabilities and solubilities under realistic repository conditions.

Acknowledgements

Funding for this research was provided by a US Department of Energy, Office of Science and Technology and International (OST&I) grant under the Source Term Thrust program. Journal reviews and the comments made by the Editor were particularly helpful in improving the presentation of this work.

References


JCT 06-203