Thermodynamic Properties of Autunite, Uranyl Hydrogen Phosphate, and Uranyl Orthophosphate from Solubility and Calorimetric Measurements

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Received May 4, 2009. Revised manuscript received August 11, 2009. Accepted August 13, 2009.

In this study, we use solubility and drop-solution calorimetry measurements to determine the thermodynamic properties of the uranyl phosphate phases autunite, uranyl hydrogen phosphate, and uranyl orthophosphate. Conducting the solubility measurements from both supersaturated and undersaturated conditions and under different pH conditions rigorously demonstrates attainment of equilibrium and yields well-constrained solubility product values. We use the solubility data and the calorimetry data, respectively, to calculate standard-state Gibbs free energies of formation and standard-state enthalpies of formation for these uranyl phosphate phases. Combining these results allows us also to calculate the standard-state entropy of formation for each mineral phase. The results from this study are part of a combined effort to develop reliable and internally consistent thermodynamic data for environmentally relevant uranyl minerals. Data such as these are required to optimize and quantitatively assess the effect of phosphate amendment remediation technologies for uranium contaminated systems.

Introduction

Uranium is a prominent contaminant in a number of groundwater aquifer settings. Its presence in these systems in soluble form is of concern due to its chemical toxicity and potential radiological exposure hazard. Subsurface poly-
TABLE 1. Thermodynamic Cycles for the Calculation of Enthalpies of Formation of HUP and UP from Oxides and Elements*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enthalpy (kJ/mol)</th>
</tr>
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<tbody>
<tr>
<td>( \text{UO}_2\text{HPO}_4-3\text{H}<em>2\text{O}</em>{25}^\circ \equiv \text{UO}_3\text{sln,702}^\circ + 0.5 \text{P}_2\text{O}_5\text{sln,702}^\circ )</td>
<td>( \Delta H_1 ) = ( \Delta H_{\text{f,el}}(\text{HUP}) = 411.02 \pm 3.46 \text{ kJ/mol (7 drops)}^b )</td>
</tr>
<tr>
<td>( \text{P}_2\text{O}_5\text{sln,702}^\circ \equiv \text{P}_2\text{O}_5\text{sln,702}^\circ + 0.5 \text{H}<em>2\text{O}</em>{25}^\circ )</td>
<td>( \Delta H_2 = \Delta H_{\text{f,el}}(\text{HUP}) )</td>
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<tr>
<td>( \text{UO}_2\text{HPO}_4-3\text{H}<em>2\text{O}</em>{25}^\circ \equiv \text{UO}_3\text{sln,702}^\circ + 0.5 \text{H}<em>2\text{O}</em>{25}^\circ )</td>
<td>( \Delta H_3 = \Delta H_{\text{f,el}}(\text{HUP}) )</td>
</tr>
<tr>
<td>( \text{H}<em>2\text{O}</em>{25}^\circ \equiv \text{H}<em>2\text{O}</em>{25}^\circ )</td>
<td>( \Delta H_4 = \Delta H_{\text{f,el}}(\text{HUP}) )</td>
</tr>
<tr>
<td>( \text{UO}_2\text{HPO}_4-3\text{H}<em>2\text{O}</em>{25}^\circ \equiv \text{UO}_3\text{sln,702}^\circ + 0.5 \text{H}<em>2\text{O}</em>{25}^\circ )</td>
<td>( \Delta H_5 = \Delta H_{\text{f,el}}(\text{HUP}) )</td>
</tr>
<tr>
<td>( \text{2P}_2\text{O}_5\text{sln,702}^\circ + 3/2\text{O}<em>2g</em>{25}^\circ \equiv \text{UO}_3\text{sln,702}^\circ + 3/2\text{O}<em>2g</em>{25}^\circ )</td>
<td>( \Delta H_6 = \Delta H_{\text{f,el}}(\text{HUP}) )</td>
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<tr>
<td>( \text{2P}_2\text{O}_5\text{sln,702}^\circ + 3/2\text{O}<em>2g</em>{25}^\circ \equiv \text{UO}_3\text{sln,702}^\circ + 3/2\text{O}<em>2g</em>{25}^\circ )</td>
<td>( \Delta H_7 = \Delta H_{\text{f,el}}(\text{HUP}) )</td>
</tr>
<tr>
<td>( \text{2P}_2\text{O}_5\text{sln,702}^\circ + 3/2\text{O}<em>2g</em>{25}^\circ \equiv \text{UO}_3\text{sln,702}^\circ + 3/2\text{O}<em>2g</em>{25}^\circ )</td>
<td>( \Delta H_8 = \Delta H_{\text{f,el}}(\text{HUP}) )</td>
</tr>
<tr>
<td>( \text{2P}_2\text{O}_5\text{sln,702}^\circ + 3/2\text{O}<em>2g</em>{25}^\circ \equiv \text{UO}_3\text{sln,702}^\circ + 3/2\text{O}<em>2g</em>{25}^\circ )</td>
<td>( \Delta H_9 = \Delta H_{\text{f,el}}(\text{HUP}) )</td>
</tr>
</tbody>
</table>

*Notes: \( x_l \) = crystalline, \( s_l \) = solution, \( l \) = liquid, \( g \) = gas, \( ox \) = oxide, \( el \) = element, \( ds \) = drop solution. Two significant figures are reported to prevent rounding errors.

Results and Discussion

High-Temperature Oxide-Melt Solution Calorimetry. Enthalpies of drop solution of \( \text{UO}_2\text{HPO}_4-3\text{H}_2\text{O} \) (HUP) and \( \text{UO}_2\text{H}_2\text{PO}_4-2\text{H}_2\text{O} \) (UP) in sodium molybdate at 702 °C are 411.02 ± 3.46 kJ/mol and 821.38 ± 13.71 kJ/mol respectively (Table 1). The calculated enthalpies of formation of the binary oxides are \( -240.95 \pm 3.89 \) kJ/mol for HUP and \( -681.51 \pm 13.82 \) kJ/mol for UP. When normalized per one uranyl unit, this corresponds to \( -240.95 \pm 3.89 \) kJ/mol for HUP and \( -227.17 \pm 4.61 \) kJ/mol for UP. These values indicate significant stability of both phases with respect to \( \text{UO}_2 \), \( \text{P}_2\text{O}_5 \) oxides, and \( \text{H}_2\text{O} \). Note that we report enthalpies, free energies, and entropies to two decimal places, although the propagated errors do not justify that accuracy. This is done to avoid accumulated round-off errors in subsequent calculations.

HUP has a layered structure composed of uranyl phosphate layers with CaU topology separated by hydrogen cations and water molecules \( (13) \). UP is a framework with uranyl phosphate layers (uranophane topology) joined by uranyl tetragonal bipyrarids with water molecules located in the pores \( (14) \). Despite the structural dissimilarities shown, formation enthalpies indicate approximately equivalent stability of phases relative to constituent oxides. Thus, to identify the structural contribution or absence of such in phase stability, more uranyl phosphates of the analogous types should be studied.
The standard enthalpies of formation from the elements are (-3223.22 ± 3.99) kJ/mol for HUP and (-7001.01 ± 13.90) kJ/mol for UP.

**Solubility Experiments.** CaUP experiments involving supersaturated initial conditions at pH 3.0 and pH 3.8 reached a steady-state within 1 d (Figure 1a and b). Experiments from undersaturated conditions required additional time, 10 and 6 d, to attain a steady-state for experiments at pH 3.5 and 3.1, respectively (Figure 1c). All samples exhibited nonstoichiometric dissolution with higher Ca and P in solution than would be predicted based on congruent dissolution/precipitation of CaUP alone. Supersaturated experiments exhibited a greater extent of nonstoichiometric dissolution/precipitation than the under-saturated experiments. U:Ca and U:P molar ratios for supersaturated experiments were 0.2 and 0.4–0.6, respectively, while under-saturated experiments had U:Ca and U:P molar ratios of 1.2 and 0.9, respectively. XRD analysis of the mineral residues indicated that CaUP with decreased crystallinity was the only detectable mineral present, although the limitations of the XRD technique do not rule out the formation of a uranyl phosphate secondary phase during the experiment. The former process would elevate the concentration of Ca and P relative to the stoichiometric concentration expected for U; the formation of a uranyl phosphate phase would depress the aqueous concentrations of U and P relative to the stoichiometric concentration expected for Ca. Our data cannot distinguish between these two possibilities and it is likely that both mechanisms may be taking place simultaneously. Preferential leaching of Ca may be partially driven by bond valence considerations (13). Reduced particle size as a result of preferential leaching can lead to artifacts in mineral residual XRD patterns consistent with decreased crystallinity such as broader peaks, a shift in peak locations, and extraneous peaks can appear. Preferential leaching of cations from uranyl minerals in aqueous solutions and decreased crystallinity in uranyl minerals resulting from leaching have been observed previously (15, 16). The formation of a leached layer or a secondary mineral phase during a solubility experiment does not nullify the results as long as there is still some contact and hence equilibration between the phase of interest and the bulk aqueous phase. The reversal measurements provide a test whether equilibrium was achieved, and $K_{sp}$ values calculated from the undersaturation and supersaturation experiments should agree within experimental uncertainty if an equilibrium state was attained during the solubility experiments.

All the HUP experiments reached steady-state conditions within 10–12 d (Figure 2), and all experiments exhibited similar extents of nonstoichiometric dissolution, with P in excess of U in solution by more than 2 orders of magnitude. Analysis of mineral residues indicated that HUP was the only mineral present. Similar to the CaUP experiments, XRD analysis of the solids after the experimental runs indicated the presence only of HUP, although the degree of crystallinity
material may be implied if a steady state between the outer leach layer and the inner bulk material is indeed achieved. The similarity of solubility product values (see discussion below) for these systems that displayed different extents of leaching provides some support for this interpretation.

**Solubility Product Calculations.** Table 2 shows the reaction stoichiometry that we used for each mineral in the solubility product calculations. Solubility product \((K_{sp})\) calculations were only performed using data points that correspond to samples taken from each system after it had achieved steady-state conditions. The measured U, P, and Ca concentrations and corresponding measured pH values for each plateau data point that we used for the calculations are compiled in the Supporting Information Tables S2–S4. Ionic strength calculations for each plateau data point accounted for the concentrations of U, P, and Ca in the case of CaUP, the pH of each sample, and the known amount of NO\(_3^−\), Na\(^+\), and K\(^+\) added from acid/base additions for pH adjustments. We used the extended Debye–Hückel equation to calculate the activity coefficients, \(γ_i\), for each experimental condition:

\[
\log γ_i = \frac{-A z_i^2 \sqrt{I}}{1 + b \sqrt{I}} + bl
\]

where \(I\) and \(z_i\) represent the ionic strength and ionic charge, respectively; \(A\) and \(B\) are constants with values of 0.51 and 0.32 \((17)\), respectively, and \(a\) and \(b\) are values for a RbNO\(_3\) electrolyte from Helgeson et al. \((17)\), with values of 5.22 and 0.062, respectively. Parameters \(a\) and \(b\) take unique values for a particular electrolyte. To simplify the experimental systems, we did not buffer ionic strength with an added electrolyte. Because values of \(a\) and \(b\) have not been determined for uranyl-dominated systems, RbNO\(_3\) was chosen as the most reasonable approximation for these experimental solutions, based on cation size, of those for which extended Debye–Hückel parameters are calculated \((17)\).

Standard states employed in this study for solid phases and for H\(_2\)O are the pure mineral or fluid, respectively, at the temperature and pressure of the experiments. The standard state for aqueous species is defined as a hypothetical one molal solution whose behavior is that of infinite H\(_2\)O dilution at the temperature and pressure of interest. Molal activity coefficients of neutral aqueous species are assumed to be unity. Solubility product calculations for each plateau data point account for the aqueous complexation reactions listed in Supporting Information Table S5 to calculate UO\(_2\)(P\(_4\))\(_3\) and Ca\(^{2+}\) activities under each experimental condition from our measurements of total U, P, and Ca concentrations. Uncertainties associated with the stability constants in Table S5 would likely have a negligible effect on calculated \(K_{sp}\) values.

Calculated solubility products, averaged for all of the equilibrium measurements, with their 2σ uncertainties for each phase are listed in Table 2. In all cases, the solubility product values determined from experiments in which equilibrium was approached from undersaturation are within experimental uncertainty of the values determined from supersaturation experiments involving the same mineral phase. In addition, experiments conducted at different pH values using the same mineral phase yield solubility product values that are within experimental uncertainty of each other. The close correspondence between solubility product values from underground and supersaturated experiments, and from experiments conducted at different pH values suggests that decreased during the equilibration time. Previous studies of uraninite mineral dissolution have also noted a decrease in crystallinity possibly with concurrent proton incorporation to maintain charge balance \((15, 16)\). A similar mechanism could be occurring in this system with the leaching of P and possible incorporation of protons and other cation impurities as well as H\(_2\)O; however, the extent of preferential leaching was large and the difference in U and P concentrations may favor simultaneous leaching and secondary amorphous uraninite phase formation as an explanation.

UP experiments reached steady-state conditions within 10–12 d under all experimental conditions (Figure 3). Similar to the HUP experiments, all UP experiments exhibited nonstoichiometric dissolution with an excess of P in solution in three of the four conditions studied. The extent of excess P varied from one experiment to another. The pH 3.1 experiments that started from undersaturated conditions (Figure 3c) yielded an average U:P molar ratio of 1.1:1 which is close to the 1.5:1 molar ratio of stoichiometric dissolution, while all other experiments yielded average U:P molar ratios that ranged from 0.89:1 (Figure 3a) to 0.28:1 (Figure 3b). Final mineral residue analysis by XRD exhibited only peaks that can be attributed to UP; however, it is possible that a small amount (less than ca. 5%) of non-UP crystalline or amorphous precipitate was present. Similar to the other experiments in this study, the final residue showed a decreased extent of crystallinity relative to the starting material.

The preferential leaching of Ca and P in these experiments may suggest a steady state in the solid between the outer leached layer of the mineral and the bulk material. Our solubility results depict steady states between the aqueous solution and the outer leach layer of the minerals. A steady state between the aqueous solution and the inner bulk material may be implied if a steady state between the outer leach layer and the inner bulk material is indeed achieved.

**FIGURE 3.** Plot of experimental measurements of the dissolved concentrations of U (squares) and P (circles) as log mol·kg\(^{-1}\) against time for UP from supersaturation for experiments at pH 3.1 (a) and pH 3.8 (b) and undersaturation for experiments at pH 3.1 (open symbols) and pH 3.5 (closed symbols) (c).
the dissolution reactions listed in Table 2 correctly describe mineral dissolution in these systems. In addition, the close correspondence of the solubility product values from all experiments involving a particular mineral phase strongly suggests that these phases were stable under the experimental conditions and that the phases acted to buffer the U, P, and Ca concentrations in the experimental solutions.

Malgalhaes et al. (16) previously measured the solubility of synthetic CaUP that yielded a log $K_{sp}$ value of $-51.4 \pm 0.11$; however, the authors only made measurements from undersaturation and did not mention any postexperiment analysis of mineral residues. Guillaumont et al. (19) reviewed a solubility study of natural CaUP from undersaturation (20) and did not include the log $K_{sp}$ value of $-50.8$ in their critical review because the composition of the mineral was not well established and the $K_{sp}$ calculations failed to account for the formation of all aqueous uranyl phosphate complexes. In contrast, our study used a well-characterized natural mineral phase; we obtained steady-state data from supersaturated and undersaturated conditions; and our calculations included up-to-date stability constant values for aqueous complexes, yielding a more rigorously determined log $K_{sp}$ value of $-48.36$ with $2\sigma$ uncertainty values of $\pm 0.03$.

Previous measurements of HUP by Vesely et al. (21) and Van Haverbeke et al. (22) produced conditional log $K_{sp}$ values (not extrapolated to infinite dilution) of $-12.17 \pm 0.07$ and $-10.38 \pm 0.24$, respectively. Markovic and Pavkovic (23) also performed solubility measurements on HUP and calculated an average log $K_{sp}$ value of $-12.33 \pm 0.06$. None of the previous studies rigorously demonstrated an equilibrium state by having the experimental systems approach equilibrium from both supersaturation and undersaturation. Postexperimental characterization by Markovic and Pavkovic (23) was extensive. Similarly, Van Haverbeke et al. (22) used XRD analysis to verify the identity of the mineral residues in their experiments, but Vesely et al. (21) did not report pre- or postexperimental XRD analysis. Our log $K_{sp}$ value with its $2\sigma$ uncertainty, $-13.17 \pm 0.11$ ($0.07$) is outside the range of the previously reported values; however, it represents a value that has been extrapolated to the infinite dilution standard state and is based upon solubility data from systems in which equilibrium was approached from both supersaturation and undersaturation.

Previously reported values for the log $K_{sp}$ of UP range from $-49.00$ to $-53.33$ (21, 23–25). Sandino et al. (24) and Rai et al. (25) performed extensive pre- and postexperimental characterization of the mineral phase. Van Haverbeke et al. (22) used XRD analysis to verify the identity of the mineral residues in their experiments, while Vesely et al. (21) did not mention pre- or postexperimental XRD analysis. All investigators gathered their data from undersaturated conditions with the exception of Sandino et al. (24) who did conduct both supersaturation and undersaturation experiments. Sandino et al. (24) and Rai et al. (25) both gathered data over a wide pH range ($\sim 3$ to $\sim 9$); however, the calculated log $K_{sp}$ values from their studies ($-53.32 \pm 0.17$ and $-49.08 \pm 0.48$, respectively) are not consistent. Our log $K_{sp}$ value of $-49.36$ ($-0.40$/$+0.02$) is consistent with the log $K_{sp}$ value calculated by Rai et al. (25).

### Gibbs Free Energy of Formation

The calculated $K_{sp}$ value for each solid phase can be used to calculate the standard.
state Gibbs free energy of formation of the phase by first translating each $K_o$ value into a standard state Gibbs free energy of reaction, $\Delta G^o_f$, for each dissolution reaction of interest using the following equation:

$$\Delta G^o_f = -2.3026RT \cdot \log K_o$$  
(2)

where $R$ is the universal gas constant and $T$ is absolute temperature. From the calculated values of $\Delta G^o_f$, we used known standard state Gibbs free energies of formation of other components in the dissolution reactions (Table 2) to calculate the standard state Gibbs free energies of formation of the three solid phases studied here. Values obtained from Cox et al. (26) for $\Delta G^o_f$(HUP) and $\Delta G^o_f$(UP) are $-592.55 \pm 1.75$, $-1025.49 \pm 1.58$, $-1095.99 \pm 1.58$, $-552.81 \pm 1.05$, and $-237.14 \pm 0.04$ kJ/mol, respectively. To obtain the $2\sigma$ errors associated with the $\Delta G^o_f$ values, we propagated the largest error associated with the respective $\log K_o$ values. Each data point from a solubility measurement yields calculated values for the Gibbs free energy of formation for the mineral of interest, and the average value for each mineral, with its $2\sigma$ error, is reported in Table 2. The $2\sigma$ errors are calculated from propagating the errors associated with the $\Delta G^o_f$ values of the mineral phase constituents and $\Delta G^o_f$.

Chen et al. (27) predicted the Gibbs free energies of formation of various uranyl minerals using an empirical approach that derives the molar contributions of the structural components to $\Delta G^o_f$ and $\Delta H^o_f$ from thermodynamic data of phases for which the crystal structures are known. Model derived values for HUP and UP are $-3063.5$ and $-6093.4$ kJ/mol, respectively. Our values for HUP $-2835.14 \pm 4.89$ kJ/mol and UP $-6138.95 \pm 12.11$ kJ/mol are not consistent with those of Chen et al.; however, the $\Delta G^o_f$ values are substantially closer to each other than the UP values. The better performance of the model for HUP is likely due to the use by Chen et al. of previous HUP solubility measurements to develop the database for their model. Conversely, their prediction of the standard Gibbs free energy of formation of UP was a “blind test” in that no solubility measurements were supported by the U.S. Department of Energy, Office of Science and Technology and International (OST&I) grant under the Source Term Thrust program, and in part by a U.S. Department of Energy, Environmental Remediation Science Program grant. Calorimetry measurements were supported by the U.S. Department of Energy (grant DE-FG02-97ER14749).

### Entropy of Formation and Standard Entropy

The entropy of formation from the elements ($\Delta S^o_f$) is calculated from Gibbs free energy of formation from the elements ($\Delta G^o_f$) determined from solubility measurements and enthalpy of formation ($\Delta H^o_f$) established by calorimetry:

$$\Delta S^o_f = \Delta H^o_f - T \Delta S^o_{el}$$  
(3)

The calculated entropy of formation $\Delta S^o_f$ is $-1302.28 \pm 21.18$ J/mol·K for HUP and $-2892.85 \pm 61.86$ J/mol·K for UP. The standard entropy $S^o_{el}$ is $-2774.13 \pm 55.28$ J/mol·K for HUP and $-5494.70 \pm 61.87$ J/mol·K for HUP and UP, respectively.

### Geologic Applications

The thermodynamic properties that have been determined in this study for CaUP, HUP, and UP can be used to determine the concentrations of aqueous species that control the relative stabilities of these phases. For example, the relationship between HUP and UP can be expressed:

$$\text{H}^+ + (\text{UO}_2^{2+})(\text{PO}_4^{3-})_2 \cdot 4\text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{HPO}_4\cdot3\text{H}_2\text{O} + 2\text{UO}_2^{2+} + \text{PO}_4^{3-} + \text{H}_2\text{O}$$  
(4)

Using standard Gibbs free energies of formation for the components in reaction 4 from Cox et al. (26) and from the results of this study yields a value for the $\Delta G^o_f$ of 136.09 kJ/mol and a log $K$ value of $-23.84$. These values can be used to determine the relative stabilities of these phases as a function of pH and uranyl and phosphate activities in solution. At a $\text{PO}_4^{3-}$ activity of 0.01 $m$, the equilibrium relationship (depicted in Figure 4a) can be expressed as:

$$\log a_{\text{UO}_2^{2+}} = -0.5 \text{ pH} - 10.92$$  
(5)

where log $a_{\text{UO}_2^{2+}}$ represents the log of the activity of the uranyl cation in solution. Under low pH conditions, where the total aqueous uranium activity is virtually identical to the activity of the uranyl cation, eq 4 indicates that UP is more stable than HUP in uranium-contaminated waters. For example, at pH 4, when log $a_{\text{UO}_2^{2+}}$ (equivalent to the total aqueous uranium activity under low pH conditions) is greater than approximately $-13$, UP is the more stable phase. However, with increasing pH above 5, the activity of the uranyl cation decreases markedly due to the increased importance of uranyl aqueous complexes with hydroxide, carbonate, organic ligands, etc. Under these conditions, HUP can be the more stable phase, depending on the exact solution composition of interest.

The conditions that favor the formation of CaUP relative to UP are depicted in Figure 4b, which shows the equilibrium relationship:

$$\text{UO}_2^{2+} + \text{H}_2\text{O} + \text{Ca}^{2+}(\text{PO}_4^{3-})_2 \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{(UO}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} + \text{Ca}^{2+}$$  
(6)

The value of $\Delta G^o_f$ for reaction 6, based on standard state Gibbs free energies of formation from this study and from Cox et al. (26), is $-5.72$ kJ/mol, corresponding to a log $K$ value of $1.00$. As the position of the equilibrium line in Figure 4b indicates, CaUP is more stable than UP whenever the activity of $\text{Ca}^{2+}$ is more than an order of magnitude larger than the activity of $\text{UO}_2^{2+}$. For contaminated geologic systems, this condition is likely met under a range of pH conditions, and UP would be more stable than CaUP only in Ca-poor waters that are highly contaminated with uranium.

### Acknowledgments

Funding for this research was provided in part by a U.S. Department of Energy, Office of Science and Technology and International (OST&I) grant under the Source Term Thrust program, and in part by a U.S. Department of Energy, Environmental Remediation Science Program grant. Calorimetry measurements were supported by the U.S. Department of Energy (grant DE-FG02-97ER14749).

### Supporting Information Available

Details of the syntheses, mineral characterization, and data points used for calculating thermodynamic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

### Literature Cited


