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A method to predict free energies of formation of mineral phases in the U(VI)–SiO_2–H_2O system

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Abstract

A method to estimate standard-state free energies of formation ($\Delta_f G°$) for U(VI)-layered oxide hydrates and silicates is described. The $\Delta_f G°$ values for these phases are estimated from the free energies for the oxide and hydroxide components in the sheet structures, defined as the solid-phase free energies ($\Delta_f G^*$). $\Delta_f G^*$ for the component oxides and hydroxides are assumed to be constant among the various sheet structures. A derivation of the $\Delta_f G^*$ parameters for structural water and the $UO_2(OH)_2$ component is presented, and used to estimate $\Delta_f G°$ for important phases in the U(VI)–SiO_2–H_2O system. Although propagated uncertainties are large, this method provides reasonable estimates of the free energies of formation for the layered U(VI) structures, but not for the infinite framework structures such as soddyite.

Keywords: Uranyl phases; Spent nuclear fuel; Solubility; Standard Gibbs free energy of formation

1. Introduction

To assess the performance of geologic repositories for the isolation of spent nuclear fuel, geochemical models (codes such as EQ3/6) are used to calculate the dissolved metal concentrations from solubilities of solid phases and the speciation of dissolved contaminants in the waste package. These calculations are then extrapolated over thousands of years. Spent nuclear fuel is essentially UO_2 with approximately 4 weight-percent actinides and fission products, which corrodes to U(VI) solid phases under aqueous oxidizing environments [1,2]. The resulting corrosion products represent a complex assemblage of U(VI) phases, the composition of which depends on groundwater conditions.

Many groundwaters are saturated with respect to silicate and contain major cations, such as Na^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}. Studies of weathering and alteration of natural uraninite (UO_2) deposits have shown that complex assemblages of U(VI) oxide hydrates and U(VI) silicate solid phases such as schoepite, metaschoepite, becquerelite, uranophane, soddyite, and many others are typically formed on a geologic timescale [2,3]. Unfortunately, the thermodynamic data necessary to predict the formation of many of the relevant solid phases do not exist or are inconsistent. In addition, the large number of possible U(VI) phases makes experimental determination a long-term research challenge. In the mean time, performance assessment activities for planned spent fuel repositories must proceed, even in the absence of essential experimental measurements.

Recently, Burns et al. [4] published a structural hierarchy for over 180 U(VI) solid phases based on the topologies of the U coordination polyhedra. This hierarchy classifies minerals of similar topologies into nine classes, with the majority (~80%) of the uranyl oxide hydrates and silicate phases classified as infinite sheet structures (Table 1). These U(VI) solid phases consist of the U-polyhedra and associated anions ordered in two-dimensional sheet structures with exchangeable cation sites located between the sheets, similar to the sheet structures of clay minerals. Another topological category for U(VI) silicate structures is the infinite framework topology, which consists of a three-dimensional network of U-polyhedra, associated anions, and exchangeable cations.

Tardy and Garrels [5] devised a method of estimating standard-state free energies of formation ($\Delta_f G°$) for layer silicates by summing free energies of 'silication' ($\Delta_f G_{sil}°$) for oxide and hydroxide components of the sheets combined with the free energies of exchange for the exchangeable cations. A similar approach was recently reported by Finch [6], where the free energy of the U(VI) oxide in the

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Table 1
Topological classification and chemical descriptions of important U(VI) mineral phases

U(VI) Mineral phase	Formula	Topological classification[a]
Uranyl oxide hydrates		
Schoepite	$[(UO_2)_8O_2(OH)_{12}]\cdot 12(H_2O)$	infinite sheet A
Metaschoepite	$[(UO_2)_8O_2(OH)_{12}]\cdot 10(H_2O)$	infinite sheet A
Becquerelite	$Ca[(UO_2)_3O_2(OH)_3]_2\cdot 8(H_2O)$	infinite sheet A
Compreignacite	$K_2[(UO_2)_3O_2(OH)_3]_2\cdot 8(H_2O)$	infinite sheet A
Uranyl silicates		
Soddyite	$(UO_2)_2SiO_4\cdot 2H_2O$	infinite framework
Uranophane	$Ca[(UO_2)(SiO_3OH)]_2\cdot 5H_2O$	infinite sheet B
Boltwoodite	$K(H_3O)[(UO_2)(SiO_4)]$	infinite sheet B
Sklodowskite	$Mg[(UO_2)(SiO_3OH)]d\cdot 6H_2O$	infinite sheet B
Weeksite	$(K_{0.62}Na_{0.38})_2(UO_2)_2(Si_5O_{13})(H_2O)_3$	infinite framework

[a] Topological classification after Burns et al. [4]. Infinite sheet A indicates infinite sheets with nets of triangles and pentagons. Infinite sheet B consists of infinite sheets with nets of triangles, pentagons and squares.

solid phase is estimated, and used to derived free energies of formation of U(VI) solid phases from the standard state. These methods require the assumption that the free energies of silication of the oxide and hydroxide components are constant among the various layered structures, although they may differ from their free energies of formation of the oxides as separate phases at standard state. For Tardy and Garrels [5], values for $\Delta_f G_{sil}{}^\circ$ of the various oxide and hydroxide components were obtained from reported $\Delta_f G^\circ$ for the Mg–Si–OH system. They then used this method to estimate the free energies of formation for montmorillonite, illite, chlorite, and micas of complex composition. Reasonable agreement between their estimates and available published values provided confidence in this approach, suggesting it may be useful for estimating the free energies of formation for U(VI) layer silicates.

An objective of this work is to apply the method of Tardy and Garrels [5] to estimate the free energies of formation for various U(VI)-layered structures. In addition, an important secondary objective is to assign uncertainties associated with these estimates. The free energy of formation for the $UO_2(OH)_2$ species in the sheet structure ($\Delta_f G^*$ $UO_2(OH)_2$) is defined as done previously [5] for metal oxide components of the clays. Uncertainties are estimated using standard error propagation. For this work, $\Delta_f G^*$ $UO_2(OH)_2$ is defined as the free energy of formation of $UO_2(OH)_2$ in the sheet structure, which differs from the formation of this species from the standard state; $\Delta_f G^*$ $UO_2(OH)_2$ is assumed to be constant among solid layered structures.

The value of $\Delta_f G^*$ for $UO_2(OH)_2$ was estimated using the published solubility for crystalline $UO_3\cdot 2H_2O$ [6]. A value for $\Delta_f G_{sil}{}^\circ$ for structural water is estimated using the linear relationship between $\Delta_f G^\circ$ and the amount of hydration for each structure. These parameters were subsequently used to estimate standard free energies of formation for other U(VI)-layer silicate minerals, and compared to available published values.

2. Methods

For all systems and calculations, standard temperature and pressure were assumed. When available, the quoted $\Delta_f G^\circ$ values reported in the NEA database for uranium were used [7]. All errors reported represent the standard propagation of uncertainties for each mathematical operation.

Following the examples for layer silicates as described by Tardy and Garrels [5], the standard-state free energies of formation ($\Delta_f G^\circ$) for U(VI)-layer oxide hydrates and silicates were estimated by summing the solid-phase free energies ($\Delta_f G^*$) for the component hydroxides and oxides in the sheet structure. The component oxides and hydroxides found in the sheet structures of U(VI) layered mineral structures include the neutral hydroxide species of the uranyl cation, $UO_2(OH)_2$ and SiO_2. The interlayer (i.e., exchangeable) cations were treated as oxides such as Na_2O_{ex} or MgO_{ex}, as described in [5]. Free energies values for the interlayer cations and SiO_2 in the U(VI) structures for this work are listed in Table 2 and were taken from Tardy and Garrels [5].

Structural water is an important component for both clay phases and the U(VI) solid phases; however, the U(VI) layered structures contain significantly more structural water than the layered silicates of clays studied by Tardy

Table 2
Estimates of the free energies of formation for the oxide and hydroxide components in the silicate matrix of the U(VI) mineral phases

Component	$\Delta_f G^*$, kJ/mol	Uncertainty
$UO_2(OH)_2$	−1390	7
SiO_2	−856	1
H_2O	−247	7
CaO_{ex}	−765	1
MgO_{ex}	−667	1
K_2O_{ex}	−787	1
Na_2O_{ex}	−734	1

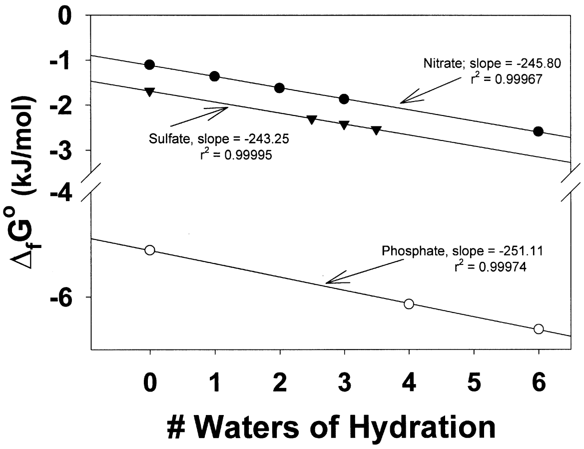

Fig. 1. The effect of hydration on the free energies of formation for various U(VI) solid phases. Values for free energies of formation are taken from Grenthe et al. [7]. Solid circles indicate the $UO_2(NO_3)_2 \cdot xH_2O$ system, open circles indicate the $(UO_2)_3(PO_4)_2 \cdot xH_2O$ system, and solid triangles are for the $UO_2(SO_4) \cdot xH_2O$ system.

and Garrels. Therefore, we estimated the $\Delta_f G^*$ for water from thermodynamic data available for other U(VI) minerals and solid phases as a function of hydration. Exchangeable water and the water component of the sheet structure were not differentiated, and a single value of $\Delta_f G^*$ H_2O in the U(VI) solids was estimated. Values of $\Delta_f G^\circ$ for the $(UO_2)(NO_3)_2 \cdot xH_2O$, $(UO_2)_3(PO_4)_2xH_2O$, and $(UO_2)(SO_4)xH_2O$ from [7] were plotted versus the number of water molecules in the structure, and this gave a linear relationship (Fig. 1); the mean of the observed slopes was used for $\Delta_f G^*$ H_2O, with an error equal to the standard deviation of the estimates.

The free energy of the $UO_2(OH)_2$ in the layered matrices was estimated using the published standard-state free energy for crystalline $UO_3 \cdot 2H_2O$. Similar to the approach of Tardy and Garrels [5], the following expression was used:

$$\Delta_f G^\circ UO_3 \cdot 2H_2O = \Delta_f G^* UO_2(OH)_2 + \Delta_f G^* H_2O \qquad (1)$$

The value of $\Delta_f G^*$ $UO_2(OH)_2$ was estimated by difference from Eq. 1 using the estimated value of $\Delta_f G^*$ H_2O, and is reported in Table 2.

Standard-state free energies of formation for the U(VI)-layered hydroxide and silicate phases were estimated by summing the appropriate contributions of the component oxides and hydroxides in Table 2, and the uncertainty was propagated. The weighting of $\Delta_f G^*$ and its uncertainty for hydroxide, oxide, and water components was determined from the mineral stoichiometry. For example, for the mineral uranophane whose formula is $Ca[(UO_2)(SiO_3OH)]_2 \cdot 5H_2O$, the component hydroxides and oxides are (1) CaO_{ex} for exchangeable Ca^{2+}; (2) UO_2 as the hydroxide species $UO_2(OH)_2$; (3) SiO_2 for silicon in the sheet; and, (4) H_2O as structural water. This gives the following relationship:

$$\Delta_f G^\circ = \Delta_f G^* CaO_{ex} + 2[\Delta_f G^* UO_2(OH)_2] + 2[\Delta_f G^* SiO_2] + 4[\Delta_f G^* H_2O] \qquad (2)$$

The weightings of the components for the various solid phases in this paper are given in Table 3 with the resulting $\Delta_f G^\circ$ values. Where possible, the estimated $\Delta_f G^\circ$ values are compared to published values.

3. Results and discussion

Tardy and Garrels demonstrated that as the cationic charge density on the metal of the component oxide or hydroxide increases, the difference between the free energy of formation in the standard state ($\Delta_f G^\circ$) and the free energy of formation in the silicate matrix (designated as $\Delta_f G_{sil}^\circ$) approaches zero. In the case of SiO_2, $\Delta_f G^\circ = \Delta_f G_{sil}^\circ$; consequently, we have chosen to use the value of $\Delta_f G^\circ$ reported in the NEA database [7] as the value for the free energy of SiO_2 in the solid phase ($\Delta_f G^*$ SiO_2), and the uncertainty assigned to $\Delta_f G^*$ SiO_2 was taken from the uncertainty assigned to $\Delta_f G^\circ$ SiO_2. As shown in Fig. 1, $\Delta_f G^\circ$ for U(VI) solid phases with various degrees of

Table 3
Weightings of the component oxides and hydroxides given with the estimates for $\Delta_f G^\circ$

	$UO_2(OH)_2$	SiO_2	H_2O	CaO_{ex}	K_2O_{ex}	MgO_{ex}	Na_2O_{ex}	Estimated $\Delta_f G^\circ$ kJ/mol	Uncertainty	Reported $\Delta_f G^\circ$ kJ/mol	Reference
Schoepite	8		10					−13590	90		
Metaschoepite	8		8					−12968	79	−13092	[8]
Becquerelite	6		5	1				−10340	55	−10780	[11]
Compreignacite	6	5		1				−10362	55	−10405	[11]
Uranophane	2	2	4	1				−6245	31	−6211	[12]
Boltwoodite	1	1	0.5		0.5			−2763	8		
Sklodowskite	2	2	5			1		−6394	38		
Soddyite	2	1						−3636	14	−3745	[12,13]
Weeksite	2	5	1		0.62		0.38	−8074	16		
Na boltwoodite	1	1	1.5				0.5	−2984	13	> −2966	[12]
Na-weeksite	2	6	2				1	−9144	21	−9088.5	[12]

hydration exhibits a linear relationship with the number of structural water molecules. The $\Delta_f G_{sil}{}^\circ$ for structural water obtained as described above is indicated in Table 2.

The estimated free energy value for structural water in the silicate matrix is consistent with the value used by Tardy and Garrels [5], although no error analysis was reported with their estimate. While the solid phases used to estimate $\Delta_f G^*$ for structural water for our work are not sheet structures, we chose this approach as the propagation of error for the value was possible. O'Hare et al. [8] reported a value of -243 kJ/mol as the free energy contribution of water to the overall $\Delta_f G^\circ$ of schoepite, which is also consistent with our estimate. The water free energy value reported by O'Hare was not used, however, as the crystal structure of schoepite has been revised recently [9], which identified additional waters of hydration in the formula. Consequently, the work of O'Hare deserves reevaluation in light of the new crystal structure for schoepite. In a recent paper by Diaz Arocas and Grambow [10], standard-state free energies of water were calculated for interlayer water and structural water in schoepite. They estimated the $\Delta_f G^\circ$ value for interlayer water to be -238.1 kJ/mol, as compared with -254.2 kJ/mol for structural water. No uncertainty was assigned to their estimate. Although we did not distinguish between structural and interlayer water in this work, our value for 'average' water is consistent with the estimates of Diaz Arocas and Grambow [10].

The value and uncertainty we estimate for $\Delta_f G^*$ $(UO_2)(OH)_2$ is consistent with the $\Delta_f G^\circ$ for crystalline β-$UO_2(OH)_2$ (-1398.683 ± 1.765 kJ/mol) reported in the NEA database [7]. Our estimate of the uncertainty associated with $\Delta_f G^*$ $UO_2(OH)_2$ is larger than that reported for $UO_2(OH)_{2(cr)}$, as we have chosen to propagate errors. Table 3 lists the estimated $\Delta_f G^\circ$ for the uranyl oxide hydrates and U(VI)-layered silicate structures in this work. When compared to reported $\Delta_f G^\circ$ values, estimates from this analysis are generally consistent although associated uncertainties with our estimates tend to be large. This approach appears to slightly underestimate $\Delta_f G^\circ$ for becquerelite, as obtained from solubility data reported by Sandino et al. [11]. The reason for this discrepancy is not clear. Our estimates of $\Delta_f G^\circ$ for uranophane and boltwoodite are consistent with the work of Nguyen et al. [12]. The experimental value reported for Na-boltwoodite was only a lower limit, due to experimental difficulties.

Interestingly, our estimate of $\Delta_f G^\circ$ for soddyite is not consistent with reported solubilities by Nguyen et al. [12] and Moll et al. [13]. In addition, our estimate for Na-weeksite does not agree with the experimental solubility reported by Nguyen et al. [12]. However, these results were anticipated. According to Burns et al. [4], the crystal structures of soddyite and weeksite are not derived from an infinite layer silicate topology, but rather an infinite framework (Table 1). As suggested by Finch [6], such differences in structural topology (e.g. sheets versus three dimensional network) are expected to yield differences in the calculated thermodynamic properties.

4. Summary and conclusions

The method described above provides reasonable estimates of $\Delta_f G^\circ$ values for sheet structures of U(VI) oxide hydrates and silicate phases, but underestimates the reported free energies of formation for nonsheet structures. Since the majority of the known U(VI) mineral structures are composed of infinite sheets and the solubilities of many of these phases have not been reported, this method provides a reasonable approach for estimating solubilities in the absence of experimental values. However, because of the uncertainties associated with the $\Delta_f G^*$ for structural water and $UO_2(OH)_2$, this method does not provide the sensitivity needed to evaluate discrepancies in solubility data of single phases, nor does it serve as a substitute for experimental thermodynamic studies. Rather, it can be used in the absence of experimental data to infer stabilities of U(VI) sheet structures in various systems, which can serve as a guide for experimental work as well as suggest important pathways for long-term U(VI) mineral transformations. In a subsequent publication, we will describe a method for estimating the free energies of formation of non-sheet structures of the U(VI) solid phases.

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