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ENTHALPIES OF FORMATION OF RARE EARTH AND ACTINIDE(III) HYDROXIDES; THEIR ACID-BASE RELATIONSHIPS AND ESTIMATION OF THEIR THERMODYNAMIC PROPERTIES

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ABSTRACT

This paper reviews the literature on rare earth(III) and actinide(III) hydroxide thermodynamics, in particular the determination of their enthalpies of formation at 25 °C. The hydroxide unit-cell volumes, lanthanide/actinide ion sizes, and solid-solution stability trends have been correlated with a generalized acid-base strength model for oxides to estimate properties for heterogeneous equilibria that are relevant to nuclear waste modeling and to characterization of potential actinide environmental interactions. Enthalpies of formation and solubility-product constants of actinide(III) hydroxides are estimated.

INTRODUCTION

The thermodynamic properties of crystalline rare earth and actinide hydroxides are needed to determine the free energies for reactions between these compounds and near-neutral aqueous solutions. Raising the pH of an aqueous rare earth or actinide solution produces gelatinous hydroxide precipitates that are not crystalline and that approach equilibrium extremely slowly. For some rare earths, long-term equilibrium studies have been made to determine the equilibrium constant of the reaction

$$M(OH)_3(\text{crystalline}) = M^{3+}(aq) + 3\ OH^-(aq). \qquad (1)$$

These studies, using "aged" and presumably crystalline hydroxides, are believed to yield thermodynamically valid solubility products K^b_{s10} [1].

A rigorous way to determine the standard free energy of reaction (1) is to prepare crystalline $M(OH)_3$ and to determine its enthalpy of formation and standard entropy. Among hydroxides, enthalpies of formation have been measured by solution calorimetry only for the lanthanides $La(OH)_3$ [2, 3] and $Nd(OH)_3$ [4]. Entropies have been determined for several rare earth hydroxides [5]. These enthalpies and entropies have been combined with literature values for $M^{3+}(aq)$ and $OH^-(aq)$ to yield solubility products $K_{sp} = K^b_{s10}$. The agreement between equilibrium measurements for reaction (1) and calculations (from enthalpy and entropy measurements) is good enough to place a high level of confidence in the equilibrium measurements for rare earth hydroxides.

The only thermodynamic properties have been determined for actinide hydroxides are equilibrium constants for solubility of $Pu(OH)_3$ [6], $Am(OH)_3$ [7], and "$Pu(OH)_4$" [8]. The hydroxides of americium(III) and curium(III) are of particular interest in nuclear waste migration studies; the lighter actinides thorium, uranium, neptunium, and plutonium exist as An(IV) hydrous oxides in near-neutral or basic solutions. Although efforts have been made to minimize radiolysis errors, to correct for oxidized species, and to remove colloidal particles, there remains doubt whether these were true equilibria; independent thermochemical or acid-base assessments should remove such doubt.

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MASTER

THERMODYNAMIC ASSESSMENTS

Hydroxides

Rare earth hydroxides (Y, La-Yb)$(OH)_3$ crystallize in trigonal space group $P6_3/m$. Baes and Mesmer [1] found a correlation between the solubility products of lanthanide hydroxides and their unit cell a parameters and published a set of recommended "smoothed" K_{sp} values. Morss [9,10] followed a similar approach but correlated unit-cell volumes with K_{sp} values.

Syntheses of crystalline hydroxides, coupled with calorimetric measurements of their enthalpies of formation, are important because they can be combined with measured entropies to determine standard free energies of formation for this isostructural class of compounds: $\Delta_f G^\circ[La(OH)_3(s)] = \Delta_f H^\circ[La(OH)_3(s)] - 298.15 \times \Delta_f S^\circ[La(OH)_3(s)]/1000 = -1415.5 - 298.15 \times 0.4334 = -(1283 \pm 2)$ kJ·mol^{-1} and $\Delta_f G^\circ[Nd(OH)_3(s)] = \Delta_f H^\circ[Nd(OH)_3(s)] - 298.15 \times \Delta_f S^\circ[Nd(OH)_3(s)]/1000 = -1403.8 - 298.15 \times 0.4453 = -(1271.0 \pm 1.0)$ kJ·mol^{-1}. For the solubility reactions we calculate, using $\Delta_f G^\circ[La^{3+}(aq) = -688$ kJ mol^{-1}, $\Delta_f G^\circ[Nd^{3+}(aq) = -672 \pm 2$ kJ mol^{-1}, and $\Delta_f G^\circ(OH^-,aq) = -157.244$ kJ mol^{-1}, we calculate for

$$La(OH)_3(s) = La^{3+}(aq) + 3\ OH^-(aq) \qquad (2)$$

$\Delta_r G^\circ = +(123 \pm \_\_)$ kJ·mol^{-1} and for

$$Nd(OH)_3(s) + Nd^{3+}(aq) + 3\ OH^-(aq) \qquad (3)$$

$\Delta G^\circ = +(127.2 \pm 3)$ kJ·mol^{-1}

The corresponding solubility products ($\log K_{sp} = -\Delta G^\circ/RT$) are given in Table I along with literature values.

Actinide hydroxides (Am, Cm)$(OH)_3$ also crystallize in trigonal space group $P6_3/m$. Baes and Mesmer [1] recommended that the solubility products of actinide(III) hydroxides be estimated from the structural correlation that they noted for lanthanide hydroxides. Morss carried out such an estimation [10]. However, his values for $Pu(OH)_3$ and $Am(OH)_3$ differ by about 2 units in $\log K_{sp}$ from those derived from equilibrium measurements [6,7]. Thus it appears that there may be an acid-base factor that distinguishes the 5f (actinide) hydroxide basicities from those of the 4f (lanthanide) hydroxides.

Sesquioxides

Smith [11] developed an empirical set of oxide acidity parameters based upon enthalpies of formation of oxy-salts and the relationship

$$\text{acidity(ACID)} - \text{acidity(BASE)} = [-\Delta H(\text{reaction})]^{1/2} \qquad (4)$$

where ΔH refers to the transfer of one mole of oxide ion from basic oxide to acidic oxide. He normalized the relationship by setting the acidity of the very weak acid H_2O equal to zero. Thus the enthalpy change of the hydrolysis reaction (normalized to one mole of oxide ion transfer)

$$H_2O(l) + 1/3\ M_2O_3(s) = 2/3\ M(OH)_3(s) \qquad (5)$$

generates a useful acidity parameter a for an oxide if the enthalpy of formation of the oxide is known: $[-\Delta H(\text{reaction } 5)]^{1/2} = a(M_2O_3)$, since $a(H_2O) = 0$. Values of a calculated from this relationship for La_2O_3 and Nd_2O_3 are given in Table I; they are significantly more negative than those of Smith.

Table I. Solubility Products of Lanthanide and ActinideIII) Hydroxides and Acidity Parameters of Sesquioxides

M	pKsp, $M(OH)_3$ [a]	$a(M_2O_3)$ [b]	M	pKsp, $M(OH)_3$ [a]	$a(M_2O_3)$ [b]
Y		-6.5?			
La	21.7 21.6 [c]	-6.1 -7.5 [e]	Ac	20.9	
Ce	22.1	-5.8			
Pr	22.1	-5.8			
Nd	23.1 22.3 [4]	-5.7 -6.9 [e]	U	22.2	
Pm	(24)		Np	22.4	
Sm	25.2	-5.1	Pu	22.6 26.2 [6]	-6.9 [d] -5.1 [e]
Eu	26.5	-5.1	Am	24.0 25.7 [7] 25.7 [f]	-5.6 [e]
Gd	26.9	-5.0	Cm	24.0 25.0 [f]	-5.8 [e]
Tb	26.3	-4.3	Bk	25.0	-4.2 [e]
Dy	25.9	-4.7	Cf	25.5	-4.2 [e]
Ho	26.5	-4.5	Es	26.0	
Er	26.6	-4.3			
Tm	26.6	-4.2			
Yb	26.6	-4.5			
Lu	27.0	-3.3			

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[a] Ref 1 (lanthanides); ref 10 (actinides) unless otherwise stated.

[b] Ref 11 unless otherwise stated.

[c] This work, calculated from refs 3 and 9.

[d] This work, equations 4 and 5.

[e] This work, $a(M_2O_3) = [\Delta H(6) - 102\ kJ]^{1/2}$.

[f] This work (see text).

The enthalpies of formation of all rare-earth sesquioxides have been determined from solution and combustion calorimetry and "best values" have been assessed [9,10]. Enthalpies of formation of Am, Cm, and Cf sesquioxides have been measured and that of Pu has been assessed [12]. Lanthanide-actinide enthalpy comparisons and actinide enthalpy-of-formation estimations have been made [12].

We generalize Smith's acid-base correlation by noting that the enthalpies of solution of lanthanide oxides in infinitely-dilute aqueous acid vary systematically [12] with ionic size:

$$2H^+(aq) + 1/3\ Ln_2O_3(s) = 2/3\ Ln^{3+}(aq) + H_2O(l) \qquad (6)$$

This generalization is useful for elements, such as the actinides, that have no enthalpy-of-formation data for oxy-salts. We adjust $\Delta H(6)$ to $\Delta H(5)$ by noting that $\Delta H(6) - \Delta H(5) = 103$ and 100 kJ mol^{-1} respectively for La and Nd. Thus $a(M_2O_3) = [\Delta H(6) - 102\ kJ]^{1/2}$. Acidities of actinide(III) oxides generated from this relationship are shown in Table I.

ACID-BASE CORRELATIONS

We accept the value of $pK_{sp} = 26.2$ for $Pu(OH)_3$ [6] and calculate $\Delta_fG°[Pu(OH)_3,s] = -1200.3$ kJ mol^{-1}. We use the most-recently assessed value of $\Delta_fH°(Pu_2O_3, s, 298\ K) = -1656$ kJ mol^{-1} [10] along with the known $S°(Pu_2O_3, s, 298\ K) = 163.0 \pm 0.6$ J mol^{-1} K^{-1} [13] and our estimate for $S°[Pu(OH)_3, s, 298\ K = 131.6$ J K^{-1} mol^{-1} [14] to derive $\Delta_fH°[Pu(OH)_3, s, 298\ K) = -1327.9$ kJ mol-1. From this value we calculate the Smith acidity parameter $a[Pu_2O_3] = -6.9$. Note that this acidity parameter is the same as that of the structurally-similar Nd_2O_3.

In a paper on the enthalpy of formation of Cf_2O_3, Morss [12] noted that the enthalpies of solution (in infinitely dilute acid) of actinide(III) oxides are systematically less exothermic than the enthalpies of solution of structurally-similar lanthanide oxides. We interpret this difference to represent the greater acidity of the actinide(III) oxides and hydroxides compared to structurally-similar lanthanide oxides and hydroxides in terms of reaction (6). This interpretation is consistent with the smaller K_{sp} (more negative log K_{sp}, greater pK_{sp}) values of actinide(III) hydroxides compared to structurally-similar lanthanide hydroxides.

It has traditionally been assumed that hydrolysis of trivalent actinide ions

$$An^{3+}(aq) + H_2O(l) = An(OH)^{2+}(aq) + H^+(aq) \quad K = \beta^*_{11} \qquad (7)$$

parallels that of lanthanide ions of the same ionic radius [15]. Recent measurements, e.g. [7], give evidence for a larger β^*_{11} (more negative log β^*_{11}, more positive $p\beta^*_{11}$) value for Am^{3+}. These recent measurements imply, as above, that actinide(III) aquo-ions are more acidic than structurally-similar lanthanide aquo-ions.

ACTINIDE(III) HYDROXIDE THERMODYNAMICS

From the acidity parameters a developed for actinide(III) oxides, and the a developed for Pu_2O_3 above, we use Smith's approach to set a parameters for Pu_2O_3, Am_2O_3, and Cm_2O_3. From these parameters we calculate enthalpies of formation of these hydroxides from $\Delta H(5)$ as follows: $\Delta_fH°[Pu(OH)_3, s, 298\ K] = -1328$ kJ mol^{-1}; $\Delta_fH°[Am(OH)_3, s, 298\ K] = -1346$ kJ mol^{-1}; and$\Delta_fH°[Cm(OH)_3, s, 298\ K] = -1341$ kJ mol^{-1}. With entropy estimates, we calculate $pK_{sp}[Am(OH)_3] = 25.7$ and $pK_{sp}[Cm(OH)_3] = 25.0$. Clearly it will be beneficial to measure enthalpies of formation for these hydroxides and pK_a for $Cm(OH)_3$ to test this extension of the acid-base systematics developed in this paper and to provide more reliable thermodynamic parameters for these and heavier actinide hydroxides.

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