

Partial Molal Entropy and Heat Capacity of the Aqueous Thorium(IV) Ion. Thermochemistry of Thorium Nitrate Pentahydrate

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Th(NO₃)₄·5H₂O(c) was prepared in high purity and its enthalpy of solution was measured in 0.01 M HClO₄ at 15, 25, and 35 °C, using a calorimeter sensitive to 5 × 10⁻⁶ K. These measurements are combined with recent literature data to derive $\bar{S}^\circ(\text{Th}^{4+}, \text{aq}) = -424 \pm 4 \text{ J mol}^{-1} \text{ K}^{-1}$, $\bar{C}^\circ_{p2}(\text{Th}^{4+}, \text{aq}) = -1 \pm 11 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\Delta H^\circ_{f1}[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{c}] = -3009 \pm 4 \text{ kJ mol}^{-1}$ at 298.15 K. \bar{S}° and \bar{C}°_{p2} are interpreted by comparison with other monatomic ions, using appropriate semiempirical equations.

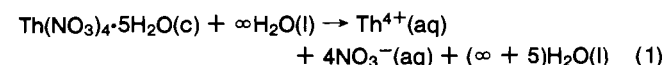
The partial molal entropy, \bar{S}° , and partial molal heat capacity, \bar{C}°_{p2} , of an aqueous ion are the essential thermodynamic properties necessary for calculating the changes of other thermodynamic properties of the aqueous ion as a function of temperature (7, 8). Since thorium is an element of great importance as a nuclear fuel and as a by-product of nuclear technology, determination of these important properties for Th⁴⁺(aq) is obviously of practical importance.

Once \bar{S}° and \bar{C}°_{p2} for several ions of a given class (e.g., monatomic cations) have been determined experimentally, there are good semiempirical methods for estimating \bar{S}° and \bar{C}°_{p2} for other ions of the same class at 25 °C and at other temperatures as well (8, 13, 14). As experimental \bar{S}° and \bar{C}°_{p2} values for more ions become available, understanding of these properties and their predictive power for other, less-tractable ions are enhanced. Data for Th⁴⁺(aq) can be extended to the important heavier tetravalent actinide ions U⁴⁺ and Pu⁴⁺.

Since Th⁴⁺ is the only tetravalent ion which exists in aqueous solution without extensive hydrolysis, it is the best tetravalent ion for which the Debye-Huckel limiting law may be tested, and for which \bar{S}° and \bar{C}°_{p2} may be calculated. However, adequate data cannot be found in the chemical literature from which these properties may be calculated.

In order to provide experimental data to satisfy the goals of determining \bar{S}° and \bar{C}°_{p2} and of testing the Debye-Huckel limiting law, thorium nitrate pentahydrate was selected as an appropriate compound which can be prepared in high purity, which dissolves readily in water, and which has an anion which does not complex appreciably with Th⁴⁺. Until recently, it was believed that the hexahydrate of thorium nitrate is the species which exists in equilibrium with Th(NO₃)₄(aq) at 25 °C. The definitive study of the Th(NO₃)₄-HNO₃-H₂O system by Ferraro et al. (16) showed that the pentahydrate is really the stable solid at 25 °C and that earlier reports of hemihydrate or hexahydrate represented mixtures of pentahydrate with hydrolyzed species and/or mother liquor. The pentahydrate has since been characterized by x-ray (37, 39) and neutron diffraction (38) crystallography. Its solubility in water has been measured (3) and its heat capacity has been measured from 6 to 349 K (6).

Measurement of \bar{S}° for Th(NO₃)₄(aq) requires the determination of ΔG° and ΔH° for the solution process (26),



The free energy for reaction 1, $\Delta G^\circ(1)$, may be calculated from literature data on the properties of the saturated aqueous solution of Th(NO₃)₄ at 25 °C, as will be described in the Results section. The only literature data on the enthalpy of solution of thorium nitrate are determinations of the enthalpy of solution (at fairly high concentration) of the tetra- and pentahydrates in various solvents (17) and a few measurements of enthalpy of dilution (25). Since these measurements are not suitable for determination of $\Delta H^\circ(1)$, measurements of the heat of solution of Th(NO₃)₄·5H₂O were undertaken at 25 °C.

Since Th⁴⁺ is appreciably hydrolyzed in water, we selected the moderately acidic pH 2.0 represented by 0.0100 M HClO₄(aq) as a solvent for our experiments. As shown below, Th⁴⁺(aq) is no more than 1.4% hydrolyzed at 25 °C and pH 2 at the Th⁴⁺ concentrations used in this work. Preliminary calorimetric experiments showed nearly identical heats of solution at pH 1.1 and pH 2.0, but markedly less exothermic heats of solution at pH 2.5 and pH 3.0.

Having measured $\Delta H(1)$ at 25 °C, we repeated the measurements at 15 and 35 °C in order to determine \bar{C}°_{p2} for Th(NO₃)₄(aq) by the "integral heat method" developed by Criss and Cobble (12). In order to determine $\Delta H^\circ(1)$, the enthalpy of solution at infinite dilution (the hypothetical 1-*m* solution), we used an extended Debye-Huckel extrapolation to infinite dilution also developed by Criss and Cobble (12).

Experimental Section

Commercial thorium nitrate, Research Organic/Inorganic "99.9+%", was analyzed by us and found to correspond nearly to a trihydrate. It was recrystallized from a warm solution of distilled, deionized water which had been mixed with nitric acid to yield a mixture in region B of Ferraro's (16) Figure 1 at 25 °C: 80.5% Th(NO₃)₄, 19% H₂O, and 0.5% HNO₃. The crystals were collected in a sintered-glass funnel, washed briefly with ice-cold dilute nitric acid, and pressed between filter papers. Since the large, initially formed crystals analyzed to a variable composition of about Th(NO₃)₄·5.2H₂O, it was assumed that they contained occluded solution and they were ground in a glass mortar to coarse granules which were stored for several weeks over saturated CaCl₂(aq) (H₂O vp 7.7 Torr at 25 °C). Two preparations were separately analyzed for thorium by ignition to ThO₂ at 900 °C and water by the Karl Fischer method. Calcd for Th(NO₃)₄·5H₂O: Th, 40.70; H₂O, 15.80. Found: Th, 40.70 ± 0.03; H₂O, 15.72 ± 0.16. The absence of any thermal anomalies in the heat-capacity measurements (6) confirmed that the granular products contained no occluded solution.

We were able to handle the pentahydrate in room air as long as the relative humidity was below 55%. Samples for calorimetry were weighed into thin-walled spherical Pyrex bulbs of ca. 1 cm³ volume. The necks of the bulbs were carefully sealed with a glass plug and Apiezon W wax using a "hot-wire" coil while immersing the bulb in water. Air-filled bulbs were sealed by the same method for measurement of the bulb-breaking correction.

The calorimetric apparatus has been described (29). For this research, when heats of solution were measured for samples yielding a final Th⁴⁺ molality of less than 0.001 mol kg⁻¹, the

Table I. Integral Heats of Solution and ρ Values of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}^a$

m , mol kg ⁻¹	l , mol kg ⁻¹	$-\Delta H(1)$, J mol ⁻¹	$10A_H I^{1/2}\alpha$, J mol ⁻¹	$-\rho$, J mol ⁻¹
15.00 °C				
0.002 27	0.0327	12 300	2617	14 917
0.000 873	0.0187	12 022	2024	14 046
0.000 498	0.0150	12 512	1851	14 363
0.000 303	0.0130	11 948	1728	13 676
0.000 322	0.0132	12 193	1740	13 933
0.001 543	0.0254	12 612	2345	14 957
0.001 606	0.0261	12 287	2374	14 661
0.001 352	0.0235	12 182	2264	14 446
0.001 952	0.0295	11 996	2506	14 502
0.000 553	0.0155	12 455	1881	14 336
0.001 084	0.0208	11 920	2148	14 068
$\Delta H^{\circ}(1) = -13\,819 \pm 154$ J/mol				
25.00 °C				
0.003 02	0.0402	16 972	3339	20 311
0.003 26	0.0426	16 934	3426	20 360
0.004 04	0.0504	17 130	3700	20 830
0.006 35	0.0735	16 609	4332	20 941
0.001 08	0.0208	17 240	2504	19 744
0.002 08	0.0308	17 065	2979	20 044
0.001 03	0.0203	17 169	2476	19 645
0.002 48	0.0348	17 048	3138	20 186
0.000 755	0.0176	17 430	2323	19 753
0.000 361	0.0136	17 478	2058	19 536
0.000 516	0.0152	17 253	2173	19 426
$\Delta H^{\circ}(1) = -19\,462 \pm 71$ J/mol				
35.00 °C				
0.001 067	0.0207	20 562	2888	23 450
0.000 783	0.0178	20 613	2704	23 317
0.002 052	0.0305	20 850	3439	24 289
0.000 547	0.0155	20 500	2544	23 044
0.000 675	0.0168	20 567	2631	23 198
0.001 43	0.0243	20 647	3112	23 759
0.001 70	0.0270	20 739	3265	24 004
0.001 087	0.0209	20 528	2911	23 439
$\Delta H^{\circ}(1) = -22\,625 \pm 38$ J/mol				

^a Uncorrected for hydrolysis.

total temperature rise was less than 0.004 K. For such experiments, the calorimeter had to be operated at its limit of temperature sensitivity (peak-to-peak noise of 5×10^{-6} K over a 5-min period) with long time-temperature "drift lines" before and after each electrical calibration or sample dissolution. A few experiments had to be rejected because of erratic sample dissolution or high noise levels, but no experiment was rejected because the measured heat was unexpectedly high or low.

For each experiment the calorimeter was charged with 878 g of 0.0100 M HClO_4 at a temperature 2° below that chosen for the experiment. The absolute temperature during each experiment was determined after calibrating the temperature-measuring thermistor Wheatstone bridge frequently against a platinum resistance thermometer (which itself had been calibrated at the ice point, 68.71 °C, and 231.97 °C) using conventional procedures (2). Each experiment consisted of a few precise electrical-heat calibrations delivering energy of the same magnitude as that expected during sample dissolution, followed by the sample dissolution, and followed again by one or two electrical-heat calibrations. The strip-chart temperature-time plots were reduced to observed heats by conventional procedures, using Dickinson's method of heat-leak correction (11, 30).

The solubility of " $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ " and of commercial $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ has been measured in water as a function of temperature. However, since we were concerned that hydrolysis polymers may appear to shift the equilibrium of eq 1 to the right, we measured the solubility of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ in an aqueous

solution such that the solvent would have $[\text{HClO}_4] = 0.0100$ M by approaching equilibrium both from an unsaturated and a supersaturated solution at 25.00 ± 0.02 °C for several days. We found that the saturated solution had $m[\text{Th}(\text{NO}_3)_4] = 3.66 \pm 0.02$ mol (kg of $\text{H}_2\text{O})^{-1}$ when equilibrium was reached from either direction.

Results

Observed heats of solution were corrected as follows; the corrected values for each experiment are shown in the third column of Table I: (a) evaporation of water into the air trapped in the bulb upon sealing, taking into account the water vapor known to be in the trapped air from the room relative humidity when the bulb was sealed. The heat attributable to bulb-breaking was 0.00 ± 0.02 J, determined by breaking air-filled bulbs and applying correction (a) to the observed heat effect. (b) a correction to the appropriate temperature of 15.00, 25.00, or 35.00 °C, since most sample dissolutions occurred at a mean temperature a few hundredths of a degree higher or lower, using the approximate ΔC_p for the solution process determined from heats of solution at all three temperatures.

From the resulting molar integral heats of solution, $\Delta H(1)$, standard-state enthalpies of solution $\Delta H^{\circ}(1)$ were determined by a second-order Debye-Huckel treatment:²⁰

$$\phi_H = \Delta H(1) = \Delta H^{\circ}(1) + \frac{\nu}{2} |z_+ z_-| A_H I^{1/2} \alpha - 2.303 RT^2 \times \left(\frac{dB}{dT} \right)_{\nu+\nu-m} \quad (2)$$

where $\alpha = [(1 + I^{1/2})^{-1} - \sigma(I^{1/2})/3]$. All symbols in eq 2 follow Pitzer and Brewer (26) and $\sigma(x)$ is tabulated by Harned and Owen (27). A convenient method of carrying out this treatment is to calculate ρ , the heat corrected by the Debye-Huckel limiting law,

$$\rho = \Delta H(1) - \frac{\nu}{2} |z_+ z_-| A_H I^{1/2} \alpha = \Delta H(1) - 10 A_H I^{1/2} \alpha \quad (3)$$

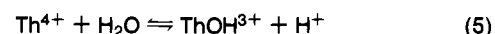
as has been done by Cobble and co-workers (12, 23), and then to extrapolate ρ to $m = 0$ by the method of least squares. The correction term and ρ value for each experiment are given in Table I and the " ρ plots" for all three temperatures are shown in Figure 1. The reported values and error limits for $\Delta H^{\circ}(1)$ at each temperature represent least-squares intercepts of ρ at $m = 0$ and the standard deviations of the intercepts,

$$s = s_y \sqrt{\frac{\sum x_i^2}{n \sum x_i^2 - (\sum x_i)^2}} \quad (4)$$

using Student's t for $n - 2$ degrees of freedom and the appropriate number of observations (42).

The resulting $\Delta H^{\circ}(1)$ values, given in Tables I and II, might not represent true values for reaction 1 because of thermal effects of hydrolysis and nitrate complexing. Each of these will be considered.

Hydrolysis. The hydrolysis of $\text{Th}^{4+}(\text{aq})$ has been considered by many investigators (1). Exhaustive survey of the literature revealed four relevant reports. Pan and Hseu (33) determined $K_h = [\text{ThOH}^{3+}][\text{H}^+]/[\text{Th}^{4+}]$ for the reaction



at 25 °C as a function of ionic strength, obtaining $K_h = 1.7 \times 10^{-4}$ in pure water. Kraus and Holmberg (24) measured K_h in 1 M NaClO_4 (ionic strength $I = 1$) at 25 °C and Baes et al. (5) extended this determination to 0 and 95°. The latter authors considered several more extensive hydrolysis reactions and calculated ΔH for each reaction. In culminating several studies on Th^{4+} hydrolysis, Hietanen and Sillen (22) confirmed and extended the results of Kraus and Holmberg and of Baes et al.

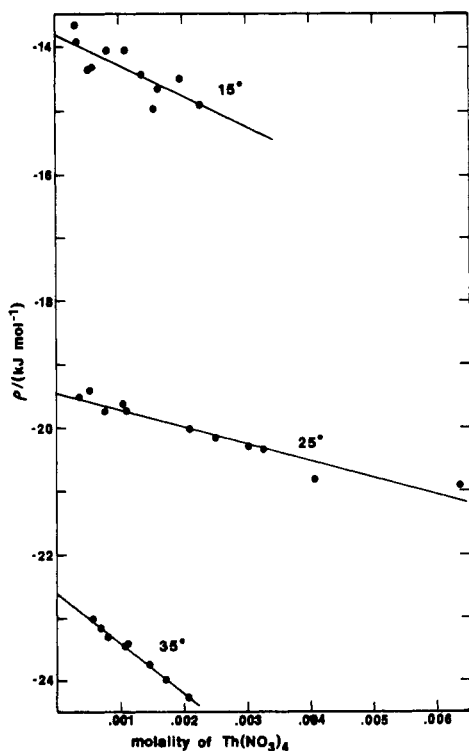
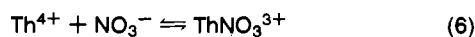


Figure 1. ρ plots for heats of solution of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$.

Under the experimental conditions of the present research, $[\text{Th}^{4+}]$ is so small and $[\text{H}^+]$ is sufficiently large that reaction 5 represents the only significant hydrolysis equilibrium. At pH 2, $I = 0.01$ when $m(\text{Th}^{4+}) = 0$; under these conditions Pan and Hseu (33) indicated $K_h = 1.4 \times 10^{-4}$ at 25 °C. Using this K_h , the $\Delta H(5)$ of Baes et al. (5), and the van't Hoff equation, we calculate $K_h = 1.0 \times 10^{-4}$ and 1.9×10^{-4} at 15 and 35 °C, respectively.

At 15 °C, $K_h = 1.0 \times 10^{-4} = [\text{ThOH}^{3+}][10^{-2} + \text{ThOH}^{3+}]/[\text{Th}^{4+}]$, so that $[\text{ThOH}^{3+}]/[\text{Th}^{4+}] \approx 0.010$; i.e., 1.0% of $\text{Th}^{4+}(\text{aq})$ is hydrolyzed at pH 2 at 15 °C. Similar calculations at 25 and 35 °C yield 1.4 and 1.9% hydrolysis as ThOH^{3+} . These results are independent of $m(\text{Th}^{4+})$ at the molalities encountered in this research. Since Baes et al. derived $\Delta H(5) = 24.7 \text{ kJ mol}^{-1}$, we have corrected $\Delta H^\circ(1)$ as shown in Table II.

Nitrate Complexing. There are three reports (15, 32, 43) which indicate that the equilibrium constant in aqueous solution for the reaction



lies between 1.5 and 4.7 at 25 °C. In our experiments, $[\text{NO}_3^-] = 4[\text{Th}^{4+}]$, so that

$$K = \frac{[\text{ThNO}_3^{3+}]}{4[\text{Th}^{4+}]^2} \quad (7)$$

Although $\Delta H(6)$ is unknown, eq 7 shows that the fraction of Th^{4+} complexed as ThNO_3^{3+} decreases linearly with $m(\text{Th}^{4+})$. Thus the ρ plots of Figure 1 correct for the effect of nitrate complexing as well as for second-order Debye-Huckel effects.

Conclusions

Limiting-Law Behavior. A recent test of the Debye-Huckel limiting law for enthalpies of dilution of 3-1 electrolytes was the study by Spedding, Csejka, and DeKock of heats of dilution of several lanthanide trichloride solutions (36). They calculated the limiting-law slope when the relative apparent molal heat content, ϕ_L , was plotted against $m^{1/2}$ and found excellent agreement with the theoretical value. The linearity of the ρ plots of Figure 1 is

Table II. $\Delta H^\circ(1)$ and $\Delta C_p^\circ(1)$ for $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$

t , °C	$\Delta H^\circ(1)_{\text{uncorr.}}$, J mol ⁻¹	% hydrolyzed	$\Delta H^\circ(1)_{\text{corr.}}$, J mol ⁻¹	$\Delta C_p^\circ(1)$, J mol ⁻¹ K ⁻¹
15	-13 819	1.0	-14 066	
20				-574
25	-19 462	1.4	-19 807	
30				-329
35	-22 625	1.9	-23 094	

good evidence that the 4-1 electrolyte $\text{Th}(\text{NO}_3)_4$ follows a second-order Debye-Huckel limiting law.

Because of the presence of 0.0100 M HClO_4 in each experiment, the range of values of $I^{1/2}$ was quite small at all three temperatures. A plot of $\Delta H(1)$ vs. $I^{1/2}$ for the 25 °C data of Table I showed a slope of $4500 \text{ J mol}^{-3/2} \text{ kg}^{1/2}$, much less than the limiting-law slope of $28 800 \text{ J mol}^{-3/2} \text{ kg}^{1/2}$ expected for a 4-1 electrolyte. We conclude that $\text{Th}(\text{NO}_3)_4$ has not reached first-order Debye-Huckel limiting-law behavior at the lowest ionic strengths encountered in this study.

Partial Molal Entropy. For reaction 1,

$$\begin{aligned} \Delta G^\circ(1) &= -RT \ln [(a_{\text{solute}})(a_{\text{H}_2\text{O}})^5] = -RT \ln [(a_{\pm})^\nu (a_{\text{H}_2\text{O}})^5] \\ &= -RT \ln [(\gamma_{\pm}^\nu)(m^\nu)(\nu^+ \nu^- \nu^-)(a_{\text{H}_2\text{O}})^5] \\ &= -RT \ln [(\gamma_{\pm}^5)(m^5)(4^4)(1^1)(a_{\text{H}_2\text{O}})^5] \quad (8) \end{aligned}$$

Apelblat et al. have recently measured the solubility of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ in water. There are two earlier reports of the solubility of $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ in water (27, 28), and because Ferraro et al. (16) showed that this "hexahydrate" is primarily pentahydrate, we might expect these earlier solubility data to be appropriate for equilibrium with the pentahydrate. However, the extrapolated molality of these earlier solubility studies, 4.04 mol kg^{-1} , is not consistent with Apelblat's reported molality of 3.74 mol kg^{-1} (Apelblat's eq 1 is on the molality scale) (3). The phase diagram (16) indicates a solubility of about 3.7 mol kg^{-1} . Our solubility at 25.00 °C, 3.66 mol kg^{-1} , is consistent with the hypothesis that hydrolysis polymers (in particular those produced by " $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ ") do shift the equilibrium of eq 1 significantly to the right. We adopt $3.7 \pm 0.1 \text{ mol kg}^{-1}$ as the concentration of the saturated solution at 25.00 °C.

There are two reports of vapor pressure data on aqueous solutions of thorium nitrate which lead to solute and solvent activities. Robinson and Levien (34) measured vapor pressures down to molality = 0.1 mol kg^{-1} . Apelblat et al. (4) measured vapor pressures to 0.2 mol kg^{-1} and extended the measurements to $0.004 \text{ mol kg}^{-1}$ by vapor pressure osmometry. Although the measurements of Apelblat et al. (4) may be extrapolated empirically to infinite dilution, their data show considerable scatter and are interpreted simply as power series in ϕ and $\ln \gamma$, yielding $\phi = 1.673$ and $\gamma = 0.320$ at the saturation molality of 3.7 mol kg^{-1} . The measurements of Robinson and Levien are more self-consistent and have been extrapolated to infinite dilution by an extended Debye-Huckel treatment (40), yielding $\gamma = 0.377$ at $m = 3.7 \text{ mol kg}^{-1}$. Thus

$$\ln a_{\text{H}_2\text{O}} = -\frac{\nu m M_{\text{H}_2\text{O}} \phi}{1000} = -\frac{5(3.7)(18.01)(1.673)}{1000} = -0.557$$

and $\Delta G^\circ(1) = -RT \ln [(0.377)^5(3.7)^5(256)(0.573)^5] = -10 970 \text{ J mol}^{-1}$.

Using this free energy and the corrected enthalpy of solution at 25 °C (Table II), $\Delta S^\circ(1) = [\Delta H^\circ(1) - \Delta G^\circ(1)]/T = [-19 807 - (-10 970)]/298.15 = -29.6 \text{ J mol}^{-1} \text{ K}^{-1}$. From reaction 1, $\bar{S}^\circ(\text{Th}^{4+}, \text{aq}, 298.15 \text{ K}) = \Delta \bar{S}^\circ(1) - 4\bar{S}^\circ(\text{NO}_3^-, \text{aq}) - 5\bar{S}^\circ(\text{H}_2\text{O}, \text{l}) + S[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{c}] = -29.6 - 4(146.94) - 5(69.95) + 543.1 = -424.0 \pm 3.6 \text{ J mol}^{-1} \text{ K}^{-1}$. Auxiliary entropy data were taken from CODATA Bulletin 10 (9) and from Cheda et al. (6).

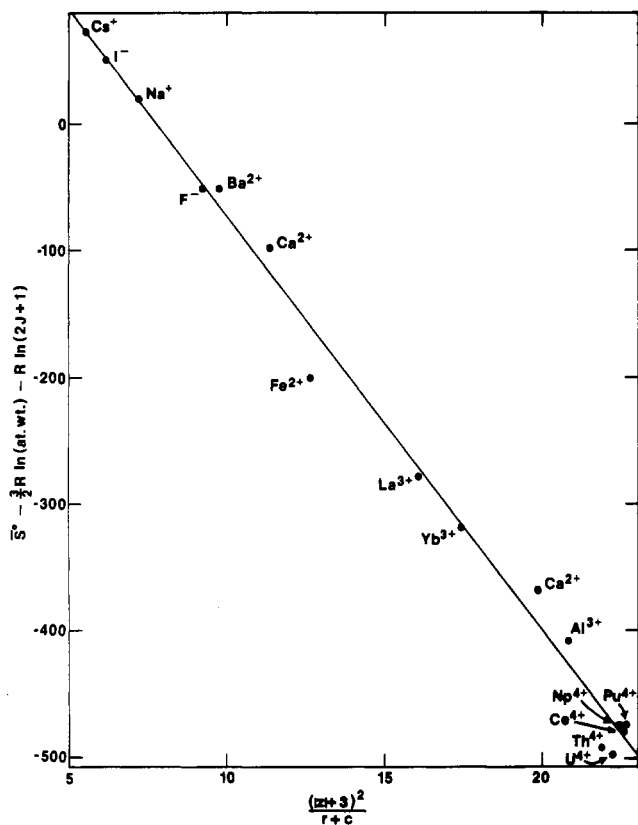


Figure 2. Entropies of monatomic aqueous ions.

Partial Molal Heat Capacity. From Table II, the mean $\Delta C_p^\circ(1)$ at 25 °C is $(-574 - 329)/2 = -452 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$. Since

$$\Delta H^\circ(1) = \Delta \bar{H}_f^\circ(\text{Th}^{4+}, \text{aq}) + 4\Delta \bar{H}_f^\circ(\text{NO}_3^-, \text{aq}) + 5\Delta H^\circ_f(\text{H}_2\text{O}, \text{l}) - \Delta H^\circ_f[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{c}] \quad (9)$$

the temperature derivative at constant pressure is

$$\Delta C_p^\circ(1) = \bar{C}_{p2}^\circ(\text{Th}^{4+}, \text{aq}) + 4\bar{C}_{p2}^\circ(\text{NO}_3^-, \text{aq}) + 5C_p(\text{H}_2\text{O}, \text{l}) - C_p[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{c}] \quad (10)$$

so that $\bar{C}_{p2}^\circ(\text{Th}^{4+}, \text{aq}, 298.15 \text{ K}) = -452 - 4(-86.61) - 5(75.29) + 480.8 = -1 \pm 11 \text{ J mol}^{-1} \text{ K}^{-1}$. Necessary heat capacities were taken from literature sources (6, 41).

$\Delta \bar{H}_f^\circ[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{c}]$. Fuger calculated $\Delta \bar{H}_f^\circ(\text{Th}^{4+}, \text{aq}) = -769.9 \text{ kJ mol}^{-1}$ (18). From eq 9 and other literature data (41) we calculate $\Delta \bar{H}_f^\circ[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}(\text{c}), 298.15 \text{ K}] = -769.9 + 4(-207.36) + 5(-285.83) - (-19.81) = -3008.7 \pm 4.2 \text{ kJ mol}^{-1}$.

Discussion

Morss and Cobble developed a semiempirical equation which successfully correlated the entropies of monatomic aqueous ions at 25 °C with their charges and radii (31). At present there are 62 monatomic aqueous ions for which entropies have been determined from experimental measurements. Using a least-squares fit of the entropies of the 61 ions, not including Th^{4+} , the equation is

$$\bar{S}^\circ(\text{M}^z, \text{aq}) = \frac{3}{2} R \ln(\text{atom wt}) + R \ln(2J + 1) + 253.4 - 32.52 \left[\frac{(z+3)^2}{r+c} \right] \quad (11)$$

where \bar{S}° is the calculated partial molal entropy of any monatomic aquoion in joules per mol per deg kelvin on the conventional scale of $\bar{S}^\circ(\text{H}^+, \text{aq}) = 0$, J is the total angular mo-

mentum quantum number for ion, z is its oxidation state, and r is its ionic radius in angstroms as quoted by Shannon and Prewitt (35) for coordination number 6, or for coordination number 8 for +4 ions. The term c is an additive correction to the ionic radius; $c = 1.20 \text{ \AA}$ for all cations and 0.40 \AA for all anions. In Figure 2 is shown the plot of the "corrected" entropy, $\bar{S}^\circ - \frac{3}{2}R \ln(\text{atom wt}) - R \ln(2J + 1)$ vs. the charge-size parameter $[(z+3)^2/(r+c)]$. Experimental values of a few "corrected" entropies of the 61 ions are shown, and the straight line represents the least-squares eq 11 for all 61 experimentally derived entropies. Although $\bar{S}^\circ(\text{Th}^{4+}, \text{aq})$ was not included in the least-squares fit, the value calculated in this paper is plotted in Figure 2 for comparison. The fit is quite good, with the value calculated from eq 11, $\bar{S}^\circ(\text{Th}^{4+}, \text{aq}, \text{calcd}) = -390 \pm 30 \text{ J mol}^{-1} \text{ K}^{-1}$, within error limits of the value calculated in this paper. Among the experimentally accessible entropies for +4 ions, all of which are plotted in Figure 2, we believe the value for $\text{Th}^{4+}(\text{aq})$ to be the most trustworthy (19). When $\bar{S}^\circ(\text{Th}^{4+}, \text{aq})$ is included in the least-squares fit to eq 11, the intercept and slope do not change significantly, becoming 256.8 and -32.84 , respectively.

Criss and Cobble (14) have shown that \bar{C}_{p2}° of an aqueous ion may be predicted from its \bar{S}° and two empirical constants. For cations at 25 °C,

$$\bar{C}_{p2}^\circ = (174.1 - 0.523\bar{S}^\circ) \text{ J mol}^{-1} \text{ K}^{-1} \quad (12)$$

where all single-ion heat capacities are scaled to "absolute" values based upon $\bar{C}_{p2}^\circ(\text{H}^+, \text{aq}) = 117 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\bar{S}^\circ(\text{H}^+, \text{aq}) = -21 \text{ J mol}^{-1} \text{ K}^{-1}$. One may test the predictive power of eq 12 for $\text{Th}^{4+}(\text{aq})$ by entering $\bar{S}^\circ(\text{Th}^{4+}, \text{aq}, \text{abs}) = -424 + 4(-21) = -508 \text{ J mol}^{-1} \text{ K}^{-1}$ into eq 12. The result is $\bar{C}_{p2}^\circ(\text{Th}^{4+}, \text{aq}, \text{abs}, \text{calcd}) = 440 \text{ J mol}^{-1} \text{ K}^{-1}$, whence $\bar{C}_{p2}^\circ(\text{Th}^{4+}, \text{aq}, \text{conventional}, \text{calcd}) = -28 \text{ J mol}^{-1} \text{ K}^{-1}$. This calculated value is in fairly good agreement with the value found in this research, indicating that eq 12 does have good predictive power for tetravalent cations.

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Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C.

1. The Rare Earth Chlorides

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The osmotic coefficients of the aqueous trichlorides of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y have been determined from 0.1 *m* to saturation at 25 °C. Semiempirical least-squares equations were obtained for the osmotic coefficients as a function of molality and these equations were used to calculate water activities and mean molal activity coefficients. The water activities of the light rare earth chlorides at constant molalities are higher than for the heavy rare earths, while the mean molal activity coefficients are larger for the heavy rare earths than for the light ones. The above effects are discussed in terms of changes in the cationic radii and hydration of the rare earth ions.

Attempts to explain irregularities in the thermodynamic (3, 10, 17, 20, 24, 25) and transport (23, 26) properties of aqueous rare earth electrolyte solutions have given rise to a model in which the light and heavy rare earth cations have different inner sphere hydration numbers, with the rare earths from Nd to Tb being mixtures of the two different coordinated forms. Transport properties (23, 26) depend mainly on overall hydration and indicate that an overall hydration increase occurs from La to Lu. The inner sphere hydration change is not seen directly in the rare earth chlorides but is reflected in the overall hydration trend. Water activities and electrolyte activity coefficients were determined since they are of fundamental importance in studying the thermodynamic behavior of these systems. In addition, the water activities are intimately related to solvation in aqueous solutions so isopiestic measurements are also of value for studying changes in hydration across the rare earth series.

Activity coefficient measurements on the rare earth chlorides have been reported by Robinson (14), Mason (7, 8), and Mason and Ernst (9). However, these measurements were for less than

half of the rare earths and extend only to 2.0 *m*. In this study, isopiestic measurements have been performed from 0.1 *m* to saturation on 14 of the rare earth chlorides, including YCl₃. A number of the the first and second derivative properties of the activities are available including the partial molal volumes (24), expansibilities (2, 3), heats of dilution (1, 11), and heat capacities (25).

Experimental Section

Apparatus and Experimental Procedure. The isopiestic apparatus employed in this research consisted of three rectangular stainless steel equilibration chambers, each containing a copper block. Each of these copper blocks had eight recesses (gold plated to reduce corrosion) in which the sample cups were firmly positioned. The cups were constructed of tantalum or of heavily gold-plated silver. A piece of platinum gauze was added to each cup to assist in the equilibration process. The equilibration chambers were slowly evacuated at the beginning of each isopiestic run. The temperature bath was controlled at 25.00 ± 0.01 °C and contained a rocking device for the chambers. The chambers were made large enough to act as thermal buffers; consequently thermal fluctuations within the chambers were much smaller than in the temperature bath. The experimental apparatus and procedure are described in more detail elsewhere (12, 15).

The isopiestic equilibrium molalities were calculated from the weight of analyzed stock solution added to each cup and the weight of solution present in these cups at the end of each equilibration period. Two samples of each solution were run and the average equilibrium molalities were used in all calculations. Each cup was covered with a tight fitting plastic cap when removed from the equilibration chambers for weighing. All weights were corrected to vacuum. Vacuum corrections for the rare earth chloride solutions were made using the density data of