# Thermodynamics of Hydration of a 4+ Aqueous Ion: Partial Molar Heat Capacities and Volumes of Aqueous Thorium(IV) from 10 to 55 °C[†]

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Densities and volumetric heat capacities for aqueous solutions containing $Th(ClO_4)_4$ in dilute ($\sim$0.12 *m*) $HClO_4$ have been determined from 10 to 55 °C. The results have been analyzed using a simple molality fraction approach (Young's rule) and an ion-interaction model (Pitzer ion-interaction scheme) that have led to calculated values for the apparent and partial molar volumes and heat capacities of $Th(ClO_4)_4(aq)$ and subsequently $Th^{4+}(aq)$ over this same temperature range. These results show the most highly negative standard state (infinitely dilute) partial molar volumes and heat capacities for any monatomic aqueous ion. The results have been examined in reference to earlier semitheoretical correlations and X-ray diffraction results for the hydration of aqueous ions and are consistent with expected Coulombic and ion−solvent interactions.

## Introduction

Knowledge of the thermodynamic properties of the aqueous actinide elements is required for a variety of applications. In particular, the properties of aqueous thorium are required because of the natural presence of thorium in groundwater and because it is a decay product of the uranium fission process. Moreover, thorium is important because of its relative ease of handling and the fact that thermodynamic data for certain thorium species can be applied to other more difficult-to-handle actinide elements.[1]

Aqueous thorium(IV) is relatively resistant to hydrolysis reactions and is less hydrolyzed in low pH solutions than many lower charged cations such as iron(III).[2,3] Because of this, the properties of unhydrolyzed, uncomplexed thorium are important in their own right for calculations of speciation in environments without significant complexed ion formation. However, in aqueous environments containing carbonate, sulfate, chloride, and even nitrate, significant ion−ligand complexing can occur.[4−7] For use in calculations of the transport of thorium and for overall speciation calculations, the properties of the uncomplexed ion are required.

Since $Th^{4+}(aq)$ is relatively unhydrolyzed in low pH environments, it makes thorium an ideal candidate for the investigation of solvation and hydration of a 4+ aqueous ion. Much of the current state of modeling of solvation reactions by semitheoretical methods involves a variety of electrostatic and nonelectrostatic components. Because of the highly localized charge density of aqueous thorium, many of these correlations based on lower charge densities, or localizations, breakdown. Since the present measurements are among the first direct determinations of the partial molar heat capacity and volume of the bare uncomplexed ion, these data will provide a severe test for many solvation theories that model the near-ion water properties. Gas phase experiments have shown in accord with simple theories of solvation that the first few water molecules solvated on multivalent ions make up for the bulk of the energetic differences of solvation between ions of different charge. Because thorium(IV) has a high electric potential field associated with it and because it is one of only a few 4+ ions that can be

investigated in solution, it is interesting here to examine such ionic solvation differences.

There are seemingly reliable thermodynamic data available for many of the solid phases involving thorium(IV) at 25 °C, although calorimetric data pertaining to species in aqueous solution are limited.[8] Much of the thermodynamic data have been extensively reviewed along with other actinide species due to the importance of these species in nuclear waste problems.[1,9−12] Values of the Gibbs free energy and standard state entropy of $Th^{4+}(aq)$ at 25 °C are in generally good agreement but are based on relatively few experimental data. Most investigations[1,8] have relied on those values selected by Fuger and Oetting[12] which are based primarily on experiments involving $ThCl_4$. The aqueous solubility of $ThO_2(cr)$ has been investigated by several authors summarized in ref 13 and most recently by Ryan and Rai[14] and Felmy *et al.*[15] These studies are important in the present context as some experiments were carried out involving the solubility of amorphous (hydrous) $ThO_2$ in solutions containing sodium perchlorate. The significantly lower solubility of hydrous $ThO_2$ in perchlorate solutions at acidic pH values compared with chloride solutions supports the conclusion that chloride forms strong complexes with $Th^{4+}(aq)$, indicated by the highly negative $\beta_2$ Pitzer ion-interaction parameter for $Th^{4+}-Cl^-$ obtained from both the solubility[15] and emf[16] data. Thus the relative poor agreement of many of the solubility and emf measurements for the thermodynamic properties of dissolved thorium are at least partially related to the strong complexing power of $Th^{4+}$.

While thorium forms strong complexes with a variety of anions (e.g. chloride, fluoride, carbonate, and sulfate) and even appreciably strong complexes with nitrate, there is no evidence that strong ion-pairs are formed with perchlorate ion. Proton NMR,[17] Raman,[18] and X-ray[19,20] spectroscopic studies are all consistent with the observation that $Th^{4+}(aq)$ is not ion-paired and is solvated by water molecules (normally considered to be eight in the first hydration shell) at the concentrations of solutions used in this investigation. At very high perchlorate concentrations (significantly higher than used here) perchlorate anion has been shown to form an outer-sphere solvent-separated complex at room temperature.[20] It is for these reasons that the present experimental measurements were undertaken using $Th(ClO_4)_4$ in dilute perchloric acid.

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[†] Dedicated to the memory of the late Professor Loren G. Hepler.
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Thermodynamic data for $Th^{4+}$(aq) and its various hydrolyzed and complexed species are required at elevated temperatures due to the importance of thorium and its species in nuclear processes under these same conditions.[1] Standard state partial molar volumes and heat capacities of $[Th(ClO_4)_4 + HClO_4]$-(aq) mixtures and subsequently $Th^{4+}$(aq) are needed for determination of key thermodynamic properties at different (usually higher) temperatures and pressures. Standard state heat capacities and volumes provide the temperature and pressure dependences of the Gibbs free energies or equilibrium constants provided that the change in enthalpy (or entropy) is known.

The present results are intended to be used to calculate standard state heat capacities and volumes of aqueous thorium-(IV) from 10 to 55 °C. These results can then be used to refine many of the low-temperature thermodynamic data or be used along with semitheoretical models to calculate results at higher temperatures. The results are also important as they represent the first direct heat capacity measurements of $Th^{4+}$(aq) in an *uncomplexed* environment. These results provide important information on the solvation of such a highly charged ion and subsequently can be used to test various theories of ionic solvation. In contradiction to earlier determinations of the standard state heat capacity of $Th^{4+}$(aq), the measured values are more negative than any other monatomic cation and are consistent with the known structure of the hydrated thorium-(IV) atom.

### Experimental Section

Water used for all experiments was first passed through an activated charcoal filter and then through a Milli-RO4/Milli-Q reagent grade mixed bed ion exchange and activated carbon system to yield purified water with a resistivity of 18 MΩ cm or greater. Solutions of NaCl (Fisher certified, ACS) were prepared by mass after drying the salt at 110 °C until constant weight.

Thorium perchlorate hexahydrate was obtained from Strem (99+%) and was recrystallized once from a slightly warm dilute perchloric acid using a rotary evaporator. The stock solution was prepared by adding the precipitate to a solution of approximately 0.1 $m$ $HClO_4$. Total thorium in the stock solution was determined through the use of precise volumetric titrations in acidic solutions using EDTA with xylenol orange as indicator.[21] Total perchlorate in the stock solution ($4m_2 + m_3$, where $m_2$ and $m_3$ are molalities of thorium perchlorate and perchloric acid, respectively) was determined by passing weighed aliquots of the solution through an ion exchange resin [Rexyn 101(H)] followed by titration of the eluent with a standard solution of sodium hydroxide. Excess perchlorate or total perchloric acid in the stock solution was obtained by difference. The stock solution was diluted by weight with a standard solution of approximately 0.1 $m$ $HClO_4$.

The densities of all solutions were determined relative to water at each of the experimental temperatures using a Sodev 03D vibrating tube densimeter[22] which was calibrated with pure water and a standard solution of NaCl. Densities of the standard NaCl solutions were calculated using data reported by Millero.[23] Volumetric heat capacities were measured relative to water with a Sodev CP-C Picker type flow microcalorimeter.[24] The heat loss correction factor[25] representing the unsymmetrical heat losses in flow calorimeters was determined by way of heat capacity measurements of standard solutions of NaCl relative to water. These measurements have led to the correction factor $f = 1.007 \pm 0.001$ at 25 °C. The heat loss factor was taken to be temperature independent over the range 10−55 °C.

Temperatures were controlled in both the densimeter and calorimeter to ±0.001 °C with separate Sodev CT-L circulating baths and monitored with calibrated thermistors. The thermistors were calibrated against a Hewlett-Packard quartz crystal thermometer traceable to NIST standards and considered accurate to ±0.01 °C.

### Results

**Apparent Molar Properties.** Several investigations have demonstrated the existence of both simple mononuclear hydrolyzed species and also more complicated and less well-defined polynuclear species.[2,12] However, because we are concerned here with acidic solutions and relatively low concentrations of thorium, only the first mononuclear hydrolyzed species is of concern. Hydrolysis of thorium(IV) occurs via

$$Th^{4+}(aq) + H_2O(l) = ThOH^{3+}(aq) + H^+(aq) \qquad (1)$$

in the absence of any heavily complexed ligands such as chloride. Equilibrium constants for this reaction are not in exceptionally good agreement; however, we can safely use an average value for the thermodynamic equilibrium constant to calculate the maximum amount of hydrolysis products present in our solutions. Values of the logarithm of the equilibrium constants at 0.1, 0.3, and 0.5 M ionic strength are reported by Pan and Hseu[26] to be −4.00, −4.12, and −4.26, respectively. These are reasonably consistent with the value at 1 M by Baes *et al.*[2] of −4.12. It can be calculated that, at worst, less than 0.6% of the thorium present in these solutions is present as hydrolyzed $ThOH^{3+}$(aq) and that the majority of our solutions should have less than 0.2% of the hydrolyzed $ThOH^{3+}$(aq) species.

Values for the density and specific heat capacity of pure water at each of the experimental temperatures were taken from Kell[27,28] and are listed later along with fitted results in Table 2. Measured values of the relative densities ($d - d_1^\circ$) and heat capacity ratios ($c_p d/c_{p,1}^\circ d_1^\circ - 1$) for all of the aqueous solutions containing $Th(ClO_4)_4$ and $HClO_4$ are listed in Table 1.

The experimentally determined apparent molar property of a solution $^\phi Y^{exptl}$ containing two noninteracting electrolytes is defined by

$$^\phi Y^{exptl} = \frac{Y_{soln} - 55.509 Y_1^\circ}{m_2 + m_3} \qquad (2)$$

where $Y_{soln}$ is the extensive property (volume or heat capacity) of a solution that contains 1 kg of solvent (water), $Y_1^\circ$ is the molar volume or heat capacity of pure solvent (water), and $m_2$ and $m_3$ are the molalities of $Th(ClO_4)_4$ and $HClO_4$, respectively. Apparent molar volumes and heat capacities were calculated from data cited in Table 2 using

$$^\phi V^{exptl} = \frac{\dfrac{1 + m_2 M_2 + m_3 M_3}{d} - \dfrac{1}{d_1^\circ}}{m_2 + m_3} \qquad (3)$$

and

$$^\phi C_p^{exptl} = \frac{c_p(1 + m_2 M_2 + m_3 M_3) - c_{p,1}^\circ}{m_2 + m_3} \qquad (4)$$

where $M$ represents the solute molecular weight, $c_p$ and $d$ are the specific heat capacity and density of the solution, and $c_{p,1}^\circ$ and $d_1^\circ$ are the specific heat capacity and density of the solvent

Thermodynamics of Hydration of a 4+ Aqueous Ion

*J. Phys. Chem. B, Vol. 101, No. 21, 1997* **4323**

**TABLE 1: Compositions of Solutions and Experimental Apparent Molar Volumes and Heat Capacities for Th(ClO$_4$)$_4$ + HClO$_4$ Mixtures**

| $m_2$ (mol kg$^{-1}$) | $m_3$ (mol kg$^{-1}$) | $10^2(d - d_1^o)$ (g cm$^{-3}$) | $^\phi V^{exptl}$ (cm$^3$ mol$^{-1}$) | $10^2((c_p d/c_{p,1}^o d_1^o) - 1)$ | $^\phi C_p^{exptl}$ (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|
| | | | 10 °C | | |
| 0.170 03 | 0.123 21 | 9.1677 | 86.757 | −3.298 | −123.49 |
| 0.127 56 | 0.117 88 | 7.0724 | 81.606 | −2.688 | −129.84 |
| 0.097 386 | 0.114 09 | 5.5666 | 76.693 | −2.230 | −131.27 |
| 0.078 056 | 0.111 67 | 4.5956 | 72.643 | −1.917 | −128.28 |
| 0.062 621 | 0.109 73 | 3.8142 | 68.825 | −1.663 | −124.01 |
| 0.048 524 | 0.107 96 | 3.0947 | 64.802 | −1.427 | −117.62 |
| 0.030 269 | 0.105 67 | 2.1613 | 58.062 | −1.106 | −103.03 |
| 0.017 196 | 0.104 03 | 1.4893 | 51.906 | −0.871 | −87.75 |
| | | | 25 °C | | |
| 0.170 03 | 0.123 21 | 8.9547 | 93.080 | −2.918 | −42.71 |
| 0.127 56 | 0.117 88 | 6.9041 | 87.667 | −2.376 | −51.28 |
| 0.097 386 | 0.114 09 | 5.4298 | 82.490 | −1.959 | −53.29 |
| 0.078 056 | 0.111 67 | 4.4799 | 78.162 | −1.681 | −53.14 |
| 0.062 621 | 0.109 73 | 3.7157 | 74.042 | −1.456 | −51.99 |
| 0.048 524 | 0.107 96 | 3.0130 | 69.606 | −1.248 | −49.51 |
| 0.030 269 | 0.105 67 | 2.1008 | 62.217 | −0.970 | −43.90 |
| 0.017 196 | 0.104 03 | 1.4424 | 55.574 | −0.766 | −36.27 |
| | | | 40 °C | | |
| 0.170 03 | 0.123 21 | 8.7831 | 97.722 | −2.774 | −4.41 |
| 0.127 56 | 0.117 88 | 6.7720 | 91.999 | −2.239 | −11.28 |
| 0.097 386 | 0.114 09 | 5.3243 | 86.563 | −1.849 | −15.85 |
| 0.078 056 | 0.111 67 | 4.3883 | 82.177 | −1.595 | −18.77 |
| 0.062 621 | 0.109 73 | 3.6386 | 77.806 | −1.380 | −19.12 |
| 0.048 524 | 0.107 96 | 2.9472 | 73.207 | −1.184 | −18.74 |
| 0.030 269 | 0.105 67 | 2.0536 | 65.252 | −0.923 | −17.75 |
| 0.017 196 | 0.104 03 | 1.4035 | 58.498 | −0.726 | −11.55 |
| | | | 55 °C | | |
| 0.170 03 | 0.123 21 | 8.6930 | 99.443 | −2.697 | 11.27 |
| 0.127 56 | 0.117 88 | 6.6984 | 93.773 | −2.178 | 4.082 |
| 0.097 386 | 0.114 09 | 5.2645 | 88.302 | −1.796 | −0.533 |
| 0.078 056 | 0.111 67 | 4.3371 | 83.898 | −1.543 | −2.318 |
| 0.062 621 | 0.109 73 | 3.5952 | 79.457 | −1.342 | −5.031 |
| 0.048 524 | 0.107 96 | 2.9095 | 74.878 | −1.148 | −4.111 |
| 0.030 269 | 0.105 67 | 2.0199 | 67.193 | −0.891 | −1.786 |
| 0.017 196 | 0.104 03 | 1.3824 | 59.893 | −0.714 | −2.993 |

**TABLE 2: Standard State Partial Molar Volumes, Heat Capacities, and Ionic Strength Parameters for Th$^{4+}$(aq) + 4ClO$_4^-$(aq) Derived from Isothermal Fits Using Young's Rule**

| $t$ (°C) | $^\phi V_2^o$ (cm$^3$ mol$^{-1}$) | $A_V$(Archer) (cm$^3$ kg$^{1/2}$ mol$^{-3/2}$) | $B_V$ (cm$^3$ kg mol$^{-2}$) | $d_1^o$ (g cm$^{-3}$) |
|---|---|---|---|---|
| 10 | 105.84 ± 0.23 | 1.6057 | 1.060 ± 0.17 | 0.999 700 |
| 25 | 115.82 ± 0.15 | 1.8305 | −0.017 ± 0.11 | 0.997 047 |
| 40 | 120.97 ± 0.23 | 2.1256 | −0.447 ± 0.16 | 0.992 219 |
| 55 | 122.55 ± 0.29 | 2.4894 | −1.557 ± 0.21 | 0.985 695 |

| $t$ (°C) | $^\phi C_{p,2}^o$ (J K$^{-1}$ mol$^{-1}$) | $A_C$(Archer) (J kg$^{1/2}$ K$^{-1}$ mol$^{-3/2}$) | $B_C$ (J kg K$^{-1}$ mol$^{-2}$) | $c_{p,1}^o$ (J K$^{-1}$ g$^{-1}$) |
|---|---|---|---|---|
| 10 | −462.4 ± 1.9 | 24.254 | 45.93 ± 1.4 | 4.1919 |
| 25 | −326.4 ± 2.5 | 31.894 | 11.56 ± 1.8 | 4.1793 |
| 40 | −271.3 ± 2.3 | 36.911 | −3.20 ± 1.7 | 4.1783 |
| 55 | −252.9 ± 4.8 | 41.646 | −17.17 ± 3.5 | 4.1821 |

(water). Calculations of these experimental apparent molar volumes and heat capacities are also listed in Table 1. Because this is a system involving a mixture of a 4:1 and 1:1 electrolyte, it is important to assess any model dependent results from both the effects of dielectric constant representations (in calculation of the Debye−Hückel slopes) and the mixed-electrolyte treatment. In this latter context, we have analyzed these results in terms of both Young's rule and the Pitzer ion-interaction model.

**Young's Rule.** The presence of excess perchloric acid in these solutions is to minimize complications due to "chemical relaxation" caused by the temperature dependence of any chemical equilibria.[29] A complete analysis of the contributions due to chemical relaxation requires accurate activity coefficients, equilibrium constants, and enthalpies of dilution, some of which

are lacking for this system. However, we are able to estimate the *total* relaxational heat capacity based on equilibrium constants cited earlier[26] and the calculated enthalpy change[3] for the reaction represented by eq 1. Simple calculations ignoring the effects of activity coefficients show that the relaxational contribution is less than 1 J K$^{-1}$ mol$^{-1}$ for each of the solutions studied. The perchloric acid present can thus be considered an additional component to the mixed electrolyte system.

In order to assess the contribution that this excess perchloric acid makes to the total experimental apparent molar properties of the mixtures, a mixed-electrolyte treatment must be employed. The desired standard state properties correspond to hypothetical solutions containing only the electrolyte (Th$^{4+}$ + 4ClO$_4^-$)(aq). Accordingly, the experimental apparent molar properties of the solutions have been separated into two components representing each of the two solutes using Young's rule:[30,31]

$$^\phi Y^{exptl} = \frac{m_2}{m_2 + m_3}{}^\phi Y_2 + \frac{m_3}{m_2 + m_3}{}^\phi Y_3 + \delta \qquad (5)$$

Here $^\phi Y_2$ and $^\phi Y_3$ apply at the total ionic strength of the solution, and $\delta$ is an excess mixing term made up of nonideal interactions of thorium and hydrogen ions. Because of the large ratio of $m_2$ to $m_3$, and the presence of a common anion, the ($\delta$) term was not sufficiently resolved by these data. As such, it is ignored in further calculations.

The ionic strength dependence of the apparent molar volumes and heat capacities of Th(ClO$_4$)$_2$ and HClO$_4$ can be represented by extended Debye−Hückel equations of the type[32,33]

$$^\phi Y = {}^\phi Y° + 1.5\frac{\omega A_Y}{I}[I - 2I^{1/2} + 2\ln(1 + I^{1/2})] +$$

$$B_Y I + C_Y I^{3/2} \quad (6)$$

where

$$I = \omega m = {}^1\!/_2 \sum m_i z_i{}^2 \quad (7)$$

$^\phi Y°$ is the standard state (infinite dilution) property, and $B$ and $C$ are parameters describing the concentration dependence of the properties. Because this is a 4:1 electrolyte, the value of $\omega$ is 10. Accordingly, the magnitude of the Debye–Hückel term is large and small uncertainties in the Debye–Hückel slopes have noticeable effects on the resultant fits and hence appropriate standard state properties.

Apparent molar volumes and heat capacities for $HClO_4$ from 10 to 55 °C were taken from Hovey and Hepler,[34] but two different sets of fits were used. Because these data for thorium perchlorate extend to higher ionic strengths than the data in ref 34, three-parameter fits were used for $HClO_4(aq)$ for the data below 1 $m$, but linear fits were used to extrapolate these data to the higher ionic strengths required here. Evaluation of best limiting standard state properties for perchloric acid required for later calculations is reported in Appendix I. Expressions of the type given by eqs 5 and 6 were fitted isothermally to the experimental apparent molar properties in Table 1 to generate values of $\bar{Y}_2°$, $B_Y$, and $C_Y$. Although lower sums of squares were observed for regressions involving both $B$ and $C$ parameters, it seems that these data are not precise enough to define the $C$ parameter. The statistical weighting of each data pair was set proportional to the square root of the molality of $Th^{4+}(aq)$. Results of these isothermal fits are listed in Table 2. All of these fits have employed the newer Debye–Hückel slopes from Archer and Wang,[35] believed to be the best values currently available.

The standard state volume ($\bar{V}°$) and heat capacity ($\bar{C}_p°$) at 25 °C for $(Th^{4+} + 4ClO_4{}^-)(aq)$ were determined to be $115.82 \pm 0.15$ cm$^3$ mol$^{-1}$ and $-326.4 \pm 2.5$ J K$^{-1}$ mol$^{-1}$, respectively. The Debye–Hückel slopes from various representations are in good agreement for the osmotic coefficient. However, because the slope for the heat capacity is related to the second temperature derivative of the static permittivities and the volume the first pressure derivative, it is interesting to examine the differences of results of these isothermal fits using the older Bradley and Pitzer[36] representation.[37] The standard state volumes and heat capacities obtained from fits using the Bradley and Pitzer slopes differ by 0.2 cm$^3$ mol$^{-1}$ and 6.2 J K$^{-1}$ mol$^{-1}$, respectively, at 25 °C, and the heat capacity differs by more than 14.3 J K$^{-1}$ mol$^{-1}$ at 10 °C, significantly larger than total estimated uncertainties. The large difference of the static permittivity representation for the infinitely dilute standard state for the *heat capacities* of a 4:1 electrolyte exemplifies uncertainties in the calculation of the double derivative. Such effects are not seen for the singly differentiated slopes (enthalpy) with respect to temperature.

Plots of $^\phi Y_2$ minus the Guggenheim form of the Debye–Hückel limiting law (eq 6) are shown in Figures 1 and 2 for the apparent molar volumes and heat capacities at 25 °C.

For convenience and for nonintegral temperatures, it is important to report results of global fits of the standard state properties ($\bar{Y}°$) and appropriate $B_Y$ parameters. Fits both with and without constraint of the 25 °C values were performed on the entire data set. Results of fits fixing the temperature
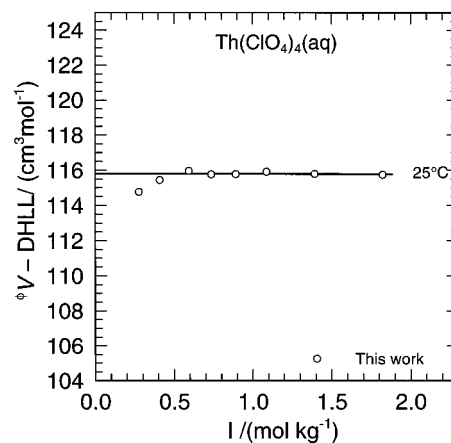


**Figure 1.** Apparent molar volumes of $Th(ClO_4)_4(aq)$ minus the Debye–Hückel limiting law (DHLL) (eq 6) as a function of ionic strength at 25 °C.



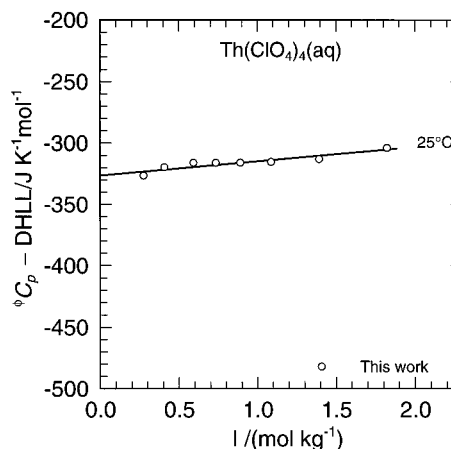**Figure 2.** Apparent molar heat capacities of $Th(ClO_4)_4(aq)$ minus the Debye–Hückel limiting law (DHLL) (eq 6) as a function of ionic strength at 25 °C.

dependence of the $\bar{Y}°$ and $B_Y$ parameters to empirical equations of the expanded form[38]

$$f(T) = p_1 + p_2 T + p_3 T^2 + \frac{p_4}{(T - 190)} + \frac{p_5}{T^2} \quad (8)$$

are listed in Table 3. Only three terms were used for both the apparent molar volumes ($p_3 = 0$, $p_5 = 0$) and heat capacities ($p_4 = 0$, $p_5 = 0$). The $p_i$ terms are fitting coefficients, and $T$ is the temperature in kelvin. Plots of $^\phi Y_2$ minus the Guggenheim form of the Debye–Hückel limiting law (eq 6) from these global fits are shown in Figures 3 and 4. The fit of 25 °C data is provided for a comparison of the isothermal and global fit qualities for this Young's rule method.

**Pitzer Ion-Interaction Model.** The Pitzer ion-interaction model[39–42] is soundly based in theory and provides a good representation of the thermodynamic properties of aqueous electrolyte solutions. Because the model is based on discrete ion–ion or particle–particle interactions, the equations become relatively complex in terms of their number of parameters when a system is comprised of many components. However, when sufficient experimental data exist, this model is clearly the most useful for a global representation of the system. The basic equation in the Pitzer treatment considers the excess free energy to result from long-range electrostatic interactions (given by Debye–Hückel theory) and short-range binary and ternary interactions. The model can be simplified for the special case of a mixture of purely ionic solutes with a common anion:[42]

**TABLE 3: Parameters Valid for the Global Representation of the Standard State Partial Molar Volumes, Heat Capacities, and Ionic Strength Parameters for Th$^{4+}$(aq) + 4ClO$_4^-$(aq) Based on Fits Using Young's Rule**[a]

| $f(T) = p_1 + p_2T + p_3T^2 + p_4/T^2 + p_5/(T - 190)$ | |
|---|---|
| parameter | value |
| $\bar{V}°$ | |
| $p_1/(\text{cm}^3 \text{ mol}^{-1})$ | $-865.1396 \pm 0.18$ |
| $p_2/(\text{cm}^3 \text{ mol}^{-1} \text{ K}^{-1})$ | $6.070\,650 \pm 0.33$ |
| $p_3/10^{-3} \times (\text{cm}^3 \text{ mol}^{-1} \text{ K}^{-2})$ | $-9.327\,992 \pm 0.54$ |
| $B_V$ | |
| $p_1/(\text{cm}^3 \text{ kg mol}^{-2})$ | $13.227\,22 \pm 0.13$ |
| $p_2/(\text{cm}^3 \text{ kg mol}^{-2} \text{ K}^{-1})$ | $-0.032\,849 \pm 0.24$ |
| $p_3/10^{-3} \times (\text{cm}^3 \text{ kg mol}^{-2} \text{ K}^{-2})$ | $-0.036\,575 \pm 0.39$ |
| $\bar{C}_p°$ | |
| $p_1/(\text{J K}^{-1} \text{ mol}^{-1})$ | $4613.890 \pm 2.4$ |
| $p_2/(\text{J K}^{-2} \text{ mol}^{-1})$ | $-10.536\,10 \pm 0.8$ |
| $p_5/10^4 \times (\text{J mol}^{-1})$ | $-19.487\,83 \pm 1.0$ |
| $B_C$ | |
| $p_1/(\text{J kg K}^{-1} \text{ mol}^{-2})$ | $-697.6349 \pm 1.8$ |
| $p_2/(\text{J kg K}^{-2} \text{ mol}^{-2})$ | $1.314\,431 \pm 0.6$ |
| $p_5/10^4 \times (\text{J kg mol}^{-2})$ | $3.453\,916 \pm 0.7$ |

[a] Note that these equations lead to the following values at 25 °C: $\bar{V}°/(\text{cm}^3 \text{ mol}^{-1}) = 115.628 \pm 0.2$; $B_V/(\text{cm}^3 \text{ kg mol}^{-2}) = 0.182\,129\,22 \pm 0.1$; $\bar{C}_p°/(\text{J K}^{-1} \text{ mol}^{-1}) = -329.37 \pm 2.4$; $B_C/(\text{J kg K}^{-1} \text{ mol}^{-2}) = 13.626\,838 \pm 1.8$.
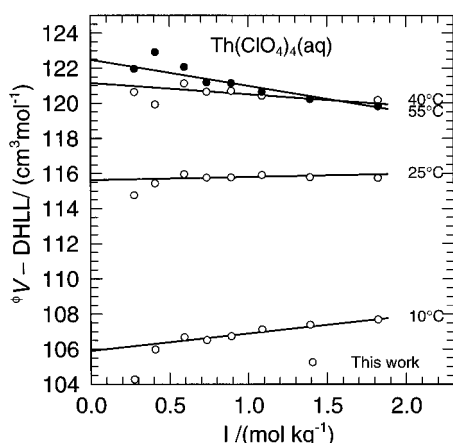


**Figure 3.** Apparent molar volumes of Th(ClO$_4$)$_4$(aq) minus the Debye–Hückel limiting law (DHLL) (eq 6) as a function of ionic strength from 10 to 55 °C: results of global fits constraining the temperature dependences to equations of type 8.
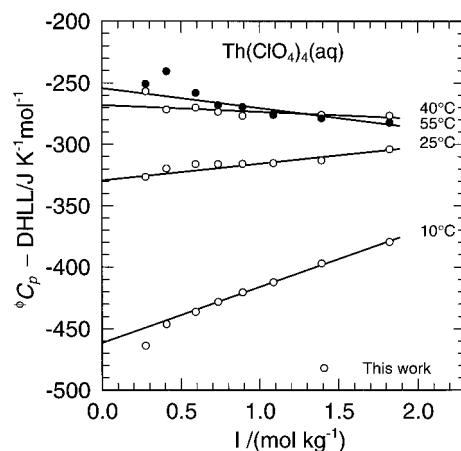
$$\frac{G^{\text{EX}}}{w_w RT} = f(I) + 2\sum_c\sum_a m_c m_a(B_{ca} + EC_{ca}) +$$
$$\sum_c\sum_{c'} m_c m_{c'}\left(2\Phi_{cc'} + \sum_a m_a \psi_{cc'a}\right) \quad (9)$$

Here $c$ and $a$ refer to individual cationic and anionic species; $f(I)$ is the Pitzer form of the extended Debye–Hückel equation and is given by

$$f(I) = -A_\phi(4I/1.2)\ln(1 + 1.2I^{1/2}) \quad (10)$$

The $B$ terms represent binary ion interactions and are functions of ionic strength of the form

$$B = \beta^{(0)} + \frac{2\beta^{(1)}}{\alpha_1^2 I}[1 - (1 + \alpha_1 I^{1/2})\exp(-\alpha_1 I^{1/2})] +$$
$$\frac{2\beta^{(2)}}{\alpha_2^2 I}[1 - (1 + \alpha_2 I^{1/2})\exp(-\alpha_2 I^{1/2})] \quad (11)$$



**Figure 4.** Apparent molar heat capacities of Th(ClO$_4$)$_4$(aq) minus the Debye–Hückel limiting law (DHLL) (eq 6) as a function of ionic strength from 10 to 55 °C: results of global fits constraining the temperature dependences to equations of type 8.

Here the $\beta$ values are adjustable parameters, as are the $\alpha$ values, although $\alpha_1$ is normally given the value 2. $E$ is an electroneutrality sum given by

$$E = \sum m_c z_c \quad (12)$$

and $\Phi$ and $\psi$ are the excess terms that arise from the nonideality of binary interactions considered with two and three particles, respectively.

Excess properties are related to the various apparent molar properties defined previously by

$$Y^{\text{EX}} = (m_2 + m_3)^\phi Y^{\text{exptl}} - m_2\bar{Y}_2° - m_3\bar{Y}_3° \quad (13)$$

and the excess volume and heat capacity are related to the excess Gibbs free energy by the standard formulas:

$$V^{\text{EX}} = \left(\frac{\partial G^{\text{EX}}}{\partial p}\right)_T \quad (14)$$

$$C_p^{\text{EX}} = -T\left(\frac{\partial^2 G^{\text{EX}}}{\partial T^2}\right)_p \quad (15)$$

Combination of these equations considering the specific mixtures here of Th(ClO$_4$)$_4$(aq) and HClO$_4$(aq) leads to

$$^\phi V^{\text{exptl}} = \frac{1}{m_2 + m_3}\left\{\left(\frac{A_V I}{1.2}\right)\ln(1 + 1.2I^{1/2}) + m_2\bar{V}_2° + m_3\bar{V}_3° +\right.$$
$$2RT[m_X m_M(B_{MX}^V + EC_{MX}^V) + m_X m_H(B_{HX}^V + EC_{HX}^V) +$$
$$\left.m_M m_H(\Phi_{MN}^V + m_X\psi_{MNX}/2)]\right\} \quad (16)$$

$$^\phi C_p^{\text{exptl}} = \frac{1}{m_2 + m_3}\left\{\left(\frac{A_J I}{1.2}\right)\ln(1 + 1.2I^{1/2}) + m_2\bar{C}_{p,2}° +\right.$$
$$m_3\bar{C}_{p,3}° - 2RT^2[m_X m_M(B_{MX}^J + EC_{MX}^J) +$$
$$\left.m_X m_H(B_{HX}^J + EC_{HX}^J) + m_M m_H(\Phi_{MN}^J + m_X\psi_{MNX}/2)]\right\} \quad (17)$$

which are general for mixtures of 4:1 and 1:1 electrolytes. Here $m_X$ refers to the molality of the common anion, ClO$_4^-$(aq), given by $m_X = 4m_2 + m_3$. The terms represented by $\Phi$ result from unsymmetrical mixing of Th$^{4+}$(aq) with H$^+$(aq) ions. These quantities contain terms both calculated from theory and derived by regression as described in Appendix II. It has been found

**TABLE 4: Results of Isothermal Fits of the Pitzer Ion-Interaction Model to Apparent Molar Volumes and Heat Capacities for $Th^{4+}(aq) + 4ClO_4^-(aq)$ Including Unsymmetrical Mixing Terms**

| $t$ (°C) | $^\phi V_2^\circ$ (cm³ mol⁻¹) | $A_V$ (cm³ kg$^{1/2}$ mol$^{-3/2}$) | $10^4 \beta^{(0)V}$ (cm³ kg J⁻¹ mol⁻¹) |
|---|---|---|---|
| 10 | $105.29 \pm 0.24$ | 1.6057 | $0.8257 \pm 0.82$ |
| 25 | $115.23 \pm 0.14$ | 1.8305 | $-5.1100 \pm 0.45$ |
| 40 | $120.48 \pm 0.25$ | 2.1256 | $-7.7894 \pm 0.78$ |
| 55 | $121.78 \pm 0.34$ | 2.4894 | $-12.616 \pm 1.00$ |

| $t$ (°C) | $^\phi C_{p,2}^\circ$ (J K⁻¹ mol⁻¹) | $A_C$ (J kg$^{1/2}$ K⁻¹ mol$^{-3/2}$) | $10^5 \beta^{(0)J}$ (kg mol⁻¹ K⁻²) | $10^5 C^J$ (kg² mol⁻² K⁻²) |
|---|---|---|---|---|
| 10 | $-467.1 \pm 4.8$ | 24.254 | $-8.0236 \pm 1.3$ | $1.942 \pm 1.2$ |
| 25 | $-324.7 \pm 7.1$ | 31.894 | $4.3425 \pm 1.8$ | $-3.196 \pm 1.5$ |
| 40 | $-276.3 \pm 5.3$ | 36.911 | $5.8705 \pm 1.2$ | $-2.238 \pm 1.0$ |
| 55 | $-239.2 \pm 9.0$ | 41.646 | $12.184 \pm 1.9$ | $-5.973 \pm 1.6$ |

that these terms are negligible for volume studies of this type but non-negligible for the heat capacity results. The contributions of nonideal ternary interactions to the excess properties have been neglected because previous experience has suggested that such interactions are unimportant in the relatively dilute solutions under consideration.

The appropriate Pitzer ion-interaction model for pure solutions of $(Th^{4+} + 4ClO_4^-)(aq)$ or $(H^+ + ClO_4^-)(aq)$ written generally in terms of $M_{\nu_M}X_{\nu_X}$ leads to[42]

$$^\phi V = \bar{V}^\circ + \nu |z_M z_X| \left(\frac{A_V}{2b}\right) \ln(1 + bI^{1/2}) + 2\nu_M \nu_X RT[mB^V + m^2(\nu_M z_M)C^V] \quad (18)$$

and

$$^\phi C_p = \bar{C}_p^\circ + \nu |z_M z_X| \left(\frac{A_J}{2b}\right) \ln(1 + bI^{1/2}) - 2\nu_M \nu_X RT^2[mB^J + m^2(\nu_M z_M)C^J] \quad (19)$$

in which $\nu = \nu_M + \nu_X$, $b = 1.2$, and other terms are defined as outlined above.

The Pitzer ion-interaction parameters for pure solutions containing $HClO_4(aq)$ were taken from sources and treatments outlined in Appendix I. The expressions represented by eqs 16 and 17 were then fitted to the experimental data in Table 1 using expressions for the apparent molar properties of $Th(ClO_4)_4$-(aq) from eqs 18 and 19 and terms representative of $\Phi$ as described in Appendix II.

It was found that the Pitzer ion-interaction treatment employing only the $\beta^{(0)}$ and $\bar{Y}^\circ$ terms led to underfitting of the experimental data. Best fits were selected from attempts at fitting the $\beta^{(1)}$, $C$, and $\Phi$ terms (the number of experimental data warranted choices of best fits from fits employing only one additional parameter from this series). As done previously, each data pair was weighted in accord of its $Th^{4+}(aq)$ concentration. The results of these fits at each individual temperature are given in Table 4. Three parameters were fitted instead of only two for the Young's rule approach, which constituted the major difference between the two methods. Fits, although, statistically inferior employing only two adjustable parameters, gave similar results to the Young's rule method.

Results of global fits of the standard state and concentration dependent properties obtained by fitting all of the experimental data simultaneously are reported in Table 5. The equations used here were three-parameter versions of those represented by eq 8.

**TABLE 5: Parameters Valid for the Global Representation of the Standard State Partial Molar Volumes, Heat Capacities, and Ionic Strength Parameters for $[Th^{4+}(aq) + 4ClO_4^-(aq)]$ in Terms of the Pitzer Ion-Interaction Model (Including Unsymmetrical Mixing Terms)[a]**

$f(T) = p_1 + p_2 T + p_3 T^2 + p_4/T^2 + p_5/(T - 190)$

| parameter | value |
|---|---|
| **$\bar{V}^\circ$** | |
| $p_1/10^3 \times$ (cm³ mol⁻¹) | $-1.067\,47 \pm 0.06$ |
| $p_2/$(cm³ mol⁻¹ K⁻¹) | $7.385\,22 \pm 0.40$ |
| $p_3/10^{-2} \times$ (cm³ mol⁻¹ K⁻²) | $-1.146\,29 \pm 0.06$ |
| **$\beta^{(0)V}$** | |
| $p_1/10^{-2} \times$ (cm³ kg J⁻¹ mol⁻¹) | $0.137\,437 \pm 0.21$ |
| $p_4/10^3 \times$ (cm³ kg J⁻¹ mol⁻¹ K²) | $-2.189\,343 \pm 0.76$ |
| $p_5/$(cm³ kg J⁻¹ mol⁻¹ K) | $2.451\,298 \pm 0.70$ |
| **$\bar{C}_p^\circ$** | |
| $p_1/10^2 \times$ (J K⁻¹ mol⁻¹) | $-2.018\,87 \pm 0.78$ |
| $p_4/10^{10} \times$ (J K mol⁻¹) | $1.323\,80 \pm 0.24$ |
| $p_5/10^5 \times$ (J mol⁻¹) | $-1.765\,41 \pm 0.21$ |
| **$\beta^{(0)J}$** | |
| $p_1/10^{-3} \times$ (kg mol⁻¹ K⁻²) | $-3.872\,42 \pm 0.62$ |
| $p_4/10^2 \times$ (kg mol⁻¹) | $1.624\,60 \pm 0.30$ |
| $p_3/10^{-8} \times$ (kg mol⁻¹ K⁻⁴) | $2.294\,30 \pm 0.32$ |
| **$C^J$** | |
| $p_1/10^{-3} \times$ (kg² mol⁻² K⁻²) | $-2.444\,79 \pm 0.15$ |
| $p_4/10^2 \times$ (kg² mol⁻²) | $5.307\,56 \pm 0.47$ |
| $p_5/10^{-1} \times$ (kg² mol⁻² K⁻¹) | $-4.877\,75 \pm 0.44$ |

*a* Note that these equations lead to the following values at 25 °C: $\bar{V}^\circ/$(cm³ mol⁻¹) $= 115.45 \pm 0.2$; $10^3 \beta^{(0)V}/$(cm³ kg J⁻¹ mol⁻¹) $= -0.589\,43 \pm 0.1$; $\bar{C}_p^\circ/$(J K⁻¹ mol⁻¹) $= -345.1 \pm 4.9$; $10^5 \beta^{(0)J}/$(kg mol⁻¹ K⁻²) $= -0.535\,75 \pm 1.2$; $10^4 C^J/$(kg² mol⁻² K⁻²) $= 0.157\,38 \pm 0.11$.
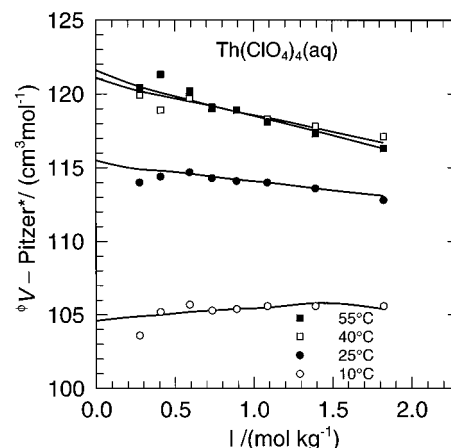


**Figure 5.** Pitzer ion-interaction model applied to apparent molar volumes for mixtures of $Th(ClO_4)_4 + HClO_4(aq)$ as a function of temperature: global regression of parameters.

Results of fitting the Pitzer ion-interaction equations to the experimental results in Table 1 are shown schematically for these global fits in Figures 5 and 6. Note that the plotted quantities are the values of the mean-ionic properties minus the Debye–Hückel limiting law and the effect of the additional perchloric acid present in the solutions. The remaining quantity after subtraction of these terms designated by "Pitzer" is a more sensitive indicator of the quality of fit.

The Pitzer ion-interaction model has previously been applied to the $(Th^{4+}-ClO_4^--Na^+-H^+-OH^-)(aq)$ system[14,15] in terms of the solubility of hydrous $ThO_2$ and thus represents the free energy parameters. The present data can be used to refine the entire Pitzer parameter representation when either temperature dependent experiments are performed or enthalpies of dilution are determined for the system $(Th^{4+}-ClO_4^--H^+)(aq)$.

Partial molar volumes and heat capacities at finite ionic strengths are easily calculated from our fitted equations from

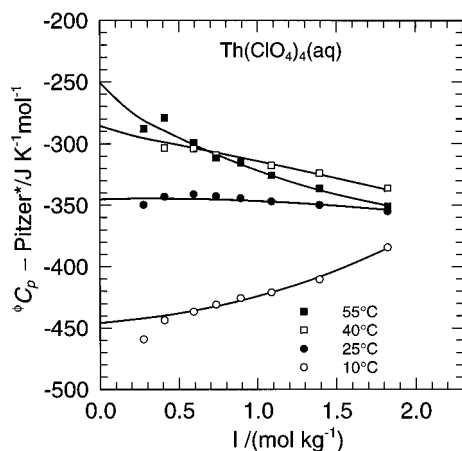Thermodynamics of Hydration of a 4+ Aqueous Ion

*J. Phys. Chem. B, Vol. 101, No. 21, 1997* **4327**



**Figure 6.** Pitzer ion-interaction model applied to apparent molar heat capacities for mixtures of $Th(ClO_4)_4$ + $HClO_4(aq)$ as a function of temperature: global regression of parameters.

either model using

$$\bar{Y}_i = {}^\phi Y_i + I\left(\frac{\partial {}^\phi Y_i}{\partial I}\right)_{T,p} \quad (20)$$

## Discussion

**Standard State Properties from Young's Rule Treatment.** The present $\bar{C}_p^\circ$ and $\bar{V}^\circ$ values resulting from the isothermal fits listed in Table 2 lead to the desired conventional ionic partial molar volumes and heat capacities for $Th^{4+}(aq)$ based on $\bar{Y}^\circ$-$(H^+,aq) \equiv 0$. The conventional ionic properties have been calculated using the refitted perchloric acid data[34] and are reported along with results of these calculations in Table 4.

The temperature dependences of standard state heat capacities and volumes of many salts have been represented by equations of the general form given by eq 8. The term $b/(T - \theta)$, where $\theta$ has the value 190, has been found to represent such data well.[38] The results of the present fits reported in Table 3 lead to

$$\bar{V}^\circ[(Th^{4+} + 4ClO_4^-)(aq)] =$$
$$-865.14 + 6.07065T - 0.00932799T^2 \quad (21)$$

$$\bar{C}_p^\circ[(Th^{4+} + 4ClO_4^-)(aq)] =$$
$$4613.89 - 10.5361T - \frac{194878}{T - 190} \quad (22)$$

which are valid from 10 to 55 °C.

As outlined in Appendix I, the temperature dependences of the standard state heat capacities of $HClO_4(aq)$ from 10 to over 75 °C and the standard state volumes from 10 to 75 °C are given by[34]

$$\bar{V}^\circ(HClO_4,aq) =$$
$$-50.255 + 0.578970T - 0.00081143T^2 - \frac{668.671}{T - 190} \quad (23)$$

$$\bar{C}_p^\circ(HClO_4^-,aq) =$$
$$1632.83 - 4.97798T + 0.0035087T^2 - \frac{52616.4}{T - 190} \quad (24)$$

Using the definition of conventional standard state properties for ionic species, we can combine these expressions to yield

$$\bar{V}^\circ(Th^{4+},aq) =$$
$$-664.12 + 3.75477T - 0.0060823T^2 + \frac{2674.68}{T - 190} \quad (25)$$

$$\bar{C}_p^\circ(Th^{4+},aq) =$$
$$-1917.43 + 9.37582T - 0.014035T^2 + \frac{15587.6}{T - 190} \quad (26)$$

for $Th^{4+}(aq)$ valid only over the temperature range 10−55 °C. These equations are more accurate for the stated temperature range than the wider range equations based on the Born model that appear later in this paper.

Similar calculations leading to the standard state heat capacities and volumes of $Th^{4+}(aq)$ derived from the Pitzer ion-interaction model are easily obtained with appropriate data in Table 5 and Appendix I. The differences between these two representations are discussed later.

**Literature Comparisons.** Several works have reviewed the available thermodynamic data for the actinide aqueous and complex ions.[1,12−14,43−45] The majority of these data are enthalpies, entropies, and corresponding Gibbs free energies. There are only a limited number of investigations that have led to definition of either the apparent molar volume or heat capacity.

Both Millero[46] and Couture and Laidler[47] cite in their review articles only those volumetric results taken from the International Critical Tables.[48] Conventional standard state partial molar volumes for $ThCl_4(aq)$ and $Th(NO_3)_4(aq)$ are given as 17.8 and 62.6 cm$^3$ mol$^{-1}$, respectively at 25 °C. Combining these values with the standard state volumes of $Cl^-(aq)^{46}$ [$\bar{V}^\circ(Cl^-,aq) = 17.83$ cm$^3$ mol$^{-1}$] and $NO_3^-(aq)^{49}$ [$\bar{V}^\circ(NO_3^-,aq) = 29.3$ cm$^3$ mol$^{-1}$] lead to $\bar{V}^\circ(Th^{4+},aq) = -53.5$ and $-54.6$ cm$^3$ mol$^{-1}$, respectively. Since both $ThCl_4(aq)$ and $Th(NO_3)_4(aq)$ are complicated by ion−ligand complexation reactions, the preferred value is the significantly more negative value reported here of $\bar{V}^\circ(Th^{4+},aq) = -60.6 \pm 0.5$ cm$^3$ mol$^{-1}$. Several investigations[50−52] have reported the results of density measurements on solutions containing $Th^{4+}(aq)$, although none of these works present data suitable for determination of the infinitely dilute standard state volume.

Measurements leading to definition of the standard state partial molar heat capacity of the aqueous thorium(IV) ion at 25 °C have been reported by Morss and McCue[53] and Apelblat and Sahar.[54] Morss and McCue have presented integral heats of solution of $Th(NO_3)_4\cdot5H_2O$ at 15, 25, and 35 °C. Differentiation of their enthalpies has led to a calculated value of $\bar{C}_p^\circ(Th^{4+},aq) = -1 \pm 11$ J K$^{-1}$ mol$^{-1}$. Recalculation of their results using the newer $\bar{C}_p^\circ(NO_3^-,aq) = -72$ J K$^{-1}$ mol$^{-1}$ [49] leads to $\bar{C}_p^\circ(Th^{4+},aq) = -60 \pm 11$ J K$^{-1}$ mol$^{-1}$. Morss and McCue's heats of solution are considered accurate, although there were complications from both hydrolysis and ion-pairing reactions. Apelblat and Sahar[54] have reported results from measurements of bulk heat capacities in the form $^\phi C_p[Th(NO_3)_4,aq] = -144 + 292 m^{1/2}$ J K$^{-1}$ mol$^{-1}$ at 30 °C. Using the value $\bar{C}_p^\circ(NO_3^-,aq) = -63.7$ J K$^{-1}$ mol$^{-1}$ [34] leads to 111 J K$^{-1}$ mol$^{-1}$ at 30 °C. The present results lead to the value $\bar{C}_p^\circ(Th^{4+},aq) = -228$ J K$^{-1}$ mol$^{-1}$ at 30 °C. Since specific molalities and heat capacities are not reported, and the improbable ability for an equation as reported to represent heat capacities over their stated molality range of 0−2.9 $m$, the discrepancy between these values is not surprising. The present value $\bar{C}_p^\circ(Th^{4+},aq) = -224 \pm 3$ J K$^{-1}$ mol$^{-1}$ at 25 °C is considered the best currently available because of its basis on measurements of solutions with minimal complications due to hydrolysis and ion-pairing equilibria.

Individual conventional ionic partial molar volumes and heat capacities are summarized in Table 6 as the result of application

**TABLE 6: Comparison of Conventional Ionic Partial Molar Volumes and Heat Capacities for $ClO_4^-$(aq) and $Th^{4+}$(aq) from 10 to 55 °C Determined Using Young's Rule and the Pitzer Ion-Interaction Model[a]**

| | $ClO_4^-$(aq) | | $Th^{4+}$(aq) | |
|---|---|---|---|---|
| $t$ | $\bar{V}°$ | $C_p°$ | $\bar{V}°$ | $C_p°$ |
| (°C) | (cm$^3$ mol$^{-1}$) | (J K$^{-1}$ mol$^{-1}$) | (cm$^3$ mol$^{-1}$) | (J K$^{-1}$ mol$^{-1}$) |
| | Young's Rule | | | |
| 10 | 41.53 | −61.1 | −60.3 | −218 |
| 25 | 44.10 | −25.6 | −60.6 | −224 |
| 40 | 46.27 | −10.1 | −64.1 | −231 |
| 55 | 47.48 | −4.7 | −67.4 | −234 |
| | Pitzer Ion-Interaction Model | | | |
| 10 | 41.54 | −60.3 | −60.9 | −226 |
| 25 | 44.07 | −25.3 | −61.0 | −224 |
| 40 | 46.25 | −10.5 | −64.5 | −234 |
| 55 | 47.42 | −5.2 | −67.9 | −218 |

[a] The values at 55 °C are slightly erratic because of the associated uncertainties of the data as listed in Table 2 and increased uncertainties in the perchloric acid data at this temperature. The smoothed values obtained from eqs 25 and 26 are preferred at this temperature, whereas all other values are preferred as listed in this table for the temperatures given.

of Young's rule using an extended Debye−Hückel equation or the Pitzer ion-interaction model at individual temperatures. There is good agreement between these two approaches considering the complications because of excess acid. The fortuitous agreement between the Pitzer model and the extended Debye−Hückel approach supports the reliability of these values. The present heat capacity data are consistent with theoretical expectations regarding the nature of the solvation of $Th^{4+}$ by water, as described in detail later.

**High-Temperature Representation.** It is extremely useful to investigate the temperature dependence of the standard state heat capacities and volumes for this 4:1 electrolyte since there are very few measurements that have been published to date. The value of the standard state partial molar heat capacity for $Th^{4+}$(aq) nearing 0 °C is comparable to a value near 300 °C for a less highly charged electrolyte. A simple model based on the Born equation can be used to derive an approximate but reliable temperature dependent function that clearly demonstrates the dramatic changing nature of these thermodynamic properties. Application of the Born model to the standard state volumes and heat capacities has proven highly reliable in the calculation of high-temperature mineral solubilities[32,55] and high-temperature ion association equilibria.[32,56]

The Born equation is a useful representation of the thermodynamic properties associated with ionic solvation when the solvent has a sufficiently low dielectric constant that is has a constant value from the surface of an ion to an infinite distance from the ion. Water as solvent approaches these criteria only at highly elevated temperatures near the critical temperature where the dielectric constant falls to values below 10. The Tanger−Helgeson[57] modification (TH-HKF) of the Helgeson−Kirkham−Flowers (HKF)[58−60] semiempirical model for ionic solvation is a useful model in which shortcomings in the Born theory are accounted for empirically at lower temperatures where water has a high dielectric constant and thus is highly structured especially near the surface of ions. For the present purpose of examining the qualitative temperature behavior of a variety of aqueous ions, this model is sufficient.

The Born theory can be represented by

$$\Delta G = \omega\left(\frac{1}{\epsilon} - 1\right) \tag{27}$$

where the free energy here applies to the difference in the work

involved in charging a rigid sphere in vacuum and in a dielectric with constant $\epsilon$. Here $\omega$ refers to the quantity $\eta z^2/r_e$ where $\eta$ is a constant equivalent to the value $6.94657 \times 10^5 z^2/r_e$ and has units J Å mol$^{-1}$. The temperature dependence of the standard state volumes and heat capacities in terms of the TH-HKF model is given generally by

$$\bar{Y}° = \Delta\bar{Y}°_{non} + \Delta\bar{Y}°_{solv} \tag{28}$$

where the terms represented by $\Delta\bar{Y}°$ are the nonsolvation and solvation terms, respectively. This latter term is defined by the Born equation, and the first term by an empirical limiting function related to the super-cooled limit of water. Specific equations are defined as

$$\bar{V}° = \sigma + \xi\left(\frac{1}{T - 228}\right) + \Delta V_{Born} \tag{29}$$

$$\bar{C}_p° = c_1 + c_2\left(\frac{1}{T - 228}\right)^2 + \Delta C_{p,Born} \tag{30}$$

where

$$\Delta V_{Born} = -\omega\frac{1}{\epsilon}\left(\frac{\partial \ln \epsilon}{\partial p}\right)_T + \left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial \omega}{\partial p}\right)_T \tag{31}$$

and

$$\Delta C_{p,Born} = \omega T\frac{1}{\epsilon}\left[\left(\frac{\partial^2 \ln \epsilon}{\partial T^2}\right)_p - \left(\frac{\partial \ln \epsilon}{\partial T}\right)_p^2\right] + \frac{2T}{\epsilon^2}\left(\frac{\partial \epsilon}{\partial T}\right)_p\left(\frac{\partial \omega}{\partial T}\right)_p - T\left(\frac{1}{\epsilon} - 1\right)\left(\frac{\partial^2 \omega}{\partial T^2}\right)_p \tag{32}$$

The TH-HKF equations allow for temperature and pressure dependent ionic radii of ions through the equation

$$r_e = r_{cr} + |z|(k_z + g) \tag{33}$$

where $r_{cr}$ is the crystallographic radius, $k_z$ is a constant that is equal to 0 for anions and 0.94 Å for cations, and $g$ is an empirical function set equal to 0 below 160 °C and always negative at elevated temperatures and pressures. This leads to a reduction in the "effective" radii of ions as temperature is increased. This has recently been supported by direct EXAFS measurements on $Ag^+$(aq) to 350 °C by Seward and co-workers.[61] Equations for calculation of $g$ and its temperature and pressure derivatives that lead to calculation of $\omega$ and its various temperature and pressure derivatives are summarized in Appendices B and C of Tanger and Helgeson.[57]

These equations were fitted to the experimental data for the standard state partial molar volumes and heat capacities listed in Table 3. Effective ionic crystallographic radii ($r_{cr}$) for the appropriate coordination number were derived from Shannon[62] (1.05 Å for $Th^{4+}$), the properties of water were derived from Hill,[63] and values of the dielectric constant and the various temperature and pressure derivatives were taken from Archer and Wang.[35] The following expressions were obtained by fitting this model to the results in Table 2:

$$\frac{\bar{V}°[Th(ClO_4)_4, aq]}{cm^3 \; mol^{-1}} = 177.152 - \frac{2934.17}{T - 228} + \Delta V_{Born} \tag{34}$$

$$\frac{\bar{C}_p°[Th(ClO_4)_4, aq]}{J \; K^{-1} \; mol^{-1}} = 233.775 - \frac{1432475}{(T - 228)^2} + \Delta C_{p,Born} \tag{35}$$

Corresponding fits to the standard state values from original or

Thermodynamics of Hydration of a 4+ Aqueous Ion

*J. Phys. Chem. B, Vol. 101, No. 21, 1997* **4329**

isothermal fits for HClO$_4$(aq) (as described in Appendix I) result in the following expressions:

$$\frac{\bar{V}°[\text{HClO}_4,\text{aq}]}{\text{cm}^3\ \text{mol}^{-1}} = 59.528 - \frac{874.598}{T - 228} + \Delta V_{\text{Born}} \quad (36)$$

$$\frac{\bar{C}_p°[\text{HClO}_4,\text{aq}]}{\text{J K}^{-1}\ \text{mol}^{-1}} = 76.70 - \frac{316358}{(T - 228)^2} + \Delta C_{p,\text{Born}} \quad (37)$$

The quantities $\Delta V_{\text{Born}}$ and $\Delta C_{p,\text{Born}}$ are equal to the the first terms in eqs 36 and 37, respectively, below 160°, because of the zero value of the $g$ function and its derivatives. As such for calculations in this region, values of $\omega$ for HClO$_4$(aq) and Th-(ClO$_4$)$_4$(aq) are equal to 4.75268 × 10$^5$ and 3.31022 × 10$^6$ J mol$^{-1}$, respectively. Equations relevant for the temperature dependence of Th$^{4+}$(aq) (referenced against the convention that the properties for H$^+$(aq) are zero at all temperatures and pressures) are easily calculated from the expressions

$$\frac{\bar{V}°[\text{Th}^{4+},\text{aq}]}{\text{cm}^3\ \text{mol}^{-1}} = -60.962 - \frac{564.227}{T - 228} + \Delta V_{\text{Born}} \quad (38)$$

$$\frac{\bar{C}_p°[\text{Th}^{4+},\text{aq}]}{\text{J K}^{-1}\ \text{mol}^{-1}} = -73.01 - \frac{167042}{(T - 228)^2} + \Delta C_{p,\text{Born}} \quad (39)$$

The temperature dependence of the partial molar volumes of Th(ClO$_4$)$_4$(aq) is compared with a series of perchlorate salts[32,34,64–66] shown in Figure 7. The standard state volumes for a 1:1, 2:1, 3:1, and 4:1 salt are plotted against temperature and pressure along the saturation surface of water. The effect of both the total number of ions in each salt and the nature of

the charge of the cation lead to the observed dependence. It is clear that the most dramatic changes in the solute−solvent interactions occur for the 4:1 electrolyte, and if these data are plotted as ionic values referenced to H$^+$(aq), we see similar trends. It is important to also examine the temperature dependence of the standard state heat capacities of the ions as shown in Figure 8, where standard state heat capacities calculated using the TH-HKF model are presented for Na$^+$(aq), Ca$^{2+}$(aq), and Al$^{3+}$(aq) from results summarized by Shock and Helgeson[67] and Th$^{4+}$(aq) from the present calculations. The effect of charge of the central ion is shown clearly here, as is the dependence on $z^2/r$. Although Th$^{4+}$(aq) is more highly charged than Al$^{3+}$(aq), its approach to −∞ is just slightly more steep than Al$^{3+}$(aq) because of the effective radius of thorium (1.05 Å) compared with that for aluminum (0.535 Å). The behavior of the standard state heat capacity of these salts at sufficiently high temperatures is dominated by purely continuum contributions from the Born model. As such, the difference between these two cations at elevated temperatures is dependent on the ratio of $z^2/r$. Within the framework of the TH-HKF model this leads to ratios of the limiting difference in high-temperature solvation of 2.7, 1.9, and 1.2 when comparing relative solvation between Ca/Na, Al/Ca, and Th/Al, respectively. This can be observed graphically by the various approaches to high temperature, as shown in Figure 8.

A similar example of the effect of the charge on the standard state heat capacities is in the region below 25 °C compared with the region above about 200 °C. In the region below 25 °C and especially that near and below 0 °C, the data are again diverging toward highly negative values in all cases. Using the approximate "absolute" heat capacity of H$^+$(aq) from Abraham and Marcus[68] of −71 J K$^{-1}$ mol$^{-1}$ valid at 25 °C as
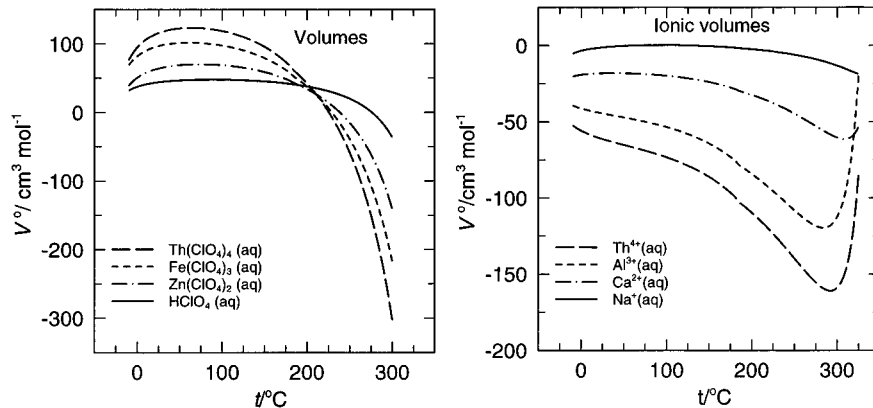


**Figure 7.** Extrapolated results for the standard volumes using the TH-HKF model for ionic solvation as a function of temperature and pressures equal to 1 bar below 100 °C and liquid vapor saturation values above for (a) metal perchlorate salts and (b) individual ions.



**Figure 8.** Extrapolated results for the standard heat capacities using the TH-HKF model for ionic solvation as a function of temperature and pressures equal to 1 bar below 100 °C and liquid vapor saturation values above for (a) metal perchlorate salts and (b) individual ions.
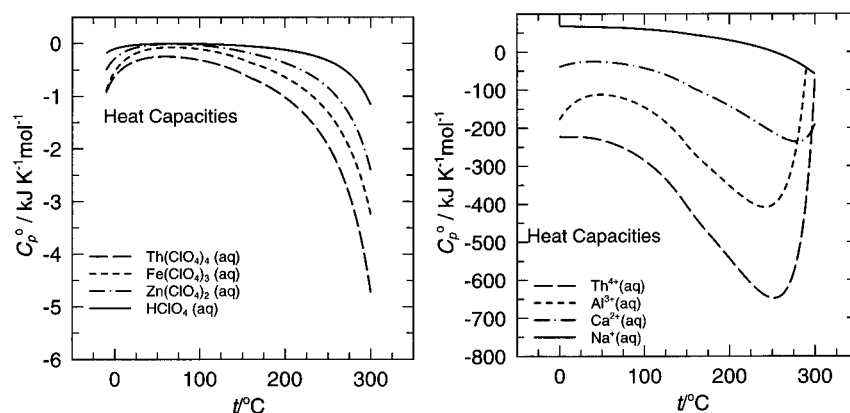
an upper estimate of this value at 10 °C to examine the approximate behavior of the bare metal ions at 10 °C leads to the values −50, −71, −190, −366, −354, and −745 J K$^{-1}$ mol$^{-1}$ for Na$^{+}$(aq), H$^{+}$(aq), Zn$^{2+}$(aq), Fe$^{3+}$(aq), Al$^{3+}$(aq), and Th$^{4+}$(aq), respectively. Consideration of these changes within dependences suggested by the Born equation ($z^2/r$), or mutual potential functions from ion−dipole equations ($z/r^2$), or other classical ion−water models, does not uniquely describe this trend. The changing nature of solvated or other water affected by the charge of the cation is dramatic over such a wide range of electrostatic fields.

At temperatures near and below room temperature, the structure of water and the near ionic structure of the hydrated ion dominate the thermodynamic behavior of aqueous ions.[68−72] The Frank and Wen model[69] of ionic hydration and the various multilayered dielectric continuum models[69−72] are all consistent with deviations or shortcomings with a purely electrostatic theory in the region near or below room temperature. The effect of placing an ion in water as can be deduced from the ion−solvent ideal interaction of the standard state properties is the disruption of the H-bonded structure by strongly removing or freezing out some of the water molecules in the primary solvation shell and less strongly in more distant shells or at distances beyond the diameter of two water molecules. In terms of partial molar volumes, this effect can be equated with the sum of crystallographic, electrostatic, and disordered contributions.[73] Considering the heat capacity of pure water, the total observed heat capacity must be reduced when placing a highly charged hydrophylic solvent into the H-bonded structure because of the removal (for Th$^{4+}$(aq) a total of eight in the primary solvation shell alone) of water molecules from the bulk to the ion. The microscopic H-bonded equilibria thus are decreased, as is the total heat capacity of the solution. Since water becomes even more highly structured as the temperature is decreased,[74] the partial molar heat capacity is expected to become very highly negative, approaching values seen for purely electrostatic interactions as the critical point of water is approached.[75,76] The region below 0 °C is a fruitful region for future experimental and theoretical research. The multilayer hydration models of Abraham and co-workers,[70−72] through the use of physically realistic models, represent the majority of the hydration quantities of ions to within reasonable levels. Difficulties of these models, however, as exemplified in determination of midlayer properties by difference calculation,[77] are expected to increase for such highly charged ions (more or larger layers required to describe the observed properties) as Th$^{4+}$(aq).

**Comparisons with Model Calculations.** Since these data, especially the results leading to the partial molar heat capacities, are believed to be the first accurate values for a 4+ aqueous cation, it is important here to examine many of the models that have been developed to describe the standard state volumes and heat capacities for the corresponding hydration reactions.

Specific values for the standard state heat capacity at 25 °C can be calculated from the hydration model presented by Abraham and Marcus.[68] Using the parameters cited in ref 68 (including sources for crystal radii) leads to a calculated $\Delta C_{p,\text{hyd}} = -1297$ J K$^{-1}$ mol$^{-1}$. This leads to $\bar{C}_p^\circ$(Th$^{4+}$,aq) = −993 J K$^{-1}$ mol$^{-1}$ using their value for the absolute heat capacity of aqueous hydrogen $\bar{C}_{p,\text{abs}}^\circ$(H$^{+}$,aq) = −71 J K$^{-1}$ mol$^{-1}$. Morss and McCue[53] calculated a value of $\bar{C}_p^\circ$(Th$^{4+}$,aq) = −28 J K$^{-1}$ mol$^{-1}$ using their determined entropy and the entropy correspondence principle of Criss and Cobble.[78] This gave good agreement with their determined $\bar{C}_p^\circ$(Th$^{4+}$,aq) = −1 ± 11 J K$^{-1}$ mol$^{-1}$ and led them to conclude that the Criss−Cobble scheme was useful for prediction of heat capacities for tetravalent and

subsequently trivalent cations. Partially on the basis of the success of the model for Th$^{4+}$(aq), Lemire and Tremaine[79] calculated the temperature dependences of a variety of equilibria involving uranium and plutonium to 200 °C. These results confirm earlier results[80] that the heat capacities of multivalent ions are not satisfactorily estimated using this model. All of these estimates are in poor agreement with the present result of $\bar{C}_p^\circ$(Th$^{4+}$,aq) = −224 ± 5 J K$^{-1}$ mol$^{-1}$ at 25 °C.

Swaddle and Mak[81] have derived an equation that represents the standard state partial molar volumes of aqueous cations often to within experimental uncertainties. Their correlation is partially based on the volumetric data for Th$^{4+}$(aq) cited earlier from Millero's 1972 compilation.[46] Since this value differs from the present value by over 7 cm$^3$ mol$^{-1}$, good agreement is not expected here. Using the appropriate radius[81] for Th$^{4+}$(aq), the model results in $\bar{V}^\circ$(Th$^{4+}$,aq) = −54.2 cm$^3$ mol$^{-1}$, in almost perfect agreement with the volumetric data the model is based upon. A revised model incorporating these new data would be expected to represent the experimental findings. An older model derived by Couture and Laidler[47] does significantly better in predicting the value $\bar{V}^\circ$(Th$^{4+}$,aq) = −58 cm$^3$ mol$^{-1}$ compared with our experimental value of −60 cm$^3$ mol$^{-1}$ even though it was based on the same older volumetric information. Updated versions of these types of correlations incorporating these new data for Th$^{4+}$(aq) are in progress.[82]

**Structure of Th$^{4+}$(aq).** Large-angle X-ray scattering experiments for Th(ClO$_4$)$_4$(aq)[20] in solutions containing excess perchloric acid have clearly defined the Th−OH$_2$ distance of 2.49 Å, in excellent agreement with earlier X-ray measurements on more concentrated solutions[19] that led to the value 2.50 Å. A total of eight water molecules were calculated as residing in the primary solvation shell, which agrees with a value of nine from earlier ^{1}H NMR data at low temperatures and higher concentrations.[17] These recent measurements, however, have provided detailed information regarding the secondary solvation shell and the fact that about 20 water molecules hydrogen bonded to the primary shell waters reside at a Th−O distance of 4.6 Å. It is informative to compare spectroscopic and thermodynamic measurements with another multivalent metal cation that also has a well-defined second solvation shell, namely, Al$^{3+}$(aq).

The maximum mutual potential energy between an ion and dipole in vacuum is proportional to $z/r^2$ and corresponds to a near-ion property. Because of the small ionic radius of Al$^{3+}$, it can easily be seen that the first ion−dipole interaction is greater than the corresponding quantity for Th$^{4+}$. However, calculations involving successive hydration steps with five or six waters of hydration lead to similarity of potential functions for thorium and aluminum. For example, in terms of an ion−dipole potential, the magnitude of the potential for aluminum (ignoring orientational effects) is greater than 2.5 times larger than that for thorium. However, the interaction of M(H$_2$O)$_5^{z+}$ moieties with a water dipole leads to virtually identical potentials of interaction (4% difference). The smaller size of aluminum compensates somewhat for its smaller charge in comparison with thorium, especially at distances equal to the primary or secondary solvation shells of the ion.

The structures of aqueous solutions containing Al$^{3+}$(aq) have been determined by X-ray scattering experiments and are summarized by Magini *et al.*[83] Al$^{3+}$(aq) has a primary solvation shell containing six water molecules at a distance of 1.9 Å and a well-defined secondary solvation shell containing 12 water molecules at a distance of about 4.0 Å. It is clear that the higher coordination of Th$^{4+}$ due in part to the charge and electronic configuration of the thorium atom leads to a greater effect of

Thermodynamics of Hydration of a 4+ Aqueous Ion

*J. Phys. Chem. B, Vol. 101, No. 21, 1997* **4331**

"freezing-out" water molecules from the bulk solution. However, because $Th^{4+}(aq)$ and $Al^{3+}(aq)$ represent cases where the second solvation shell is well-defined experimentally by X-ray data and have associated experimental data for the standard state partial molar volumes and heat capacities, a simple approximate calculation can be made to estimate the thermodynamic properties of water in the primary and secondary solvation shells in reference to the solvated standard state. The fact that the solvation shells do not contain the same number of water molecules allows for estimation of contributions from both of these differently solvated water molecules.

Here it is assumed that the water in both primary solvation shells is bound (electrostatically) in similar fashion (not in terms of the nature of electronic orbitals of the species) for these two metal ions (as partially supported by earlier ion–dipole arguments). It is also assumed that the Born equation can be used to correct for "bulk" solvation beyond the second solvation shell. As such, the absolute heat capacities and volumes of solvated thorium and aluminum species can be represented by the following individual steps:

$$\bar{Y}^{abs}[M^{z+}(aq)] = \bar{Y}^{abs}[M(H_2O,I)_a(H_2O,II)_b{}^{z+}(aq)] + \Delta\bar{Y}_{Born} \quad (40)$$

where $\bar{Y}^{abs}[M(H_2O,I)_a(H_2O,II)_b{}^{z+}(aq)]$ represents the ion with its primary and secondary solvation shells, and $a$ and $b$ are the numbers of solvated water in shell I (primary) and shell II (secondary). $\Delta\bar{Y}^\circ_{Born}$ is the continuum electrostatic contribution on going from the ion with two solvation shells to the total solvated species in bulk solution. For the purposes of quantifying the contributions that the solvation shell water molecules make to the total experimentally observed values, this ion is written as

$$\bar{Y}^{abs}[M(H_2O)_a(H_2O)_b{}^{z+}(aq)] = \\ \bar{Y}^{abs}(M^{z+}) + a\bar{Y}^{abs}(H_2O,I) + b\bar{Y}^{abs}(H_2O,II) \quad (41)$$

The bare contribution of $\bar{Y}^{abs}(M^{z+})$ is small and can be estimated from crystallographic or ideal-gas statistical mechanics results, thus equating the bulk of the effect to ion–water interactions in the first two solvation shells. These calculations should provide results independent of assumed dielectric constants of solvation layers but ignore further perturbations in the water structure outside of the secondary solvation shell and are limited to ions with similar charge/size ratios.

The various derived quantities from this simple model are given in Table 7. Although not expected to be universally applicable, these quantities are informative in terms of both $Th^{4+}(aq)$ and $Al^{3+}(aq)$, where both solvation shells are well-defined. It can be seen that each primary shell water molecule contributes approximately $-23$ J K$^{-1}$ mol$^{-1}$ to the total observed heat capacity, whereas secondary shell water molecules contribute less than half of this value, $-10$ J K$^{-1}$ mol$^{-1}$. Since these calculations are referenced to contributions to the partial molar quantities in the hypothetical 1 $m$ standard state, it is important to note that they illustrate approximate relative contributions to the heat capacity, *not* the internal heat capacity of a water molecule in this state. A value of 0 would imply that the water molecules are indistinguishable from the state of water in bulk solvent. The magnitude of the contribution that the secondary shell water molecules make to the heat capacity indicates that further coordination spheres are likely to make appreciable contributions to the heat capacity. The lack of direct structural evidence for more distant shells hampers more detailed calculations. Examination of similar quantities for the volume

**TABLE 7: Estimation of the Contribution of Primary and Secondary Solvation Shell Water Molecules to the Absolute Molar Volumes and Heat Capacities for Th⁴⁺(aq) and Al³⁺(aq) at 25 °C[a]**

|  | Al³⁺ | Th⁴⁺ |
|---|---|---|
| $r(M^{z+})$/Å | 0.535 | 1.04 |
| $r[M(H_2O,I)_a(H_2O,II)_b{}^{z+}]$/Å | 5.4 | 6.0 |
| *Heat Capacity/J mol⁻¹ K⁻¹* | | |
| $C_p^{abs}(M^{z+})$ | 21.0 | 21.0 |
| $\Delta C_{p,Born}(II \rightarrow bulk)$ | $-95.6$ | $-152.9$ |
| $C_p^{abs}(M^{z+},aq)$ | $-332$ | $-516$ |
| $C_p^{abs}(H_2O,I)$ | *−23* | |
| $C_p^{abs}(H_2O,II)$ | *−10.0* | |
| *Volume/cm³ mol⁻¹* | | |
| $V^{abs}(M^{z+})$ | 0.4 | 2.9 |
| $\Delta V_{Born}(II \rightarrow bulk)$ | $-6.9$ | $-11.0$ |
| $V^{abs}(M^{z+},aq)$ | $-63.3$ | $-84.7$ |
| $V^{abs}(H_2O,I)$ | *−9.0* | |
| $V^{abs}(H_2O,II)$ | *−0.2* | |

[a] Absolute values of the heat capacities of the ions were estimated from gas phase properties of ions and volumetric properties from the appropriate crystallographic radii derived from Shannon.[62] Born constributions were calculated from sources described earlier.

changes associated with hydration of these ions clearly shows that the major contribution to the observed standard state volume is due to the primary solvation shell. As shown in Table 7, the contribution that water molecules make to the total observed volumetric results is $-9.0$ cm³ mol⁻¹ for primary shell waters and $-0.2$ cm³ mol⁻¹ for secondary shell waters. Even though these ions disrupt the water structure well beyond the primary solvation shell, the partial molar volumes are less sensitive to such perturbations and secondary shell waters are at least volumetrically similar to bulk water. These values can be used to calculate appropriate standard state heat capacities and volumes for cations with similar size to charge ratios such as the lanthanide aqueous ions. Precise X-ray data are available for most 3+ lanthanide metal ions, and as an example, Er³⁺-(aq) is known to have eight water molecules in the primary solvation shell and about 13 in the second solvation shell.[84] Using radii information from ref 84 and the data in Table 7, the standard state heat capacity and volume of Er³⁺(aq) can be calculated to be $-122$ J K⁻¹ mol⁻¹ and $-43$ cm³ mol⁻¹, respectively. These values are in good agreement with the experimental values[46,85] $-101$ J K⁻¹ mol⁻¹ and $-43$ cm³ mol⁻¹, respectively.

The nature of the hydration reactions of ions is more clearly defined by rigorous calculation of each individual hydration step in bringing an ion from the gas phase to that in bulk solution. At present there are direct experimental data for the initial hydration steps of many singly charged cations,[86] and *ab initio* calculations have led to a variety of data[87] and are becoming more accurate and more extensive. Molecular dynamic results[88] are qualitatively accurate but also rely on some degree of empiricism, as do many of the continuum models of ionic hydration. A combination of experimentally determined primary solvation shell enthalpies and corresponding Gibbs energies combined with either molecular dynamic or continuum electrostatic theory from the outer surface of the primary shell to the bulk solvent are expected to be more informative than strictly electrostatic models described above. Pitzer[89] has performed such calculations for the self-ionization of water, and similar but extended continuum calculations were presented by Tanger and Pitzer.[90,91] An important complement to the direct solution experiments is investigation of the thermodynamics of hydration and solvation of multivalent electrolytes by novel experimental methods such as electrospray ionization mass spectrometry[92,93]

**TABLE 8: Results of Fitting Extended Debye−Hückel and Pitzer Equations to the Apparent Molar Volumes and Heat Capacities of HClO₄(aq) at Selected Temperatures**

| | | | Extended Debye−Huckel Equations of Type (A1) | | | |
|---|---|---|---|---|---|---|
| $t$ (°C) | $\phi V_2^\circ$ (cm³ mol⁻¹) | $B_V$ (cm³ kg mol⁻²) | $C_V$ (cm³ kg³/² mol⁻⁵/²) | $\phi C_{p,2}^\circ$ (J K⁻¹ mol⁻¹) | $B_C$ (J kg K⁻¹ mol⁻²) | $C_C$ (J kg³/² K⁻¹ mol⁻⁵/²) |
| 10 | 41.53 ± 0.11 | 0.6240 ± 0.54 | −0.5417 ± 0.45 | −61.1 ± 0.7 | 50.803 ± 3.4 | −19.968 ± 2.8 |
| 25 | 44.10 ± 0.03 | −0.6634 ± 0.03 | 0.1436 ± 0.04 | −25.6 ± 0.6 | 23.198 ± 4.1 | −8.565 ± 3.7 |
| 40 | 46.27 ± 0.05 | −0.6569 ± 0.06 | | −10.1 ± 0.4 | 7.2662 ± 0.59 | |
| 55 | 47.48 ± 0.09 | −1.3131 ± 0.21 | 0.3023 ± 0.11 | −4.7 ± 1.3 | 3.1179 ± 1.7 | |

| | | | Pitzer Ion−Interaction Equations of Type (A2) | | | |
|---|---|---|---|---|---|---|
| $t$ (°C) | $\phi V_2^\circ$ (cm³ mol⁻¹) | $10^4\beta^{(0)V}$ (cm³ kg J⁻¹ mol⁻¹) | $10^4 C^V$ (cm³ kg² J⁻¹ mol⁻²) | $\phi C_{p,2}^\circ$ (J K⁻¹ mol⁻¹) | $10^5\beta^{(0)J}$ (kg mol⁻¹ K⁻²) | $10^5 C^J$ (kg² mol⁻² K⁻²) |
| 10 | 41.54 ± 0.09 | 0.3926 ± 0.61 | −0.5126 ± 0.46 | −60.3 ± 0.6 | −2.8028 ± 0.14 | 0.6895 ± 0.10 |
| 25 | 44.07 ± 0.03 | −1.384 ± 0.01 | 0.1240 ± 0.03 | −25.3 ± 0.6 | −1.0281 ± 0.16 | 0.2214 ± 0.13 |
| 40 | 46.25 ± 0.05 | −1.533 ± 0.01 | | −10.5 ± 0.4 | −0.2927 ± 0.04 | |
| 55 | 47.42 ± 0.07 | −2.301 ± 0.2 | 0.2161 ± 0.06 | −5.2 ± 1.3 | −2.14 ± 9.4 | |

and higher order quantum mechanical calculations.[94] It is expected that a combination of these research areas will provide direct structural and thermochemical information regarding long-range ion−ligand interactions well beyond the first solvation shell, particularly important for lanthanide, actinide, and other multivalent cations.

## Appendix I

**Data Representations for HClO₄(aq).** *Apparent Molar Volumes.* There are several sources of experimental determinations of the apparent molar volumes and heat capacities of aqueous perchloric acid. Apparent molar volumes over the range 10−200 °C were taken from Hovey and Hepler[34] (10−55 °C), Pogue and Atkinson[95] (15−55 °C), Herrington et al.[96] (25−75 °C), and Lemire et al.[97] (25−100 °C) and values for the standard state limiting volumes only were derived using auxiliary data from Ellis[98,99] (100−200 °C). Weighted isothermal fits at each of the experimental temperatures of concern here were performed for both the normal extended Debye−Hückel equations given by

$$\phi Y = \phi Y^\circ + 1.5\frac{A_Y}{I}[I - 2I^{1/2} + 2\ln(1 + I^{1/2})] + B_Y I + C_Y I^{3/2}$$

$$(A1)$$

and the Pitzer ion-interaction equations for the apparent molar volumes:[42]

$$\phi V = \bar{V}^\circ + \left(\frac{A_V}{b}\right)\ln(1 + bI^{1/2}) + 2RT(mB^V + m^2 C^V) \quad (A2)$$

where $B^V$ is a function of ionic strength as defined by eq 11 in the regular text. The various best fits are shown for each temperature in Table 8.

The full set of experimental data were then used in global fits of all appropriate volumetric parameters and the temperature dependences of these parameters. The data of Ellis were included in the Pitzer-model fits to guide $\bar{V}^\circ$ to higher temper-

**TABLE 9: Parameters Valid for the Temperature Dependences of the Extended Debye−Hückel Parameters from Global Fits of Apparent Molar Volumes and Heat Capacities of HClO₄(aq) According to Eq A1[a]**

| $f(T) = p_1 + p_2 T + p_3 T^2 + p_4/T^2 + p_5/(T - 190)$ | | | |
|---|---|---|---|
| molar volumes | | molar heat capacities | |
| $\bar{V}^\circ$ | | $\bar{C}_p^\circ$ | |
| $p_1/10^{+1}$ | −5.025 526 6 | $p_1/10^{+3}$ | 1.632 828 1 |
| $p_2/10^{-1}$ | 5.789 698 8 | $p_2/10^0$ | −4.977 977 1 |
| $p_3/10^{-4}$ | −8.114 251 2 | $p_3/10^{-3}$ | 3.508 682 2 |
| $p_5/10^{+2}$ | −6.686 707 6 | $p_5/10^{+4}$ | −5.261 635 4 |
| $B^V$ | | $B^J$ | |
| $p_1/10^0$ | −6.332 483 5 | $p_1/10^{+2}$ | −2.681 362 3 |
| $p_5/10^{+2}$ | 7.162 257 9 | $p_3/10^{-4}$ | 9.570 083 0 |
| $C^V$ | | $C^J$ | |
| $p_1/10^0$ | 3.650 873 2 | $p_1/10^{+1}$ | 5.477 823 3 |
| $p_5/10^{+2}$ | −5.052 141 3 | $p_5/10^{+3}$ | −6.752 433 1 |
| $D^V$ | | | |
| $p_1/10^{-1}$ | −7.180 063 0 | | |
| $p_5/10^{+2}$ | 1.162 735 2 | | |

[a] Overall resultant units are cm³ mol⁻¹ for volumes and J K⁻¹ mol⁻¹ for heat capacities when temperature is in kelvin.

atures. The data of Lemire et al.[97] were measured at slightly higher pressure and were not consistent with the other data sets at the same temperatures and were not used for either approach.

The various parameters were constrained to temperature dependent equations of the form

$$f(T) = p_1 + \frac{p_2}{T} + p_3 T + p_4 T^2 +$$

$$\frac{p_5}{T - 190} + \frac{p_6}{T - 647} + p_7 \ln T \quad (A3)$$

where the number of parameters varied depending on the fit model and quantity to be fitted. All of the various coefficients for both of the approaches are listed in Table 9.

*Apparent Molar Heat Capacities.* There are significantly fewer data that lead to the determination of apparent molar heat capacities for perchloric acid. Heat capacities of pure solutions containing HClO₄(aq) have been measured by Lemire et al.,[97] Hovey and Hepler,[34] Pogue and Atkinson,[95] and Singh et al.[100] (25 °C). The data of Pogue and Atkinson are in poor agreement with the other studies perhaps because unsymmetrical heat losses were not considered. The results from Lemire et al.[97] are systematically more negative (after appropriate pressure correction) than the results of Hovey and Hepler[34] and Singh et al.,[100] although extending to higher temperatures. Accordingly, the results from Hovey and Hepler,[34] Singh et al.,[100] and Lemire et al.[97] above 55 °C were used to refine the various extended

Thermodynamics of Hydration of a 4+ Aqueous Ion

*J. Phys. Chem. B, Vol. 101, No. 21, 1997* **4333**

**TABLE 10: Parameters Valid for the Temperature Dependences of Pitzer Ion-Interaction Model Parameters from Global Fits for Partial Molar Volumes and Heat Capacities of HClO$_4$(aq) According to Eqs A2 and A3[a]**

| $f(T) = p_1 + p_2/T + p_3T + p_4T^2 + p_5/(T-190) + p_6/(T-647) + p_7 \ln T$ | | | |
|---|---|---|---|
| molar volumes | | molar heat capacities | |
| $\bar{V}^\circ$ | | $\bar{C}_p^\circ$ | |
| $p_1$ | 625 520.664 | $p_1$ | 1082.058 18 |
| $p_2$ | −151 60131.2 | $p_3$ | −2.305 772 00 |
| $p_3$ | 302.470 502 | $p_5$ | −45 480.1748 |
| $p_4$ | −0.13 828397 | | |
| $p_5$ | 773 40.4811 | | |
| $p_6$ | −118 694.404 | | |
| $p_7$ | −114 710.429 | | |
| $\beta^{(0)V}$ | | $\beta^{(0)J}$ | |
| $p_1/10^{-1}$ | 1.775 187 429 | $p_1/10^{-4}$ | 3.315 500 611 |
| $p_3/10^{-4}$ | −4.670 502 984 | $p_3/10^{-7}$ | −6.403 740 723 |
| $p_4/10^{-6}$ | 1.691 050 818 | $p_5/10^{-2}$ | −1.636 773 341 |
| $p_6/10^{+1}$ | 6.587 111 156 | | |
| $\beta^{(1)V}$ | | | |
| $p_1/10^{-3}$ | −6.685 921 147 | | |
| $p_3/10^{-3}$ | 1.668 255 482 | | |
| $p_4/10^{-6}$ | −6.375 129 630 | | |
| $p_6/10^{+2}$ | −2.575 252 071 | | |
| $C^V$ | | $C^J$ | |
| $p_1/10^{-1}$ | −5.290 164 776 | $p_1/10^{-6}$ | −7.388 662 556 |
| $p_4/10^{-8}$ | −4.882 268 220 | $p_3/10^{-8}$ | −2.541 746 960 |
| $p_6/10^0$ | −3.370 691 016 | $p_5/10^{-3}$ | 1.855 086 422 |

[a] Overall resultant units are cm$^3$ mol$^{-1}$ for volumes and J K$^{-1}$ mol$^{-1}$ for heat capacities when temperature is in kelvin.

Debye−Hückel or Pitzer ion-interaction parameters. The apparent molar heat capacity of a 1:1 electrolyte is given by eq A1 for the extended Debye−Hückel approach and by the following equation for the Pitzer ion-interaction model:

$$\phi C_p = \bar{C}_p^\circ + \left(\frac{A_J}{b}\right)\ln(1 + bI^{1/2}) - 2RT^2(mB^J + m^2 C^J) \quad (A4)$$

Isothermal fits to appropriate data at temperatures of interest here are provided in Table 8 for both approaches. Global representations of the data by constraint of the temperature dependence of the various parameters to equations of type A3 are reported in Table 10 for both approaches.

The discrepancies of the various data sets is troublesome in the case of perchloric acid, as it is such a simple and pure electrolyte. Appropriate wider molality range measurements over the temperature range 4−90 °C are under way.[66]

## Appendix II

**Unsymmetrical Mixing Terms for the Partial Molar Volume and Heat Capacity.** There are theoretical methods that can be employed to calculate various terms arising from unsymmetrical and symmetrical mixing of ions.[42,101−103] In the present system containing the electrolyte mixture with a common anion, there are no contributions that arise from mixing of ions of similar charge and magnitude of charge. However, because the unsymmetrical terms are proportional to the charge on common cations with different charge magnitudes, it is expected that these terms might be non-negligible. As such, it was necessary to derive a method for determination of these quantities.

$\Phi_{ij}$ is the term representative of the non-negligible contributions to the excess Gibbs energy that result from mixing (unsymmetrical) of ions (same sign but with differing absolute charge). The equations defining $\Phi_{ij}$ appropriate for the Gibbs energy, osmotic coefficient, and activity coefficient are given by

$$\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (A5)$$

$$\Phi'_{ij} = \frac{\partial \Phi_{ij}}{\partial I} = {}^E\theta'_{ij}(I) \quad (A6)$$

$$\Phi^\theta_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) + I^E\theta'_{ij}(I) \quad (A7)$$

The quantities ${}^E\theta_{ij}(I)$ and ${}^E\theta'_{ij}(I)$ are concentration dependent, as indicated, and are calculated from theory. The $\theta_{ij}$ term is an empirical parameter without an appreciable ionic strength dependence. Because here we are concerned with the partial molar volumes and heat capacities, we need to generate appropriate values for the theoretical terms for these quantities. These terms are related to the temperature and pressure derivatives of ${}^E\theta_{ij}(I)$ in the normal way:

$$\Phi^V_{ij} = \left(\frac{\partial \Phi_{ij}}{\partial p}\right)_T$$

$$= \left(\frac{\partial \theta_{ij}}{\partial p}\right)_T + \left(\frac{\partial\, {}^E\theta_{ij}(I)}{\partial p}\right)_T$$

$$= \theta^V_{ij} + {}^E\theta^V_{ij}(I) \quad (A8)$$

$$\Phi^J_{ij} = \left(\frac{\partial^2 \Phi_{ij}}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial \Phi_{ij}}{\partial T}\right)_p$$

$$= \left(\frac{\partial^2 \theta_{ij}}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial \theta_{ij}}{\partial T}\right)_p + \left(\frac{\partial^2\, {}^E\theta_{ij}(I)}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial\, {}^E\theta_{ij}(I)}{\partial T}\right)_p$$

$$= \theta^J_{ij} + {}^E\theta^J_{ij}(I) \quad (A9)$$

As such, derivatives for the first pressure derivative of ${}^E\theta_{ij}(I)$ as well as the first and second derivatives of ${}^E\theta_{ij}(I)$ are required. These quantities were calculated using numerical derivatives from the method of Harvie[104] using two Chebyshev polynomial approximations and the various parameters for the terms outlined by Pitzer.[42] Appropriate values were derived from the present data and the dielectric constant treatment of Archer and Wang.[35] It was found that the contributions to the partial molar volume were very small (on the order of $10^{-12}$), although those for heat capacity were much larger. In terms of the same units as derived for the $\beta^{(0)}$ terms, the unsymmetrical contribution term ${}^E\theta^J_{ij}(I)$ ranged in value from $-0.4 \times 10^{-4}$ to $-0.2 \times 10^{-3}$ for these solutions. However, it was found that although these additional terms had almost no effect on the quality of fit, they did have a non-negligible effect on the exact magnitude of the individual ion-interaction parameters.

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