Thermodynamic Properties of Aqueous Gadolinium Perrhenate and Gadolinium Chloride from High Dilution Calorimetry at Extreme Temperatures and Pressures

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The heat of solution of solid cubic gadolinium oxide has been measured in noncomplexing perrhenic acid solutions at very high dilutions (10^{-4} *m*) up to 596.30 K, from which the standard state thermodynamic properties of aqueous gadolinium perrhenate were determined up to 623.15 K. From the measured differences between similar properties of aqueous sodium chloride and perrhenate, thermodynamic properties for aqueous gadolinium chloride were obtained by ionic additivity. Data for the hydrolysis of Gd^{3+}(aq) were obtained by separate determinations. The enthalpy of solution of gadolinium chloride at 623.15 K obtained from this research (-2.7 MJ mol^{-1}) is apparently larger than any other recorded for a chemical reaction involving aqueous systems. Standard state partial molal heat capacities for $ThCl_4$(aq) were predicted up to 623.15 K.

Introduction

Due to increasing nonideality of the electrolytes at high temperatures in even dilute solutions,[1] the use of extremely low concentrations in measuring properties of aqueous electrolytes is important for all electrolytes but particularly for the highly charged ions. The difficulties involved in making high dilution measurements under high pressures and temperatures are challenging. As a consequence, there are no 3:1 electrolytes whose standard state thermodynamic properties have been extended to high temperatures, although $GdCl_3$(aq) has been characterized up to 373.15 K.[2] The advantage of the integral heat method[3] is that measurements to give extremely dilute solutions of the electrolyte are possible; $10^{-2}-10^{-4}$ *m* is the normal operating range, and even concentrations down to 10^{-5} *m* are feasible. Gadolinium ion, Gd^{3+}, was chosen as a model 3:1 electrolyte because the relatively large size (0.938 Å) suggests less hydrolysis, and there are no other available stable aqueous oxidation states.

In this communication, thermodynamic data for $Gd(ReO_4)_3$(aq) are reported up to 623.15 K, obtained in a high dilution calorimeter described elsewhere.[4] In order to avoid possible complexes of Gd^{3+}(aq), the solution of cubic Gd_2O_3(cr) was carried out in noncomplexing $HReO_4$(aq) acidic solutions:

$$\tfrac{1}{2}Gd_2O_3(cr, cubic) + 3HReO_4(aq) =$$
$$Gd(ReO_4)_3(aq) + \tfrac{3}{2}H_2O(l) \quad (1)$$
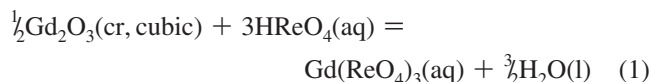
More details regarding properties of the strong acid $HReO_4$(aq) are described elsewhere.[4,5] The thermodynamic properties of $GdCl_3$(aq) were then determined by additivity:

$$\bar{X}^\circ_{GdCl_3(aq)} = \bar{X}^\circ_{Gd(ReO_4)_3(aq)} - 3\bar{X}^\circ_{NaReO_4(aq)} + 3\bar{X}^\circ_{NaCl(aq)} \quad (2)$$

where $\bar{X}^\circ$ represents any standard state partial molal thermodynamic property.

The solubility reaction 1 is also superior to the direct measurement of the heat of solution of solid $Gd(ReO_4)_3$, because there is partial cancelation of the heats of dilution of the electrolytes on both sides of reaction 1, and because the heat of solution of a solid gadolinium salt in water would be too large (see later discussion).

Baes and Mesmer[6] have critically reviewed the hydrolysis of trivalent lanthanides at 298.15 K. A calorimetric investigation of the hydrolysis of Gd^{3+}(aq) was carried out in this study at the highest experimental temperature (596.30 K); the results are given elsewhere.[4] In the range of pH (≤ 2.5) and the concentration (10^{-4} *m*) studied, Gd^{3+}(aq) is not expected to undergo appreciable hydrolysis beyond the first step:[7]

$$Gd^{3+}(aq) + H_2O(l) = Gd(OH)^{2+}(aq) + H^+(aq) \quad (3)$$

In addition, no inner-sphere complexes have been detected by UV−visible[8] or luminescence spectroscopy.[9]

The standard state partial molal heat capacities and molal volume for some lanthanide trivalent ions have been reported from 283 to 338 K,[10] and partial molal volumes for Gd^{3+}(aq) (based on the convention $\bar{V}_2^\circ(H^+, aq) = 0$) at p_{sat} from 283.15 to 473.15 K are known.[11] No other high temperature values of $\bar{C}_{p,2}^\circ$ and $\bar{V}_2^\circ$ have been reported for the trivalent rare-earth ions, or any other trivalent ion under standard state (high dilution) conditions.

Experimental Section

Materials. Distilled water used in the measurements and in the calorimeter was passed through a Milli-Q reagent grade mixed bed ion exchange column/activated charcoal system (conductivity less than 18 MΩ cm).

Gd_2O_3(cr,cubic) (99.998%) purchased from Alfa-Aesir was dried in an oven at 1000 K for 24 h and was stored in a

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desiccator containing solid P_2O_5. The impurities reported were 3 ppm Fe, 2 ppm Ca, 1 ppm Si, <1 ppm Mg, and <1 ppm Ag. No other rare-earth metals were detected. Quartz bulbs containing the dried material were sealed under a vacuum. There is one report[12] that solid Gd_2O_3 powder is hygroscopic, but that was not observed to be the case in the present research.[4]

Apparatus. The integral heats of reaction 1 were measured from 393.18 to 596.30 K in the high temperature, high dilution calorimeter.[4] The molar heat capacities of Gd_2O_3(cr,cubic) were measured using a Perkin-Elmer model DSC-2 scanning calorimeter. The apparatus was calibrated using sapphire as a reference material.[13]

Procedures. The experimental procedures used have been described previously.[3,4] The calorimeter was calibrated electrically for each experimental run, and was confirmed by also measuring the energy of vaporization of water, $\Delta \bar{E}_{vap}(T, p_{sat})$, by breaking empty bulbs of known volumes. The overall accuracy of the calorimetric measurements by this separate test is on average approximately $\pm 0.2\%$, when compared to values given in the steam tables.[14]

Calculations and Results

The heats of solution (reaction 1) in excess dilute perrhenic acid from 393.18 to 596.30 K were analyzed by procedures outlined previously.[4,15] These are summarized in Table 1 together with estimated errors of the individual measurements. The values of rho, ρ, were obtained by subtracting the extended Debye−Hückel heat of dilution at a given temperature and concentration from the measured heat of solution. The extrapolated value of rho at infinite dilution, $\rho°$, and at each temperature was obtained using a weighted linear least-squares analysis, where each data point was weighted according to its estimated uncertainty. In Figure 1, the values of rho at 596.30 K are plotted against the final ionic strength, I. The linearity of the rho plots indicates that the measurements were carried out at sufficient dilutions and that the heats of dilution between Gd^{3+}(aq) and $3H^+$(aq) could reliably be extrapolated to infinite dilution (Figure 1).

The $3H^+$ on one side of eq 1 cancels much of the heat of dilution and molal volume effects of Gd^{3+}(aq).[4] The enthalpy correction due to the volume change of the liquid placed in the calorimeter as the result of introduction of the solute, dH_v, must be added to the extrapolated value of rho, $\rho°$, in order to obtain the experimental standard state enthalpy. These standard state enthalpies, $\Delta_{sol}\bar{H}°(T, p_{sat})$, for reaction 1, from 393.18 to 596.30 K and estimated propagated errors at each experimental temperature are summarized in Supporting Information Table S1.

The values for $\Delta_{sol}\bar{H}°(T, p_{sat})$, for reaction 1 at each temperature have been corrected for hydrolysis (reaction 3). The experimental values of $\Delta_{sol}\bar{H}°(T, p_{sat})$ for reaction 1 were measured down to 393.18 K and extrapolated to 298.15 K using available heat capacities for reaction 1 (Figure 2), and are discussed further in the Discussion section.

The experimental enthalpies for reaction 1, $\Delta_{sol}\bar{H}°(T, p_{sat})$, were empirically fitted to eq 4:

$$\Delta_{sol}\bar{H}° = a_1 + a_2 T + a_3 T^2 + \frac{a_4 T^2}{(a_5 - T)^2} + \frac{a_6 T^2}{(T - a_7)^2} \quad (4)$$

The resulting parameters are summarized in Table 2. It is noted that the average deviation of the experimental data from the

smooth function (eq 4) is less than $\pm 0.05\%$, and confirms the overall precision of the data over almost a 300° temperature range.

The heat capacities for reaction 1 are calculated from eq 5:

$$\Delta_{sol}\bar{C}_p° = \left(\frac{\partial \Delta_{sol}\bar{H}°}{\partial T}\right)_{sat} + \left[\Delta_{sol}\bar{V}° - T\left(\frac{\partial \Delta_{sol}\bar{V}°}{\partial T}\right)_p\right]\left(\frac{\partial p}{\partial T}\right)_{sat} \quad (5)$$

It is known at lower temperature that the differences in partial molal volumes ($\bar{V}_2°(Gd^{3+}, aq) - 3\bar{V}_2°(H^+, aq)$) have smaller errors than those for the individual ions, due to partial cancelation effects. For example, the values for $\bar{V}_2°(GdCl_3, aq)$ and $3\bar{V}_2°(HCl, aq)$ at 598 K are −1414 and −1233 cm^3 mol^{-1}, a difference of only −181 cm^3 mol^{-1}. Predicted values[4] for $\Delta_{sol}\bar{V}°$ and $(\partial \Delta_{sol}\bar{V}°/\partial T)_p$ are given in Supporting Information Table S2.

The values of $\Delta_{sol}\bar{C}_p°$ for reaction 1 and the calculated standard state partial molal heat capacities of aqueous gadolinium chloride, $\bar{C}_{p,2}°$, as a function of temperature and at p_{sat} from additivity[4] are listed in Table 3.

Discussion

At the lowest experimental temperature (393.18 K) and lowest concentration of the acid ($I < 0.0025$), it was observed that traces of Gd_2O_3(cr) were still not dissolved after any reasonable time for the calorimetric run, and that the data point was not used in the analysis of data. This prevented an overlap comparison of the results from the present study with a previous study[3] on soluble $GdCl_3$(cr) up to 368.02 K.

However, the enthalpy of solution for reaction 1 at 393.18 K was extrapolated to 298.15 K using eq 6, which makes it possible to join the previous data for $GdCl_3$(aq)[3] with that for $Gd(ReO_4)_3$(aq).

$$\Delta_{sol}\bar{H}°(T) = \Delta_{sol}\bar{H}°(393.18 \text{ K}) + \int_{393.18 \text{ K}}^{T} \Delta_{sol}\bar{C}_P°(T, 1 \text{ bar}) \, dT + \int_1^{P_{sat}}\left(\Delta_{sol}\bar{V}° - T\left(\frac{\partial \Delta_{sol}\bar{V}°}{\partial T}\right)_P\right) dp \quad (6)$$

where $\bar{C}_p°(GdCl_3, aq)$ are from the study up to 368.02 K,[2] $\bar{C}_p°(HCl, aq)$ from refs 4 and 15, $C_p°(Gd_2O_3, cr)$ from the present study (Supporting Information Table 3S), and $C_p°(H_2O, l)$ from the steam tables.[14] The third term in eq 6 is negligible in this temperature range (<0.006 kJ mol^{-1}). The extrapolation of $\bar{C}_p°(GdCl_3, aq)$ from 368.02 to 393.18 K does not result in any appreciable error in joining the two sets of data.

An average value for $\Delta_{sol}\bar{H}°$ for reaction 1 at 393.18 K was calculated from each experimental temperature (393.18−596.30 K) from eq 7:

$$\Delta_{sol}\bar{H}°(393.18 \text{ K}) = \Delta_{sol}\bar{H}°(T) - \int_{393.18 \text{ K}}^{T}\left(\frac{\partial \Delta_{sol}\bar{H}°}{\partial T}\right)_{sat} dT \quad (7)$$

The average value at 393.18 K of -243.202 ± 0.144 kJ mol^{-1} is a better value for $\Delta_{sol}\bar{H}°$ at 393.18 K than was determined from more limited measurements at that single temperature.

Aqueous Gadolinium Perrhenate and Gadolinium Chloride

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TABLE 1: Heat of Solution of Cubic Gadolinium Oxide in Excess Dilute Perrhenic Acid as a Function of Temperature (Corrected for Hydrolysis)^a

$n_{Gd_2O_3}$ ($\times 10^4$)	$I_{initial}$ ($\times 10^3$)	I_{final} ($\times 10^3$)	q_{obs}^b (J)	q_b^c (J)	q_{vp}^d (J)	q_{sol}^e (J)	$\delta_{Hydrol}H^f$ (kJ mol^{-1})	$\Delta_{sol}\bar{H}^g$ (kJ mol^{-1})	ρ^h (kJ mol^{-1})	$\pm\sigma^i$ (kJ mol^{-1})
					393.18 K					
1.1848	2.4750	4.0162	−53.330	3.100	0.037	−56.393	0.327	−238.303	−241.636	2.137
1.1412	4.9510	6.4386	−51.511	2.991	0.037	−54.465	0.083	−238.705	−240.794	0.449
1.1038	9.9029	11.3423	−49.249	2.899	0.036	−52.112	0.031	−236.092	−239.091	0.552
	0.0000								−243.030	0.122^j
					418.78 K					
1.0287	2.4750	3.8058	−44.150	5.741	0.033	−49.858	0.749	−243.083	−245.257	0.517
1.1261	19.8000	21.2683	−49.388	3.968	0.038	−53.318	0.030	−236.771	−242.014	0.882
1.3548	4.9500	6.7124	−60.550	4.869	0.045	−65.374	0.242	−241.517	−244.442	0.622
1.6014	9.9000	11.9868	−71.411	5.172	0.054	−76.529	0.086	−239.033	−242.962	0.508
	0.0000								−245.820	0.416^j
					445.27 K					
9.2552	2.4750	3.6558	−33.578	11.540	0.047	−45.071	2.038	−245.529	−248.396	1.642
9.6056	9.9000	11.1495	−32.008	14.385	0.050	−46.343	0.254	−241.484	−246.650	0.526
13.5477	4.9500	6.7027	−55.539	10.662	0.069	−66.132	0.758	−244.828	−248.736	0.684
16.3366	19.8000	21.9285	−70.913	7.389	0.087	−78.215	0.105	−239.491	−246.559	0.612
	0.0000								−248.591	0.693^j
					485.17 K					
9.2552	2.4750	3.5866	−28.300	16.082	0.105	−44.277	7.694	−246.894	−251.470	0.765
12.8497	4.9500	6.5741	−45.840	16.382	0.148	−62.074	3.013	−244.550	−250.847	0.669
13.8511	9.9000	11.6855	−48.878	17.949	0.163	−66.664	1.140	−241.786	−250.280	0.412
15.4015	19.8000	21.7998	−56.455	16.855	0.185	−73.125	0.441	−237.837	−249.328	0.347
	0.0000								−251.631	0.163^j
					500.32 K					
5.9393	2.4750	3.1788	−9.827	18.362	0.067	−28.122	8.983	−245.730	−250.794	1.381
6.0855	29.7900	30.5810	−9.896	18.472	0.079	−28.289	0.338	−232.769	−248.371	0.931
6.5931	19.8000	20.6547	−12.748	18.418	0.084	−31.082	0.597	−236.314	−249.349	1.302
7.6580	9.9029	10.8862	−20.302	16.535	0.094	−36.743	1.529	−241.428	−251.010	1.511
8.4949	29.7900	30.8942	−20.366	19.032	0.110	−39.288	0.343	−231.588	−247.225	0.816
9.0373	4.9510	6.0821	−18.556	24.833	0.107	−43.282	3.971	−243.433	−250.502	0.712
9.8180	9.9029	11.1652	−26.986	19.922	0.121	−46.787	1.403	−239.675	−249.320	1.109
	0.0000								−251.200	0.616^j
					542.38 K					
4.5435	29.8500	30.4385	−19.466	0.000	0.063	−19.403	0.746	−214.274	−242.448	1.381
5.9393	2.4875	3.1045	−7.528	18.362	0.061	−25.829	21.797	−239.236	−248.040	1.901
6.0855	29.8500	30.6382	−7.901	18.472	0.084	−26.289	0.748	−216.742	−244.957	0.975
6.5931	19.9000	20.7486	−10.751	18.418	0.089	−29.080	1.420	−221.956	−245.532	2.118
7.6580	9.9500	10.9120	−18.000	16.535	0.097	−34.438	3.957	−228.807	−246.053	1.852
9.0373	4.9750	6.0397	−16.089	24.833	0.105	−40.817	10.364	−236.187	−248.750	0.998
9.8180	9.9500	11.1824	−24.733	19.922	0.125	−44.530	4.035	−230.815	−248.162	1.025
10.4632	14.9250	16.2613	−32.852	14.111	0.138	−46.825	2.234	−225.996	−246.852	1.115
19.9504	4.9750	7.2418	−63.398	25.016	0.227	−88.187	13.800	−234.816	−247.915	1.925
22.9629	19.9000	22.8529	−80.101	20.153	0.309	−99.945	1.512	−219.135	−243.248	1.832
30.8829	9.9500	13.7828	−113.873	22.397	0.390	−135.880	5.194	−225.186	−243.440	1.762
	0.0000								−249.289	1.470^j
					572.56 K					
5.5311	9.9029	10.5757	10.286	33.122	0.153	−22.683	8.986	−214.037	−242.053	0.913
14.5159	4.9510	6.4705	−22.604	34.649	0.350	−56.903	26.297	−222.299	−242.354	0.933
19.7463	9.9029	12.2683	−49.217	31.109	0.543	−79.783	10.870	−212.890	−241.316	0.552
27.4981	19.8058	23.2915	−76.930	31.428	0.818	−107.540	3.751	−199.292	−238.245	0.767
	0.0000								−244.010	0.130^j
					596.30 K					
1.1059	4.9510	5.9687	−11.357	23.188	0.281	−34.264	54.500	−209.412	−209.412	0.940
2.4944	7.5705	12.6022	−54.025	21.053	0.717	−74.361	37.130	−186.189	−186.189	0.403
2.7126	3.2000	11.7359	−22.078	36.272	0.551	−57.799	95.389	−201.928	−201.928	0.575
2.7824	33.6700	37.2283	−55.858	22.322	1.004	−77.176	3.615	−142.303	−142.303	0.329
2.8853	9.9029	13.0808	−72.705	21.425	0.865	−93.264	28.787	−190.409	−190.409	0.988
2.9352	4.9515	12.4493	−56.745	19.363	0.727	−75.381	64.324	−192.733	−192.733	0.676
5.8748	33.6700	41.1761	−108.482	53.091	2.125	−159.448	3.783	−139.488	−139.488	0.231
	0.0000								−237.058	0.322^j

^{a} $^1/_2$Gd$_2$O$_3$(cr,cubic) + 3H$^+$(aq) = Gd^{3+}(aq) + $^3/_2$H$_2$O(l). ^{b} Observed heat. ^{c} Calculated bulb-breaking heat, from the steam tables.[14] ^{d} Heat due to vapor pressure correction. ^{e} Heat of solution, $q_{sol} = q_{obs} − q_b + q_{vp}$. ^{f} Enthalpy contribution due to hydrolysis. ^{g} Enthalpy of reaction, corrected for contribution from hydrolysis. ^{h} Obtained by subtracting the extended Debye−Hückel heat of dilution from each enthalpy of solution at a given temperature and concentration.[4] ^{i} Estimated uncertainty. ^{j} Estimated standard deviation of the fit.

Finally, the complete set of $\Delta_{sol}\bar{H}°$ for reaction 1 from 298.15 to 596.30 K was fitted with eq 4 and the values of the resulting parameters are listed in Table 2.

Similarly, the enthalpies of solutions of GdCl$_3$(cr) relative to the reference temperature of 298.15 K were calculated up to 623.15 K for the direct solution:
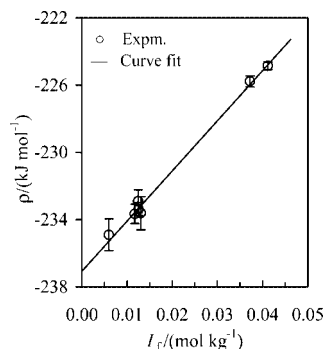
**Figure 1.** ρ plot (corrected for hydrolysis) of the heat of solution of Gd_2O_3(cubic,cr) in excess dilute $HReO_4$(aq) at 596.30 K. The multiple data points near $I = 0.012$ are from hydrolysis studies at nearly constant ionic strength.
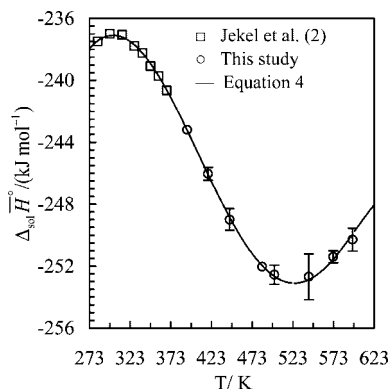
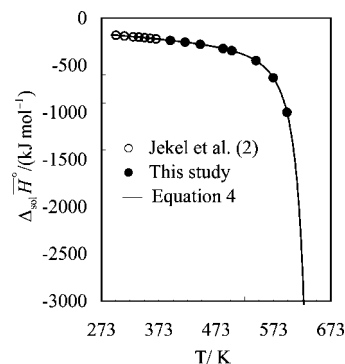**Figure 2.** Standard state enthalpies of solution of Gd_2O_3(cubic,cr) in $HReO_4$(aq) at p_{sat}.

TABLE 2: Fitting Parameters (eq 4) for Standard State Enthalpies of Solution of Cubic Gadolinium Oxide in Perrhenic Acid (Reaction 1) and for Standard State Enthalpies of Solution of Solid Gadolinium Chloride in Water (Reaction 8) at p_{sat}

	reaction 1	reaction 8
a_1	3.28905E+02	4.14672E+03
a_2	−1.34548E+01	−1.09210E+00
a_3	7.57884E-03	5.19084E-04
a_4	−4.15610E+01	7.52704E+00
a_5	1.01708E+03	6.58673E+02
a_6	1.04134E+04	−3.93813E+03
a_7	−2.78998E+02	3.92745E+00

$$GdCl_3(cr) = GdCl_3(aq) \qquad (8)$$
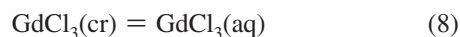
These standard state molal enthalpies of solution, $\Delta_{sol}\bar{H}°$($GdCl_3$,cr), are summarized in Figure 3. They were empirically fitted to eq 4, and the resulting parameters are listed in Table 2. The joining of the two sets of data, from the direct solution of solid $GdCl_3$ in water (up to 368.02 K) and of solid Gd_2O_3 in perrhenic acid (down to 393.18 K), unambiguously fixes the $\bar{C}_p°$($Gd(ReO_4)_3$,aq) and $\bar{C}_p°$($GdCl_3$,aq) between 298 and 623 K (Table 3).

From Table 3, it can be seen that at the higher temperatures ($T > 473.15$ K) the difference between $\bar{C}_{p,2}°$(Gd^{3+},aq) and $3\bar{C}_{p,2}°$(H^+,aq) is close to zero and within the estimated experimental uncertainty at these temperatures. A similar observation has been previously noted[4,16] when comparing divalent ions, $\bar{C}_{p,2}°$(M^{2+},aq) and $2\bar{C}_{p,2}°$(H^+,aq), where M^{2+}(aq) = Ba^{2+}(aq), Co^{2+}(aq), Cu^{2+}(aq). This (first order) balancing of $\bar{C}_{p,2}°$(M^{z+},aq) − $z\bar{C}_{p,2}°$(H^+,aq), for $z > 1$, at high temperatures may be used as a powerful predictive tool to estimate $\bar{C}_{p,2}$ at high temperatures,

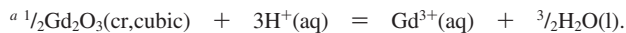**Figure 3.** Standard state enthalpies of solution of $GdCl_3$(cr) in water at p_{sat}.
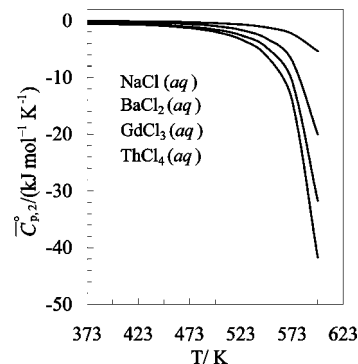
Figure 4. Standard state partial molal heat capacities of some representative electrolytes at p_{sat} ($ThCl_4$(aq) values are predicted).

TABLE 3: Standard State Heat Capacities for Reaction 1 and Calculated Standard State Heat Capacities for Gadolinium Perrhenate and Gadolinium Chloride at p_{sat}

T (K)	$\Delta_{sol}\bar{C}_p°$ [a,b] (J mol^{-1} K^{-1})	$\bar{C}_{p,2}°$ [c] (J mol^{-1} K^{-1})	$\bar{C}_{p,2}°$ [d] (J mol^{-1} K^{-1})
298.15	8.1	−121.6	−433.3
323.15	−38.0	−57.0	−422.5
348.15	−74.7	−85.5	−475.2
373.15	−99.3	−163.9	−536.5
398.15	−110.4	−272.0	−608.4
423.15	−108.4	−413.1	−703.9
448.15	−94.3	−594.3	−851.4
473.15	−70.4	−852.8	−1104.9
498.15	−40.4	−1273.5	−1580.1
523.15	−11.1	−2073.2	−2550.2
548.15	2.8	−3898.6	−4762.2
573.15	−45.0	−9180.2	−10712.1
598.15	−385.1	−31620.0	−31805.9

[a] $\frac{1}{2}Gd_2O_3$(cr,cubic) + $3H^+$(aq) = Gd^{3+}(aq) + $\frac{3}{2}H_2O$(l). [b] Standard state molal heat capacities at p_{sat} calculated using eq 4 and parameters from Table 2 (see also Supporting Information Table S3). [c] Standard state partial molal heat capacity of $Gd(ReO_4)_3$(aq). [d] Standard state partial molal heat capacity of $GdCl_3$(aq).

and is a more refined empirical rule than those given by Lindsay[17a] and Cobble[17b] several years ago. The values for $\bar{C}_{p,2}°$($ThCl_4$,aq) can be estimated up to 623.15 K from the above empirical observation and are summarized in Figure 4. The standard state thermodynamic properties of highly charged ions, M^{4+}(aq), are extremely difficult to obtain at high temperatures due to extensive hydrolysis even in very dilute solutions.

$\bar{C}_p°$($GdCl_3$,aq) in Figure 4 shows the same gross features as the other electrolytes at high temperatures (but much larger) and further confirms the dominance of electrostatic effects over structural chemical effects[18] of the solvent. A large number of

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water molecules must lose some of their heat capacity to produce an effect as large as $-180\,000$ J mol^{-1} K^{-1} at 623.15 K and p_{sat}.

Further, the absolute values of the partial molal heat capacities at the highest temperatures are in themselves noteworthy. At 623.15 K, where $\bar{C}_p^{\circ}$(GdCl$_3$,aq) is about $-180\,000$ J mol^{-1} K^{-1}, the addition of 1 mol of the GdCl$_3$(cr) to an infinite amount of water changes the enthalpy of solution by -180 kJ for every degree change in temperature.

Finally, the results from this study show that the enthalpies of solution of simple electrolytes approach megajoules at the highest temperature studied (Figure 3). Such large thermal effects come from the release of thermal energy as an increasing number of water molecules are affected by the field of the ions.[18] For GdCl$_3$(aq) at 598.15 K, the molar heat capacity of pure water is 128 J mol^{-1} K^{-1}. Estimating that each water molecule involved in these thermal effect losses, on average, about one-quarter of its normal heat capacity,[19] on introduction of the ions, the $\bar{C}_{p,2}^{\circ}$ for GdCl$_3$(aq) of $-32\,000$ J mol^{-1} K^{-1} at 598.15 K represents the loss of some thermal motion for about 1000 (solvent) water molecules, contrasted to a few molecules at room temperature, for each gadolinium chloride group of ions involved. At 623.15 K, the corresponding number of (solvent) water molecules is >2400.

Between 623.15 K and the critical temperature of water (647.29 K), the megajoules heat of solution of a simple salt will continue to increase sharply with temperature. We estimate the standard state enthalpies of solution of GdCl$_3$(cr) in water to be -87 MJ mol^{-1} at 645 K. These energies are in the kiloelectronvolts (keV) range and under some conditions could give rise to high energy ultraviolet or low energy X-ray production from a simple solution reaction.

Supporting Information Available: Standard state enthalpies of solution of cubic gadolinium oxide in perrhenic acid at T and p_{sat}. Standard state volumes of GdCl$_3$(aq) and HCl(aq) and the T and p derivatives. Standard state heat capacities for GdCl$_3$(aq) and Gd(ReO$_4$)$_3$(aq) from experimentally derived heat capacities of solution (reaction 1). Comparison of experimental and calculated enthalpies of solution of GdCl$_3$(cr) at p_{sat}.

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