

Standard State Thermodynamic Properties of $\text{Ba}^{2+}(\text{aq})$, $\text{Co}^{2+}(\text{aq})$, and $\text{Cu}^{2+}(\text{aq})$ up to 598.15 K, and Temperature Effect on Ligand Field

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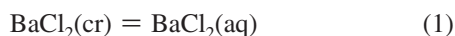
Integral heat of solution measurements of barium chloride to 619.81 K, copper oxide in an excess of perrenic acid to 585 K, and cobalt perrenate in perrenic acid to 573 K were measured in a high dilution calorimeter ($\leq 10^{-3} m$) at p_{sat} , from which the high temperature thermodynamic properties of aqueous barium chloride, copper perrenate, and cobalt perrenate were obtained. From the known differences between the corresponding properties for aqueous perrenate and chloride ions, the thermodynamic properties of completely ionized aqueous copper and cobalt chloride were obtained from ionic additivity. The enthalpy and derived heat capacity data at higher temperatures ($T > 473.15 \text{ K}$) suggest that the ligand field stabilization energy of $\text{Co}^{2+}(\text{aq})$ may be disappearing.

Introduction

Although divalent ions in the periodic table include many species of importance, most previous thermodynamic studies were carried out using chloride as the supporting ion. Chloride complexes of metallic ions become stronger at higher temperatures.¹ Measurements at extremely low concentrations of aqueous electrolytes are important at high temperatures for all electrolytes, but particularly for multicharged ions. Higher temperature extrapolation of thermal measurements from concentrations ($m \geq 0.05$) to infinite dilution cannot be guided by strong electrolyte models and is model dependent.² This situation pertains even in the case of $\text{NaCl}(\text{aq})$ at $T > 573 \text{ K}$.³

Wood and co-workers⁴ reported flow calorimetric measurements of apparent molal heat capacities for some pure $\text{MCl}_2(\text{aq})$ species of Ca, Ni, Mg, and Fe in concentrated solutions ($m > 0.05$) at 17.7 MPa from 298 to 573 K. However, these data at higher temperatures cannot be reliably extrapolated to infinite dilution, and hydrolysis and complex ion formation are probably involved as well. Enthalpies of dilution of $\text{CaCl}_2(\text{aq})$ from 7.26 to 0.008 mol kg^{-1} at 7 and 40 MPa were measured by Holmes et al.;⁵ however, even $\text{Ca}^{2+}(\text{aq})$ may be hydrolyzed and complexed with $\text{Cl}^{-}(\text{aq})$ at the highest temperature, 523.15 K.

We report here the standard state thermodynamic properties for $\text{BaCl}_2(\text{aq})$ to 623 K, $\text{Cu}(\text{ReO}_4)_2(\text{aq})$, and $\text{Co}(\text{ReO}_4)_2(\text{aq})$ to 598 K, obtained using the integral heat of solution method⁶ from high dilution calorimetric measurements, under conditions where hydrolysis and complex ion formation are avoided. The solution processes measured were



The barium ion is a good model +2 species, and it can be assumed to have little hydrolysis under the conditions used in

the present research. Further, at the dilutions of these experiments, there is no evidence of complex ion formation with chloride ion. It will be shown that the concentration dependence of the heat of solution indicates that barium chloride is completely ionized at the highest temperature and dilutions studied ($\leq 0.009 m$). The $\text{Co}(\text{ReO}_4)_2$ study was carried out in aqueous perrenic acid at very low dilutions ($\leq 0.001 m$), and $\text{CuO}(\text{cr})$ was dissolved in low dilution (excess) perrenic acid solutions ($\leq 0.1 m$). In the later case, eq 3 indicates that concentration effects are minimized because of the cancelation of heats of dilution of $\text{Cu}^{2+}(\text{aq}) - 2\text{H}^{+}(\text{aq})$.

From these data and the known differences between the corresponding properties for $\text{ReO}_4^{-}(\text{aq})$ and $\text{Cl}^{-}(\text{aq})$ ⁷ ions, the standard state thermodynamic properties of completely ionized $\text{CoCl}_2(\text{aq})$ and $\text{CuCl}_2(\text{aq})$ were obtained from ionic additivity, and compared with those of $\text{BaCl}_2(\text{aq})$.

Experimental Section

Materials. Water used in the measurements was singly distilled and passed through a Milli-Q reagent grade mixed bed ion exchange column and activated charcoal system (conductivity less than 18 $\text{M}\Omega \text{ cm}$).

Solid barium chloride (99.995%) from Alfa-Aesar was dried in an oven at 623.15 K for 48 h. Solid copper oxide was obtained from Alfa-Aesar. The copper(II) content was analyzed by iodimetric titration: obsd, 79.84%; calcd, 79.88%. Cobalt perrenate was prepared by dissolving cobalt carbonate-hydroxide in excess aqueous perrenic acid. The resulting hydrated pink cobalt perrenate salt was recrystallized twice. The hydrate was then transferred to a quartz tube attached to a vacuum line and was dehydrated by gradually increasing the temperature for 12 h up to 573 K. The temperature was gradually lowered to room temperature, and the sample tube was sealed under a vacuum. The anhydrous salt has a bright purple color. Handling and weighing of the anhydrous salt was done in a glovebox containing solid P_2O_5 as a desiccant. The salt was analyzed gravimetrically for $\text{ReO}_4^{-}(\text{aq})$ content: obsd, 89.36%; calcd, 89.46%.

Apparatus. The measurements of enthalpies of solution and reaction were carried out in the high pressure and temperature calorimeter (HP-1) similar to the one previously described.⁷

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Procedures. Details of the experimental procedures were the same as described previously.⁷ The calorimeter was calibrated electrically for each experimental run, which was confirmed by measuring the energy of vaporization of water, $\Delta\bar{E}_{\text{vap}}(T, p_{\text{sat}})$. The average accuracy of the measurements was approximately $\pm 0.5\%$, when compared to the steam tables.⁸

Results and Discussion

Aqueous Barium Chloride. The integral heats of solutions of barium chloride (reaction 1) from 548 to 619.81 K were extrapolated to infinite dilution using the convenient rho method,^{6,7} where the extended Debye–Hückel heat of dilution was subtracted from each enthalpy of solution at a given temperature and concentration:

$$\rho = \Delta_{\text{sol}}\bar{H} - \nu/2[Z_+Z_-|A'_H I^{1/2} \alpha((I/m^\circ)^{1/2})] = \Delta_{\text{sol}}\bar{H} + BI \quad (4)$$

where ν and m are the number and molality of the dissolved ionic species, $A'_H = {}^{3/2}A_H$, B is an adjustable but constant parameter, at low concentrations, and $m^\circ = 1$. The limiting law enthalpy, A_H , values used in this research at various temperatures are from Bradley and Pitzer.⁹ The factor $\alpha((I/m^\circ)^{1/2})$ is a mathematical function of ionic strength, I , and is given by

$$\alpha(x) = [1/(1 + x^{1/2}) - \sigma(x)/3] \quad (5)$$

and

$$\sigma(x) = 3/x^3[(1 + x) - 1/(1 + x) - 2 \ln(1 + x)] \quad (6)$$

The linearly extrapolated value of ρ vs ionic strength to infinite dilution, ρ° , at each temperature was obtained using a weighted linear least-squares method where each point was weighted according to the estimated uncertainty of each individual measurement. The observed linearity of the ρ plot with I confirms that the measurements were carried out at sufficient dilutions and could be reliably extrapolated to infinite dilution (Figure 1). These results are summarized in Supporting Information Table S1. The reported value at 619.81 K is preliminary in the sense that only one data point was obtained.

The enthalpy correction due to the volume change of the liquid in the calorimeter as the result of introduction of the solute, dH_v , must be added to the extrapolated value of rho, ρ° , in order to obtain the experimental standard state enthalpy.

To combine present and previous results, the data on BaCl₂(aq)^{6,10} up to 473 K have been recalculated using more recent values of limiting law slopes,⁹ so as to be consistent with the data of this study to 619.81 K. These standard state enthalpies, $\Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})$, for reaction 1, from 288.18 to 619.81 K and estimated errors at each experimental temperature are summarized in Supporting Information Table S1.

Aqueous Cobalt(II) Perrhenate and Cobalt(II) Chloride. The experimental heats of solution of cobalt(II) chloride from 277.45 to 368.39 K were measured,^{11a} and from these, the standard state thermodynamic properties of CoCl₂(aq) were calculated. To avoid complex ion formation between cobalt and chloride ions at higher temperatures, the heats of solution of Co(ReO₄)₂(cr) were carried out in very dilute perrhenic acid solutions from 437 to 573 K^{7b} (Table 1).

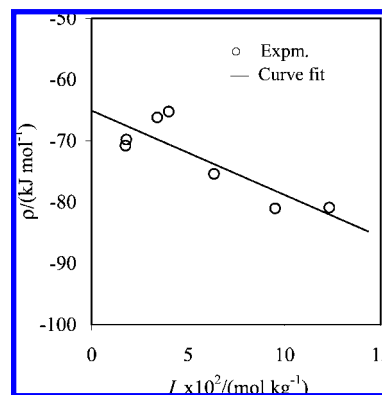


Figure 1. Rho plot of the heats of solution of copper(II) oxide in dilute excess HReO₄(aq) at 584.45 K.

The standard state enthalpies of solution of CoCl₂(cr) at lower temperatures ($T < 373$ K) were converted into the corresponding values for perrhenate using ionic additivity and necessary auxiliary data.^{12,13} The thermodynamic properties of uncomplexed Co(ReO₄)₂(aq) from 277 to 573.15 K were calculated through combination of these two sets of experimental data.^{7a} The standard state thermodynamic properties for CoCl₂(aq) were then calculated from the standard state thermodynamic properties of Co(ReO₄)₂(aq) and from the known differences between the corresponding properties of ReO₄[−](aq) and Cl[−](aq)⁷ using ionic additivity (Supporting Information Table S2).

Aqueous Copper(II) Perrhenate and Copper(II) Chloride. For comparison with the thermodynamic properties of BaCl₂(aq) and CoCl₂(aq), the thermodynamic properties of CuCl₂(aq) from 298 to 598 K were calculated from experimental high dilution calorimetric measurements as follows.

The experimental heats of solution of copper(II) chloride from 277 to 368 K were measured^{11b} from which the standard state thermodynamic properties of CuCl₂(aq) can be calculated. Above 373 K, Cu²⁺(aq) probably forms chloride complexes. To determine the thermodynamic properties of uncomplexed Cu²⁺(aq), the heats of solution of copper(II) oxide in excess dilute perrhenic acid, HReO₄(aq) (reaction 3), were measured from 489.45 to 584.45 K. The experimental data were treated by the procedure outlined elsewhere⁷ and are given in Table 1. The lower temperature data ($T < 373$ K) on CuCl₂(aq) solutions were converted through ionic additivity into the CuO(cr) solution reaction in HReO₄(aq), reaction 3. These results were then combined with higher temperature data on Cu(ReO₄)₂(aq) to give a continuous set of data from 277 to 584 K.^{7a}

The experimental results for reaction 3 on CuO(cr) from this study together with data on HReO₄(aq)^{7a,c} and other auxiliary data from reference tables^{12,13} give the standard state thermodynamic properties for Cu(ReO₄)₂(aq). The standard state thermodynamic properties for CuCl₂(aq) were then calculated from the similar properties of Cu(ReO₄)₂(aq) using ionic additivity.⁷ These results fix the standard state thermodynamic properties of uncomplexed CuCl₂(aq) at p_{sat} from 273 to 598 K and are given in Supporting Information Table S3.

The experimental enthalpies for reactions 1–3, $\Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})$, were empirically fitted by a least-squares method to eq 7, and each point was weighted by its variance:

$$\Delta_{\text{sol}}\bar{H}^\circ = a_1 + a_2T + a_3T^2 + \frac{a_4T^2}{(a_5 - T)^2} + \frac{a_6T^2}{(T - a_7)^2} \quad (7)$$

TABLE 1: The Integral Heats of Solutions at p_{sat}^a

solute	solvent	T (K)	moles ($\times 10^4$)	molality ($\times 10^4$)	I_{initial}^b ($\times 10^3$)	I_{final}^c ($\times 10^3$)	q_{sol}^d (J)	$\Delta_{\text{sol}}\bar{H}^e$ (kJ mol $^{-1}$)	ρ^f (kJ mol $^{-1}$)
BaCl ₂	H ₂ O	548.16	4.172	8.345	0.000	2.503	−73.514	−176.189	−182.381
		548.16	6.354	12.708	0.000	3.812	−110.953	−174.618	−182.195
		548.16	18.198	36.395	0.000	10.919	−307.222	−168.824	−181.269
		548.16	36.759	73.519	0.000	22.056	−592.464	−161.173	−178.341
		573.15	4.630	10.760	0.000	3.228	−118.335	−255.584	−266.492
		573.15	4.837	9.667	0.000	2.900	−126.775	−262.116	−272.477 ^g
		573.15	8.738	20.307	0.000	6.092	−181.557	−207.778	−222.539 ^g
		573.15	10.486	24.369	0.000	7.311	−245.435	−234.060	−250.145
		573.15	13.194	30.663	0.000	9.199	−289.512	−219.427	−237.340
		573.15	18.481	42.949	0.000	12.885	−384.261	−207.922	−228.867
		573.15	24.234	56.319	0.000	16.896	−472.763	−195.082	−218.799
		573.15	25.724	59.782	0.000	17.935	−486.168	−188.994	−213.364
		573.15	29.064	67.543	0.000	20.263	−622.149	−214.064	−239.821 ^g
		573.15	39.548	91.908	0.000	27.572	−801.965	−202.783	−232.360 ^g
Co(ReO ₄) ₂	HReO ₄ (aq)	437.50	0.977	2.269	1.001	1.682	−10.312	−105.600	−107.377
		437.50	6.796	15.792	1.001	5.739	−55.690	−81.948	−84.661
		437.50	4.026	9.355	1.001	3.808	−38.073	−94.571	−96.898
		437.50	1.190	2.765	1.001	1.830	−12.307	−103.445	−105.268
		437.50	5.749	13.359	1.001	5.009	−52.687	−91.646	−94.222
		437.50	4.365	10.144	0.961	4.004	−38.347	−87.847	−90.206
		437.50	7.295	16.951	1.009	6.094	−62.500	−85.680	−88.459
		497.15	2.451	5.695	3.846	5.554	−31.229	−127.424	−133.810
		497.15	2.252	5.233	3.623	5.192	−27.716	−123.085	−129.279
		497.15	1.602	3.723	3.846	4.963	−19.499	−121.700	−127.896
		497.15	2.206	5.126	6.804	8.341	−27.332	−123.918	−131.922
		497.15	1.756	4.081	15.810	17.034	−18.750	−106.763	−118.217
		497.15	4.071	9.460	15.810	18.648	−41.675	−102.374	−114.078
		497.15	2.718	6.316	8.356	10.251	−31.896	−117.353	−126.165
		497.15	4.966	11.539	8.356	11.818	−56.773	−114.324	−123.466
		539.15	1.470	3.415	3.622	4.647	−23.770	−161.724	−172.038
		539.15	3.380	7.853	3.622	5.978	−55.338	−163.732	−174.783
		539.15	1.748	4.062	15.631	16.850	−24.278	−138.892	−158.439
		539.15	4.217	9.800	15.631	18.571	−58.576	−138.892	−158.899
		539.15	1.752	4.071	7.871	9.092	−27.747	−158.381	−172.862
		539.15	3.273	7.606	7.871	10.152	−51.514	−157.381	−172.270
		539.15	2.454	5.703	9.078	10.789	−38.604	−157.297	−172.883
		539.15	1.746	4.057	15.371	16.588	−25.250	−144.641	−164.044
		539.15	2.898	6.735	3.698	5.718	−47.380	−163.481	−174.438
		539.15	1.790	4.160	8.730	9.978	−26.649	−148.879	−164.037
		539.15	3.978	9.244	8.730	11.503	−59.743	−150.185	−165.895
		572.79	3.477	8.081	4.304	6.728	−74.020	−212.861	−233.774
		572.79	1.165	2.707	10.630	11.442	−23.681	−203.309	−232.301
		572.79	2.427	5.640	10.630	12.322	−51.255	−211.187	−240.702
		572.79	6.230	14.476	10.630	14.973	−124.053	−199.129	−230.137
		572.79	2.404	5.586	10.630	12.306	−50.260	−209.079	−238.584
		572.79	3.856	8.960	1.000	3.688	−86.766	−225.016	−238.733
		572.79	4.288	9.965	1.000	3.990	−96.973	−226.128	−240.242
		572.79	4.528	10.529	1.500	4.659	−104.613	−231.057	−246.746
		572.79	2.915	6.773	1.500	3.532	−68.503	−235.011	−249.318
		572.79	4.905	12.144	1.000	4.643	−112.802	−229.982	−244.910
		572.79	2.382	5.535	5.161	6.822	−49.830	−209.183	−230.958
		572.79	1.638	3.086	5.377	6.303	−36.667	−223.894	−245.420
CuO	HReO ₄ (aq)	489.45	4.491	9.613	15.709	16.670	−25.365	−56.479	−59.914
		489.45	11.310	23.190	47.671	49.990	−69.894	−61.798	−67.404
		489.45	12.300	27.080	11.552	14.260	−63.147	−51.339	−54.434
		489.45	18.290	34.790	19.901	23.380	−96.683	−52.861	−56.777
		489.45	18.530	57.100	10.340	16.050	−77.716	−41.940	−45.062 ^g
		489.45	22.860	46.510	24.779	29.430	−134.238	−58.722	−63.053
		539.30	2.350	5.460	78.740	84.200	−10.669	−45.401	−50.126
		539.30	2.860	6.650	213.750	220.400	−13.640	−47.692	−55.102
		539.30	4.330	10.060	213.840	223.900	−18.619	−43.000	−50.438
		539.30	6.460	15.010	78.690	93.700	−33.179	−51.361	−56.211
		539.30	10.100	23.470	154.130	177.600	−49.288	−48.800	−55.359
		539.30	18.120	41.850	256.750	298.600	−80.249	−44.288	−52.559
		584.45	11.380	2.617	14.983	17.600	−63.555	−55.848	−70.785
		584.45	12.540	2.883	15.147	18.030	−68.659	−54.752	−69.812
		584.45	17.910	4.076	29.984	34.060	−82.341	−45.975	−66.205
		584.45	25.950	5.911	34.129	40.040	−113.261	−43.646	−65.220
		584.45	43.650	9.521	54.039	63.560	−214.221	−49.077	−75.395
		584.45	45.010	9.845	85.285	95.130	−222.978	−49.540	−81.021
		584.45	53.300	11.440	111.860	123.300	−244.178	−45.812	−80.880

^a For reactions 1–3. ^b Initial concentration of HReO₄(aq). ^c Final ionic strength. ^d $q_{\text{sol}} = q_{\text{obs}} - q_{\text{b}} - q_{\text{vp}}$. ^e Enthalpy of solution, $q_{\text{sol}}/n_{\text{solute}}$. ^f See eq 4 for definition of ρ . ^g These data points were not used in the extrapolation to obtain ρ° .

TABLE 2: Parameters for Calculation of Standard State Enthalpies of Solution at p_{sat} from eq 5

eq 5	reaction 1	reaction 2	reaction 3
a_1	1.26179E+02	-1.73618E+02	3.09658E+01
a_2	-6.09977E-01	6.61992E-01	-6.47287E-01
a_3	5.19501E-04	-1.13556E-03	1.18962E-03
a_4	-6.14245E+00	-2.18380E+00	-3.97317E+01
a_5	6.62795E+02	6.52715E+02	9.16411E+02
a_6	7.10281E-05	2.88097E+00	0.00000E+00
a_7	2.85035E+02	1.89245E+02	0.00000E+00

TABLE 3: Standard State Thermodynamic Functions of BaCl₂(aq) at p_{sat}

T (K)	$\bar{H}_2^{\circ}(T) - \bar{H}_2^{\circ}(T_r)$ (kJ mol ⁻¹)	$\bar{G}_2^{\circ}(T) - \bar{G}_2^{\circ}(T_r)$ (kJ mol ⁻¹)	\bar{S}_2° (J mol ⁻¹ K ⁻¹)
298.15	0.000	0.000	122.40 ^a
323.15	-6.780	-2.747	100.30
348.15	-13.371	-4.979	80.58
373.15	-20.013	-6.740	62.23
398.15	-27.019	-8.049	44.20
423.15	-34.899	-8.898	25.18
448.15	-44.488	-9.243	3.32
473.15	-57.238	-8.988	-24.29
498.15	-75.848	-7.951	-62.67
523.15	-105.759	-5.802	-121.40
548.15	-159.217	-1.911	-221.13
573.15	-268.434	5.039	-413.83
598.15	-541.078	18.269	-864.55

^a NBS tables.¹³**TABLE 4: Standard State Thermodynamic Functions of CuCl₂(aq) at p_{sat}**

T (K)	$\bar{H}_2^{\circ}(T) - \bar{H}_2^{\circ}(T_r)$ (kJ mol ⁻¹)	$\bar{G}_2^{\circ}(T) - \bar{G}_2^{\circ}(T_r)$ (kJ mol ⁻¹)	\bar{S}_2° (J mol ⁻¹ K ⁻¹)
298.15	0.000	0.000	13.40 ^a
323.15	-6.706	-0.053	-8.22
348.15	-12.369	0.367	-25.11
373.15	-17.669	1.180	-39.81
398.15	-23.132	2.355	-53.98
423.15	-29.462	3.894	-69.39
448.15	-37.716	5.849	-88.30
473.15	-49.609	8.335	-114.02
498.15	-68.146	11.565	-152.00
523.15	-99.116	15.913	-212.24
548.15	-155.124	22.064	-315.96
573.15	-268.792	31.399	-516.79
598.15	-549.951	47.278	-991.78

^a NBS tables.¹³

The resulting parameters are summarized in Table 2. The standard state thermodynamic properties for the representative electrolytes using experimental results from this study are listed in Tables 3–5.

It is interesting to compare the enthalpies as a function of temperature of several of the divalent ions. The standard state partial molal enthalpies relative to 298.15 K, $\bar{H}_2^{\circ}(T) - \bar{H}_2^{\circ}(298.15 \text{ K})$, for M²⁺(aq) = 2H⁺(aq) (M = Ba, Co, Cu, Ca), are summarized in Figure 2. The smooth curves were calculated from the empirical fitting constant of eq 7 given in Table 2. The comparison of the ions alone is accomplished by subtracting the values for H⁺(aq), such as Ba²⁺(aq) - 2H⁺(aq), for example. In Figure 2, the temperature behavior is remarkably similar for Cu²⁺(aq), Ba²⁺(aq), and Ca²⁺(aq). Thermodynamic data for Ca²⁺(aq) is available in the literature⁵ up to 523.15 K below which hydrolysis and complex ion formation in CaCl₂(aq) is minimal. In fact, Ca²⁺(aq) and Ba²⁺(aq) are quite similar and both are similar to Cu²⁺(aq) within 8 kJ mol⁻¹.

TABLE 5: The Standard State Thermodynamic Functions of CoCl₂(aq) at p_{sat}

T (K)	$\bar{H}_2^{\circ}(T) - \bar{H}_2^{\circ}(T_r)$ (kJ mol ⁻¹)	$\bar{G}_2^{\circ}(T) - \bar{G}_2^{\circ}(T_r)$ (kJ mol ⁻¹)	\bar{S}_2° (J mol ⁻¹ K ⁻¹)
298.15	0.000	0.000	0.00 ^a
323.15	-6.770	0.251	-20.27
348.15	-13.837	1.021	-41.33
373.15	-21.411	2.318	-62.39
398.15	-29.295	4.135	-82.92
423.15	-37.450	6.457	-103.03
448.15	-46.175	9.280	-123.58
473.15	-56.362	12.626	-146.51
498.15	-70.018	16.577	-175.76
523.15	-91.554	21.337	-219.70
548.15	-131.363	27.381	-297.58
573.15	-217.886	35.851	-461.39
598.15	-454.221	49.906	-890.84

^a NBS tables.¹³**TABLE 6: Comparison of Standard State Partial Molal Heat Capacities of Some Representative MCl₂(aq) at p_{sat} ^a**

T (K)	$\bar{C}_{p,2}^{\circ}$ BaCl ₂ (aq)	$\bar{C}_{p,2}^{\circ}$ CuCl ₂ (aq)	$\bar{C}_{p,2}^{\circ}$ CoCl ₂ (aq)
298.15	-280.5	-310.0	-272.3
323.15	-265.8	-242.1	-267.8
348.15	-263.0	-210.0	-298.6
373.15	-270.6	-204.8	-329.6
398.15	-294.4	-227.1	-359.9
423.15	-344.6	-285.0	-401.0
448.15	-439.8	-396.0	-469.0
473.15	-616.7	-593.4	-601.4
498.15	-953.7	-946.7	-862.9
523.15	-1634.5	-1614.9	-1392.5
548.15	-3154.5	-3023.4	-2532.2
573.15	-7132.5	-6570.7	-5301.5
598.15	-20692.9	-18555.4	(-14971.8)

^a J mol⁻¹ K⁻¹.

The behavior of Co²⁺(aq) is so different from the other species that some other phenomenon is likely to be involved. Only two reasons would give such a large effect: the change in coordination number (resulting in an effective radius change) or loss in crystal field energy in Co²⁺(aq) as the temperature increases. Since the effective radius as defined and calculated from the unified theory^{7a,14} does not change with temperature, it is possible that the behavior is caused by loss of crystal field energy due to the increase in thermal motion of the primary hydration water molecules around a still constant center of gravity. Why Cu²⁺(aq) does not show such an effect but is rather similar to Ba²⁺(aq) and Ca²⁺(aq) is at present not known. We have not found any other explanation for the results summarized in Figure 2 up to the present time.

The heat capacities for reactions 1–3 are calculated from the following equation:

$$\Delta_{\text{sol}} \bar{C}_p^{\circ} = \left(\frac{\partial \Delta_{\text{sol}} \bar{H}^{\circ}}{\partial T} \right)_{\text{sat}} + \left[\Delta_{\text{sol}} \bar{V}^{\circ} - T \left(\frac{\partial \Delta_{\text{sol}} \bar{V}^{\circ}}{\partial T} \right)_p \right] \left(\frac{\partial p}{\partial T} \right)_{\text{sat}} \quad (8)$$

The values of $\bar{C}_{p,2}^{\circ}$ for BaCl₂(aq), CoCl₂(aq), and CuCl₂(aq) are summarized in Table 6 and compared with CaCl₂(aq) in Figure 3.

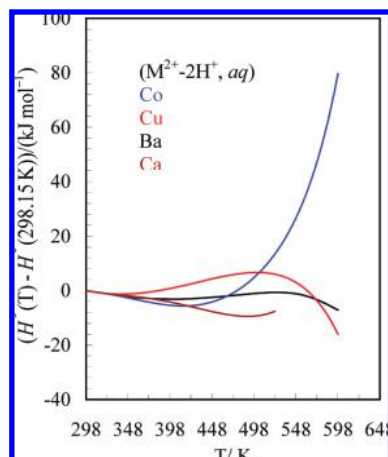


Figure 2. Standard state partial molal enthalpies relative to 298.15 K for $M^{2+}(aq) - 2H^{+}(aq)$ at p_{sat} .

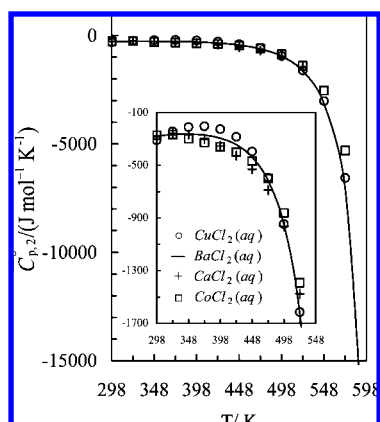


Figure 3. Standard state partial molal heat capacities of some representative 2:1 electrolytes at p_{sat} .

Tables 3–5 confirm the original hypothesis of Cobble et al.¹⁵ that the standard state enthalpies and entropies change very rapidly as the critical temperature is approached, and largely cancel each other out in the resulting standard state free energies. While others¹⁶ have also verified this hypothesis for lower charged ions at higher concentrations, the absolute values of the standard state heat capacities still seem astonishing. For example, at 623 K, $\bar{C}_{p,2}$ for $BaCl_2(aq)$ is over $-85 \text{ kJ mol}^{-1} \text{ K}^{-1}$.

A previous estimation by Cobble et al.¹⁷ at 573 K suggested 164 water molecules lost some of their energy to the surroundings on introduction of $Ba^{2+} + 2Cl^{-}$ ions. The present higher temperature data indicates over 1700 water molecules are influenced at 623 K by the same reasoning. Wood and his co-workers¹⁸ have observed similar effects from flow calorimetric studies for lower charged ions at higher concentrations, and believe $\bar{C}_{p,2}$ values go to infinity at the critical temperature of water, T_c . The present data are based upon a direct thermal measurement of heat, q , which cannot go to infinity. Nevertheless, many of the standard state functions are changing so rapidly in the critical region (as in a phase transition) that it is remarkable that the standard state Gibbs free energies appear to pass through this region smoothly with temperature into the critical region (e.g., standard state Gibbs free energy of ionization of water¹⁹).

Conclusions

As far as can be determined, this communication reports the first complete $(\bar{G}_2, \bar{H}_2, \bar{S}_2, \bar{C}_{p,2}, \bar{V}_2, (\partial\bar{V}_2/\partial T)_p, (\partial\bar{V}_2/\partial p)_T)$ thermodynamic characterization of some representative 2:1 electrolytes from measurements at low enough concentrations that the standard state values are insensitive to the model chosen for extrapolation of experimental data to infinite dilution. Further, it appears that the data confirms a behavior similar to $CaCl_2(aq)$ ⁵ at lower temperatures ($T < 523 \text{ K}$) (see Figure 3). The standard state partial molal enthalpy and derived heat capacity data suggest that at higher temperatures ($T > 474.15 \text{ K}$) the ligand field stabilization energy of $Co^{2+}(aq)$ may be disappearing.

Supporting Information Available: Experimental enthalpies of solution of barium chloride at p_{sat} . Experimental and calculated enthalpies of solution of cobalt perrenate at p_{sat} . Experimental enthalpies of solution of copper(II) oxide in perrenic acid at p_{sat} . Standard state partial molal volume and its first T and p derivatives for $BaCl_2(aq)$, $CoCl_2(aq)$, and $CuCl_2(aq)$ at p_{sat} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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