

# A Unified Theory of the Thermodynamic Properties of Aqueous Electrolytes to Extreme Temperatures and Pressures

Essmaïl Djamali<sup>\*,†,‡</sup> and James W. Cobble<sup>\*,‡</sup>

Center for Hydrothermal Research, San Diego State University, San Diego, California 92182, and Department of Chemistry, San Diego State University, San Diego, California 92182

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A new theoretical treatment has been developed for predicting the thermodynamic properties of electrolytes up to and beyond the critical temperature of water (973 K and at pressures up to 1000 MPa). The model is based upon the classical Born equation corrected for non-Born hydration effects. The temperature and pressure behavior of electrolytes can now be accurately predicted from existing low temperature data. Only two constants are needed for each electrolyte at all temperatures and pressures, where data exist to test the theory.

## Introduction

The field of high temperature and pressure chemistry of electrolytes is of both practical and theoretical importance for many chemical processes involved in aqueous corrosion (found in all power plants using steam/water as the thermal fluid), geochemistry, including geothermal sources of hot water/steam, in oceanic chemistry near fumaroles, and in the search for electrolytic systems for high temperature batteries and fuel cells.

Theoretically, it is of interest to look at key thermodynamic functions of aqueous electrolytes, particularly the Gibbs energy, between the ice and critical point of water. Between these temperatures, water transitions from a highly structured low temperature solvent to a nonstructured but still ionizing fluid at high temperature.<sup>1</sup> A number of empirical and theoretical treatments have been developed over the last 40 years to predict the Gibbs free energy at higher temperatures. However, starting with the Criss–Cobble entropy correspondence principle in 1964<sup>2</sup> until the present, no one has to date succeeded in predicting, from first principles, free energies to the desired accuracy of chemical interest over the liquid range of water, although a number of semiempirical extrapolation procedures have been useful over a more limited temperature range.<sup>3–9</sup> Chemical accuracy is defined here to mean errors in the Gibbs free energy of less than a kilojoule at  $T \geq 573$  K. Larger errors give equilibrium constants with uncertainties that can be too large to be very useful for most chemical purposes.

To date, all continuum theoretical models have used the Born charging equation<sup>10</sup> to account for the electrostatic interaction between ions and a continuous dielectric medium. The main difficulties in the use of continuum models are obtaining or even defining the ionic radius to the required degree of accuracy and lack of detailed knowledge of the dielectric constant of the solvent at the surface and immediate vicinity of an ion.

## The Proposed Unified Model

The model developed for the calculation of the standard state Gibbs free energies of hydration of ions,  $\Delta_h \bar{G}^\circ$ , at  $T$  and  $p$  can be summarized as

$$\Delta_h \bar{G}^\circ = \Delta_{el} \bar{G}^\circ + \Delta_{nel} \bar{G}^\circ + \Delta_{ss} \bar{G}^\circ \quad (1)$$

where  $\Delta_{el} \bar{G}^\circ$  is the electrostatic contribution and  $\Delta_{nel} \bar{G}^\circ$  represents the nonelectrostatic contribution to hydration from short-range and structural effects and compensates for the errors in the electrostatic representation of the primary hydration shell. The standard state conversion term,  $\Delta_{ss} \bar{G}^\circ$ , for the hypothetically ideal 0.1 MPa gaseous ions being hydrated to the hypothetically ideal 1  $m$  aqueous solution is given by eq 2:

$$\Delta_{ss} \bar{G}^\circ = \nu RT \ln \left( \frac{m^\circ d^\circ RT}{1000 p^\circ} \right) \quad (2)$$

where  $m^\circ$  is equal to 1 mol/kg,  $d^\circ$  is the density of the pure solvent in g/cm<sup>3</sup>,<sup>11</sup> and  $p^\circ$  is equal to 0.1 MPa. Other researchers<sup>12,13</sup> concur that the transfer of ions between two different standard states requires such a correction.

The electrostatic term,  $\Delta_{el} \bar{G}^\circ$ , is given by

$$\Delta_{el} \bar{G}^\circ = \Delta_B \bar{G}^\circ + \Delta_{NB} \bar{G}^\circ \quad (3)$$

where  $\Delta_B \bar{G}^\circ$  is the Born charging equation (eq 4) and  $\Delta_{NB} \bar{G}^\circ$  covers all of the electrostatic contributions of a non-Born type. To avoid the arbitrary and nonthermodynamic division of thermodynamic properties into cationic and anionic contributions, the electrolyte form of the equation will be used:

$$\Delta_B \bar{G}^\circ = -\frac{Ne^2}{2R_B} \left[ 1 - \frac{1}{D(T, p)} \right] \quad (4)$$

where  $N$  is Avogadro's number,  $e$  is the value of electrostatic charge,  $R_B$  is the Born radius of the electrolyte, to be determined as described below, and  $D$  is the bulk dielectric constant of the

\* Corresponding authors. E-mail: hydrothermal@projects.sdsu.edu or djamali@sciences.sdsu.edu (E.D.); jcobble@sbcglobal.net (J.W.C.). Phone: (619)-594-7395 or (858)-454-4767 (E.D.); (858)-454-4767 (J.W.C.). Fax: (619)-594-7311 (E.D.).

<sup>†</sup> Center for Hydrothermal Research.

<sup>‡</sup> Department of Chemistry.

solvent. The Born radius for a neutral aqueous electrolyte is defined by

$$\frac{1}{R_B} = \sum_i \frac{\nu_i Z_i^2}{R_i} \quad (5)$$

where  $\nu_i$  is the stoichiometric number of ions in the electrolyte,  $R_i$  is the effective electrostatic radius of the spherical cavity in the dielectric continuum which contains the ions, and  $Z_i$  is the ionic charge number. The effective electrostatic radius is defined here as the distance beyond which the bulk dielectric constant of the solvent is applicable.

The nonelectrostatic and the non-Born-type electrostatic contributions to the hydration process are combined and are represented by two constants (eq 6)

$$\Delta_{\text{nel}}\bar{G}^\circ + \Delta_{\text{NB}}\bar{G}^\circ = C_H - C_S T \quad (6)$$

where  $C_H$  and  $C_S$  represent the enthalpy and entropy loss of the solvent molecules in the primary hydration shell, respectively, and will be assumed to be independent of  $T$  and  $p$ . The standard state corrected experimental Gibbs free energy of hydration,  $\Delta_h\bar{G}^*$ , is then given by eq 7:

$$\Delta_h\bar{G}^* = \Delta_h\bar{G}^\circ - \Delta_{\text{ss}}\bar{G}^\circ = \Delta_h\bar{G}^\circ - \nu RT \ln\left(\frac{m^\circ d^\circ RT}{1000p^\circ}\right) \quad (7)$$

where the second equality is from eq 2. Combining eqs 1–7 yields

$$\Delta_h\bar{G}^* = -\frac{Ne^2}{2R_B} \left[1 - \frac{1}{D(T,p)}\right] - C_S T + C_H \quad (8)$$

For the prediction of hydration properties from this model (eq 8), accurate dielectric properties of water as a function of temperature and pressure are required. Bradley and Pitzer,<sup>14</sup> Uematsu and Franck,<sup>15</sup> Helgeson and Kirkham,<sup>16</sup> and Archer and Wang<sup>17</sup> have all analyzed the existing data. In this research, the Bradley and Pitzer<sup>14</sup> values are adopted for calculations for the proposed model (eq 8) up to 623.15 K.

One very important part of the present model is to avoid the question of the structural details of the primary hydration layer of water around an ion by letting the experimentally observed standard state (corrected) Gibbs free energy of hydration itself define the effective radius. Rearranging eq 8:

$$-\frac{Ne^2}{2R_B} = \frac{(\Delta_h\bar{G}^*(T,p) - C_H + C_S T)}{\left(1 - \frac{1}{D(T,p)}\right)} \quad (9)$$

The experimental standard state corrected Gibbs free energies of hydration can be used to fix the radius parameter very accurately (eq 9). In Table 1, the values of  $R_B$  were calculated from the available data for some representative electrolytes from 298 to 598 K.<sup>18,19</sup> The average constancy is good to a few parts in ten thousand. It was observed that the two constants,  $C_H$  and  $C_S$ , give a constant value of  $R_B$ , determined from the experimental Gibbs energy data for some representative electrolytes from 298.15 to 598.15 K. For the purpose of this treatment, we

**TABLE 1: The Constancy of the Born Radius Parameters (in Å),  $R_B$ , Calculated from eq 9 at  $p_{\text{sat}}$**

$T$ (K)	NaCl	BaCl <sub>2</sub>	GdCl <sub>3</sub>
298.15	0.8252	0.3557	0.2069
373.15	0.8251	0.3556	0.2068
423.15	0.8251	0.3557	0.2069
473.15	0.8251	0.3557	0.2069
523.15	0.8252	0.3557	0.2069
573.15	0.8253	0.3557	0.2068
598.15	0.8251	0.3557	0.2069

have used 298.15 K and 0.1 MPa as the reference state, although any temperature or pressure could be used if free energy data were available. Equation 9 can now be written as

$$-\frac{Ne^2}{2R_B} = \frac{(\Delta_h\bar{G}^*(T_r, p_r) - C_H + C_S T_r)}{\left(1 - \frac{1}{D(T_r, p_r)}\right)} \quad (10)$$

Substitution of eq 10 in eq 8 yields the following useful function for the proposed model:

$$\Delta_h\bar{G}^*(T, p) = [\Delta_h\bar{G}^*(T_r, p_r) + C_S T_r - C_H] F_1(D) - C_S T + C_H \quad (11a)$$

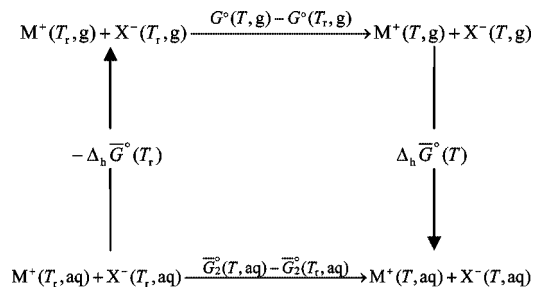
where

$$F_1(D) = \left[ \frac{D(T, p) - 1}{D(T_r, p_r) - 1} \right] \left[ \frac{D(T_r, p_r)}{D(T, p)} \right] \quad (11b)$$

The model parameters  $C_H$  and  $C_S$  are fixed from eq 11 and experimental standard state Gibbs free energies of hydration,  $\Delta_h\bar{G}^\circ$ , for at least two temperatures besides  $T_r$ . The values of  $\Delta_h\bar{G}^\circ(T_r, p_r)$  used in this research were obtained from the NBS<sup>20</sup> and JANAF<sup>21</sup> tables at 298.15 K.

## Results and Discussion

To obtain the Gibbs free energies, it is more accurate to use the smaller differences between the two very large hydration energies at  $T_r$  and the temperature of interest,  $T$ , according to the following thermodynamic cycle: The difference between the



hydration energies at two temperatures is conveniently related to the experimental free energies of transfer of an electrolyte from one temperature to the other,  $\bar{G}_2^\circ(T, \text{aq}) - \bar{G}_2^\circ(T_r, \text{aq})$ :

$$\bar{G}_2^\circ(T, p_{\text{sat}}, \text{aq}) - \bar{G}^\circ(T_r, p_r, \text{aq}) = \Delta_h(\bar{G}^\circ(T, p_{\text{sat}}) - \bar{G}^\circ(T_r, p_r)) + G^\circ(T, \text{g}) - G^\circ(T_r, \text{g}) \quad (12)$$

**TABLE 2: Differences between the Experimental and Predicted (eq 11) Gibbs Free Energies of Transfer from 298.15 K to  $T$  at  $p_{\text{sat}}$  in  $\text{kJ mol}^{-1}$** 

$T$ (K)	HCl	NaCl	CsCl	BaCl <sub>2</sub>	CoCl <sub>2</sub>	CuCl <sub>2</sub>	GdCl <sub>3</sub>	NaReO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	NaOH	KCl	FeCl <sub>2</sub>
323	−0.095	−0.043	0.272	−0.311	−0.420	−0.198	−0.707	0.137	0.164	−0.085	0.145	
373	−0.061	−0.033	0.385	−0.274	−0.460	−0.025	−0.584	0.212	0.307	−0.183	0.165	0.169
423	0.078	−0.009	0.228	0.075	0.169	0.225	0.008	0.016	−0.052	−0.110	0.015	−0.026
473	0.140	−0.013	−0.014	0.226	0.726	0.104	0.322	−0.203	−0.359	0.117	−0.142	−0.060
523	0.000	0.002	−0.204	−0.033	0.381	−0.308	0.253	−0.172	0.153	−0.002	−0.151	0.181
573	−0.223	0.108	−0.024	0.011	−1.057	0.331	−0.231	0.071	−0.227		0.458	0.236
598	0.114	−0.094					−0.114	0.010				

**TABLE 3: Parameters for Representative Primary Electrolytes Calculated from eq 11**

electrolyte	$-C_S$ (J mol <sup>−1</sup> )	$C_H$ (kJ mol <sup>−1</sup> )	$\Delta_h \bar{G}^\circ(298.15 \text{ K})^a$ (kJ mol <sup>−1</sup> )
HCl <sup>b</sup>	82.493	−413.917	−1408.05
NaCl	71.517	66.720	−727.17
CsCl	30.031	209.251	−609.79
HReO <sub>4</sub>	76.254	−513.680	−1390.00
NaReO <sub>4</sub>	65.278	−33.043	−709.12
NaOH	169.498	−218.982	−854.66
BaCl <sub>2</sub>	157.683	−102.927	−1960.10
CoCl <sub>2</sub>	297.809	−910.010	−2621.23
CuCl <sub>2</sub>	273.497	−1009.740	−2716.42
GdCl <sub>3</sub>	389.713	−1338.252	−4505.37

<sup>a</sup> Calculated from refs 18, 20, and 21. <sup>b</sup> Calculated from ionic additivity relationships.

where values of  $G^\circ(T, g) - G^\circ(T_r, g)$  for heating of the gaseous ions are calculated from statistical thermodynamics<sup>18,22,23</sup> and from data in the JANAF tables.<sup>21</sup>

The standard state Gibbs free energies of transfer calculated from the present unified model (eq 11) and eq 12 are compared with the experimentally derived standard state Gibbs free energies of transfer in Table 2. The standard state data obtained from high dilution ( $10^{-3}$ – $10^{-4}$  *m*) calorimetric studies in this laboratory are summarized in ref 18. In Table 2, the unified model predictions are also tested against a secondary set of standard state data, which are not considered as reliable (and therefore not used to verify the model) obtained from measurements in more concentrated solutions (KCl,<sup>24</sup> FeCl<sub>2</sub><sup>25</sup>). However, the agreement between the theory and experiment for these electrolytes is also good to within the average experimental error of the measurements. The parameters of the present model are summarized in Table 3.

The present model assumes that the parameters of the model,  $C_H$  and  $C_S$ , are temperature and pressure independent. These assumptions of the theory can be tested again with the experimental data for the ionization reaction of water (these data were not used in developing the theory):



The ionization constant,  $K_w^\circ$ , has been measured to very high temperatures and pressures above the critical point by a number of investigators and is summarized by Marshall and Franck<sup>26</sup> in an empirical equation, which reproduces the experimental data. The values of  $K_w^\circ$  calculated from the Marshall and Franck equation<sup>26</sup> can then be compared with the corresponding values for  $K_w^\circ$  predicted from the present unified model.

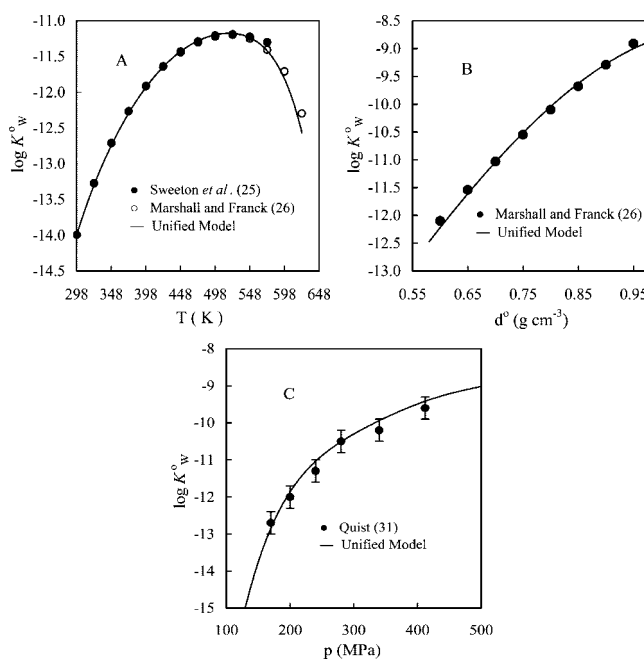
The parameters,  $C_H$  and  $C_S$ , for  $\text{H}^+\text{OH}^-(\text{aq})$  were obtained by ionic additivity from the corresponding parameters for HCl(aq), NaCl(aq), and NaOH(aq) in Table 3. Values for NaOH(aq) were calculated from the experimental calorimetric

data of Simonson et al.<sup>27</sup> up to 473 K; their higher temperature data cannot reliably be extrapolated to standard state conditions without making assumptions regarding ion associations. The present model parameters for  $\text{H}^+\text{OH}^-(\text{aq})$  are therefore fixed using only data from 298.15 to 473.15 K at  $p_{\text{sat}}$ . Auxiliary data are from the JANAF tables.<sup>21</sup>

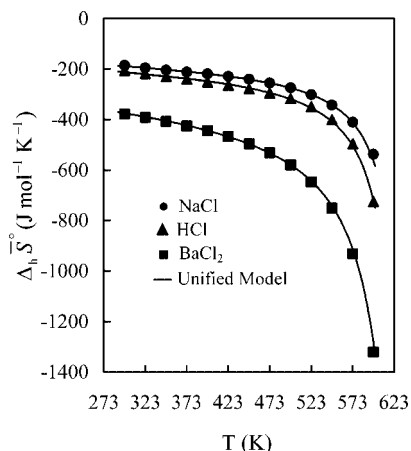
The  $\log K_w^\circ$  values calculated from the present unified model at  $p_{\text{sat}}$  agree well with those calculated from the Marshall and Franck empirical equation<sup>26</sup> from 298.15 to 623.15 K, as well as the experimental data of Sweeton et al.<sup>28</sup> to within the combined uncertainties of the experimental data<sup>28</sup> and the uncertainty of the dielectric constant data used in the present model. The comparison is summarized in Figure 1.

At lower temperatures ( $\leq 423.15$  K) and at pressures up to 500 MPa, the values for  $\log K_w^\circ$ , predicted from the unified model at high pressures, are in better agreement with the experimental data<sup>29</sup> than the corresponding values predicted from the semicontinuum model of Tanger and Pitzer,<sup>30</sup> which requires 11 adjustable parameters, compared to 2 parameters for the present model fixed from only lower temperature data at  $p_{\text{sat}}$ .

The values of  $\log K_w^\circ$ , predicted from the present model, to supercritical temperatures up to 973.15 K and pressures up to 500 MPa, were compared with the experimental<sup>31</sup>  $\log K_w^\circ$  and the corresponding values given by Marshall and Franck.<sup>26</sup> At 673.15 K and at water densities from 0.60 to 0.95 g/cm<sup>3</sup>,  $\log K_w^\circ$  values from the present model are in excellent agreement. At



**Figure 1.** Comparison of the literature values of  $\log K_w^\circ$  with those calculated from the unified model (parameters obtained from  $T \leq 473.15$  K and at  $p_{\text{sat}}$ ): (A)  $p_{\text{sat}}$ ; (B) 673.15 K as a function of water density; (C) 973.15 K as a function of pressure.



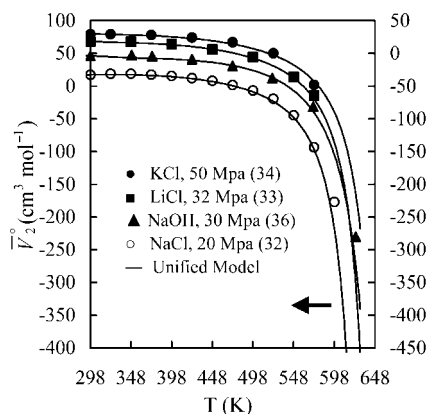
**Figure 2.** Comparison of the experimental entropies of hydration<sup>18</sup> with those calculated from the unified model at  $p_{\text{sat}}$ .

all densities, they are also in good agreement with the experimental conductance data of Quist<sup>31</sup> to within the stated experimental uncertainties. Furthermore, at pressures from 100 to 500 MPa and at 973.15 K, the present model predictions are, again, in excellent agreement with the experimental conductance data of Quist<sup>31</sup> (see Figure 1). At temperatures above 623.15 K, the Archer and Wang<sup>17</sup> dielectric constants were used for prediction of the  $\log K_W$ , since the Bradley and Pitzer<sup>14</sup> values did not extend beyond 623.15 K.

It is important to re-emphasize that the parameters of the present unified model for the prediction of  $\log K_W$  were fixed at lower temperatures ( $T \leq 473.15$  K) and at relatively low pressures (namely,  $p_{\text{sat}}$ ). Those same parameters,  $C_H$  and  $C_S$ , were used to predict  $\log K_W$  values in good agreement with the existing experimental data from low temperatures to supercritical temperatures and to high pressures (500 MPa). This is very satisfactory, and substantiates that  $C_H$  and  $C_S$  are constant over wide ranges of temperature and pressure. The unified model is a powerful tool for extrapolation of Gibbs free energy data to higher temperatures and pressures once the parameters of the model are fixed from lower temperature and pressure data.

### The Standard State Entropies of Hydration

It is also important to note that calculation of the entropies of hydration provides an independent test of the accuracy and validity of the present model. The free energy of hydration depends on  $1/D$ , while the entropy of hydration is proportional to  $(1/D^2)(\partial D/\partial T)_p$  at each temperature.



The first temperature derivative of the Gibbs free energy of hydration is obtained from eq 14 as

$$\Delta_h \bar{S}^\circ(T, p) = -(\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H) F_2(D) - C_S + \Delta_{ss} \bar{S}^\circ \quad (14a)$$

where

$$F_2(D) = \left[ \frac{D(T_r, p_r)}{D(T_r, p_r) - 1} \right] \left[ \frac{1}{D(T, p)^2} \right] \left( \frac{\partial D}{\partial T} \right)_p \quad (14b)$$

and

$$\Delta_{ss} \bar{S}^\circ = -\nu R \left[ \ln(RT d^\circ) + T \left( \frac{\partial \ln d^\circ}{\partial T} \right)_T + 1 \right] \quad (14c)$$

The standard state entropies of hydration for NaCl(aq), HCl(aq), and BaCl<sub>2</sub>(aq) were calculated from eq 14 and are compared with experimental values in Figure 2. Although Bradley and Pitzer<sup>14</sup> believe the uncertainty in  $(\partial D/\partial T)_p$  could be less than 5% at temperatures below 573.15 K but as much as 25% above 573.15 K near the saturation pressure up to 623.15 K, the agreement between the experimental and predicted standard state entropies of hydration is better than that.

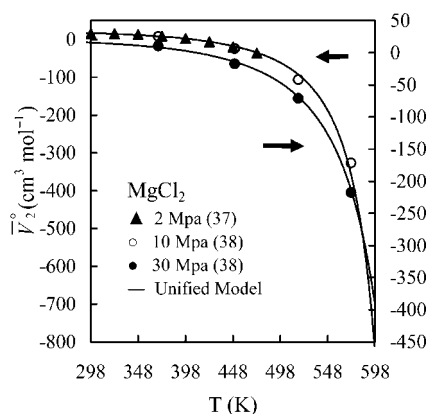
### The Standard State Partial Molal Volumes of Electrolytes

The pressure derivative of the standard state Gibbs free energy, the standard state partial molal volume, is given in this treatment as

$$\bar{V}_2^\circ(T, p) = \{ \bar{V}_2^\circ(T_r, p_r) - (\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H) F_3(T_r, p_r) \} F_1(T, p) + (\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H) F_3(T, p) + [\Delta_{ss} \bar{V}^\circ(T, p) - \Delta_{ss} \bar{V}^\circ(T_r, p_r) F_1(T, p)] \quad (15a)$$

where

$$F_3(D) = \left[ \frac{D(T_r, p_r)}{D(T_r, p_r) - 1} \right] \left[ \frac{1}{D(T, p)^2} \right] \left( \frac{\partial D}{\partial p} \right)_T \quad (15b)$$



**Figure 3.** Comparison of literature values for the standard state partial molal volume of aqueous electrolytes with those calculated from the unified model at different temperatures and pressures.



and

$$\Delta_{ss}\bar{V}^\circ = \nu RT \left( \frac{\partial \ln(d^\circ)}{\partial p} \right)_T \quad (15c)$$

where  $\Delta_{ss}\bar{V}^\circ$  is the standard state correction term. The properties for pure water are obtained from the steam tables.<sup>11</sup>

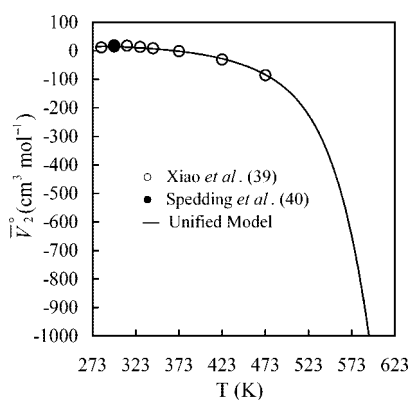
The experimental standard state partial molal volumes,  $\bar{V}_2^\circ$ , for NaCl(aq),<sup>32</sup> LiCl(aq),<sup>33</sup> KCl(aq),<sup>34</sup> NaOH(aq),<sup>35,36</sup> and MgCl<sub>2</sub>(aq)<sup>37,38</sup> are compared with the values of  $\bar{V}_2^\circ$  predicted from the present model (eq 15) at different temperatures and pressures in Figure 3. It is important to note that  $C_H$  and  $C_S$  were those used previously to fit the standard state Gibbs free energies and that no new parameters are required. The agreement between the experimental and predicted values of  $\bar{V}_2^\circ$  of the above representative electrolytes is good; differences are well within the experimental uncertainties the various authors reported in extrapolating the molal volume data to infinite dilution from relatively concentrated solutions ( $m \geq 0.05$ ), as well as uncertainties in  $(\partial D/\partial p)_T$ .

The values of Xiao et al.<sup>39</sup> for  $\bar{V}_2^\circ(\text{GdCl}_3, \text{aq})$  to 473.15 K and at  $p_{\text{sat}}$  are compared with the values calculated from the present model in Figure 4. The agreement is well within the experimental uncertainty up to 473.15 K. Direct experimental density measurements from which  $\bar{V}_2^\circ(\text{GdCl}_3, \text{aq})$  can be estimated at higher temperature are difficult to interpret, due to hydrolysis and complex ion formation, both of which increase with rising temperature. However, it is now possible to predict  $\bar{V}_2^\circ(\text{GdCl}_3, \text{aq})$  up to high temperatures and pressures from the present model whose parameters are fixed at lower temperatures where hydrolysis and complex formation are avoided. The predicted standard state partial molal volumes for aqueous gadolinium chloride from 298.15 to 623.15 K are summarized in Figure 4. Aqueous gadolinium chloride is an important model electrolyte involving a +3 ion.

### The Standard State Partial Molal Heat Capacities of Electrolytes

Still another test of the present theory is to compare the predicted and observed heat capacities of hydration, which involve the second derivative of the Gibbs free energy of hydration with respect to temperature.

The second temperature derivative of the standard state Gibbs free energy, the standard state partial molal heat capacity, is given by



**Figure 4.** Comparison of literature values for the standard state partial molal volume of aqueous gadolinium chloride<sup>39,40</sup> with those calculated from the unified model at  $p_{\text{sat}}$ .

$$\bar{C}_{p,2}^\circ(T, p) = -T(\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H) F_4(D) + \nu C_p^\circ(\text{g}) + \Delta_{ss} \bar{C}_p^\circ \quad (16a)$$

where

$$F_4(D) = \left( \frac{D(T_r, p_r)}{D(T, p_r) - 1} \right) \left( \frac{1}{D(T, p)^2} \right) \left[ \left( \frac{\partial^2 D}{\partial T^2} \right)_p - \frac{2}{D(T, p)} \left( \frac{\partial D}{\partial T} \right)_p \right] \quad (16b)$$

and

$$\Delta_{ss} \bar{C}_p^\circ = -\nu R \left[ 1 - 2T\alpha^\circ - T^2 \left( \frac{\partial \alpha^\circ}{\partial T} \right)_p \right] \quad (16c)$$

where

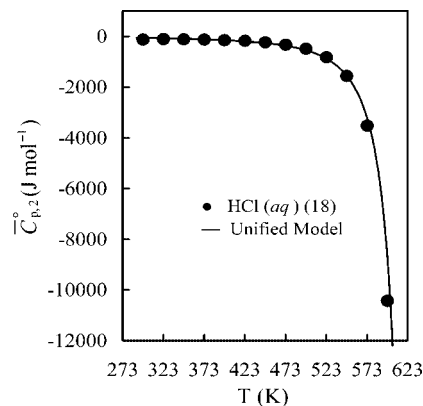
$$\alpha^\circ = -\frac{1}{d^\circ} \left( \frac{\partial d^\circ}{\partial T} \right)_p \quad (16d)$$

$\alpha^\circ$  is the coefficient of thermal expansion of water,<sup>11</sup> and  $C_p^\circ(\text{g})$  are the molar heat capacities of the gaseous ions.<sup>18,21</sup>

The standard state partial molal heat capacities,  $\bar{C}_{p,2}^\circ$ , for HCl(aq) calculated from the model (eq 16) are compared with the experimental values<sup>18</sup> in Figure 5. The agreement is good to 573 K, and any differences are well within the combined uncertainties of  $(\partial D/\partial T)_p$  and  $(\partial^2 D/\partial T^2)_p$  used in the present model.

### Conclusions

The unified model developed in this research has successfully predicted the thermodynamic properties of representative aqueous electrolytes within the combined uncertainties associated with the dielectric constant of water and its temperature and pressure derivatives for 15 electrolytes. The parameters of the model ( $C_H$  and  $C_S$ ) reported in this communication were derived from the experimental ( $T \leq 598$  K) standard state partial molal Gibbs free energies of electrolytes (except for NaOH(aq), where the highest temperature was 473 K). Once these parameters are fixed, the model has been used to predict the standard state partial molal Gibbs free energies of electrolytes up to supercritical temperature (973 K). The model has also been used



**Figure 5.** Comparison of the values for the standard state partial molal heat capacities of hydrochloric acid<sup>18</sup> with those calculated from the unified model at  $p_{\text{sat}}$ .

successfully to predict the standard state partial molal entropies, heat capacities, and volumes of electrolytes to the highest temperatures of the experimental data (623 K). It is clear, however, the parameters can be fixed from much lower temperature data, as is indicated in Tables 1 and 2.

Thermodynamic data for a substantial number of electrolytes are available over more limited temperature ranges, 273–373 K. In fact, off-the-shelf experimental equipment can be purchased (such as flow calorimeters) to make these lower temperature measurements. An added advantage of the lower temperature measurements is that extrapolation of thermal and free energy data to infinite dilution is much easier than at higher temperatures. This means that the present model can now also be used to predict high temperature thermodynamic parameters for many more electrolytes.

The modified Born equation (eq 11) and only two constants for each electrolyte,  $C_H$  and  $C_S$ , fit the experimentally observed standard state Gibbs free energy data to chemical accuracy over the entire temperature range (essentially 298–973 K). Using the same constants, the theory reproduces the standard state entropy, heat capacity, and molal volume data over the same temperature and pressure range (when available).

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