

Standard State Thermodynamic Properties of Aqueous Sodium Chloride Using High Dilution Calorimetry at Extreme Temperatures and Pressures

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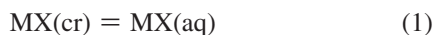
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In this communication, we report the first calorimetric data for the standard state enthalpies of a solution of sodium chloride obtained from high dilution, down to ($10^{-3} m$), integral heats of solution measurements to 596.30 K. Although there are no comparable thermodynamic data available at such high dilutions in the literature, the present results for NaCl(aq) can be used for many thermodynamic studies by others to achieve a complete thermodynamic description of this key electrolyte over very wide ranges of concentration. From the recently developed unified theory of electrolytes, the experimental data from this study were used to predict Gibbs free energies of hydration of sodium chloride up to 1100 K. These Gibbs free energies of hydration at different pressures and densities compare well with reported values obtained from *ab initio* calculations by others.

1. Introduction

A unified theory of electrolytes for the prediction of the standard state thermodynamic properties of electrolytes at high temperatures and pressures has been developed.¹ Key to this development was the availability of very accurate thermodynamic functions of important representative electrolytes under standard state conditions. The extrapolated experimental thermodynamic values to standard state conditions become more uncertain as the temperature increases because of increasing nonideality of the electrolytes in even dilute solutions.² Most of the data in the literature are for calorimetric measurements at concentrations greater than 0.05 *m* because of equipment limitations. The difficulty of making flow calorimetric and dilution measurements under the pressures and temperatures of interest is known to be quite challenging.^{3,4} The approach adopted for this research has been to use “batch calorimetry” wherein enthalpy measurements can be carried out using a suitable chemical reaction where the thermodynamic properties of all other reactants and products are known. The simplest of these reactions is the enthalpy of solution of a pure salt:



Since the thermodynamic functions of many solid salts of interest have already been characterized,⁵ the enthalpies of solution in effect give the thermodynamic properties of the dissolved solute. The advantage of this batch calorimetry is that measurements to give extremely dilute solutions of the electrolyte are possible; 10^{-2} to $10^{-4} m$ is the normal operating range, and even concentrations down to $10^{-5} m$ are possible. Indeed, in some of the data to be reported,⁶ extrapolation to infinite dilution must take into account the contribution of water itself from self-ionization.

These dilutions make it possible to obtain standard state enthalpies of solution or reaction values, which are not sensitive to the theoretical model used for the extrapolation or to the exact value of “limiting law” slopes.

The high pressure calorimeters used in this research are described in detail elsewhere; two separate devices were used over the time involved, HP-1 and HP-2,⁷ the later being of an improved design. To date, the highest temperature reached by these devices is 620 K. It is possible to go to even higher temperatures, indeed through the critical region, but the thickness of the special titanium–palladium alloy used in the present calorimeters precluded pressures greater than 17 MPa.

Of all electrolytes, the key electrolyte sodium chloride has been studied more extensively and over wider ranges of temperature and pressure than any other species, and data have been reported to 623.15 K. Up to 473.15 K, the thermodynamic properties of aqueous sodium chloride, NaCl(aq), have been extensively measured at dilutions sufficient to obtain standard state properties.^{8,9} However, above 473.15 K, where the non-ideality of ionic solution becomes much more pronounced, measurements applicable to accurately defining standard state values are scarce. Liu and Lindsay^{10,11} measured vapor pressures of sodium chloride solutions from 346.15 to 573.15 K and from 0.1 *m* to *m*_{sat}, and Busey et al.¹² obtained enthalpies of dilution from 298.15 to 623.15 K in concentrated solutions (*m* ≥ 0.1) using a flow calorimeter. Apparent molal heat capacity, *C_{p,q}*, measurements were reported by Wood and co-workers using flow calorimetry,¹³ at *m* ≥ 0.1.

In this communication, we report data for the standard state enthalpies of solution of NaCl up to 596.30 K from measurements all less than 0.01 *m*.

2. Experimental Section

2.1. Materials. Water used in the measurements and in the calorimeter was singly distilled and passed through a Milli-Q reagent grade mixed bed ion exchange column and activated charcoal system (conductivity less than 18 MΩ cm). Solid sodium chloride (99.995%) (Alfa-Aesar) was dried in an oven at 623 K overnight and was stored in a desiccator containing P₂O₅.

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TABLE 1: Experimental Integral Heats of Solution of Sodium Chloride

| moles ($\times 10^3$) | I^a ($\times 10^3$) | q_{obs}^b (J) | q_b^c (J) | q_{vp}^d (J) | q_{sol}^e (J) | $\Delta_{\text{sol}}\bar{H}^{f,g}$ (kJ mol $^{-1}$) | ρ^h (kJ mol $^{-1}$) | σ_p^i (kJ mol $^{-1}$) |
|-------------------------|-------------------------|------------------------|-------------|-----------------------|------------------------|--|----------------------------|--------------------------------|
| 547.95 K | | | | | | | | |
| 2.2049 | 4.4716 | -124.580 | 20.579 | -2.202 | -142.957 | -64.836 | -67.554 | 0.715 |
| 3.0334 | 6.1979 | -176.898 | 20.438 | -3.087 | -194.249 | -64.037 | -67.209 | 0.732 |
| 5.2065 | 10.5680 | -314.486 | 17.241 | -5.082 | -326.645 | -62.738 | -66.811 | 0.670 |
| 7.5592 | 15.3430 | -456.123 | 14.834 | -7.276 | -463.681 | -61.340 | -66.178 | 0.692 |
| 10.5510 | 21.4160 | -652.847 | 12.066 | -10.012 | -654.901 | -62.070 | -67.700 | 0.660 |
| 10.6364 | 21.5701 | -632.868 | 12.530 | -10.065 | -635.333 | -59.732 | -65.379 | 0.715 |
| 0 | | | | | | | -67.496 | 0.896 ^j |
| 572.15 K | | | | | | | | |
| 7.2379 | 1.4835 | -36.901 | 33.277 | -0.892 | -69.286 | -95.727 | -98.278 | 0.978 |
| 15.0318 | 2.7569 | -120.504 | 24.765 | -1.637 | -143.632 | -95.552 | -98.990 | 0.959 |
| 17.7798 | 3.9015 | -142.530 | 24.468 | -2.297 | -164.701 | -92.634 | -96.695 | 0.958 |
| 35.4364 | 7.2635 | -298.818 | 31.085 | -4.197 | -325.706 | -91.913 | -97.365 | 1.290 |
| 57.0729 | 11.6995 | -482.083 | 25.991 | -6.639 | -501.435 | -87.859 | -94.670 | 0.940 |
| 0 | | | | | | | -99.076 | 1.296 ^j |
| 596.30 K | | | | | | | | |
| 5.5765 | 1.2157 | -50.709 | 33.737 | -1.555 | -82.891 | -148.644 | -152.551 | 0.908 |
| 13.7213 | 2.9914 | -178.812 | 24.694 | -3.748 | -199.758 | -145.582 | -151.623 | 0.712 |
| 15.3195 | 3.3398 | -191.545 | 34.246 | -4.172 | -221.619 | -144.665 | -151.034 | 0.701 |
| 31.0479 | 6.7688 | -415.192 | 33.749 | -8.254 | -440.687 | -141.938 | -150.849 | 0.522 |
| 0 | | | | | | | -152.615 | 0.412 ^j |

^a Ionic strength. ^b Observed heat. ^c Calculated bulb-breaking heat from the steam tables (eq 5). ^d Heat due to vapor pressure correction (see eq 10). ^e $q_{\text{sol}} = q_{\text{obs}} - q_b - q_{\text{vp}}$. ^f $\Delta_{\text{sol}}\bar{H} = q_{\text{sol}}/n_{\text{solute}}$. ^g For the reaction $\text{NaCl}(\text{cr}) = \text{NaCl}(\text{aq})$. ^h See eq 15 for the definition of ρ . ⁱ Estimated uncertainty. ^j Estimated standard deviation of the fit.

2.2. Apparatus and Procedures. The heats of solution of solid sodium chloride were measured at 548 and 572 K in a newly designed calorimeter similar to HP-1.^{7b} At 596.30 K, the measurements were carried out in HP-2.^{7a} The main calorimeter reaction vessel is a cylindrical pressure vessel about 17 cm in length and 13 cm in diameter, machined out of a titanium-0.2% palladium alloy ingot, and has a volume of approximately 865 mL. The reaction vessel is placed inside a stainless steel vacuum jacket, which is contained in a large air thermostat. All of the electrical connections inside the calorimeter system use gold wire, and connections are made either by fusing the gold wires or by silver soldering.

The calorimeter vessel has a lid that is pressure sealed with a gold O-ring and positioned inside a stainless steel vacuum jacket, and is placed inside a large air thermostat. The calorimeter is stirred magnetically, and an electromagnetic trip assembly causes a quartz bulb containing a chemical sample to break under the solvent. A thermistor serves as the temperature-sensing element, and a high resolution (16-Bit) Analog/Digital (A/D) Input/Output (I/O) board used with a personal computer was used for data acquisition and control. The calorimeter has a maximum thermal drift of 3×10^{-6} K/min at 600 K and a sensitivity of 1×10^{-6} K.

The experimental procedures used were described in detail elsewhere.⁷ The calorimeter was calibrated electrically for each experimental run, which was confirmed by measuring the molar energy of vaporization of water, $\Delta_{\text{vap}}\bar{E}$. The overall accuracy of the measurements was approximately $\pm 0.2\%$ for HP-2 and $\pm 0.5\%$ for HP-1, compared to values given in the steam tables.¹⁴

2.3. Treatment of Data. The molal enthalpies of solution, $\Delta_{\text{sol}}\bar{H}$, are calculated from the experimentally observed heats, q_{obs} , in the present calorimeters as follows. The heat observed, q_{obs} , in the solution process contains contributions from several sources:

$$q_{\text{obs}} = q_{\text{sol}} + q_{\text{bulb}} + q_{\text{vp}} \quad (2)$$

where q_{sol} is the integral heat of solution of the salt, q_{bulb} is the heat involved when liquid water is evaporated in the calorimeter due to the breaking and collapse of the evacuated bulb containing the salt, and q_{vp} is the heat due to condensation of some vapor because of the small lowering of the vapor pressure of water when the solute is introduced. There is an additional correction due to the resulting change in the volume of the solution upon introduction of solute sample. This correction, $\delta\bar{H}_v$, is added as a molal correction to the resulting molal enthalpies and is calculated as follows:

$$\delta\bar{H}_v = \Delta_{\text{sol}}\bar{V}^\circ\Delta_{\text{vap}}\bar{E}/\Delta_{\text{vap}}\bar{V} \quad (3)$$

$$\Delta_{\text{sol}}\bar{V}^\circ = \bar{V}_2^\circ - V^\circ(\text{cr}) \quad (4)$$

where $\Delta_{\text{sol}}\bar{V}^\circ$ is the molal volume change for the process of solution of the sample, \bar{V}_2° is the standard state partial molal volume of the electrolyte, $V^\circ(\text{cr})$ is the molar volume of solid solute, and $\Delta_{\text{vap}}\bar{E}$ and $\Delta_{\text{vap}}\bar{V}$ respectively are the molar energy and molar volume of vaporization of water from the steam tables.¹⁴ The heats of bulb breaking, q_{bulb} , were also determined experimentally at each temperature (and at saturation steam pressure). These experimental heats of bulb breaking can be compared with the known energy values of vaporization of water from the steam tables,¹⁴ according to eq 5:

$$q_{\text{bulb}} = \Delta_{\text{vap}}\bar{E}V_{\text{bulb}}/\Delta_{\text{vap}}\bar{V} \quad (5)$$

where V_{bulb} is the void space inside the sample bulb (corrected for the volume of a sample if present).

As the solute is introduced into the solvent, the vapor pressure of the solvent, p° , is lowered to a new value, p . This vapor pressure lowering effect is often represented by¹⁵

$$\ln p/p^\circ = -M_1mv\varphi/1000 \quad (6)$$

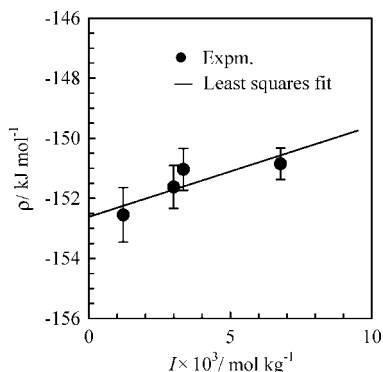


Figure 1. Rho plot (weighted values) of the heat of solution of sodium chloride at 596.30 K.

where m° is equal to 1 mol kg^{-1} and ν and m are the number and molality of the dissolved ionic species, respectively. M_1 is the molecular weight of water, and φ is the osmotic coefficient for the solution. Since the electrolyte solution studied here has very low concentrations ($\leq 10^{-2} m$), the small vapor pressure changes are reliably calculated from the limiting law for the solvent. For example, at 598 K and $0.01 m$, $\Delta p = -0.023 \text{ MPa}$, or 0.19% . The osmotic coefficient, φ , was evaluated using the extended Debye–Hückel equation:¹⁵

$$\varphi = 1 - A_\varphi (I/m^\circ)^{1/2} \sigma((I/m^\circ)^{1/2}) \quad (7)$$

where A_φ is the Debye–Hückel limiting constant for the osmotic coefficient given by

$$A_\varphi = 1/3(2\pi N_A d_1^\circ / 1000)^{1/2} (e^2 / DkT)^{3/2} \quad (8)$$

where N_A is Avogadro's number, d_1° is the density of pure water, D is the static dielectric constant of pure water, k is Boltzmann's constant, e is the absolute electronic charge, and I is the final ionic strength. The factor $\sigma((I/m^\circ)^{1/2})$ is a mathematical function of ionic strength, I , and is given by

$$\sigma(x) = 3/x^3 [(1+x) - 1/(1+x) - 2 \ln(1+x)] \quad (9)$$

A_φ values used in this research at various temperatures are from Bradley and Pitzer.¹⁶

The heat involved in the vapor pressure lowering is

$$q_{vp} = (\partial d_1^\circ / \partial p)_T \Delta p V_{\text{steam}} \Delta_{\text{vap}} \bar{E} \quad (10)$$

where $(\partial d_1^\circ / \partial p)_T$ is the change of water vapor density with pressure, Δp is the change in vapor pressure ($p - p^\circ$), and V_{steam} is the volume of water vapor in the reaction vessel. The quantity, $\Delta_{\text{sol}} \bar{H} = (q_{\text{sol}}/n)$, where n is the number of moles of solute, must be extrapolated to infinite dilution to obtain the desired standard state value, $\Delta_{\text{sol}} \bar{H}^\circ$.

Since

$$\Delta_{\text{sol}} \bar{H} = \Delta_{\text{sol}} \bar{H}^\circ + L_\varphi(m) \quad (11)$$

experimental enthalpies of dilution ($L_\varphi = -\Delta_{\text{dilution}} \bar{H}$) are normally used in obtaining the molality dependence of L_φ , and the extrapolated value, $\Delta_{\text{sol}} \bar{H}^\circ$, is obtained as the average of

$$\Delta_{\text{sol}} \bar{H}^\circ = \Delta_{\text{sol}} \bar{H}(m_i) - L_\varphi(m_i) \quad (12)$$

However, since L_φ data are not available at higher temperatures at the low concentrations ($< 0.01 m$) involved in present research, values of L_φ had to be estimated. We have found that the rho function defined by Criss and Cobble⁸ as an extension of the Debye–Hückel limiting law and first introduced by Guggenheim¹⁷ is very convenient. Sanahuja and Gómez-Estévez¹⁸ concur that this extended form of the Debye–Hückel limiting law appears to be adequate

$$\Delta_{\text{sol}} \bar{H} = \Delta_{\text{sol}} \bar{H}^\circ - 2.303RT^2 \nu_+ \nu_- dB/dT (I/m^\circ) + (\nu/2) |Z_+ Z_-| A'_H (I/m^\circ)^{1/2} [1/(1 + (I/m^\circ)^{1/2}) - \sigma((I/m^\circ)^{1/2})/3] \quad (13)$$

where $A'_H = 3/2A_H$, and dB/dT is an adjustable but constant parameter, at low concentrations. If the second term on the right-hand side is subtracted from both sides of the eq 13 and the left side is plotted against I , a straight line with the slope $(-2.303RT^2 \nu_+ \nu_- dB/dT)$ should be obtained. Rewriting eq 13 as

$$\rho = \Delta_{\text{sol}} \bar{H}^\circ - 2.303RT^2 \nu_+ \nu_- (I/m^\circ) dB/dT \quad (14)$$

where

$$\rho \equiv \Delta_{\text{sol}} \bar{H} - (\nu/2) |Z_+ Z_-| A'_H (I/m^\circ)^{1/2} \alpha((I/m^\circ)^{1/2}) \quad (15)$$

and

$$\alpha(x) = [1/(1 + x^{1/2}) - \sigma(x)/3] \quad (16)$$

A heat correction, $\delta \bar{H}_v$, must be added to ρ° in order to obtain the experimental standard state enthalpy of the solution at each temperature at the saturated steam pressure, $\Delta_{\text{sol}} \bar{H}^\circ(T, p_{\text{sat}})$:

$$\begin{aligned} \Delta_{\text{sol}} \bar{H}^\circ &= \Delta_{\text{sol}} \bar{H}^\infty + \delta \bar{H}_v \\ &= \rho^\circ + \Delta_{\text{sol}} \bar{V} \Delta_{\text{vap}} \bar{E} / \Delta_{\text{vap}} \bar{V} \end{aligned} \quad (17)$$

where the second equality is from eq 3.

3. Calculations and Results

Integral heats of solution measurements of NaCl(cr) up to 596.30 K were treated by the procedures outlined above and are given in Table 1. The value of rho, ρ , calculated from each heat of solution measurement at 596.30 K is plotted against the final ionic strength, I (Figure 1). The extrapolated value of rho to infinite dilution, ρ° , at each temperature was obtained using a weighted linear least-squares method, and these values are also given in Table 1. For a consistent treatment of the previously reported high temperature data from this laboratory, the experimental observed heats, q_{obs} , from Criss and Cobble⁸ and Gardner et al.⁹ were used, but their rho values used to extrapolate to infinite dilution were recalculated using more recent values of the limiting slopes.¹⁶ These recalculated ρ values were in all cases within the estimated uncertainties reported in the original data. Table 2 summarizes the extrapolated ρ° values

TABLE 2: Experimental Enthalpies of Solution of Sodium Chloride at p_{sat}

| T (K) | ρ^{oa} (kJ mol $^{-1}$) | σ_p^b (kJ mol $^{-1}$) | δH_V^c (kJ mol $^{-1}$) | σ_V^d (kJ mol $^{-1}$) | $\Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})^e$ (kJ mol $^{-1}$) | $\sigma_{p,V}^f$ (kJ mol $^{-1}$) |
|---------|--------------------------------------|--------------------------------|----------------------------------|--------------------------------|---|------------------------------------|
| 293.12 | 4.481 | 0.033 | 0.000 | 0.000 | 4.481 | 0.033 |
| 298.15 | 3.824 | 0.021 | −0.001 | 0.000 | 3.849 | 0.021 |
| 308.11 | 2.573 | 0.025 | −0.001 | 0.000 | 2.572 | 0.025 |
| 318.15 | 1.423 | 0.021 | −0.001 | 0.000 | 1.421 | 0.021 |
| 327.98 | 0.335 | 0.021 | −0.002 | 0.000 | 0.332 | 0.021 |
| 338.01 | −0.858 | 0.021 | −0.022 | 0.000 | −0.880 | 0.021 |
| 348.16 | −2.038 | 0.021 | −0.005 | 0.000 | −2.043 | 0.021 |
| 358.13 | −3.222 | 0.033 | −0.008 | 0.000 | −3.230 | 0.033 |
| 368.33 | −4.540 | 0.033 | −0.012 | 0.000 | −4.552 | 0.033 |
| 387.40 | −7.113 | 0.105 | −0.026 | 0.000 | −7.139 | 0.105 |
| 423.05 | −12.866 | 0.105 | −0.088 | 0.002 | −12.954 | 0.105 |
| 472.65 | −24.772 | 0.209 | −0.421 | 0.012 | −25.193 | 0.210 |
| 547.95 | −67.496 | 0.896 | −4.345 | 0.190 | −71.841 | 0.915 |
| 572.15 | −99.076 | 1.296 | −9.939 | 0.403 | −109.015 | 1.357 |
| 596.30 | −152.615 | 0.412 | −26.134 | 1.880 | −178.749 | 1.925 |
| 623.15 | | | | | (−360.771) ^g | (3.600) |

^a Extrapolated heat of solution to infinite dilution. Values below 473 K are recalculated from data of Criss and Cobble⁸ and Gardner et al.⁹

^b Estimated uncertainty in ρ° . ^c Heat contribution due to volume change on introduction of solute (eq 3). ^d Estimated uncertainty for δH_V .

^e Enthalpy of solution at p_{sat} . ^f Propagated error for enthalpy of solution at p_{sat} . ^g Estimated value from eq 18 and Table 3.

TABLE 3: Empirical Parameters for Calculating Standard State Enthalpies of Solution of Sodium Chloride at p_{sat} from eq 18

| | |
|-------|---------------------------|
| a_1 | 2.85169×10^1 |
| a_2 | -9.20949×10^{-2} |
| a_3 | 4.66601×10^{-5} |
| a_4 | -4.57306×10^0 |
| a_5 | 6.94366×10^2 |
| a_6 | 4.45486×10^{-2} |
| a_7 | 2.40993×10^2 |

at infinite dilution up to 596.30 K together with the estimated uncertainty at each experimental temperature. The heat corrections due to volume change of the liquid placed in the calorimeter as the result of introduction of the solute, δH_V , are given in column 4, and the estimated errors of these heat corrections, σ_V , at each experimental temperature are listed in column 5. These small errors, σ_V , are mainly due to uncertainties in the estimation of the values of the standard state partial molal volumes, \bar{V}_2° , of the electrolyte. These enthalpies are given in column 6, and the propagated errors, $\sigma_{p,V}$, as the result of the uncertainties in ρ° and δH_V are listed in column 7.

The standard state enthalpies of solution as a function of temperature at saturated steam pressure, $\Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})$, were empirically fitted by a least-squares method to eq 18 (each experimental result was weighted by final propagated error, $\sigma_{p,V}$):

$$\Delta_{\text{sol}}\bar{H}^\circ = a_1 + a_2T + a_3T^2 + a_4T^2/(a_5 - T)^2 + a_6T^2/(T - a_7)^2 \quad (18)$$

This equation, while purely empirical, has been used for enthalpies of solution of a wide variety of electrolytes,^{6,19,20} and the extrapolated values of the enthalpy of solution at 623.15 K are believed to be reliable. The resulting parameters from eq 18 for $\Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})$ are summarized in Table 3.

The standard state partial molal heat capacities of NaCl(aq) at p_{sat} can now be calculated from eq 19 and the parameters from Table 3 and are listed in Table 4.

$$\bar{C}_{p,2}^\circ = C_p^\circ(\text{cr}) + (\partial \Delta_{\text{sol}}\bar{H}^\circ / \partial T)_{\text{sat}} + [\Delta_{\text{sol}}\bar{V}^\circ - T(\partial \Delta_{\text{sol}}\bar{V}^\circ / \partial T)](\partial p / \partial T)_{\text{sat}} \quad (19)$$

The contribution to $\bar{C}_{p,2}^\circ$ from the molal volume, the third term in eq 19, indicates that a 10% uncertainty at 598.15 K in this term will introduce an error of less than 2% to the overall value of $\bar{C}_{p,2}^\circ$. The molar heat capacity of the solid is from the literature.⁵

The standard state Gibbs free energies of solution of sodium chloride are calculated (Table 5) from eq 20 together with eq 18, parameter values from Table 3, $(\partial p / \partial T)_{\text{sat}}$ from the steam tables,¹⁴ and the values of the standard state molal volume of solution, $\Delta_{\text{sol}}\bar{V}^\circ$:

$$\Delta_{\text{sol}}\bar{G}^\circ(T, p_{\text{sat}}) = T/T_r \Delta_{\text{sol}}\bar{G}^\circ(T_r, p_r) - T \int_{T_r}^T \Delta_{\text{sol}}\bar{H}^\circ(T, p_{\text{sat}})/T^2 dT + T \int_{T_r}^T \Delta_{\text{sol}}\bar{V}^\circ(T, p_{\text{sat}})/T(\partial p / \partial T)_{\text{sat}} dT \quad (20)$$

and

$$\Delta_{\text{sol}}\bar{V}^\circ = \bar{V}_2^\circ(\text{NaCl, aq}) - V^\circ(\text{NaCl, cr}) \quad (21)$$

where T_r and p_r are the reference temperature (298.15 K) and the reference pressure (0.1 MPa) and $\Delta_{\text{sol}}\bar{G}^\circ(298.15 \text{ K}, 0.1 \text{ MPa})$ is calculated from NBS tables.²¹ The values of $\bar{V}_2^\circ(\text{NaCl, aq})$ are given in Table 6, and $V^\circ(\text{cr})$ for NaCl is calculated from its density.²²

The uncertainty associated with the calculation of $\Delta_{\text{sol}}\bar{G}^\circ(T, p_{\text{sat}})$ from the above equation is mainly due to the uncertainty in estimation of the standard state partial molal volume, \bar{V}_2° , at p_{sat} . Fortunately, even a 10% uncertainty in \bar{V}_2° will result in less than 0.1% error in $\Delta_{\text{sol}}\bar{G}^\circ(T, p_{\text{sat}})$ at the highest temperature due to the fact that the contribution of \bar{V}_2° to the second and third terms in eq 20 has opposite sign and comparable magnitude. Consequently, as the result of this partial cancelation of the effect of \bar{V}_2° , the total contribution of \bar{V}_2° at the highest temperature of this study is less than 1% of $\Delta_{\text{sol}}\bar{G}^\circ(T, p_{\text{sat}})$.

4. Discussion

As a check of the self-consistency of the enthalpy and heat capacity data, the enthalpy of solution, $\Delta_{\text{sol}}\bar{H}^\circ$, at 298.15 K can

TABLE 4: Comparison of the Standard State Partial Molal Heat Capacities of Aqueous Sodium Chloride ($\text{J mol}^{-1} \text{K}^{-1}$) Reported by Various Authors

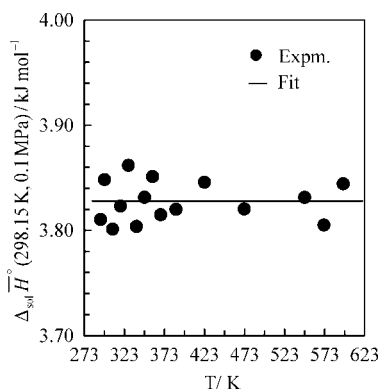
| T (K) | p_{sat} (MPa) | this study, p_{sat} | Pitzer et al., ^a p_{sat} | Archer, ^b p_{sat} | Shock et al., ^c p_{sat} | Gates et al. ^d (4 MPa) | Gates et al. ^e (4 MPa) |
|---------|------------------------|------------------------------|--|---------------------------------------|---|-----------------------------------|-----------------------------------|
| 298.15 | 0.1 | -78.4 | -83.8 | -85.0 | -85.3 | -82.4 | -81.9 |
| 323.15 | 0.1 | -63.5 | -62.6 | -60.1 | -61.3 | -72.9 | -71.6 |
| 348.15 | 0.1 | -67.5 | -63.3 | -60.6 | -60.8 | -66.8 | -68.3 |
| 373.15 | 0.1 | -80.4 | -76.7 | -74.2 | -71.9 | -68.3 | -76.2 |
| 398.15 | 0.2 | -102.4 | -100.0 | -97.8 | -92.8 | -83.7 | -97.6 |
| 423.15 | 0.5 | -136.8 | -132.6 | -132.2 | -126.1 | -119.2 | -133.2 |
| 448.15 | 0.9 | -190.8 | -178.8 | -181.2 | -169.8 | -181.3 | -184.3 |
| 473.15 | 1.6 | -277.8 | -245.5 | -254.6 | -231.7 | -278.5 | -257.6 |
| 498.15 | 2.5 | -424.1 | -346.7 | -366.1 | -330.4 | -431.1 | -387.8 |
| 523.15 | 4.0 | -684.9 | -517.8 | -554.8 | -500.4 | -663.0 | -618.1 |
| 548.15 | 5.9 | -1191.9 | -851.1 | -917.9 | -832.3 | | |
| 573.15 | 8.6 | -2313.5 | -1640.7 | -1756.4 | -1611.8 | | |
| 598.15 | 12.0 | -5389.3 | | -4585.9 | -4077.3 | | |

^a Pitzer et al.²⁴ ^b Archer.³⁰ ^c Shock et al.³³ estimated from low temperature data ($T \leq 423.15$ K). ^d Gates et al.²³ using A_j from Uematsu and Frank.³⁴ ^e Gates et al.²³ using A_j from Bradley and Pitzer.¹⁶

TABLE 5: Standard State Gibbs Free Energies of Solution of Sodium Chloride at p_{sat}

| T (K) | $\Delta_{\text{sol}}\bar{G}^{\text{oa}}$ (kJ mol^{-1}) | $\Delta_{\text{sol}}\bar{G}^{\text{ob}}$ (kJ mol^{-1}) | $\Delta_{\text{sol}}\bar{G}^{\text{oc}}$ (kJ mol^{-1}) | σ^d (kJ mol^{-1}) |
|---------|--|--|--|--|
| 298.15 | -8.995 | | | |
| 323.15 | -9.946 | | | |
| 348.15 | -10.673 | -10.778 | -10.674 | 0.018 |
| 373.15 | -11.185 | -11.365 | -11.205 | 0.020 |
| 398.15 | -11.477 | -11.625 | -11.456 | 0.040 |
| 423.15 | -11.527 | -11.588 | -11.530 | 0.049 |
| 448.15 | -11.301 | -11.406 | -11.305 | 0.061 |
| 473.15 | -10.745 | -10.911 | -10.765 | 0.063 |
| 498.15 | -9.773 | -10.062 | -9.745 | 0.085 |
| 523.15 | -8.251 | -8.754 | -8.277 | 0.119 |
| 548.15 | -5.956 | -6.847 | -5.918 | 0.259 |
| 573.15 | -2.506 | -4.006 | -3.118 | 0.399 |
| 598.15 | 2.784 | | | |

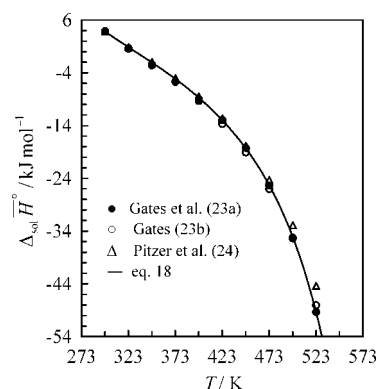
^a Calculated from thermal data, eq 20. ^b Liu and Lindsay.^{10,11} ^c Recalculated from Liu and Lindsay.^{10,11} ^d Estimated errors from the recalculated values of Liu and Lindsay.^{10,11}

**Figure 2.** Analysis of standard state molal enthalpies for a solution of sodium chloride at 298.15 K and 0.1 MPa from data at higher temperatures (eq 22). The least-squares fit has a slope of exactly zero (as required). The scale is greatly expanded.

be calculated from the enthalpy of solution at each experimental temperature:

$$\Delta_{\text{sol}}\bar{H}^{\circ}(298.15 \text{ K}) = \Delta_{\text{sol}}\bar{H}^{\circ}(T) - \int_{298.15}^T \Delta_{\text{sol}}\bar{C}_p^{\circ} dT - \int_{298.15}^T [\Delta_{\text{sol}}\bar{V}^{\circ} - T(\partial\Delta_{\text{sol}}\bar{V}^{\circ}/\partial T)_p](\partial p/\partial T)_{\text{sat}} dT \quad (22)$$

Values of $\Delta_{\text{sol}}\bar{H}^{\circ}(298.15 \text{ K})$ for sodium chloride calculated from experimental $\Delta_{\text{sol}}\bar{H}^{\circ}(T)$ at each experimental temperature

**Figure 3.** Standard state enthalpies of solution of sodium chloride at p_{sat} . Enthalpy data for Gates²³ are calculated from reported $\bar{C}_{p,2}^{\circ}$.

at p_{sat} are plotted in a greatly expanded scale in Figure 2. While such an analysis gives a better value for $\Delta_{\text{sol}}\bar{H}^{\circ}(298.15 \text{ K})$ than can be determined from measurements at that one temperature, it is used here to check the internal consistency of the adopted standard state heat capacities, the molal volumes, and their temperature derivatives at each temperature. The average of all of the calculated $\Delta_{\text{sol}}\bar{H}^{\circ}(298.15 \text{ K})$ values for NaCl, $3.829 \pm 0.021 \text{ kJ mol}^{-1}$, can be compared to the best direct measurements at 298.15 K of $3.884 \text{ kJ mol}^{-1}$ given in the NBS tables.²¹ The slope of the line in Figure 2 is zero (as required), and the average value of $\Delta_{\text{sol}}\bar{H}^{\circ}(298.15 \text{ K})$ agrees very well with the accepted 298.15 K NBS²¹ value to $\pm 55 \text{ J mol}^{-1}$.

The standard state Gibbs free energies of solution of sodium chloride at p_{sat} , $\Delta_{\text{sol}}\bar{G}^{\circ}(T, p_{\text{sat}})$, calculated from this study can be compared with those reported by Liu and Lindsay^{10,11} from 348 to 573 K, in Table 5. The calculated free energy values from this study agree with those of Liu and Lindsay^{10,11} to better than 1% on average up to 473 K. Above 473 K, the differences increase with temperature, and at $T > 473 \text{ K}$, the values of $\Delta_{\text{sol}}\bar{G}^{\circ}(T, p_{\text{sat}})$ from this study are consistently less negative than those reported by Liu and Lindsay.^{10,11} The differences could result from systematically propagated errors in the calculated $\Delta_{\text{sol}}\bar{G}^{\circ}(T, p_{\text{sat}})$ of Liu and Lindsay.^{10,11} This could in part be the result of extrapolation of their measured osmotic coefficients from the concentrated solutions ($m > 0.1$) to infinite dilution. The difficulties involving the extrapolations of various thermodynamic functions from regions outside the validity of a simple limiting law (Debye–Hückel) have been discussed in more detail elsewhere.^{7a,23}

The values of $\Delta_{\text{sol}}\bar{G}^{\circ}(T, p_{\text{sat}})$ for sodium chloride at p_{sat} were recalculated^{7a} from the vapor pressure measurements of Liu and

TABLE 6: Standard State Thermodynamic Properties of NaCl(aq)^a

| T (K) | $(\bar{H}_2^o(T) - \bar{H}_2^o(T_r))^b$ (kJ mol ⁻¹) | $(\bar{G}_2^o(T) - \bar{G}_2^o(T_r))^c$ (kJ mol ⁻¹) | \bar{S}_2^o (J mol ⁻¹ K ⁻¹) | $\bar{C}_{p,2}^o$ (J mol ⁻¹ K ⁻¹) | \bar{V}_2^o (cm ³ mol ⁻¹) | $(d\bar{V}_2^o/dT)_p^f$ (cm ³ mol ⁻¹ K ⁻¹) | $(d\bar{V}_2^o/dp)_T^f$ (cm ³ mol ⁻¹ MPa ⁻¹) |
|---------|--|--|--|--|--|---|---|
| 298.15 | 0.000 | 0.000 | 115.50 ^g | -78.4 | 18.8 | -4.845×10^{-2} | 3.801×10^{-2} |
| 323.15 | -1.711 | -2.806 | 109.95 | -63.5 | 17.9 | -4.898×10^{-2} | 4.285×10^{-2} |
| 348.15 | -3.327 | -5.486 | 105.11 | -67.5 | 16.7 | -6.583×10^{-2} | 4.916×10^{-2} |
| 373.15 | -5.156 | -8.044 | 100.02 | -80.4 | 15.0 | -8.967×10^{-2} | 5.854×10^{-2} |
| 398.15 | -7.410 | -10.465 | 94.16 | -102.4 | 12.5 | -1.247×10^{-1} | 7.426×10^{-2} |
| 423.15 | -10.349 | -12.723 | 86.99 | -136.8 | 9.1 | -1.783×10^{-1} | 1.043×10^{-1} |
| 448.15 | -14.351 | -14.779 | 77.80 | -190.8 | 3.9 | -2.635×10^{-1} | 1.559×10^{-1} |
| 473.15 | -20.021 | -16.572 | 65.49 | -277.8 | -3.8 | -4.055×10^{-1} | 2.525×10^{-1} |
| 498.15 | -28.395 | -18.011 | 48.28 | -424.1 | -16.0 | -6.568×10^{-1} | 4.441×10^{-1} |
| 523.15 | -41.349 | -18.955 | 23.02 | -684.9 | -36.3 | -1.138×10^0 | 8.559×10^{-1} |
| 548.15 | -62.575 | -19.178 | -16.35 | -1191.9 | -72.4 | -2.169×10^0 | 1.843×10^{-0} |
| 573.15 | -100.105 | -18.289 | -82.66 | -2313.5 | -144.3 | -4.771×10^0 | 4.633×10^{-0} |
| 598.15 | -174.070 | -15.598 | -207.37 | -5389.3 | -314.7 | -1.336×10^1 | 1.489×10^1 |

^a $T_r = 298.15$ K. ^b Equation 18. ^c Equation 20. ^d $\bar{S}_2^o(T) = [(\bar{H}_2^o(T) - \bar{H}_2^o(T_r)) - (\bar{G}_2^o(T) - \bar{G}_2^o(T_r))]/T + T_r \bar{S}_2^o(T_r)/T$. ^e Equation 19. ^f Calculated from the unified theory of electrolytes.¹ ^g From NBS tables.²¹

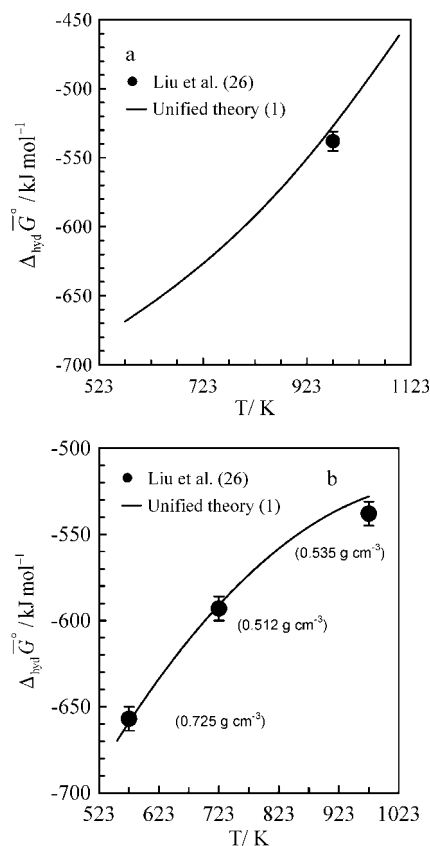


Figure 4. Comparison of predicted Gibbs free energies of hydration of sodium chloride from the unified theory of electrolytes¹ with results from Liu et al.²⁶ as a function of temperature at 225 MPa (a) and density (b).

Lindsay^{10,11} using the limiting law slope for osmotic coefficient A_ϕ obtained from the dielectric constant of water, as tabulated by Brady and Pitzer.¹⁶ The recalculated osmotic coefficients, ϕ , differed from the original data of Liu and Lindsay^{10,11} by less than 1%, well within the authors' reported errors. However, the small differences in osmotic coefficients can add up and propagate to give a difference as large as ± 0.015 in the activity coefficients in the more concentrated solutions.^{7a,23} The recalculated $\Delta_{\text{sol}} \bar{G}^o(T, p_{\text{sat}})$ from data of Liu and Lindsay^{10,11} are in good agreement with the results from this study up to 573 K to within the estimated uncertainties of their vapor pressure measurements data. These recalculated values of $\Delta_{\text{sol}} \bar{G}^o(T, p_{\text{sat}})$ at p_{sat} are listed in column 4 of Table 5, and in column 5, the

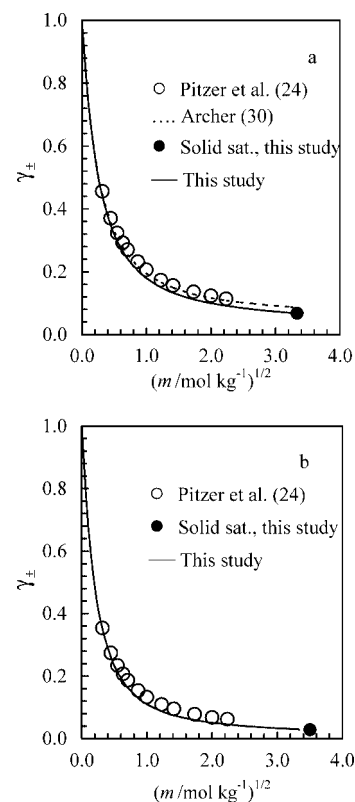


Figure 5. Comparison of stoichiometric mean activity coefficient of aqueous sodium chloride at p_{sat} with literature (a) 598.15 K and (b) 623.15 K.

estimated uncertainties for the recalculated values are listed. The resulting differences in the activity coefficients of saturated sodium chloride solution at 573.15 K are now only 0.008 units, which is gratifying in the light of the extremely difficult but different methods used to obtain the data. However, very small errors in the vapor pressure measurements are greatly magnified in calculation of second law enthalpy values and the agreement at the highest temperature, 573 K, is not as good.

The standard state enthalpies of solution of sodium chloride, $\Delta_{\text{sol}} \bar{H}^o(T, p_{\text{sat}})$, from this study can be compared with those reported in the literature up to 523.15 K and are summarized in Figure 3. The $\Delta_{\text{sol}} \bar{H}^o(T, p_{\text{sat}})$ calculated from the $\bar{C}_{p,2}^o$ values of NaCl(aq) reported by Gates et al.²³ at 4 MPa, and corrected to p_{sat} , indicate agreement at all temperatures from 398 to 523 K to better than 1%. This may be partly fortuitous in this

TABLE 7: Unified Theory Equations for the Thermodynamic Properties of Electrolytes^a

$$\Delta_{\text{h}}\bar{G}^*(T, p) = [\Delta_{\text{h}}\bar{G}^*(T_{\text{r}}, p_{\text{r}}) + C_{\text{S}}T_{\text{r}} - C_{\text{H}}]F_1(D) - C_{\text{S}}T + C_{\text{H}} \quad (23a)$$

$$\Delta_{\text{h}}\bar{G}^* = \Delta_{\text{h}}\bar{G}^{\circ} - \Delta_{\text{ss}}\bar{G}^{\circ} = \Delta_{\text{h}}\bar{G}^{\circ} - \nu RT \ln\left(\frac{m^{\circ}d^{\circ}RT}{1000p^{\circ}}\right) \quad (23b)$$

$$F_1(D) = \left[\frac{D(T, p) - 1}{D(T_{\text{r}}, p_{\text{r}}) - 1} \right] \left[\frac{D(T_{\text{r}}, p_{\text{r}})}{D(T, p)} \right] \quad (23c)$$

$$\bar{S}_2^{\circ}(T, p) = -(\Delta_{\text{h}}\bar{G}^*(T_{\text{r}}, p_{\text{r}}) + C_{\text{S}}T_{\text{r}} - C_{\text{H}})F_2(D) - C_{\text{S}} + \nu S^{\circ}(\text{g}) + \Delta_{\text{ss}}\bar{S}^{\circ} \quad (24a)$$

$$F_2(D) = \left[\frac{D(T_{\text{r}}, p_{\text{r}})}{D(T_{\text{r}}, p_{\text{r}}) - 1} \right] \left[\frac{1}{D(T, p)^2} \right] \left(\frac{\partial D}{\partial T} \right)_p \quad (24b)$$

$$\Delta_{\text{ss}}\bar{S}^{\circ} = -\nu R \left[\ln(RTd^{\circ}) + T \left(\frac{\partial \ln d^{\circ}}{\partial T} \right)_T + 1 \right] \quad (24c)$$

$$\begin{aligned} \bar{V}_2^{\circ}(T, p) = & \{ \bar{V}_2^{\circ}(T_{\text{r}}, p_{\text{r}}) - (\Delta_{\text{h}}\bar{G}^*(T_{\text{r}}, p_{\text{r}}) + \\ & C_{\text{S}}T_{\text{r}} - C_{\text{H}})F_3(T_{\text{r}}, p_{\text{r}}) \} F_1(T, p) + (\Delta_{\text{h}}\bar{G}^*(T_{\text{r}}, p_{\text{r}}) + \\ & C_{\text{S}}T_{\text{r}} - C_{\text{H}})F_3(T, p) + [\Delta_{\text{ss}}\bar{V}^{\circ}(T, p) - \Delta_{\text{ss}}\bar{V}^{\circ}(T_{\text{r}}, p_{\text{r}})F_1(T, p)] \end{aligned} \quad (25a)$$

$$F_3(D) = \left[\frac{D(T_{\text{r}}, p_{\text{r}})}{D(T_{\text{r}}, p_{\text{r}}) - 1} \right] \left[\frac{1}{D(T, p)^2} \right] \left(\frac{\partial D}{\partial p} \right)_T \quad (25b)$$

$$\Delta_{\text{ss}}\bar{V}^{\circ} = \nu RT \left(\frac{\partial \ln(d^{\circ})}{\partial p} \right)_T \quad (25c)$$

$$\bar{C}_{p,2}^{\circ}(T, p) = -T(\Delta_{\text{h}}\bar{G}^*(T_{\text{r}}, p_{\text{r}}) + C_{\text{S}}T_{\text{r}} - C_{\text{H}})F_4(D) + \nu \bar{C}_p^{\circ}(\text{g}) + \Delta_{\text{ss}}\bar{C}_p^{\circ} \quad (26a)$$

$$F_4(D) = \left(\frac{D(T_{\text{r}}, p_{\text{r}})}{D(T_{\text{r}}, p_{\text{r}}) - 1} \right) \left(\frac{1}{D(T, p)^2} \right) \left[\left(\frac{\partial^2 D}{\partial T^2} \right)_p - \frac{2}{D(T, p)} \left(\frac{\partial D}{\partial T} \right)_p \right] \quad (26b)$$

$$\Delta_{\text{ss}}\bar{C}_p^{\circ} = -\nu R \left[1 - 2T\alpha^{\circ} - T^2 \left(\frac{\partial \alpha^{\circ}}{\partial T} \right)_p \right] \quad (26c)$$

$$\alpha^{\circ} = -\frac{1}{d^{\circ}} \left(\frac{\partial d^{\circ}}{\partial T} \right)_p \quad (26d)$$

^a Definition of symbols: D is the bulk dielectric constant of the solvent; C_{S} and C_{H} are constant parameters specific to each solute; ν is the stoichiometric number of ions in the solute; m° is equal to 1 mol/kg; d° is the density of the pure solvent in g/cm³; p° is equal to 0.1 MPa; α° is the coefficient of thermal expansion of water, $S_p^{\circ}(\text{g})$ and $C_p^{\circ}(\text{g})$ are the molar entropies and molar heat capacities of the gaseous ions; $\Delta_{\text{ss}}\bar{X}^{\circ}$, $X = V, C, S, G$, are the standard state correction terms.

temperature range in light of the uncertainties of the results of Gates et al.²³ at low molalities, and extrapolated further to infinite dilution.

The values for $\Delta_{\text{sol}}\bar{H}^{\circ}(T, p_{\text{sat}})$ of sodium chloride from this study are compared with the compilation of Pitzer et al.²⁴ from 298 to 573 K. This comparison indicates agreement to within their stated uncertainties, ($\leq 3\%$), up to 473.15 K. Above 473 K, their results are consistently less negative than the present research and at 573 K the difference is well outside their estimated uncertainty; the results are also not in agreement with the enthalpies calculated from the more recent low pressure measured heat capacities.²³ These detailed comparisons are important because NaCl(aq) is such a key electrolyte and the new high dilution data reported here will be extremely valuable in recalculating previous higher concentration data.

The $\bar{C}_{p,2}^{\circ}$ values from this study are compared with the published results in the literature in Table 4, and compare well with those of Gates et al.²³ from 298 to 523 K to within their stated uncertainties.

Recently, we reported a new functional form for the Gibbs free energy of hydration of electrolytes in aqueous solutions, a unified theory of electrolytes (UTE) for prediction of the standard state thermodynamic properties of electrolytes to extreme temperatures and pressures.¹ This functional form not only fits direct measurements of Gibbs free energies of solutions over a wide range of temperature and pressure up to the critical point of water and even to the supercritical region, but it also acts as an equation of state in the sense that its derivatives account for all known measurements of standard state partial molal entropies and volumes of +1, +2, and +3 electrolytes. It is a simple model to implement and corrects empirically for deficiencies of the classical Born model.

The UTE model requires only two parameters, C_{H} and C_{S} , for each electrolyte at temperatures above 298.15 K. Once these parameters were fixed, the model has been used to predict the standard state partial molal Gibbs free energies of electrolytes up to supercritical temperatures.¹

The temperature and pressure behavior of electrolytes can now be accurately predicted from existing low temperature data alone. The model has also been used successfully to predict and tabulate the standard state partial molal entropies, heat capacities, and volumes of 15 important electrolytes to the highest temperatures of the experimental data, 623 K.^{1,7a}

The experimental data from this study were used to predict the Gibbs free energies of hydration of NaCl up to 1100 K from

TABLE 8: Standard State Gibbs Free Energies of Formation of NaCl(aq) at p_{sat}^a

| T (K) | $\Delta_{\text{f}}\bar{G}_2^{\circ}(\text{NaCl, aq})$ (kJ mol ⁻¹) |
|---------|---|
| 298.15 | -393.133 ^b |
| 323.15 | -391.887 |
| 348.15 | -390.335 |
| 373.15 | -388.509 |
| 398.15 | -386.420 |
| 423.15 | -384.062 |
| 448.15 | -381.413 |
| 473.15 | -378.425 |
| 498.15 | -375.016 |
| 523.15 | -371.052 |
| 548.15 | -366.313 |
| 573.15 | -360.411 |
| 598.15 | -352.658 |
| 623.15 | (-339.443) ^c |

^a Based on $\Delta_{\text{f}}\bar{G}^{\circ}$ of elements equal to zero at 298.15 K. ^b NBS tables.²¹ ^c Predicted from the unified theory of electrolytes.¹

the UTE model (Table 7), using dielectric constants of water from Archer and Wang²⁵ and other auxiliary data from the literature.^{5,21} These Gibbs free energies of hydration at different pressures and densities compare well with reported values by Lin et al.²⁶ obtained from ab initio calculations. The predicted values were calculated at very small temperature intervals, and the resulting smooth curve is given in Figure 4.

The Gibbs free energies of formation of NaCl(aq) from 298.15 to 623.15 K listed in Table 8 are calculated as follows:

$$\Delta_f \bar{G}^\circ(\text{NaCl, aq}) = \bar{G}_2^\circ(\text{NaCl, aq}) - G^\circ(\text{Na, r}) - 1/2 G^\circ(\text{Cl}_2, \text{g}) \quad (23)$$

where $\bar{G}_2^\circ(\text{NaCl, aq})$ are the standard state partial molal Gibbs free energies from Table 6 and G° are molar Gibbs free energies from the literature.⁵

Finally, it is important to note that $\Delta_{\text{sol}} \bar{G}^\circ(T, p_{\text{sat}})$ derived from thermal measurements unambiguously defines the activity of the solute in a solid-saturated solution of the electrolyte at any temperature:

$$\Delta_{\text{sol}} \bar{G}^\circ = -\nu RT \ln(\gamma_{\text{sat}} m_{\text{sat}}) \quad (24)$$

where γ_{sat} and m_{sat} are the activity coefficient and the solubility of the solid-saturated solution at temperature T , respectively.

As an illustration, the values for γ_{sat} of NaCl(aq) at p_{sat} for temperatures of 598.15 and 623.15 K were calculated from eq 24 using solubility data in the literature.²⁷ These activity coefficients at solid-saturated solution, γ_{sat} , can be extended to all concentrations using the modified Meissner model.^{28,29} This is a simple empirical equation of an extended Debye–Hückel form. The Meissner model provides the activity coefficients at all concentrations at a given T and p when an experimental value at only one concentration is given at the same T and p . The activity coefficients of NaCl(aq) at all concentrations ($0 \leq m \leq m_{\text{sat}}$) at p_{sat} calculated from this study are compared with the corresponding literature values^{24,30} in Figure 5. The activity coefficients of NaCl(aq) reported by Pitzer et al.²⁴ are calculated from apparent relative molal enthalpies, L_φ . The experimental L_φ must be extrapolated to infinite dilution in order to calculate the γ_{\pm} , and if the extrapolation of L_φ to infinite dilution is significantly in error, even precise enthalpy of dilution measurements will produce large errors in calculated activity coefficients.³¹ Moreover, the extrapolation of L_φ to infinite dilution even at the low concentrations ($\geq 0.1 m$) has been shown³² to be model dependent and, therefore, the activity coefficients derived from them as well. Over the whole concentration range, the activity coefficients of aqueous sodium chloride from this study are in reasonable agreement, within the combined uncertainty, with those reported in the literature.^{24,30}

5. Conclusion

The standard state thermodynamic properties for an aqueous sodium chloride solution from this study are in agreement within the uncertainties resulting from extrapolation to infinite dilution from relatively concentrated solutions (and for pressure corrections) in the published literature. The standard state thermodynamic properties for NaCl(aq) from this study are recommended because the results are based on measurements down to $10^{-3} m$, from which more reliable extrapolations to standard state conditions are possible, and which are not sensitive to various extrapolation models. Others can now use these standard state properties to calculate a large body of data on the

thermodynamics of more concentrated solutions, and these are some of the most useful results of the present research.

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