

# Thermodynamic Properties of the NaCl + H<sub>2</sub>O System

## II. Thermodynamic Properties of NaCl(aq), NaCl·2H<sub>2</sub>O(cr), and Phase Equilibria

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Equations that described the thermodynamic properties of the NaCl + H<sub>2</sub>O system were obtained from a fit to experimental results for this system. The experimental results included in the fit spanned the range of temperature of approximately 250 to 600 K and, where available, the range of pressure from the vapor pressure of the solution to 100 MPa. New equations and/or values for the following properties are given in the present work: 1)  $\Delta_f G_m^\circ$  and  $\Delta_f H_m^\circ$ , for formation from the elements, for NaCl(cr) for 298.15 K and 0.1 MPa, 2)  $\Delta_f G_m^\circ$  and  $\Delta_f H_m^\circ$  from the elements, as well as  $S_m^\circ$  and  $C_{p,m}^\circ$ , all for 298.15 K, 0.1 MPa, for NaCl·2H<sub>2</sub>O(cr), 3) the change in chemical potential for both NaCl and H<sub>2</sub>O in NaCl(aq) as a function of temperature, pressure, and molality, valid from 250 to 600 K and, where available, from the vapor pressure of the solution to 100 MPa. Comparison of the accuracies of experimental methods, where possible, has also been performed.

Keywords: activity coefficient; apparent molar properties; aqueous; compressibility; dehydration; density; enthalpy; equation of state; expansivity; formation properties; Gibbs energy; heat capacity; osmotic coefficient; partial molar properties; sodium chloride; sodium chloride dihydrate; solubility; thermodynamics; vapor pressure.

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## List of Symbols

$A_\phi, A_H, A_C, A_V$	Debye-Hückel coefficients for osmotic coefficient, apparent molar enthalpy, apparent molar constant-pressure heat capacity and apparent molar volume.
$a_w$	Activity of water in a solution.
$b$	A constant in Pitzer's ion-interaction equation, chosen to be $1.2 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ .
$C_p^\circ$	$1.0 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .
$C_{p,\phi}$	Apparent molar constant-pressure heat capacity.
$C_{p,m,2}^\circ$	Standard-state constant-pressure molar heat capacity of the solute.
$C_{p,m,cr}^\circ$	Standard-state constant-pressure molar heat capacity of a crystalline phase.
$c_{p,s}$	Specific constant-pressure heat capacity of a solution.
$c_{p,w}$	Specific constant-pressure heat capacity of one kg of water.
$C_p(m_r)$	Constant-pressure heat capacity of a quantity of solution of molality $m_r$ and containing one kg of solvent.
$C_{MX}, C_{MX}^{(0)}, C_{MX}^{(1)}$	Ion-interaction parameters for Pitzer's equation.
$G$	Gibbs energy (extensive).
$G^{\text{ex}}$	Excess Gibbs energy of a solution (extensive).
$G_{m,1}^\circ, G_{m,2}^\circ$	Standard-state molar Gibbs energy of the solvent and the solute, respectively.
$G_{m,cr}^\circ$	Standard-state molar Gibbs energy of a crystalline phase.
$G_{m,1,g}^\circ$	Standard-state molar Gibbs energy of the solvent gas phase.
$H_{m,cr}^\circ$	Standard-state molar enthalpy of a crystalline phase.
$I$	Ionic strength ( $I = 0.5\sum m_i z_i^2$ ).
$K_{\phi,s}^\circ$	Apparent molar isentropic compressibility.
$L^\circ$	$1.0 \text{ kJ}\cdot\text{mol}^{-1}$ .
$L_\phi$	Relative apparent molar enthalpy.
$L_{m,1}$	Partial molar enthalpy of the solvent.
$M_1$	Molar mass of the solvent, $18.0153 \times 10^{-3} \text{ kg}\cdot\text{mol}^{-1}$ .
$m$	Molality.
$m^\circ$	$1.0 \text{ mol}\cdot\text{kg}^{-1}$ .
$m_r$	Reference molality.
$n_i$	Moles of the $i$ 'th substance.
$p$	Pressure.
$p^\circ$	$1.0 \text{ MPa}$ .
$p_w$	Vapor pressure of pure water.
$p_r$	Reference pressure; as a subscript to a property it denotes that the value of the property is that for the reference pressure.
$R$	Gas constant, $8.3144 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}$ .
$S^{\text{ex}}$	Excess entropy of a solution (extensive).

$S_{m, cr}^{\circ}$	Standard-state molar entropy of a crystalline phase.
$S_{1, m}^{\circ}, S_{2, m}^{\circ}$	Standard-state molar entropy of the solvent and the solute.
$T$	Temperature.
$T^{\circ}$	1.0 K.
$T_r$	A reference temperature; as a subscript to a property it denotes that the value of the property is that for the reference temperature.
$u$	Speed of sound.
$V^{\circ}$	1.0 cm <sup>3</sup> ·mol <sup>-1</sup> .
$V_{\phi}$	Apparent molar volume.
$V_{m, 2}^{\circ}$	Standard-state molar volume of the solute.
$V_{m, cr}^{\circ}$	Standard-state molar volume of a crystalline phase.
$V(m_r)$	Volume of a quantity of solution of molality $m_r$ and containing 1 kg of solvent.
$z_M, z_X$	The charges of ions M and X.
$\alpha$	A constant in Pitzer's equation, chosen to be 2.0 kg <sup>1/2</sup> ·mol <sup>-1/2</sup> .
$\alpha_2$	A constant in revised Pitzer's equation, chosen to be 2.5 kg <sup>1/2</sup> ·mol <sup>-1/2</sup> .
$\alpha_s$	Expansivity of a solution.
$\beta$	Isothermal compressibility.
$\beta_s$	Isentropic compressibility.
$\beta_{MX}^{(0)}, \beta_{MX}^{(1)}$	Ion-interaction parameters in Pitzer's ion interaction equation.
$\Delta_f G_m^{\circ}$	The standard-state molar Gibbs energy change for formation from the elements.
$\Delta_{dec} G_m^{\circ}$	The standard-state molar Gibbs energy change for decomposition of a material.
$\Delta_{sol} G_{anhydrous}^{\circ}$	The standard-state molar Gibbs energy change for solution of an anhydrous solute.
$\Delta_{sol} G_{dihydrate}^{\circ}$	The standard-state molar Gibbs energy change for solution of a dihydrate solute.
$\Delta_f H_m^{\circ}$	The standard-state molar enthalpy change for formation from the elements.
$\Delta_{fus} T$	The difference in freezing point temperature for a solvent from a solution and the pure solvent.
$\Delta_{dil} V_{\phi}$	The change in apparent molar volume for a change in molality.
$\delta$	The average deviation (unweighted) of a set of experimental results from the fitted equation.
$\gamma_{\pm}$	Stoichiometric activity coefficient of the solute.
$\phi$	Osmotic coefficient.
$\rho$	Density.
$\rho^{\circ}$	1.0 g·cm <sup>-3</sup> .
$\sigma_{fit}$	The root mean square difference (un-

weighted) of a set of experimental results from the fitted equations.

$\nu$   
 $\nu_M, \nu_X$

$\nu_M + \nu_X$

The stoichiometric number of M and X ions in the electrolyte  $M\nu_M X\nu_X$ .

$v_w$

Volume of one kg of water.

## 1. Introduction

Two recent treatments of the thermodynamic properties of NaCl(aq) have been given by Pitzer *et al.*<sup>1</sup> (which incorporated the volumetric-property equation of Rogers and Pitzer<sup>16</sup>) and by Clarke and Glew.<sup>2</sup> The Pitzer *et al.* equation was a representation of experimental values ranging from the freezing point of the solution to 573 K and to pressures of 100 MPa. Their equation used two sets of parameters, one for low temperatures, the other, comprised of 53 least-squares estimated parameters, for the entire range of temperature. The Pitzer *et al.* treatment represented the available results, for temperatures greater than 373 K, within reasonable agreement of the experimental uncertainties. However, as Clarke and Glew noted, various measurements at near-ambient temperatures, primarily enthalpy and free energy results, were not represented within experimental errors. Clarke and Glew gave a representation of experimental results for temperatures less than 423 K that represented these lower temperature results more accurately than did the Pitzer *et al.* equation. The Clarke and Glew equation contained 35 variable parameters and did not attempt to represent the pressure dependence of the thermodynamic properties, i.e. volumetric results. Clarke and Glew obtained this improvement over the Pitzer *et al.* treatment, in part, by including terms of  $Dm^4$  and  $Em^5$  to the Pitzer equation for excess Gibbs energy. Both of these representations satisfied their respective authors' goals. Since the time the Pitzer *et al.* equation was published, a significant number of experimental results for temperatures greater than 373 K, many of them of significantly greater accuracy than the previously available results, has become available. Not all of these high-temperature results agreed with the Pitzer *et al.* equation within expected experimental uncertainties. For many purposes, but not all, the small discrepancies of the Pitzer *et al.* equation from the experimental results is not a significant problem.

One purpose for which these discrepancies are important is the determination of instrument accuracies by comparison with previous experiment. With the vast  $T, p$  space available to high-temperature experiments today, comparison at specific  $T, p, m$  points, as is done with experimental methods that provide values only for very-near-ambient conditions, is unnecessarily cumbersome. What is desired is an equation that represents all of the best measurements within their accuracies and that spans this  $T, p$  space so that comparisons with new experiments may be made without a constant fussing with exact

temperature and pressure settings. A second purpose is to supply values with which instruments that require a chemical standard for calibration may be so calibrated. Often a chemical-standard calibration may consume less resource than an absolute calibration and give an adequate degree of experimental accuracy, provided sufficiently accurate values for the properties of the chemical standard are available.

A few examples are described here. In mass-flow relative heat-capacity calorimeters it is fairly well known that systematic errors arise from unaccounted heat transfers between calorimeter and surroundings. Because the time and costs of determining the heat losses in this type of calorimeter are far from trivial, calls for chemical standard calibrations of these calorimeters have appeared throughout the literature. Less well known are systematic differences that can appear in results obtained with high-temperature enthalpy of dilution calorimeters. An example of systematic differences between high-temperature enthalpy of dilution calorimeters is given in Appendix 2.

Because NaCl(aq) is an ubiquity in many realms of nature, and is inexpensive and easy to purify, it is often chosen as the first system with which to demonstrate a new instrument. As such, there is an extent of reported experimental measurements for NaCl(aq) that is greater and more accurate than that available for any other two-component chemical system. (This is the author's perception and so could be entirely incorrect.) In the present work it was desired to generate a representation for NaCl(aq) that represents the best available experimental results for NaCl(aq) within their uncertainties, so that the above two purposes, these being perhaps the most demanding uses of such a representation, may be satisfied.

Three equations were used to represent experimental results for the NaCl + H<sub>2</sub>O system. These were: 1) the equation of state for water given by Hill<sup>3</sup>; 2) a representation for the change in chemical potential of NaCl(cr) as a function of temperature,<sup>4</sup> the pressure dependence of which is described here; and, 3) an equation for the changes in chemical potentials for the components of the aqueous solution. Section 2 describes the representation of the chemical potential for NaCl(cr). Section 3 gives a value of the density of NaCl·2H<sub>2</sub>O, obtained from fitting experimental observations of a univariant equilibria, a value of the compressibility, and an estimate of the heat capacity of NaCl·2H<sub>2</sub>O(cr). The equation for the changes in chemical potentials of the solution components with respect to temperature, pressure, and molality for NaCl(aq) was obtained from a global fit to values from thermodynamic measurements for the aqueous system. The matrix of experimental values contained measurements of volumetric properties, solvent and solute activities, enthalpy changes, heat capacities, and solubilities from the solid phases. Because one of the intended purposes of the present work is to provide assistance in the calibration of instruments, certain types of data have not been included in the representation for NaCl(aq). Generally, these are results of measurements that can be termed relative, in other words, the measurement of a

property for NaCl(aq) relative to another aqueous electrolyte. The equation for NaCl(aq) and its agreement with experimental values is described in Sec. 4. Section 5 describes the thermodynamic properties for some of the invariant and univariant equilibria of the NaCl + H<sub>2</sub>O system. A program that calculates values of the thermodynamic properties of NaCl(aq) will be available from the author for a reasonable period of time. A few calculated values, presented only as a means to test the validity of coding, (Tables 7 through 10) may be found at the end of the paper.

## 2. Thermodynamic Properties of NaCl(cr)

Calorimetric results for NaCl(cr), for a 0.1 MPa nominal isobar, were recently reviewed and represented.<sup>4</sup> That review was performed because of the significant differences of "critically evaluated" values of the heat capacity of NaCl(cr) from the experimental results. Because the difference between the different sets of heat capacities was about 1 per cent near 270 K, and larger at lower temperatures, the 298.15 K molar entropy of NaCl(cr), 72.27 J·K<sup>-1</sup>·mol<sup>-1</sup>, cannot be claimed to be more accurate than ± 1 per cent. Details of the NaCl(cr) representation were given in Ref. 4.

Bockris *et al.*<sup>5</sup> measured the expansion of NaCl(cr) from 300 K to near the melting point. They gave the density of NaCl(cr) as:

$$\rho/\rho^\circ = a + b(T - 273.15 \text{ K})/T^\circ - c[(T - 273.15 \text{ K})/T^\circ]^2 \quad (1)$$

where  $T^\circ$  and  $\rho^\circ$  are 1.0 K and 1.0 g·cm<sup>-3</sup>, respectively, and  $a$ ,  $b$ , and  $c$  are given in Table 1. The compressibility of NaCl(cr) was taken to be  $4.2 \times 10^{-5}$  MPa<sup>-1</sup>.<sup>6</sup> The calculations discussed in this paper were not very sensitive to this value.

TABLE 1. Parameters for Eq. (1)

Parameter	Value
$a$	2.168
$b$	$-1.267 \times 10^{-4}$
$c$	$-1.754 \times 10^{-7}$

The equation for the molar Gibbs energy of NaCl(cr) is:

$$G_{m,cr}^\circ = G_{m,cr,T_r,p_r}^\circ - (T - T_r)S_{m,cr,T_r,p_r}^\circ + \int_{T_r}^T C_{p,m,cr,p_r}^\circ dT - T \int_{T_r}^T (C_{p,m,cr,p_r}^\circ / T) dT + \int_{p_r}^p V_{m,cr}^\circ dp \quad (2)$$

where  $T_r$  and  $p_r$  were chosen as 298.15 K and 0.1 MPa. The integrals of the molar heat capacity were calculated from the spline given in Ref. 4 and the molar volume was calculated from Eq. (1) and the compressibility.  $G_{m,cr,T_r,p_r}^\circ$  is, of course, not experimentally accessible. (The value of  $S_{m,cr,T_r,p_r}^\circ$  used in the calculations was 72.2653 J·K<sup>-1</sup>·mol<sup>-1</sup> as obtained from the equations described in Ref. 4.) The thermodynamic properties for formation

( $\Delta_f G_m^\circ$ ,  $\Delta_f H_m^\circ$ ) of both NaCl(cr) and NaCl·2H<sub>2</sub>O(cr) for 298.15 K and 0.1 MPa are discussed in a subsequent section.

### 3. Thermodynamic Properties of NaCl·2H<sub>2</sub>O(cr)

There are few accurate measurements of the thermodynamic properties of NaCl·2H<sub>2</sub>O(cr). A value for  $C_{p,m,NaCl\cdot 2H_2O(cr)}^\circ$  for 298.15 K, 0.1 MPa was estimated to be 137 J·K<sup>-1</sup>·mol<sup>-1</sup> by combining the value of  $C_{p,m,cr}^\circ$  for NaCl(cr) with 87 J·K<sup>-1</sup>·mol<sup>-1</sup>, an approximate value for the heat capacity contribution for two waters of hydration. This value was obtained by comparison with other electrolytes; the dihydrates of MgCl<sub>2</sub>, BaCl<sub>2</sub> and CaSO<sub>4</sub>, the monohydrates of MgCl<sub>2</sub> and MgSO<sub>4</sub> and the hemihydrate of CaSO<sub>4</sub> were used to obtain this value. This value was slightly larger than that used by Pabalan and Pitzer<sup>171</sup> in their treatment of mineral solubilities. Pabalan and Pitzer obtained their value, 83 J·K<sup>-1</sup>·mol<sup>-1</sup>, from the heat capacity values for the mono-, di-, tetra- and hexa-hydrates of MgCl<sub>2</sub> and the mono- and hexa-hydrates of MgSO<sub>4</sub>. The more hydrated salts were not used to obtain the value used here because of the possibility of a non-identical increment for each additional stoichiometric mole of water. A value for  $S_{m,NaCl\cdot 2H_2O(cr)}^\circ$  for 298.15 K and 0.1 MPa, 162.5 J·K<sup>-1</sup>·mol<sup>-1</sup>, was determined from fitting to the experimental solubilities of the dihydrate phase, decomposition pressures, and thermodynamic results for NaCl(aq). The density of NaCl·2H<sub>2</sub>O(cr), for 273.15 K and 0.1 MPa, 1629 kg·m<sup>-3</sup>, was determined from the experimental determinations of the univariant equilibrium: NaCl(cr) + NaCl·2H<sub>2</sub>O(cr) + NaCl(aq). The compressibility of NaCl·2H<sub>2</sub>O(cr) was taken to be 4.8 × 10<sup>-5</sup> MPa<sup>-1</sup>.<sup>7</sup> Only the dihydrate appears in the literature; this, of course, cannot be taken to mean that other hydrates do not exist.

## 4. Thermodynamic Properties of NaCl(aq)

### 4.1. Description of Equations

A modified form<sup>8</sup> of the ion-interaction model described by Pitzer<sup>9</sup> was used in the present work to express the thermodynamic properties of the solution. Description of Pitzer's equation can be found elsewhere<sup>10</sup> and so only sufficient exposition to allow use of the present equations is presented here. Pitzer's equation for the excess Gibbs energy per kg of water,  $n_w$ , is:

$$\frac{G^\alpha}{n_w RT} = -4|z_M z_X| A_\phi \ln(1 + bI^{1/2}) + 2\nu_M \nu_X (m^2 B_{MX} + m^3 \nu_M z_M C_{MX}) \quad (3)$$

$$B_{MX} = \beta_{MX}^{(0)} + 2\beta_{MX}^{(1)} [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] / (\alpha^2 I). \quad (4)$$

In Eqs. (3, 4),  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$ , and  $C_{MX}$  are adjustable parameters (ion-interaction parameters) that are dependent on temperature and pressure,  $z_M$  and  $z_X$  are the

charges of the cation and the anion, respectively,  $\alpha$  and  $b$  were chosen to be constants with the values 2.0 kg<sup>1/2</sup>·mol<sup>-1/2</sup> and 1.2 kg<sup>1/2</sup>·mol<sup>-1/2</sup>, respectively, and  $\nu_M$  and  $\nu_X$  are the stoichiometric numbers of cations and anions formed upon dissociation.  $A_\phi$  is the Debye-Hückel coefficient for the osmotic coefficient.

In the present work, as in previous work for NaBr(aq),<sup>8</sup> an ionic-strength dependence of the third virial coefficient was assumed. It was further assumed that the functional form of the ionic-strength dependence of the third virial coefficient was similar in nature to that for the second virial coefficient, for the osmotic coefficient. In other words, the third virial coefficient contribution for the osmotic coefficient, was taken to have the an ionic-strength dependence given by the general form:

$$(C_{MX}^{(0)} + C_{MX}^{(1)} \exp(-\alpha_2 I^{1/2})).$$

This assumption results in an ionic-strength dependent  $C_{MX}$  that is expressed as:

$$C_{MX} = C_{MX}^{(0)} + 4C_{MX}^{(1)} [6 - (6 + 6\alpha_2 I^{1/2} + 3\alpha_2^2 I + \alpha_2^3 I^{3/2}) \exp(-\alpha_2 I^{1/2})] / (\alpha_2^4 I^2), \quad (5)$$

where  $C_{MX}^{(0)}$  and  $C_{MX}^{(1)}$  are adjustable parameters, dependent on temperature and pressure. This ionic-strength dependence of the third virial coefficient significantly improved the quality of fit for NaCl(aq) compared to that obtained with Eqs. (3, 4). As will be shown below, the quality of fit of the near-ambient results was similar to that obtained by Clarke and Glew,<sup>2</sup> but was achieved without the added difficulty of controlling the behavior of terms in  $D_{MX} m^4$  and  $E_{MX} m^5$  appended to Eq. (3), especially as the solubility of NaCl(aq) approximately doubles from near ambient to 600 K. The difficulties associated with representations obtained by means of high-order polynomials is well recognized.<sup>11</sup>

For NaCl(aq), the optimum value of  $\alpha_2$  was found to be near 2.5 kg<sup>1/2</sup>·mol<sup>-1/2</sup>. This value gave the best results for fitting the experimental results for temperatures from the freezing point to the 0.1 MPa boiling point of the solution. This value of  $\alpha_2$  can also be shown to improve representation of the experimental osmotic coefficient results from Rard and Miller<sup>12</sup> for Na<sub>2</sub>SO<sub>4</sub> (aq). The systematic pattern of residuals that was present when the Na<sub>2</sub>SO<sub>4</sub> (aq) results were fitted using  $\alpha$  equal to either 2.0 kg<sup>1/2</sup>·mol<sup>-1/2</sup>, or 1.4 kg<sup>1/2</sup>·mol<sup>-1/2</sup> as in Ref. 13, and not using the ionic-strength dependence of the third virial coefficient was not present when using Eqs. (3-5) and the values for  $\alpha_2$  and  $\alpha$  of 2.5 and 2.0 kg<sup>1/2</sup>·mol<sup>-1/2</sup>, respectively, for the representation. A value of 2.0 kg<sup>1/2</sup>·mol<sup>-1/2</sup> was used for  $\alpha_2$  in a previous representation for NaBr(aq).<sup>8</sup> However, the quality of representation of the experimental results for NaBr(aq) was approximately the same when refitted using 2.5 kg<sup>1/2</sup>·mol<sup>-1/2</sup> for  $\alpha_2$ . The lack of sensitivity of the quality of fit for NaBr(aq) on the exact value of  $\alpha_2$  reflected, in part, the lesser accuracies of the experimental results for NaBr(aq) as compared to NaCl(aq) and Na<sub>2</sub>SO<sub>4</sub>(aq).

The excess Gibbs energy,  $G^E$ , is related to the Gibbs energy of the solution,  $G$ , as:

$$G^E = G - n_1 G_{m,1}^\circ - n_2 G_{m,2}^\circ + RT\nu m_2(1 - \ln m/m^\circ) \quad (6)$$

where  $n_1$  and  $n_2$  are the number of moles of solvent and solute, respectively,  $m$  is the stoichiometric molality,  $\nu$  is the number of ions formed upon complete dissociation of the electrolyte and  $m^\circ$  is  $1.0 \text{ mol}\cdot\text{kg}^{-1}$ . The standard-state molar Gibbs energy for solvent and solute are  $G_{m,1}^\circ$  and  $G_{m,2}^\circ$ , respectively. The standard states were chosen to be pure liquid for the solvent and the hypothetical one molal ideal solution for the solute, at the temperature and pressure of interest, rather than at the temperature of interest and an arbitrary pressure. The Debye-Hückel coefficients used in the present work were calculated from the equation of state for water from Hill,<sup>3</sup> the dielectric-constant equation from Archer and Wang,<sup>14</sup> and the definitions given by Bradley and Pitzer.<sup>15</sup>

Appropriate differentiation of Eq. (3-5) leads to the osmotic coefficient,  $\phi$ , and the stoichiometric activity coefficient,  $\gamma_{\pm}$ :

$$\begin{aligned} \phi - 1 = & -|z_M z_X| A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} \\ & + m \frac{2\nu_M \nu_X}{\nu} \left( \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2}) \right) \\ & + m^2 \frac{4\nu_M^2 \nu_X}{\nu} \left( C_{MX}^{(0)} + C_{MX}^{(1)} \exp(-\alpha_2 I^{1/2}) \right) \quad (7) \end{aligned}$$

$$\begin{aligned} \ln \gamma_{\pm} = & -|z_M z_X| A_\phi \left( \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right) + \\ & m \frac{2\nu_M \nu_X}{\nu} \left\{ 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{\alpha_2 I} \left[ 1 - \left( 1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2} \right) \exp(-\alpha I^{1/2}) \right] \right\} \\ & + m^2 \frac{2\nu_M^2 \nu_X z_M}{\nu} \left\{ 3C_{MX}^{(0)} + 4C_{MX}^{(1)} \left[ 6 - (6 + 6\alpha_2 I^{1/2} \right. \right. \\ & \left. \left. + 3\alpha_2^2 I + \alpha_2^3 I^{3/2} - \alpha_2^4 I^2/2) \exp(-\alpha_2 I^{1/2}) \right] / (\alpha_2^4 I^2) \right\}. \quad (8) \end{aligned}$$

The osmotic coefficient is related to the activity of water as:  $\phi = -\ln a_w (M_1 \nu m)^{-1}$ , where  $M_1$  is the molar mass of the solvent. The relative apparent molar enthalpy,  $L_\phi$ , is:

$$\begin{aligned} L_\phi = & \nu |z_M z_X| A_H \ln(1 + bI^{1/2})/2b \\ & - 2\nu_M \nu_X RT^2 (m B_{MX}^L + m^2 \nu_M z_M C_{MX}^L) \quad (9) \end{aligned}$$

where:

$$\begin{aligned} B_{MX}^L = & \left( \frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_P + 2 \left( \frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_P \\ & \times [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2}) / \alpha^2 I] \quad (10) \end{aligned}$$

$$\begin{aligned} C_{MX}^L = & \left( \frac{\partial C_{MX}^{(0)}}{\partial T} \right)_P + 4 \left( \frac{\partial C_{MX}^{(1)}}{\partial T} \right)_P \times \\ & [6 - (6 + 6\alpha_2 I^{1/2} + 3\alpha_2^2 I + \alpha_2^3 I^{3/2}) \exp(-\alpha_2 I^{1/2})] / (\alpha_2^4 I^2) \quad (11) \end{aligned}$$

and where  $A_H$  is the Debye-Hückel coefficient for apparent molar enthalpy. The constant-pressure apparent molar heat capacity,  $C_{p,\phi}$ , is:

$$\begin{aligned} C_{p,\phi} = & C_{p,m,2}^\circ + \nu |z_M z_X| A_C \ln(1 + bI^{1/2})/2b \\ & - 2\nu_M \nu_X RT^2 (m B_{MX}^C + m^2 \nu_M z_M C_{MX}^C) \quad (12) \end{aligned}$$

where:

$$\begin{aligned} B_{MX}^C = & \left( \frac{\partial^2 \beta_{MX}^{(0)}}{\partial T^2} \right)_P + \frac{2}{T} \left( \frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_P \\ & + 2 \left\{ \left( \frac{\partial^2 \beta_{MX}^{(1)}}{\partial T^2} \right)_P + \frac{2}{T} \left( \frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_P \right\} \\ & [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2}) / \alpha^2 I] \quad (13) \end{aligned}$$

$$\begin{aligned} C_{MX}^C = & \left( \frac{\partial^2 C_{MX}^{(0)}}{\partial T^2} \right)_P + \frac{2}{T} \left( \frac{\partial C_{MX}^{(0)}}{\partial T} \right)_P \\ & + 4 \left\{ \left( \frac{\partial^2 C_{MX}^{(1)}}{\partial T^2} \right)_P + \frac{2}{T} \left( \frac{\partial C_{MX}^{(1)}}{\partial T} \right)_P \right\} \times \\ & [6 - (6 + 6\alpha_2 I^{1/2} + 3\alpha_2^2 I + \alpha_2^3 I^{3/2}) \\ & \exp(-\alpha_2 I^{1/2})] / (\alpha_2^4 I^2) \quad (14) \end{aligned}$$

and where  $A_C$  is the Debye-Hückel coefficient for apparent molar heat capacity and  $C_{p,m,2}^\circ$  is the standard-state molar heat capacity of the solute. The apparent molar volume of a solution,  $V_\phi$ , is:

$$\begin{aligned} V_\phi = & V_{m,2}^\circ + \nu |z_M z_X| A_V \ln(1 + bI^{1/2})/2b \\ & + 2\nu_M \nu_X RT (m B_{MX}^V + m^2 \nu_M z_M C_{MX}^V) \quad (15) \end{aligned}$$

where:

$$\begin{aligned} B_{MX}^V = & \left( \frac{\partial \beta_{MX}^{(0)}}{\partial p} \right)_T + 2 \left( \frac{\partial \beta_{MX}^{(1)}}{\partial p} \right)_T \times \\ & [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2}) / \alpha^2 I] \quad (16) \end{aligned}$$

$$C_{MX}^V = \left( \frac{\partial C_{MX}^{(0)}}{\partial p} \right)_T + 4 \left( \frac{\partial C_{MX}^{(1)}}{\partial p} \right)_T$$

$$[6 - (6 + 6\alpha_2 I^{1/2} + 3\alpha_2^2 I + \alpha_2^3 I^{3/2})$$

$$\exp(-\alpha_2 I^{1/2})]/(\alpha_2^4 I^2) \quad (17)$$

and where  $A_V$  is the Debye-Hückel coefficient for apparent molar volume and  $V_{m,2}^\circ$  is the standard-state volume of the solute.

In order to avoid the complex temperature and pressure behavior of  $V_{m,2}^\circ$  and  $C_{p,m,2}^\circ$ , Eqs. (15, 12) were rewritten, following, in part, the example of Rogers and Pitzer<sup>16</sup>. The analogous equation for a reference molality was subtracted from the appropriate equation for the molality of interest to obtain, in the case of  $V_\phi$ ,

$$V_\phi = V_{\phi, m_r} + \nu |z_M z_X| A_V \ln \{ (1 + bI^{1/2}) / (1 + bI_r^{1/2}) \} / 2b + 2\nu_M \nu_X RT \{ (m - m_r) B_{MX}^V + (m^2 - m_r^2) \nu_M z_M C_{MX}^V \} \quad (18)$$

where  $m_r$  is the chosen reference molality and  $I_r$ ,  $V_{\phi, m_r}$  are the ionic strength and the apparent molar volume that correspond to  $m_r$ , respectively.  $V_{\phi, m_r}$  has a less extreme temperature and pressure dependence than does  $V_{m,2}^\circ$ , however, this temperature and pressure dependence may be reduced further by rewriting Eq. (18) as:

$$V_\phi + \nu_w/n_r = V(m_r)/n_r + \nu |z_M z_X| A_V \ln \{ (1 + bI^{1/2}) / (1 + bI_r^{1/2}) \} / 2b + 2\nu_M \nu_X RT \{ (m - m_r) B_{MX}^V + (m^2 - m_r^2) \nu_M z_M C_{MX}^V \} \quad (19)$$

where  $\nu_w$  is the volume of 1 kg of water,  $V(m_r)$  is the volume of a quantity of solution of molality  $m_r$  which contains 1 kg of water and  $n_r$  is the number of moles of solute in this quantity of solution. This rearrangement requires the definition of the apparent molar property, which is:

$$X_\phi = \frac{X - n_1 X_{m,1}^\circ}{n_2} \quad (20)$$

where  $X$  is the measured property for a quantity of solution containing  $n_1$  moles of solvent and  $n_2$  moles of solute.  $X(m_r)$  is the desired slowly changing function, if  $m_r$  is chosen to be sufficiently large. In the present work  $m_r$  was chosen to be 6 mol·kg<sup>-1</sup>. Equations similar to Eq. (19) may be written for the other apparent molar properties. The analogous equation for apparent molar heat capacity is:

$$C_{p,\phi} + c_{p,w}/n_r = C_p(m_r)/n_r + \nu |z_M z_X| A_C \ln \{ (1 + bI^{1/2}) / (1 + bI_r^{1/2}) \} / 2b$$

$$- 2\nu_M \nu_X RT^2 \{ (m - m_r) B_{MX}^C + (m^2 - m_r^2) \nu_M z_M C_{MX}^C \} \quad (21)$$

where  $C_p(m_r)$  is the heat capacity of a quantity of solution containing one kg of solvent at the desired temperature and pressure and  $c_{p,w}$  is the heat capacity of one kg of water. The pressure dependence of  $C_p(m_r)/n_r$  is contained in  $V(m_r)/n_r$  and so the only additional variable parameters introduced were those that described the behavior of  $C_p(m_r)/n_r$  along an isobar. This isobar was chosen to be 0.1 MPa.  $C_p(m_r)/n_r$  along this 0.1 MPa isobar will be referred to as  $C_{p,p}(m_r)/n_r$ .

The partial molar Gibbs energy of the solute in its standard state at temperature  $T$  and pressure  $p$ ,  $G_{m,2,T,p}^\circ$ , may be written in terms of the above equations as:

$$G_{m,2,T,p}^\circ = G_{m,2,T_r,p_r}^\circ + \frac{n_1 G_{m,1,T_r,p_r}^\circ - n_1 G_{m,1,T,p}^\circ}{n_r}$$

$$+ \frac{G_{T_r,p_r,m_r}^{\text{ex}} - G_{T,p,m_r}^{\text{ex}}}{n_r}$$

$$- (T - T_r) \left( S_{m,2,T_r,p_r}^\circ + \frac{n_1 S_{m,1,T_r,p_r}^\circ}{n_r} + \frac{S_{T_r,p_r,m_r}^{\text{ex}}}{n_r} \right)$$

$$- T \int_{T_r}^T \frac{1}{T^2} \int_{T_r}^T C_{p,p}(m_r)/n_r \, dT \, dT$$

$$+ \int_{p_r}^p V(m_r)/n_r \, dp \quad (22)$$

where:

$$S_{T_r,p_r}^{\text{ex}} = - \left( \frac{\partial G_{T_r,p_r}^{\text{ex}}}{\partial T} \right)_p, \quad (23)$$

evaluated at  $T_r$ . (Eq. 25 of Ref. 8 is typed incorrectly, it should appear as Eq. (23) above.)  $T_r$  and  $p_r$  were chosen to be 298.15 K and 0.1 MPa, respectively. The value of  $S_{m,1,T_r,p_r}^\circ$  was taken from Cox *et al.*<sup>17</sup> to be 69.95 J·K<sup>-1</sup>·mol<sup>-1</sup>.

The equations describing the solubility of the anhydrous and dihydrate solid phases are:

$$\Delta_{\text{sol}} G_{\text{anhydrous}}^\circ = G_{m,2}^\circ - G_{m,\text{cr},\text{anhydrous}}^\circ$$

$$= -2RT \ln(m_s \gamma_{\pm,s}/m^\circ) \quad (24)$$

and

$$\Delta_{\text{sol}} G_{\text{dihydrate}}^\circ = G_{m,2}^\circ + 2G_{m,1}^\circ - G_{m,\text{cr},\text{dihydrate}}^\circ$$

$$= -2RT \ln(m_s \gamma_{\pm,s}/m^\circ) - 2RT \ln a_{w,s} \quad (25)$$

where  $G_{m,2}^\circ$ ,  $G_{m,1}^\circ$ , and  $G_{m,\text{cr},i}^\circ$  are the molar Gibbs energies for the solute, the pure liquid, and the  $i^{\text{th}}$  crystal phase all at a given  $T$  and  $p$ , respectively,  $\Delta_{\text{sol}} G_i^\circ$  is the standard-state molar Gibbs energy for the solution process of the  $i^{\text{th}}$  crystal phase and  $m_s$ ,  $\gamma_{\pm,s}$  and  $a_{w,s}$  are the saturation molality, the mean stoichiometric activity coefficient for the solute at saturation, and the activity of water for the saturation molality, respectively. Of course,  $G_{m,2}^\circ$ ,  $G_{m,1}^\circ$  and  $G_{m,\text{cr},i}^\circ$  cannot be evaluated and so Eqs. (24, 25) were rewritten as:

$$\begin{aligned} \Delta_{\text{sol}}G_{\text{anhydrous}, T}^{\circ} &= \Delta_{\text{sol}}G_{\text{anhydrous}, T_r}^{\circ} + \{G_{\text{m}, 2, T}^{\circ} - G_{\text{m}, 2, T_r}^{\circ}\} \\ &\quad - \{G_{\text{m}, \text{cr}, \text{anhydrous}, T}^{\circ} - G_{\text{m}, \text{cr}, \text{anhydrous}, T_r}^{\circ}\} \\ &= -2RT \ln(m_s \gamma_{\pm, s}/m^{\circ}) \quad (26) \end{aligned}$$

and

$$\begin{aligned} \Delta_{\text{sol}}G_{\text{dihydrate}, T}^{\circ} &= \Delta_{\text{sol}}G_{\text{dihydrate}, T_r}^{\circ} + \{G_{\text{m}, 2, T}^{\circ} - G_{\text{m}, 2, T_r}^{\circ}\} \\ &\quad - \{G_{\text{m}, \text{cr}, \text{dihydrate}, T}^{\circ} - G_{\text{m}, \text{cr}, \text{dihydrate}, T_r}^{\circ}\} \\ &\quad + 2\{G_{\text{m}, 1, T}^{\circ} - G_{\text{m}, 1, T_r}^{\circ}\} \\ &= -2RT \ln(m_s \gamma_{\pm, s}/m^{\circ}) - 2RT \ln a_{w, s} \quad (27) \end{aligned}$$

The first braced term of Eqs. (26, 27) was obtained from Eq. (22), the second braced term of Eq. (26) was obtained from Eq. (2), the third braced term of Eq. (27) was obtained from the equation of Hill.<sup>1</sup> The second braced term of Eq. (27) was expressed as:

$$\begin{aligned} \{G_{\text{m}, \text{cr}, \text{dihydrate}, T}^{\circ} - G_{\text{m}, \text{cr}, \text{dihydrate}, T_r}^{\circ}\} &= -(T - T_r) \\ S_{\text{m}, \text{cr}, \text{dihydrate}, T_r, p_r}^{\circ} &+ 137 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \{ (T - T_r) - T \ln(T/T_r) \}. \quad (28) \end{aligned}$$

Solubility measurements were included in the global data fit. The two Gibbs energies of solution at the reference temperature,  $T_r$ , and reference pressure,  $p_r$ , were treated as adjustable parameters, as was  $S_{\text{m}, \text{cr}, \text{dihydrate}, T_r, p_r}^{\circ}$  and  $S_{\text{m}, T_r, p_r}^{\circ}$ . In addition, the experimental solubility results make some contribution to the determination of the parameters for the excess Gibbs energy for the solution through Eq. (22).

For the dehydration (decomposition) reaction:



the Gibbs energy of reaction for 298.15 K and 0.1 MPa, per mole of  $\text{H}_2\text{O}$ , is:

$$\begin{aligned} \Delta_{\text{dec}}G_{\text{m}, T_r, p_r}^{\circ} &= (\Delta_f G_{\text{anhydrous}, T_r, p_r}^{\circ} + 2\Delta_f G_{\text{H}_2\text{O}(\text{g}), T_r, p_r}^{\circ} \\ &\quad - \Delta_f G_{\text{dihydrate}, T_r, p_r}^{\circ})/2 \quad (30) \end{aligned}$$

where  $\Delta_f G_{\text{anhydrous}, T_r, p_r}^{\circ}$  and  $\Delta_f G_{\text{dihydrate}, T_r, p_r}^{\circ}$  are the standard-state Gibbs energies of formation of the anhydrous and dihydrate sodium chloride phases at  $T_r$  and  $p_r$ . The standard-state Gibbs energy of formation of  $\text{H}_2\text{O}$  at  $T_r$  and  $p_r$ ,  $\Delta_f G_{\text{H}_2\text{O}(\text{g}), T_r, p_r}^{\circ}$ , was taken from Cox *et al.* At any given temperature, the Gibbs energy of decomposition,  $\Delta_{\text{dec}}G_{\text{m}, T, p_r}^{\circ}$ , is:

$$\begin{aligned} \Delta_{\text{dec}}G_{\text{m}, T, p_r}^{\circ} &= \Delta_{\text{dec}}G_{\text{m}, T_r, p_r}^{\circ} \\ &\quad + (S_{\text{m}, \text{H}_2\text{O}(\text{g}), T_r, p_r}^{\circ} + 0.5S_{\text{m}, \text{anhydrous}, T_r, p_r}^{\circ} \\ &\quad - 0.5S_{\text{m}, \text{dihydrate}, T_r, p_r}^{\circ})(T_r - T) \\ &\quad + \int_{T_r}^T (C_{p, \text{m}, \text{H}_2\text{O}(\text{g}), p_r}^{\circ} + 0.5C_{p, \text{m}, \text{anhydrous}, p_r}^{\circ} \\ &\quad - 0.5C_{p, \text{m}, \text{dihydrate}, p_r}^{\circ}) dT \\ &\quad - T \int_{T_r}^T (C_{p, \text{m}, \text{H}_2\text{O}(\text{g}), p_r}^{\circ} + 0.5C_{p, \text{m}, \text{anhydrous}, p_r}^{\circ} \\ &\quad - 0.5C_{p, \text{m}, \text{dihydrate}, p_r}^{\circ})/T dT, \quad (31) \end{aligned}$$

again per mole of water. The heat capacities and entropies for Eq. (31) have been referred to previously. The vapor pressures of water over the dihydrate solid, from 233.15 to 273.3 K were included in the global data fit.

The ion-interaction parameters for the excess Gibb energy for the  $\text{NaCl}(\text{aq})$  solution were expressed as:

$$\beta_{\text{MX}}^{(0)} = f(1, p, T)/m^{\circ} \quad (32)$$

$$\beta_{\text{MX}}^{(1)} = f(2, p, T)/m^{\circ} \quad (33)$$

$$C_{\text{MX}}^{(0)} = f(3, p, T)/m^{\circ 2} \quad (34)$$

$$C_{\text{MX}}^{(1)} = f(4, p, T)/m^{\circ 2} \quad (35)$$

where:

$$\begin{aligned} f(i, p, T) &= [b_{i, 1} + b_{i, 2}T/(1000T^{\circ}) + b_{i, 3}\{T/(500T^{\circ})\}^2 \\ &\quad + b_{i, 4}T^{\circ}/(T - 200 \text{ K}) + b_{i, 5}T^{\circ}/T \\ &\quad + b_{i, 6}\{100 T^{\circ}/(T - 200 \text{ K})\}^2 \\ &\quad + b_{i, 7}(200 T^{\circ}/T)^2 + b_{i, 8}\{T/(500T^{\circ})\}^3 \\ &\quad + b_{i, 9}\{T^{\circ}/(650 \text{ K} - T)\}^{1/2} \\ &\quad + b_{i, 10}1 \times 10^{-5}(p/p^{\circ}) + b_{i, 11}2 \times 10^{-4}(p/p^{\circ}) \\ &\quad \{T^{\circ}/(T - 225 \text{ K})\} + b_{i, 12}100(p/p^{\circ}) \\ &\quad \{T^{\circ}/(650 \text{ K} - T)\}^3 \\ &\quad + b_{i, 13}1 \times 10^{-5}(p/p^{\circ})\{T/(500T^{\circ})\} \\ &\quad + b_{i, 14}2 \times 10^{-4}(p/p^{\circ})\{T^{\circ}/(650 \text{ K} - T)\} \\ &\quad + b_{i, 15}1 \times 10^{-7}(p/p^{\circ})^2 \\ &\quad + b_{i, 16}2 \times 10^{-6}(p/p^{\circ})^2\{T^{\circ}/(T - 225 \text{ K})\} \\ &\quad + b_{i, 17}(p/p^{\circ})^2\{T^{\circ}/(650 \text{ K} - T)\}^3 \\ &\quad + b_{i, 18}1 \times 10^{-7}(p/p^{\circ})^2\{T/(500T^{\circ})\} \\ &\quad + b_{i, 19}1 \times 10^{-7}(p/p^{\circ})^2\{T/(500T^{\circ})\}^2 \\ &\quad + b_{i, 20}4 \times 10^{-2}(p/p^{\circ})\{T^{\circ}/(T - 225 \text{ K})\}^2 \\ &\quad + b_{i, 21}1 \times 10^{-5}(p/p^{\circ})\{T/(500T^{\circ})\}^2 \\ &\quad + b_{i, 22}2 \times 10^{-8}(p/p^{\circ})^3\{T^{\circ}/(T - 225 \text{ K})\} \\ &\quad + b_{i, 23}1 \times 10^{-2}(p/p^{\circ})^3\{T^{\circ}/(650 \text{ K} - T)\}^3 \\ &\quad + b_{i, 24}200\{T^{\circ}/(650 \text{ K} - T)\}^3] \quad (36) \end{aligned}$$

and where  $T^{\circ}$  is 1.0 K,  $p^{\circ}$  is 1.0  $\text{g} \cdot \text{cm}^{-3}$  and  $m^{\circ}$  is 1.0  $\text{mol} \cdot \text{kg}^{-1}$ .  $V(m_r)/n_r$  and  $C_p(m_r)/n_r$  were taken as functions of  $T$  and  $p$  as:

$$\begin{aligned} V(m_r)/n_r &= [0.1b_{5, 1} + b_{5, 2}T/(3 \times 10^4 T^{\circ}) \\ &\quad + b_{5, 3}1 \times 10^{-7}T\{(p + 10 \text{ MPa})/p^{\circ}\}^{1.5}/(300T^{\circ}) \\ &\quad + b_{5, 4}1 \times 10^{-3}\{T/(300T^{\circ})\}^3 \\ &\quad + b_{5, 5}1 \times 10^{-3}p/p^{\circ} + b_{5, 6}pT/(p^{\circ}3000T^{\circ}) \\ &\quad + b_{5, 7}1 \times 10^{-3}pT^2/\{p^{\circ}(300T^{\circ})^2\} \\ &\quad + b_{5, 8}1 \times 10^{-3}p^2T/(p^{\circ 2}300T^{\circ})]V^{\circ} \quad (37) \end{aligned}$$



$$C_{p,p_r}(m_r)/n_r = [b_{6,1} + b_{6,2}T/(300 \text{ K}) + b_{6,3}(T/300 \text{ K})^2 + b_{6,4}(100T^\circ/T)]C_p^\circ \quad (38)$$

where  $V^\circ$  is  $1.0 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $C_p^\circ$  is  $1.0 \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ,  $p^\circ$  is  $1.0 \text{ MPa}$ . The functions of Eqs. (36–38) were scaled, in the fitting procedure, so that all of the least-squares estimated parameters would be of approximately the same order of magnitude. The least-squares estimated param-

eters,  $b_{i,j}$ , are found in Table 2. The absence of a value for a particular  $b_{i,j}$  from Table 2 indicates that it was not used in the final least-squares procedure.

#### 4.2. Agreement with Experimental Results for NaCl(aq)

The weighting of experimental results to reflect their different variances is essential for the correct application

TABLE 2. Least-squares estimated parameters for Eqs. (3–37)

Parameter	Value	Parameter	Value	Parameter	Value
$h_{1,1}$	0.242408292826506	$b_{2,1}$	-1.90196616618343	$b_{3,1}$	
$h_{1,2}$		$b_{2,2}$	5.45706235080812	$b_{3,2}$	-0.0412678780636594
$h_{1,3}$	-0.162683350691532	$b_{2,3}$		$b_{3,3}$	0.0193288071168756
$h_{1,4}$	1.38092472558595	$b_{2,4}$	-40.5376417191367	$b_{3,4}$	-0.338020294958017
$h_{1,5}$		$b_{2,5}$		$b_{3,5}$	
$h_{1,6}$		$b_{2,6}$		$b_{3,6}$	0.0426735015911910
$h_{1,7}$	-67.2829389568145	$b_{2,7}$	485.065273169753	$b_{3,7}$	4.14522615601883
$h_{1,8}$		$b_{2,8}$	-0.661657744698137	$b_{3,8}$	-0.00296587329276653
$h_{1,9}$	0.625057580755179	$b_{2,9}$		$b_{3,9}$	
$h_{1,10}$	-21.2229227815693	$b_{2,10}$		$b_{3,10}$	1.39697497853107
$h_{1,11}$	81.8424235648693	$b_{2,11}$	242.206192927009	$b_{3,11}$	-3.80140519885645
$h_{1,12}$	-1.59406444547912	$h_{2,12}$		$h_{3,12}$	
$h_{1,13}$		$b_{2,13}$	-99.0388993875343	$b_{3,13}$	
$h_{1,14}$		$b_{2,14}$		$b_{3,14}$	-16.8888941636379
$h_{1,15}$	28.6950512789644	$b_{2,15}$		$b_{3,15}$	-2.49300473562086
$h_{1,16}$	-44.3370250373270	$b_{2,16}$	-59.5815563506284	$b_{3,16}$	3.14339757137651
$h_{1,17}$	1.92540008303069	$b_{2,17}$		$b_{3,17}$	
$h_{1,18}$	-32.7614200872551	$b_{2,18}$		$b_{3,18}$	2.79586652877114
$h_{1,19}$		$b_{2,19}$		$b_{3,19}$	
$h_{1,20}$		$b_{2,20}$		$b_{3,20}$	
$h_{1,21}$	30.9810098813807	$b_{2,21}$		$b_{3,21}$	
$h_{1,22}$	2.46955572958185	$b_{2,22}$		$b_{3,22}$	
$h_{1,23}$	-0.725462987197141	$b_{2,23}$		$b_{3,23}$	
$h_{1,24}$	10.1525038212526	$b_{2,24}$		$b_{3,24}$	-0.502708980699711
$h_{4,1}$	0.788987974218570	$b_{6,1}$	1.62690371649145	$\Delta_{\text{sol}}G_{\text{anhydrous}, T_r, p_r}^\circ$	-9.040721 ± 0.0062 kJ·mol <sup>-1</sup>
$h_{4,2}$	-3.67121085194744	$b_{6,2}$	-0.767143070769565	$\Delta_{\text{sol}}G_{\text{dihydrate}, T_r, p_r}^\circ$	-8.953775 ± 0.041 kJ·mol <sup>-1</sup>
$h_{4,3}$	1.12604294979204	$b_{6,3}$	0.211473310430416	$S_{\text{m, cr, dihydrate}, T_r, p_r}^\circ$	162.5115 ± 1.1 J·K <sup>-1</sup> ·mol <sup>-1</sup>
$h_{4,4}$		$b_{6,4}$	-1.00267947284134	$S_{\text{m, NaCl(aq)}, T_r, p_r}^\circ$	115.5108 ± 0.029 J·K <sup>-1</sup> ·mol <sup>-1</sup>
$h_{4,5}$					
$h_{4,6}$	-10.1089172644722	$b_{5,1}$	1.73695617448715		
$h_{4,7}$		$b_{5,2}$	0.966200843424027		
$h_{4,8}$		$b_{5,3}$	5.65834170020827		
$h_{4,9}$		$b_{5,4}$	5.29304128387387		
$h_{4,10}$		$b_{5,5}$	-11.4549171718081		
$h_{4,11}$		$b_{5,6}$	0.139613287266584		
$h_{4,12}$		$b_{5,7}$	-8.04750349624935		
$h_{4,13}$		$b_{5,8}$			
$h_{4,14}$			0.189614646216723		
$h_{4,15}$					
$h_{4,16}$					
$h_{4,17}$					
$h_{4,18}$					
$h_{4,19}$					
$h_{4,20}$					
$h_{4,21}$					
$h_{4,22}$					
$h_{4,23}$					
$h_{4,24}$	16.6503495528290				

\*The ± values are 95% confidence intervals within the global data representation.

of the usual least-squares method.<sup>18</sup> However, the assignment of estimated variances to the observations is usually not a simple matter. The investigator's description of the accuracy of his measurements might not always be reliable. Some investigators report extremely optimistic error estimates that are not truly representative of the measurements. Others adopt overly conservative error estimates (this occurs less frequently than the former, but it does occur). It also sometimes happens that an investigator's accuracy estimate is actually a description of the precision of the measurement and thus is not particularly useful for the assignment of weighting factors. The process of assignment of variances to a large number of sets of experimental data legitimately implores the critical question: "At what point does the subjectivity involved in the assignment of variances to observations reduce the nominally objective least-squares process into a non-objective enterprise?"

Clarke and Glew<sup>2</sup> described a method by which they attempted to remove the subjective component of the assignment of variances. Their procedure (for brevity, details such as the concentration dependence of the variance are omitted here) was to assign unit weighting to all measurements, apply a least-squares regression, calculate the root-mean-square (r.m.s.) deviations from the fitted function for groups of observations, calculate weighting factors assuming that the r.m.s. deviations approximated the square root of the variances of the groups of data and iterate this process until convergence. Their converged variances for most data sets were very reasonable when compared to experiment. However, an occasional data set may have been overweighted. The cause of this overweighting can be explained with a simple one parameter case. (For heuristic purposes our simple explanation will apply the method of Clarke and Glew to a problem to which they clearly would not apply it.) Consider five observations of a single point for which, unbeknownst to us, each observation has the same variance. A weighted average of the five measurements is desired. If the method of Clarke and Glew is applied to this set of five measurements, each measurement eventually possesses a converged variance. The observed value closest to the final average would have the smallest converged variance; that furthest away would have the largest. Yet all of the observations had the same variance. In this case, the converged variances clearly are not the same as the actual variances.

The differences between the best few enthalpy of solution data sets, for 298.15 K, in Clarke and Glew's represented database can be described as mostly independent of concentration and offset from one another, in other words, for the six lowest variance data sets the absolute value of the average error was close to the r.m.s. error. Of these six data sets there was a pair of enthalpy of solution data sets obtained in the same laboratory, with essentially the same instrument, yet they had quite different converged variances. The smaller of these two sets of converged variances appeared to be significantly smaller than what would be expected from the reproducibility of

the measurements between the two data sets. This situation with the enthalpy of solution data sets is analogous to the above described heuristic example. This is a relatively minor difficulty in Clarke and Glew's method. might have been avoided by establishing a minimum variance for a data set, below which the converging variance would not have been reduced. The previous observations were presented because it was desired to use many Clarke and Glew's variances in the present work. However, an estimate of a minimum variance for a particular experiment was used here if it was larger than Clarke and Glew's converged variance for that data set.

Clarke and Glew's method of determining variances for sets of data worked well, in large part, because the large number of sets and types of experimental results was sufficient for the central limit theory<sup>18</sup> to be applicable. For temperatures greater than 370 K, the same scope of experimental results does not yet exist. Thus, the method described by Clarke and Glew for assigning variances was not used for those results that were considered here but not included in Clarke and Glew's representation. For these results, which included the volumetric results, the weighting factors for a set of data were first calculated from an expected experimental uncertainty for the actual measurement. These variances were then adjusted to bring the weighted r.m.s. error for a data set to a value near unity.

As in previous work for NaBr(aq),<sup>8</sup> reported experimental results were reduced to forms that were a compromise between values that were as close to the actually measured experimental quantity as possible and convenience. This reduction was used so as to remove the influence of changes in the properties of water on the input data set (i.e. the effect of a chosen value for a water property on the calculation of an apparent molar property, the effect of a water property on calibration of an instrument etc.) and to simplify the weighting of experimental results. At the time the least-squares procedure was executed these experimental values were converted into the appropriate quantities for fitting.

Experimental results included in the present data representation for NaCl(aq) spanned the temperature and pressure ranges of 248 to 600 K and, where available, from near the vapor pressure of water to 100 MPa. Literature sources for volumetric results considered for the global data fit, and the quality of representation of these results are listed in Table 3. Similar information for the activity and thermal properties of NaCl(aq) and for the relation of NaCl(cr) and of NaCl·2H<sub>2</sub>O(cr) to NaCl(aq) is given in Table 4. The estimated square root of the variance,  $\sigma_{\text{est}}$ , used for calculating weighting factors are given in Tables 3 and 4.

#### 4.2.1. Volumetric Results

The reported experimental volumetric measurements for NaCl(aq) were classified in one of several different categories. Pycnometric and other results in which a calibration with a single reference fluid (water) was per-

TABLE 3. Literature sources for the volumetric properties of NaCl(aq)

Reference	Temperature range (K)	Pressure range <sup>a</sup> (MPa)	Molality range (mol·kg <sup>-1</sup> )	n	Type	$\sigma_{est}^b$	$\sigma_{fit}$	$\delta_{fit}$
19	273.95	0.1	0.015–0.126	11	$\rho_s^c$	$5 \times 10^{-6}$	$4 \times 10^{-6}$	$0.6 \times 10^{-6d}$
20	278.15	0.1	0.05–3.5	19	$V_\phi$	0.028	0.030	-0.013 <sup>e</sup>
21	298.15	0.1	0.17–5.86	13	$\rho_s/\rho_w$	$40 \times 10^{-6}$	$14 \times 10^{-6}$	$2 \times 10^{-6d}$
22	298.15	0.1	0.0026–0.75	15	$\rho_s/\rho_w$	$3 \times 10^{-6}$	$4 \times 10^{-6}$	$-2 \times 10^{-6d}$
23	298.15	0.1	0.04–6.14	11	$\rho_s/\rho_w$	$30 \times 10^{-6}$	$24 \times 10^{-6}$	$16 \times 10^{-6d}$
24(set 1)	298.15	0.1	0.06–2.1	21	$\rho_s-\rho_w$	U	$29 \times 10^{-6}$	$-26 \times 10^{-6d}$
24(set 2)	298.15	0.1	0.06–2.8	18	$\rho_s-\rho_w$	U	$60 \times 10^{-6}$	$43 \times 10^{-6d}$
25	298.15	0.1	0.05–3.5	19	$V_\phi$	0.017	0.016	-0.002 <sup>e</sup>
26	298.15	0.1	0.02–0.31	5	$\rho_s-\rho_w$	$5 \times 10^{-6}$	$3 \times 10^{-6}$	$0 \times 10^{-6d}$
27	298.15	0.1	1.0–6.0	7	$\rho_s/\rho_w$	U	$416 \times 10^{-6}$	$-230 \times 10^{-6d}$
28	298.15	0.1	0.21–0.82	2	$\rho_s/\rho_w$	$10 \times 10^{-6}$	$9 \times 10^{-6}$	$0.5 \times 10^{-6d}$
28	298.15	0.1	0.004–0.82	1	$\Delta_{dil}V_\phi$	0.02	0.006	-0.006 <sup>e</sup>
29	323.15	0.1	0.005–0.98	10	$\rho_s-\rho_w$	$20 \times 10^{-6}$	$22 \times 10^{-6}$	$9 \times 10^{-6d}$
30	298.15	0.1	0.01–1.0	12	$\rho_s-\rho_w$	$3 \times 10^{-6}$ ; 0.064%	$15 \times 10^{-6}$	$-12 \times 10^{-6d}$
31	298.15	0.1	0.17–5.0	9	$\rho_s/\rho_w$	U	$193 \times 10^{-6}$	$137 \times 10^{-6d}$
32	298.15	0.1	0.1–0.5	10	$\rho_s-\rho_w$	U	$85 \times 10^{-6}$	$49 \times 10^{-6d}$
33	298.15	0.1	0.28–5.10	10	$\rho_s-\rho_w$	U	$108 \times 10^{-6}$	$-74 \times 10^{-6d}$
34	298.15	0.1–40	0.06–5.0	40	$\rho_s-\rho_w$	$20 \times 10^{-6}$ ; 0.1%	$93 \times 10^{-6}$	$-13 \times 10^{-6d}$
33	298.15	0.1	0.28–5.10	10	$\alpha_s-\alpha_w$	$\sigma E_\phi = 2 \times 10^{-6}$ $m_L = 2.0$	$3.2 \times 10^{-6}$	$1.8 \times 10^{-6f}$
35	303.15	0.1	0.1–1.0	8	$V_\phi$	0.3	0.31	-0.29 <sup>e</sup>
36	308.15	0.1	0.002–1.08	13	$\rho_s/\rho_w$	$30 \times 10^{-6}$ ; 1.3%	$81 \times 10^{-6}$	$-52 \times 10^{-6d}$
37	280.15–306.19	0.1	0.25–5.7	21	$\rho_s/\rho_w$	$100 \times 10^{-6}$	$96 \times 10^{-6}$	$59 \times 10^{-6d}$
38	273.15–323.19	0.1	0.25–5.9	15	$\rho_s/\rho_w$	$100 \times 10^{-6}$	$104 \times 10^{-6}$	$-70 \times 10^{-6d}$
39	273.15–298.15	0.1	0.002–1.02	18	$\rho_s/\rho_w$	$15 \times 10^{-6}$	$15 \times 10^{-6}$	$3 \times 10^{-6d}$
40	273.2–338.15	0.1	0.23–0.9	27	$\Delta_{dil}V_\phi$	0.12	0.16	-0.10 <sup>e</sup>
40	273.2–338.15	0.1	0.21–1.0	17	$\rho_s/\rho_w$	$30 \times 10^{-6}$	$40 \times 10^{-6}$	$24 \times 10^{-6d}$
41	273.15–328.15	0.1	0.01–0.96	83	$\rho_s-\rho_w$	$5 \times 10^{-6}$ ; 0.14%	$21 \times 10^{-6}$	$-3 \times 10^{-6d}$
42	273.15–318.15	0.1	0.25–5.0	34	$\beta_s-\beta_w$	$0.6 \times 10^{-6}$	$0.54 \times 10^{-6}$	$0.02 \times 10^{-6g}$
43	273.15–308.15	0.1	0.01–1.5	47	$\rho_s-\rho_w$	$4 \times 10^{-6}$ ; 0.085%	$10 \times 10^{-6}$	$-4 \times 10^{-6d}$
44	274.65–318.15	0.1	0.03–3.0	58	$\rho_s-\rho_w$	$7.5 \times 10^{-6}$ ; 0.15%	$45 \times 10^{-6}$	$4 \times 10^{-6d}$
45	283.15–313.15	0.1	0.19–1.89	20	$\alpha_s-\alpha_w$	$\sigma E_\phi = 2 \times 10^{-6}$ $m_L = 2.0$	$3.2 \times 10^{-6}$	$-0.3 \times 10^{-6f}$
46	288.15–318.15	0.1	0.17–5.9	58	$\rho_s-\rho_w$	0.045%	$20 \times 10^{-6}$	$1 \times 10^{-6d}$
47	288.15–313.15	0.1	0.06–2.9	55	$\rho_s-\rho_w$	U	$25 \times 10^{-6}$	$5 \times 10^{-6d}$
48	293.15–313.15	0.1	0.114	21	$V_\phi$	U	0.13	0.08 <sup>e</sup>
49	273.15–323.15	10–100	0.03–2.0	178	$\Delta\rho(P_2-P_1)$	$\sigma V_\phi = 0.1$ ; $m_L = 1.0$	0.44	0.2 <sup>e</sup>
50	293.15–571.65	10–100	0.017–5.7	216	$\rho_s$	$860 \times 10^{-6}$	$800 \times 10^{-6}$	$420 \times 10^{-6d}$
51, 52	298.15–358.15	0.1–100	0.89–5.68	104	$\rho_s/\rho_w$	$40 \times 10^{-6}$	$35 \times 10^{-6}$	$-2.5 \times 10^{-6d}$
53	323.16–548.05	***–40	0.056–5.0	250	$\rho_s-\rho_w$	$50 \times 10^{-6}$ ; 0.5%	$290 \times 10^{-6}$	$-120 \times 10^{-6d}$
53	321.6–549.7	***–32	0.01–3.09	163	$\rho_s-\rho_w$	$36 \times 10^{-6}$ ; 0.36%	$277 \times 10^{-6}$	$7 \times 10^{-6d}$
54	348.15–473.15	2.03	0.1–1.0	24	$\rho_s$	<sup>b</sup>	$159 \times 10^{-6}$	$-116 \times 10^{-6d}$
55	348.15–473.15	2.03	0.053–4.39	48	$\rho_s/\rho_w$	<sup>b</sup>	$180 \times 10^{-6}$	$-2 \times 10^{-6d}$
56	450–600	20.	0.1–4.0	59	$\rho_s$	U	0.016	0.0057 <sup>d</sup>
57	473.15–573.15	1.5–100	1.1–4.3	30	$\rho_s$	$3 \times 10^{-3}$	$3.7 \times 10^{-3}$	$2.0 \times 10^{-3d}$
58	448.15–573.15	$p_s$	0.5–3.0	24	$\rho_s$	$10 \times 10^{-3}$	$5.6 \times 10^{-3}$	$-4.6 \times 10^{-3d}$
53	597.45	21–39	0.01–5.05	30	$\rho_s-\rho_w$	$130 \times 10^{-6}$ ; 1.3%	$1.03 \times 10^{-3}$	$-0.47 \times 10^{-3d}$
59	604.4	27–38	0.01–3.1	87	$\rho_s-\rho_w$	$480 \times 10^{-6}$ ; 1.2%	$1.27 \times 10^{-3}$	$-0.14 \times 10^{-3d}$
169	308.15–368.15	0.101	0.26–6.2	141	$\rho_s-\rho_w$	$50 \times 10^{-6}$ ; 0.1%	$73 \times 10^{-6}$	$16 \times 10^{-6d}$

\*\*\*indicates that the lowest pressure for the data set changed with the experimental temperature.

<sup>b</sup> The letter U indicates that these points were given an insignificant weight in the least-squares procedure. When two values are given the  $\sigma_{exp}$  was taken to be the larger of the two values given. In the cases where a value is given for  $m_L$ ; the expected square root of variance is taken to be the first value for  $m > m_L$  and taken to be the first value divided by  $m_L$  for  $m < m_L$ .

<sup>c</sup> Values of density were calculated from the data given only as a figure.

<sup>d</sup> Units are g·cm<sup>-3</sup>.

<sup>e</sup> Units are cm<sup>3</sup>·mol<sup>-1</sup>.

<sup>f</sup> Units are K<sup>-1</sup>.

<sup>g</sup> Units are MPa<sup>-1</sup>.

<sup>h</sup> Values of  $\sigma_{exp}$  depended on temperature. Values were  $2 \times 10^{-4}$ ,  $2.8 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$ ,  $4.2 \times 10^{-4}$ , and  $5 \times 10^{-4}$  g·cm<sup>-3</sup>, for temperatures of 348.15 and 373.15, 398.15, 423.15, 448.15, and 473.15 K, respectively.

formed were recorded as the ratio of solution density to water density,  $\rho_s/\rho_w$ , where the water density value was that reported as having been used in the calibration of the apparatus. Vibrating-tube densimeter and magnetic-float densimeter results were used as the difference in density between solution and water,  $\rho_s - \rho_w$ . Vibrating-tube densimeters require a calibration with, at least, two reference fluids of known densities and so are not as amenable to reduction as pycnometric results. Results from vibrating-tube densimeters, including those designed for operation at near-ambient conditions, are subject to systematic errors in the calibration constant. These errors appear to be dependent on, among other things the choice of calibrating fluid. Another possible source of systematic error in results obtained from vibrating-tube densimeters may arise from adsorption of solute on the inner wall of the densimeter tube. Indications of adsorption effects for vibrating-tube densimeters, as well as

methods which may be used to correct for such effect have been reported by Archer *et al.*<sup>60</sup> for aqueous surfactants and by Majer *et al.*<sup>53</sup> for aqueous electrolytes. Thus the potentially lower accuracy of these instruments, for concentrated solutions, does not warrant reduction of these values for water calibration errors. Values obtained by means of a dilatometer are the change in volume for a given change in concentration and were described as  $\Delta_{dil}V_\phi$ . These values were treated in the same way as enthalpy of dilution values,  $\Delta_{dil}L_\phi$ . Values of  $V_\phi$  and  $\rho_s$  for which insufficient information existed with which to reduce these values to their experimentally measured quantities were recorded as such. These values were usually but not always, given lesser weight for the least-square procedure. Measurements of the expansivity and the compressibility of a solution were treated as the differences in the property for the solution and the property for water.

TABLE 4. Literature sources for the activity and thermal properties of NaCl(aq)

Reference	Temperature range (K)	Pressure range <sup>a</sup> (MPa)	Molality range (mol·kg <sup>-1</sup> )	n	Type <sup>b</sup>	$\sigma_{est}$ <sup>c</sup>	$\sigma_{fit}$	$\Delta_{fit}$
70	273.15	0.1	$m_s$	1	$m_s$ (NaCl·2H <sub>2</sub> O)	0.022	0.006	0.006 <sup>d</sup>
71	251.55–269.15	0.1	$m_s$	4	$m_s$ (NaCl·2H <sub>2</sub> O)	0.024	0.027	0.007 <sup>d</sup>
72	252.05–273.25	0.1	$m_s$	2	$m_s$ (NaCl·2H <sub>2</sub> O)	0.022	0.003	0.002 <sup>d</sup>
73	252.05–273.15	0.1	$m_s$	7	$m_s$ (NaCl·2H <sub>2</sub> O)	0.015	0.016	-0.003 <sup>d</sup>
74	252.15–271.15	0.1	$m_s$	5	$m_s$ (NaCl·2H <sub>2</sub> O)	0.040	0.038	0.035 <sup>d</sup>
75	252.34	0.1	$m_s$	1	$m_s$ (NaCl·2H <sub>2</sub> O)	0.3	0.03	-0.03 <sup>d</sup>
76	273.15–380.15	0.1, $p_s$	$m_s$	8	$m_s$ (NaCl)	0.040	0.028	-0.020 <sup>d</sup>
77	298.15	0.1	$m_s$	2	$m_s$ (NaCl)	0.010	0.014	0.014 <sup>d</sup>
70	278.15–356.15	0.1	$m_s$	16	$m_s$ (NaCl)	0.010	0.009	0.000 <sup>d</sup>
78	293.6–323.15	0.1	$m_s$	6	$m_s$ (NaCl)	0.010	0.004	0.000 <sup>d</sup>
79	288.15–298.15	0.1	$m_s$	3	$m_s$ (NaCl)	0.020	0.010	-0.009 <sup>d</sup>
71	273.15–381.95	0.1, $p_s$	$m_s$	13	$m_s$ (NaCl)	0.030	0.028	-0.020 <sup>d</sup>
80	273.15–373.15	0.1	$m_s$	5	$m_s$ (NaCl)	0.063	0.062	-0.055 <sup>d</sup>
72	273.25–373.15	0.1	$m_s$	6	$m_s$ (NaCl)	0.010	0.008	0.005 <sup>d</sup>
72	393.15–462.55	$p_s$	$m_s$	4	$m_s$ (NaCl)	0.040	0.042	-0.006 <sup>d</sup>
81	423.15–573.15	$p_s$	$m_s$	6	$m_s$ (NaCl)	0.100	0.098	0.037 <sup>d</sup>
82	375.5–441.45	$p_s$	$m_s$	2	$m_s$ (NaCl)	0.050	0.048	-0.039 <sup>d</sup>
74	273.15–333.15	0.1	$m_s$	4	$m_s$ (NaCl)	0.025	0.015	-0.002 <sup>d</sup>
83	348.15–573.15	$p_w$	$m_s$	11	$m_s$ (NaCl)	0.030	0.033	0.006 <sup>d</sup>
84	422–603	$p_s$	$m_s$	13	$m_s$ (NaCl)	0.064	0.044	0.012 <sup>d</sup>
85	283.15–308.15	0.1	$m_s$	4	$m_s$ (NaCl)	0.010	0.008	0.007 <sup>d</sup>
86	290.8–373.14	0.1	$m_s$	13	$m_s$ (NaCl)	0.05	0.042	0.037 <sup>d</sup>
87	235–256			11	$p_{dec}$	6%	7%	-2%
88	251.95–273.3			5	$p_{dec}$	20	21	-3.8 <sup>e</sup>
89	$T_{fus}$	0.1	1.0–5.2	12	$\Delta_{fus}T$	U	0.010	-0.010 <sup>f</sup>
73	$T_{fus}$	0.1	2.24–5.13	5	$\Delta_{fus}T$	0.005	0.005	0.0042 <sup>f</sup>
90	$T_{fus}$	0.1	0.0008–1.3	28	$\Delta_{fus}T$	0.00075, $m_L = 0.2$	0.0038	0.0017 <sup>f</sup>
74	$T_{fus}$	0.1	1.5–5.12	4	$\Delta_{fus}T$	0.005, $m_L = 5.0$	0.012	-0.0059 <sup>f</sup>
91	$T_{fus}$	0.1	0.02–3.07	21	$\Delta_{fus}T$	0.0007, $m_L = 1.0$	0.0057	0.002 <sup>f</sup>
92	$T_{fus}$	0.1	0.14–3.6	32	$\Delta_{fus}T$	0.002, $m_L = 1.0$	0.0018	0.0013 <sup>f</sup>
93	$T_{fus}$	0.1	0.007–4.2	32	$\Delta_{fus}T$	0.0008, $m_L = 0.2$	0.0026	-0.0014 <sup>f</sup>
94	373	0.1	0.07–2.8	15	$\Delta_{vap}T$	0.003	0.0032	-0.0021 <sup>f</sup>
95	333–343	0.1	0.05–1.0	24	$\Delta_{vap}T$	0.0006	0.00060	-0.00021 <sup>f</sup>
95	353–373	0.1	0.05–1.0	36	$\Delta_{vap}T$	0.00037	0.00039	0.00006 <sup>f</sup>
96	333.15	0.05	1.5–3.5	10	$\Delta_{vap}T$	0.005	0.0049	0.0039 <sup>f</sup>
96	343.15–373.15	0.07	1.5–3.5	43	$\Delta_{vap}T$	0.003	0.0023	0.00005 <sup>f</sup>
97	298.15–373.15	0.1	1.0–6.1	56	$\phi$	0.0039	0.0044	-0.0034 <sup>f</sup>
98	293.15–303.15	0.1	2.4–6.1	36	$\phi$	0.0036	0.0034	-0.0023 <sup>f</sup>
99	298.15	$p_s$	4.0–5.9	9	$p_s - p_w$	0.0023	0.0021	0.0001 <sup>f</sup>

TABLE 4. Literature sources for the activity and thermal properties of NaCl(aq) — Continued

Reference	Temperature range (K)	Pressure range <sup>a</sup> (MPa)	Molality range (mol·kg <sup>-1</sup> )	n	Type <sup>b</sup>	$\sigma_{\text{est}}^c$	$\sigma_{\text{fit}}$	$\Delta_{\text{fit}}$
100	293.43	$p_s$	6.1	2	$p_s - p_w$	0.0020	0.0022	-0.0017 <sup>f</sup>
100	298.15	0.1	4.3-6.0	6	$p_s - p_w$	0.007	0.0056	0.0042 <sup>f</sup>
101	293.43-298.15	$p_s$	4.7-6.1	3	$p_s - p_w$	0.002	0.0027	0.00030 <sup>f</sup>
102	298.15	$p_s$	0.76-5.9	12	$p_s - p_w$	0.0046	0.0043	-0.0027 <sup>f</sup>
83	348.15-423.15	$p_s$	3.8-7.2	7	$p_s - p_w$	0.0075	0.0054	0.0040 <sup>f</sup>
83	473.15-498.15	$p_s$	3.9-8.4	13	$p_s - p_w$	0.005	0.0033	0.0030 <sup>f</sup>
83	523.15-573.15	$p_s$	4.1-10.4	18	$p_s - p_w$	0.003	0.0026	0.0009 <sup>f</sup>
103	422-541	$p_s$	1.0-3.0	22	$p_s - p_w$	0.01	0.0098	-0.0032 <sup>f</sup>
104	440-512.4	$p_s$	0.5-1.0	7	$p_s - p_w$	0.025	0.014	0.0057 <sup>f</sup>
105	398.15-573.15	$p_s$	0.25-1.0	38	$p_s - p_w$	U	0.013	-0.0072 <sup>f</sup>
106	423.15-573.15	$p_s$	1.2-5.55	20	$p_s - p_w$	U	0.030	-0.010 <sup>f</sup>
107	273.15-323.15	0.1	0.001-4.0	60	$\ln(\gamma_2/\gamma_1)$	0.005	0.0044	0.00018
108	288.15-323.15	0.1	0.02-1.0	32	$\ln(\gamma_2/\gamma_1)$	U	0.0041	0.0010
109	298.15-343.15	0.1	0.03-5.0	48	$\ln(\gamma_{\pm})$	U	0.019	-0.00056
110	273.45-313.15	0.1	0.05-4.0	76	$\ln(\gamma_2/\gamma_1)$	0.005	0.0049	-0.0013
111	298.15	0.1	0.03-2.97	4	$\Delta_{\text{aII}}L_{\phi}$	80	51	-22 <sup>g</sup>
112	298.15	0.1	0.4-1.23	66	$\Delta_{\text{aII}}L_{\phi}$	0.09, $m_L = 0.8$	0.13	0.007 <sup>g</sup>
113	298.15	0.1	0.1-0.83	21	$\Delta_{\text{aII}}L_{\phi}$	15	15	-8.4 <sup>g</sup>
114	348.35-372.85	6.6-41.1	0.03-5.2	33	$\Delta_{\text{aII}}L_{\phi}$	2%, 20.	24	-4.4 <sup>g</sup>
114	423.25-473.05	6.6-41.6	0.03-5.2	47	$\Delta_{\text{aII}}L_{\phi}$	2%, 20.	52	13 <sup>g</sup>
114	523.45	6.6-41.7	0.03-5.2	31	$\Delta_{\text{aII}}L_{\phi}$	2%	190	67 <sup>g</sup>
114	572.85	10.5-41.7	0.03-5.2	141	$\Delta_{\text{aII}}L_{\phi}$	2%	517	-34 <sup>g</sup>
115	283.15-298.15	0.1	0.0003-0.40	56	$\Delta_{\text{aII}}L_{\phi}$	8.0	8.1	-2.0 <sup>g</sup>
116	298.15	0.1	0.005-1.0	23	$\Delta_{\text{aII}}L_{\phi}$	2.5	2.2	1.3 <sup>g</sup>
117	303.15	0.1	0.2-1.0	7	$\Delta_{\text{aII}}L_{\phi}$	3.0	2.3	-2.0 <sup>g</sup>
118	298.15	0.1	0.04-5.0	19	$\Delta_{\text{aII}}L_{\phi}$	6.0	6.3	-3.8 <sup>g</sup>
118	323.15	0.1	0.04-5.0	23	$\Delta_{\text{aII}}L_{\phi}$	10	10.3	-2.7 <sup>g</sup>
118	348.15	0.1	0.04-5.0	18	$\Delta_{\text{aII}}L_{\phi}$	10	7.4	2.7 <sup>g</sup>
119	298.15	0.1	0.0008-0.1	24	$\Delta_{\text{aII}}L_{\phi}$	5	4.7	-0.4 <sup>g</sup>
120	298.08	0.1	0.046-0.45	2	$\Delta_{\text{aII}}L_{\phi}$	12	12.0	12.0 <sup>g</sup>
120	298	0.1	0.44-6.14	17	$\Delta_{\text{aII}}L_{\phi}$	1	0.81	0.42 <sup>g</sup>
121	273.4	0.1	0.09-6.1	21	$\Delta_{\text{aII}}L_{\phi}$	0.5, $m_L = 0.5$	0.82	0.06 <sup>g</sup>
121	285.8	0.1	0.2-6.1	18	$\Delta_{\text{aII}}L_{\phi}$	0.5, $m_L = 0.5$	0.51	-0.38 <sup>g</sup>
121	298.2	0.1	0.19-6.1	17	$\Delta_{\text{aII}}L_{\phi}$	0.3, $m_L = 0.5$	0.29	0.042 <sup>g</sup>
122	298.15	0.1	0.00025-1.0	7	$\Delta_{\text{aII}}L_{\phi}$	2.5	2.6	1.0 <sup>g</sup>
123	348.15	0.1	0.035-6.0	21	$\Delta_{\text{aII}}L_{\phi}$	5.0, $m_L = 0.3$	5.4	-0.2 <sup>g</sup>
123	373.15	0.11	0.009-6.0	28	$\Delta_{\text{aII}}L_{\phi}$	10.0	6.6	4.3 <sup>g</sup>
123	423.65	0.5	0.007-6.0	46	$\Delta_{\text{aII}}L_{\phi}$	<sup>h</sup>	16.5	10.5 <sup>g</sup>
123	450.95	0.9	0.04-6.0	25	$\Delta_{\text{aII}}L_{\phi}$	<sup>h</sup>	15.0	12.2 <sup>g</sup>
123	472.95	1.55	0.20-6.0	11	$\Delta_{\text{aII}}L_{\phi}$	30	29	14 <sup>g</sup>
124	349.2	1.03	0.03-3.0	18	$\Delta_{\text{aII}}L_{\phi}$	20	16	-12 <sup>g</sup>
124	398.3	1.03	0.03-3.0	19	$\Delta_{\text{aII}}L_{\phi}$	<sup>h</sup>	34	-26 <sup>g</sup>
124	448.3	1.03	0.01-3.0	22	$\Delta_{\text{aII}}L_{\phi}$	<sup>h</sup>	80	-59 <sup>g</sup>
124	498.3	3.35	0.01-3.0	21	$\Delta_{\text{aII}}L_{\phi}$	<sup>h</sup>	78	-26 <sup>g</sup>
125	313.15	0.1	0.005-6.0	42	$\Delta_{\text{aII}}L_{\phi}$	20	16	10 <sup>g</sup>
125	323.15	0.1	0.004-5.7	31	$\Delta_{\text{aII}}L_{\phi}$	20	22	11 <sup>g</sup>
125	333.15	0.1	0.008-5.7	32	$\Delta_{\text{aII}}L_{\phi}$	20	16	8 <sup>g</sup>
125	343.15	0.1	0.007-5.7	32	$\Delta_{\text{aII}}L_{\phi}$	20	21	-1.0 <sup>g</sup>
125	353.15	0.1	0.007-5.7	29	$\Delta_{\text{aII}}L_{\phi}$	U	68	26 <sup>g</sup>
126	298.15	0.1	0.27-3.0	6	$\Delta_{\text{aII}}L_{\phi}$	20	15	-5 <sup>g</sup>
127	293.15	0.1	0.02-0.04	9	$\Delta_{\text{sol}}H_m$	250	168	-49 <sup>g</sup>
128	298.15	0.1	0.05-1.3	24	$\Delta_{\text{sol}}H_m$	40	21	19 <sup>g</sup>
129	278.15-348.15	0.1	0.46	5	$\Delta_{\text{sol}}H_m$	40	40	-39 <sup>g</sup>
130	298.15	0.1	0.5-5.6	14	$\Delta_{\text{sol}}H_m$	40	30	28 <sup>g</sup>
129	278.15-313.15	0.1	0.0003-4.1	41	$\Delta_{\text{sol}}H_m(m_2-m_1)$	120	126	-98 <sup>g</sup>
131	275.15	0.1	0.06-6.0	18	$\Delta_{\text{sol}}H_m$	230	230	-136 <sup>g</sup>
132	387.4-472.65	$p_s$	0.01-0.04	17	$\Delta_{\text{sol}}H_m$	300	296	-106 <sup>g</sup>
133	273.2-368.3	0.1	0.003-0.02	58	$\Delta_{\text{sol}}H_m$	150	146	-100 <sup>g</sup>
134	298.15	0.1	0.02-0.72	23	$\Delta_{\text{sol}}H_m$	40	22	12 <sup>g</sup>
135	298.15	0.1	0.01-0.03	5	$\Delta_{\text{sol}}H_m$	40	27	-23 <sup>g</sup>
136	278.15-298.15	0.1	0.05-5.0	88	$\Delta_{\text{sol}}H_m$	170	169	-80 <sup>g</sup>
137	303-313	0.1	0.006-0.12	48	$\Delta_{\text{sol}}H_m$	190	182	142 <sup>g</sup>
138	298.15	0.1	0.01-0.12	16	$\Delta_{\text{sol}}H_m$	100	101	18 <sup>g</sup>
139	293.15-298.15	0.1	0.8-5.9	17	$\Delta_{\text{sol}}H_m$	40	17	0.6 <sup>g</sup>

TABLE 4. Literature sources for the activity and thermal properties of NaCl(aq) — Continued

Reference	Temperature range (K)	Pressure range <sup>a</sup> (MPa)	Molality range (mol·kg <sup>-1</sup> )	<i>n</i>	Type <sup>b</sup>	$\sigma_{\text{est}}^c$	$\sigma_{\text{fit}}$	$\Delta_{\text{fit}}$
140	298.15	0.1	0.07–5.5	20	$\Delta_{\text{sol}}H_m$	40	10	-2 <sup>g</sup>
141	298	0.1	0.25–0.5	4	$\Delta_{\text{sol}}H_m$	40	5	3 <sup>g</sup>
142	323.14–573.15	7–36	1.0–6.0	127	$c_{p,s}/c_{p,w}$	0.00125	2.1	0.8 <sup>h</sup>
142	598.01	20.1	1.0–6.0	24	$c_{p,s}/c_{p,w}$	0.005	18.7	11.2 <sup>h</sup>
146	349–573	***–17.9	0.08–5.0	402	$c_{p,s}/c_{p,w}$	*	12.3	-0.8 <sup>i</sup>
146	597.8	17.9	0.085–3.0	18	$c_{p,s}/c_{p,w}$	*	83	52 <sup>i</sup>
147	348.2–598.6	17.7	3.0	7	$c_{p,s}/c_{p,w}$	*	4.3	-2.7 <sup>j</sup>
148	358.3, 573.95	17.7	1.0–3.0	6	$c_{p,s}/c_{p,w}$	*	2.3	1.6 <sup>j</sup>
150	598.11	17.7	1.0–3.0	6	$c_{p,s}/c_{p,w}$	*	5.0	-3.3 <sup>j</sup>
149	353.15–473.15	***	0.35–2.13	35	$C_{p,s}$	0.012	5.4	-0.2 <sup>j</sup>
143	278.15	0.1	0.076–6.0	20	$C_{p,\phi}$	0.5, $m_L = 1.5$	1.7	-0.9 <sup>k</sup>
143	298.15	0.1	0.04–6.0	30	$C_{p,\phi}$	0.5, $m_L = 1.5$	1.8	-0.3 <sup>k</sup>
143	318.15	0.1	0.04–6.0	26	$C_{p,\phi}$	0.5, $m_L = 1.5$	1.9	-0.2 <sup>k</sup>
143	338.15	0.1	0.08–6.0	22	$C_{p,\phi}$	0.5, $m_L = 1.5$	0.9	0.3 <sup>k</sup>
143	358.15	0.1	0.08–6.0	17	$C_{p,\phi}$	0.5, $m_L = 1.5$	1.4	0.3 <sup>k</sup>
24	298.15	0.1	1.0–3.2	13	$C_{p,\phi}$	0.4, $m_L = 2.5$	0.6	-0.1 <sup>k</sup>
144	298.15	0.1	0.011–5.32	22	$C_{p,\phi}$	0.75, $m_L = 0.1$	1.0	-0.3 <sup>k</sup>
145	298.15	0.1	0.05–2.5	11	$C_{p,\phi}$	1.0, $m_L = 0.6$	3.4	-1.9 <sup>k</sup>
27	298.15	0.1	1.0–6.0	8	$c_{p,s}/c_{p,w}$	U	1.1	0.6 <sup>k</sup>
115	298.15	0.1	0.01–3.0	22	$C_{p,\phi}$	U	2.8	2.4 <sup>k</sup>
44	274.65	0.1	0.07–1.8	12	$C_{p,\phi}$	U	4.9	-2.4 <sup>k</sup>
44	278.15	0.1	0.03–1.0	11	$C_{p,\phi}$	U	3.2	-0.5 <sup>k</sup>
44	288.15	0.1	0.03–3.0	16	$C_{p,\phi}$	U	1.3	0.3 <sup>k</sup>
44	308.15	0.1	0.03–3.0	16	$C_{p,\phi}$	U	4.2	4.0 <sup>k</sup>
44	318.15	0.1	0.03–2.5	15	$C_{p,\phi}$	U	3.1	2.9 <sup>k</sup>
32	298.15	0.1	0.08–0.5	10	$C_{p,\phi}$	U	1.3	-0.5 <sup>k</sup>
24	298.15	0.1	0.06–2.1	21	$C_{p,\phi}$	U	2.4	2.4 <sup>k</sup>
24	298.15	0.1	0.07–2.8	19	$C_{p,\phi}$	U	5.5	5.2 <sup>k</sup>
47	283.15–313.15	0.1	0.04–2.9	53	$C_{p,\phi}$	U	1.0	0.1 <sup>k</sup>
33	298.15	0.1	0.28–5.1	10	$C_{p,\phi}$	U	1.7	1.3 <sup>k</sup>
152	423.15–573.15	$p_s$	0.4–6.04	24	$c_{p,s}/c_{p,w}$	U	70	37 <sup>k</sup>
163	248.15	0.1	2.0–6.0	6	$C_{p,s}$	10, $m_L = 6.0$	17	9 <sup>k</sup>

\*\*\* indicates that the lowest pressure for the data set changed with the experimental temperature

<sup>b</sup> Type  $m_s$  refers to solubility of the indicated substance;  $p_{\text{dec}}$  refers to the vapor pressure of water in equilibrium with the dihydrate; The symbol  $p_s-p_w$  refers to the difference in vapor pressure between solution and solvent.

<sup>c</sup> The letter U indicates that these points were given an insignificant weight in the least-squares procedure. When two values are given the  $\sigma_{\text{exp}}$  was taken to be the larger of the two values given. In the cases where a value is given for  $m_L$ , the expected square root of the variance is taken to be the first value for  $m > m_L$  and taken to be the first value divided by  $m_L$  for  $m < m_L$ .

<sup>d</sup> Units are kJ·mol<sup>-3</sup>.

<sup>e</sup> Units are Pa.

<sup>f</sup> Values given in terms of the osmotic coefficient.

<sup>g</sup> Units are J·mol<sup>-1</sup>.

<sup>h</sup> Values of  $\sigma_{\text{exp}}$  were unitless, other values given in terms of  $C_{p,\phi}$ , units are J·K<sup>-1</sup>·mol<sup>-1</sup>.

<sup>i</sup> Values of  $\sigma_{\text{exp}}$  were unitless and were those given in the cited reference, other values given in terms of  $C_{p,\phi}$ , units are J·K<sup>-1</sup>·mol<sup>-1</sup>.

<sup>j</sup> Values of  $\sigma_{\text{exp}}$  had units of J·K<sup>-1</sup>·g<sup>-1</sup>, other values given in terms of  $C_{p,\phi}$ , units are J·K<sup>-1</sup>·mol<sup>-1</sup>.

<sup>k</sup> Units are J·K<sup>-1</sup>·mol<sup>-1</sup>.

All of the significantly weighted results included by Rogers and Pitzer<sup>16</sup> in their representation of the volumetric properties of NaCl(aq) were included in the present work. They gave one or two standard deviations of fit for each of the 12 data sets that they included in their representation. Their two standard deviations corresponded to either their low-temperature or their high-temperature representation. The agreement of the present fitted equation with 11 of those 12 data sets was comparable to the better of their two listed standard deviations. The one data set for which the present equation showed poorer agreement was that of Hilbert.<sup>50</sup> The

larger difference of Hilbert's results from the fitted equation is attributable to the inclusion of the results of Majer *et al.*,<sup>53</sup> Gehrig *et al.*,<sup>57</sup> and of Majer *et al.*,<sup>59</sup> none of these results were available to Rogers and Pitzer.

The error in experimental determinations of solution densities arises from errors in measurement of the concentration, the density itself, temperature and pressure. For 298.15 K and 0.1 MPa the determination of the temperature and pressure should introduce negligible errors into the determination of the density. Figure 1 shows the differences between experiment and fitted equation for density results, for 298.15 K and 0.1 MPa, where the den-

sities were determined by means of either a pycnometer, a dilatometer, or a magnetic-float densimeter. Six of the seven sets of results shown in the figure agree, for the most part, within  $50 \times 10^{-6} \text{ g cm}^{-3}$ . At large molalities an uncertainty in molality determination of  $\pm 0.02\%$  corresponds to an uncertainty of  $\pm 50 \times 10^{-6} \text{ g cm}^{-3}$  in the density and thus composition determination becomes a significant factor in the accuracy to which the density may be determined, for near-ambient conditions. Figure 2 shows the differences between experimental values of the density, obtained with vibrating-tube densimeters, from the fitted equation, again for 298.15 K and 0.1 MPa. Comparison of Figs. 1 and 2 is a direct comparison of the accuracies of the respective experimental methods, assuming that solutions were prepared with the same accuracy in the vibrating-tube densimeter (VTD) studies as they were for the results shown in Fig. 1. The results from Gates and Wood<sup>34</sup> agreed with the fitted equation within their stated uncertainties. Their results showed a somewhat random pattern of residuals that would be related primarily to the accuracy of concentration determination. For most of the remainder of the data sets shown in Fig. 2, differences of the VTD results from the more accurate results, e.g. those shown in Fig. 1, can be described as possessing systematic errors that generally increase

with increasing concentration, a characteristic similar to what one expects for inaccuracies in the calibration of the VTD. These systematic errors corresponded to inaccuracies in the calibration constant that range to 0.1% or larger. Of special note are the results of Olofsson,<sup>24</sup> who gave values of  $V_\phi$  for "calorimeter 1" and "calorimeter 2" that showed systematic biases of different sign from the fitted equation, relative to each other. The 298.15 K  $V_\phi$  results of Allred and Woolley<sup>47</sup> showed a small systematic bias, however, their results for 313.15 K exhibited systematic differences from the equation that were as large as 0.8% of  $\rho_s - \rho_w$ . The differences of the results of Singh *et al.*<sup>32</sup> from the fitted equation were significantly larger than the other VTD results.

Systematic differences were also found in the VTD results for higher temperatures. Figures 3 and 4 show the differences of the fitted equation from the experimental results for Majer *et al.*'s<sup>53</sup> "Set 1" and "Set 2" results for nominal temperatures of 323 and 448 K. These two sets of results were obtained with a VTD with different materials of construction for the vibrating tube and with different calibration methods. For 323 K, the fitted equation was determined primarily by the results of Gibson and Loeffler,<sup>51,52</sup> as well as, but to a lesser extent, by the results of Rogers *et al.*<sup>55</sup> and of Ellis.<sup>54</sup> From the present re-

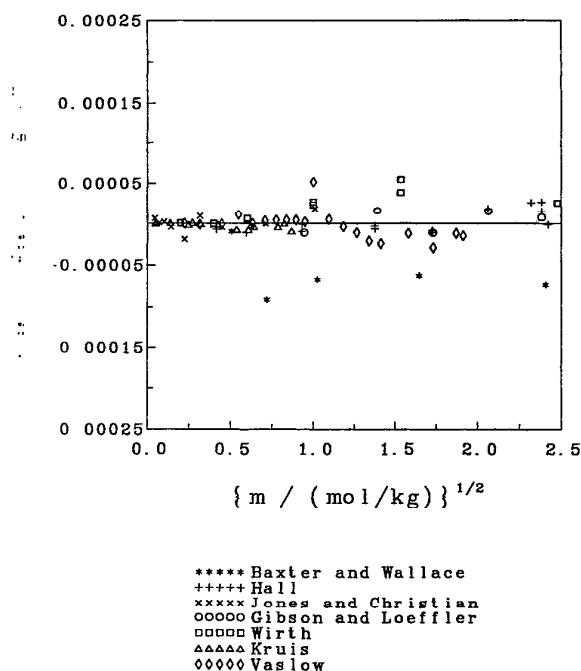


FIG. 1. Difference of experimental densities from the fitted equation for 298.15 K 0.1 MPa. The experimental results were from: Baxter and Wallace,<sup>38</sup> Hall,<sup>21</sup> Jones and Christian,<sup>39</sup> Gibson and Loeffler,<sup>51,52</sup> Wirth,<sup>23</sup> Kruis,<sup>22</sup> and Vaslow.<sup>25</sup>

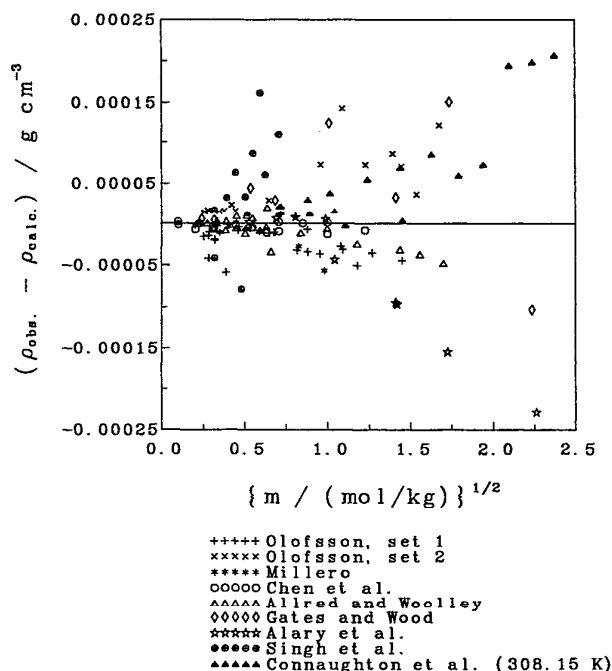


FIG. 2. Difference of experimental densities, obtained from vibrating-tube densimeters, from the fitted equation for 298.15 K 0.1 MPa. The experimental results are: Olofsson "set 1",<sup>24</sup> Olofsson "set 2",<sup>24</sup> Millero,<sup>41</sup> Chen *et al.*,<sup>43</sup> Allred and Woolley,<sup>47</sup> Gates and Wood,<sup>34</sup> Alary *et al.*,<sup>33</sup> Singh *et al.*<sup>32</sup> and Connaughton *et al.*<sup>169</sup>

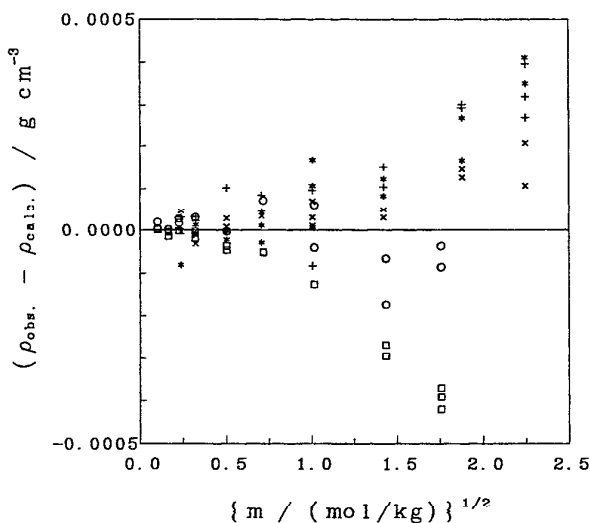
sults it can be concluded that: 1) for near-ambient temperatures, the accuracy of densities determined with VTD's has been less than what can be obtained with other methods, *e.g.* pycnometers, magnetic-float densimeters and dilatometers; 2) for significantly non-ambient conditions and for dilute solutions, the greater resolution in measurement of  $\rho_s - \rho_w$  by VTD provides for a significantly more accurate (orders of magnitude) determination of this quantity than that obtained with static-vessel type  $pVT$  methods; 3) for non-ambient conditions and for concentrated solutions the accuracy of current VTD methods is a factor of two or three times more accurate than static-vessel type  $pVT$  methods.

Wirth and Bangert<sup>61</sup> did not report their experimental values but reported obtaining density values from a combination of pycnometric and dilatometric methods that were  $200 \times 10^{-6} \text{ g}\cdot\text{cm}^{-3}$  larger than the results of Vaslow<sup>25</sup> for concentrations larger than  $2.0 \text{ mol}\cdot\text{kg}^{-1}$ . The agreement of the several sets of results shown in Fig. 1 as well as the agreement of the expansivities and densities at other temperatures, indicated that Wirth and Bangert's results were probably in error. J. Rard supplied a copy of a correspondence with H. E. Wirth regarding the results of Ref. 61. This correspondence included the measured values. This additional information was not able to re-

solve the discrepancies between the Wirth and Bangert results and the representation; both the dilatometric results and the one reference-solution density result disagreed with the representation.

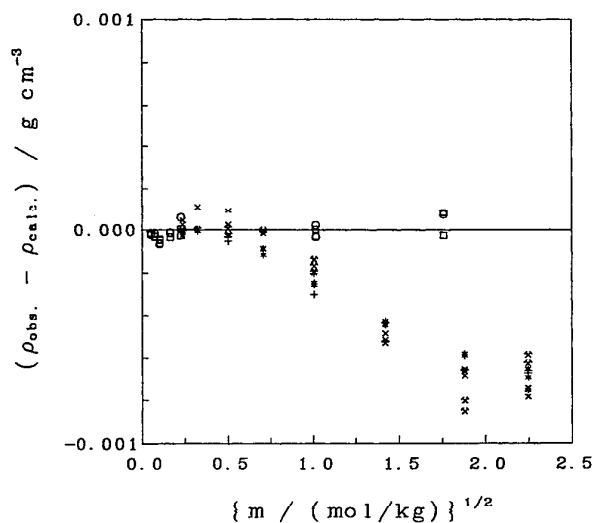
As in the work of Rogers and Pitzer,<sup>16</sup> the results of Khaibullin and Borisov,<sup>62</sup> of Fabuss and Korosi,<sup>63,64</sup> and of Zarembo and Federov<sup>65</sup> were given no significant weight in the representation due to their low accuracies. The high-temperature results of Grant-Taylor<sup>56</sup> showed differences from the fitted equation that increased with increasing molality and increasing temperature and were not given a significant weight. Additionally, the very near-ambient density results of Epikhin and Stakhanova,<sup>27</sup> Olofsson,<sup>24</sup> Allred and Woolley,<sup>47</sup> Gucke *et al.*,<sup>31</sup> Alary *et al.*,<sup>33</sup> and Singh *et al.*<sup>32</sup> were given no significant weight in the least-squares procedure because of the presence of systematic biases of their results from other results in regions of the independent variables where more accurate results existed.

Figure 5 shows agreement of the isothermal compressibility measurements of Millero *et al.*<sup>42</sup> with the fitted equation. Comparison of isentropic compressibilities for temperatures from 278.15 to 353.15 K and 0.1 MPa is also shown in Fig. 5. The agreement was reasonable. As in Rogers and Pitzer's<sup>16</sup> work, the compressibility results of



\*\*\*\*\* Majer et al. set 1; 323 K 0.1 MPa  
 +++++ Majer et al. set 1; 323 K 30 MPa  
 xxxxx Majer et al. set 1; 323 K 37 MPa  
 ooooo Majer et al. set 2; 323 K 0.6 MPa  
 □□□□ Majer et al. set 2; 323 K 32 MPa

FIG. 3. Difference of experimental densities from Majer *et al.*,<sup>53</sup> obtained from two slightly different vibrating-tube densimeters for approximately 323 K.



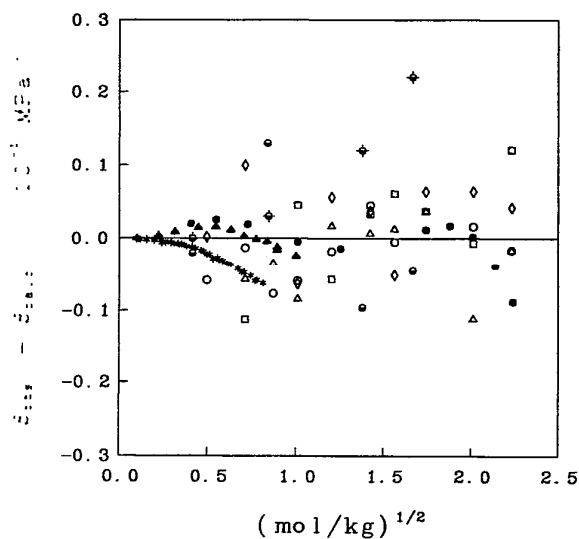
\*\*\*\*\* Majer et al. set 1; 450 K 3.3 MPa  
 +++++ Majer et al. set 1; 450 K 11 MPa  
 xxxxx Majer et al. set 1; 450 K 29 MPa  
 \*\*\*\*\* Majer et al. set 1; 450 K 38 MPa  
 ooooo Majer et al. set 2; 448 K 4.5 MPa  
 □□□□ Majer et al. set 2; 448 K 33 MPa

FIG. 4. Difference of experimental densities from Majer *et al.*,<sup>53</sup> obtained from two slightly different vibrating-tube densimeters for approximately 450 K.



Rowe and Chou<sup>66</sup> showed large differences from the fitted equation and were given no significant weight in the representation.

Figure 6 shows values of the expansivity of NaCl(aq) for 0.1 MPa. The dilatometric results of Gibson and Loeffler<sup>51,52</sup> and of Wirth and LoSurdo<sup>67</sup> agreed well with each other and with the fitted equation. The results of Alary *et al.*<sup>33</sup> and of Fortier *et al.*<sup>45</sup> were obtained with a commercial mass-flow heat-capacity calorimeter. Their results showed a systematic bias that increased with increasing concentration for concentrations greater than 1.0 mol·kg<sup>-1</sup>. Alary *et al.* claimed an accuracy of 2% in expansivity. Agreement is within this accuracy limit. The values in Fig. 6 indicated that expansivities obtained by the flow-calorimetric method of Fortier *et al.* were about a factor of two to three less accurate than those obtained with dilatometric apparatus, for non-dilute solutions. The r.m.s. errors for Rogers *et al.*'s<sup>55</sup> dilatometric values to 473.15 K was significantly smaller than their estimated accuracies. The r.m.s. error for Ellis's<sup>54</sup> dilatometric results was slightly smaller than that found in the representation from Rogers and Pitzer.<sup>16</sup>



○○○○  $\beta_T$  273.15 K, Millero *et al.*  
 □□□□  $\beta_T$  288.15 K, Millero *et al.*  
 △△△△  $\beta_T$  303.15 K, Millero *et al.*  
 ◇◇◇◇  $\beta_T$  318.15 K, Millero *et al.*  
 ●●●●  $\beta_S$  298.15 K, Gucker *et al.*  
 ▲▲▲▲  $\beta_S$  298.15 K, Millero *et al.*  
 \*\*\*\*\*  $\beta_S$  278.15 K, Sakurai *et al.*  
 ◆◆◆◆  $\beta_S$  293.15 K, Mikhailov & Shutilov  
 ○○○○  $\beta_S$  353.15 K, Mikhailov & Shutilov

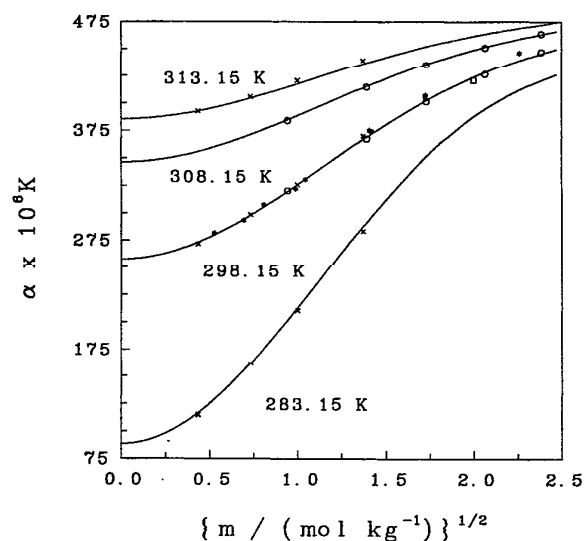
FIG. 5. Difference between experimental compressibilities for 0.1 MPa and values calculated from the fitted equation. The experimental isothermal compressibilities are from: Millero *et al.*,<sup>42</sup> The adiabatic compressibilities are from: Gucker *et al.*,<sup>31</sup> Millero *et al.*,<sup>30</sup> Sakurai *et al.*,<sup>69</sup> and Mikhailov and Shutilov.<sup>68</sup>

#### 4.2.2. Activity Results

Osmotic coefficients were calculated from the difference in vapor pressure between the solution and the solvent as:

$$\phi = \frac{(G_{m,1,g}^{\circ} - G_{m,1}^{\circ})}{RTvmM_1} \quad (45)$$

where the difference in chemical potentials for the vapor and the liquid at the temperature and pressure of the solution,  $G_{m,1,g}^{\circ} - G_{m,1}^{\circ}$ , was calculated from the equation of state for water. Osmotic coefficients were calculated from the difference in freezing temperature of water in the solution from that of pure water by means of the equation given by Scatchard *et al.*<sup>153</sup> The osmotic coefficients given by Gibbard *et al.*<sup>97</sup> and by Olynk *et al.*<sup>98</sup> were used as given as the original vapor pressures were not given. Values of the osmotic coefficient that were, in principle, determinable from isopiestic molalities were not included in the data representation for the following reason. Isopiestic molality determinations equate the ac-



○○○○ Gibson and Loeffler  
 □□□□ Wirth and LoSurdo  
 \*\*\*\*\* Alary *et al.*  
 ◆◆◆◆ Fortier *et al.*

FIG. 6. Experimental and calculated values of the 0.1 MPa expansivity of NaCl(aq). The experimental results are from: Gibson and Loeffler,<sup>51,52</sup> Wirth and LoSurdo,<sup>67</sup> Alary *et al.*,<sup>33</sup> and Fortier *et al.*<sup>45</sup>

tivity of water in a solution of one solute to the activity of water in a solution of a different solute. The measurement is a relative one; some solute, or solutes, must serve as a standard. NaCl(aq) is one of the few solutes that can serve as an accurate isopiestic standard, i.e. there are sufficient experimental results available to define the required thermodynamic properties with no recourse to measurements of a solution of NaCl(aq) relative to another solution of a different substance. Inclusion of relative measurements in the determination of the equation for the "standard" invalidates the original intent. This point has been observed by Rard and Platford<sup>154</sup> regarding equations for the isopiestic "standards" used for water activities less than those that can be obtained with NaCl(aq), namely, H<sub>2</sub>SO<sub>4</sub>(aq) and CaCl<sub>2</sub>(aq).

Differences of the present equation from the osmotic and activity coefficient measurements, for temperatures less than 373 K and for molalities less than 6.2 mol·kg<sup>-1</sup>, were nearly identical to that obtained with Clarke and Glew's equation. The results from Scatchard and Prentiss<sup>90</sup> were somewhat less well represented by the present

equation than by Clarke and Glew's<sup>2</sup> equation, however comparison of the present equation with all of the freezing-point results, Fig. 7, indicates a substantial agreement. The results of Liu and Lindsay<sup>105</sup> (those greater than 4 mol·kg<sup>-1</sup> and greater than 348 K) were somewhat better represented by the present equation than by the equation of Clarke and Glew. For temperatures greater than 423 K, the representation of the results of Liu and Lindsay was comparable to that obtained by Pitzer *et al.*<sup>1</sup> The osmotic coefficients, calculated from the vapor pressures given by Mashovets *et al.*<sup>106</sup> did not agree well with the other results (Fig. 8) and thus were given no significance in the data representation. Similar differences of Mashovets *et al.*'s results were also found for NaBr(aq).<sup>8</sup> The difference of the present equation from that of Clarke and Glew's, for the osmotic coefficient, is shown in Fig. 9. The differences shown in the figure for the combination of large molality and large temperature were directly attributable to the differences in representation of the vapor-pressure results of Lindsay and Liu. Because both equations gave very similar representa-

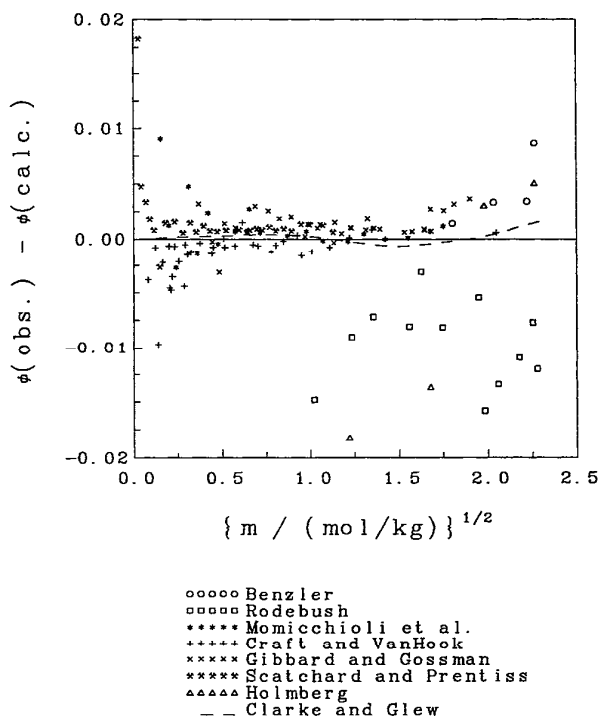


FIG. 7. Differences between osmotic coefficients calculated from solvent freezing-point measurements and values calculated from the fitted equation. The experimental results are from: Benzler,<sup>73</sup> Rodebush,<sup>89</sup> Momicchioli *et al.*,<sup>91</sup> Craft and VanHook,<sup>93</sup> Gibbard and Gossman,<sup>92</sup> Scatchard and Prentiss,<sup>90</sup> and Holmberg.<sup>74</sup> The dashed line is the difference of values calculated from Clarke and Glew's<sup>2</sup> representation from the present fitted equation.

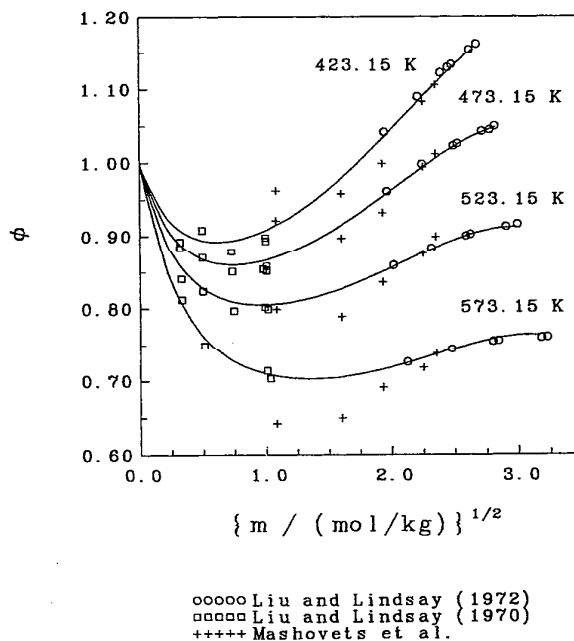


FIG. 8. Values of the osmotic coefficient calculated from vapor pressure measurements and calculated from the fitted equation for 423 K, 473 K, 523 K and 573 K. The experimental results are: Lindsay and Liu,<sup>83</sup> Lindsay and Liu,<sup>105</sup> and Mashovets *et al.*<sup>106</sup>

tions of the remainder of the experimental results, other differences observed in the figure were attributable to model biases between the two equations. The agreement of the present equation with Clarke and Glew's for 298.15 K, 0.1 MPa and for all molalities less than saturation, indicated that the differences of Clarke and Glew's equation from that of Hamer and Wu,<sup>155</sup> Pitzer *et al.*<sup>1</sup> and Gibbard *et al.*,<sup>97</sup> for these conditions, would also be observed with the present equation. Clarke and Glew showed that the difference of their equation from the others resulted from the differences of the osmotic coefficients calculated from isopiestic molalities as compared to the remainder of the fitted experimental results. Clarke and Glew gave these osmotic coefficients reduced weight in their representation; the present work has not included them. Because these osmotic coefficients appear to be less accurate than other sources of the solvent activity and because the other three equations are heavily based on these osmotic coefficients, the present equation, and that of Clarke and Glew, should be considered as more accurate.

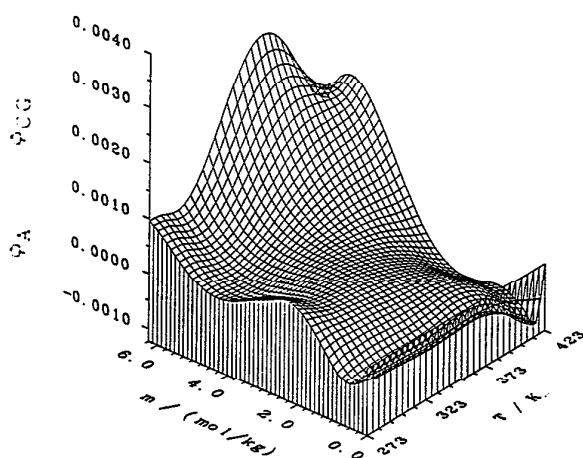


Fig. 9. Difference in calculated values of the osmotic coefficient between the present equation and that of Clarke and Glew.<sup>2</sup>

#### 4.2.3. Enthalpy of Dilution Results

For experimental enthalpies of dilution obtained for temperatures less than 343 K, the r.m.s. errors, the average deviations, and the pattern of residuals, obtained from the present representation, were comparable to those calculated from Clarke and Glew's<sup>2</sup> equation. Some of these data sets were slightly better represented by the present equation, others were slightly better represented by Clarke and Glew's equation.

Very accurate results exist for near-ambient temperatures. Young and co-authors<sup>120, 121</sup> measured the enthalpy change for very small changes in solute molality. The results from Young and Machin<sup>121</sup> spanned the tempera-

ture range of 273.3 to 298.15 K. The r.m.s. difference for their measurements, for molalities greater than 0.4 mol·kg<sup>-1</sup>, was approximately 0.35 J·mol<sup>-1</sup>. The present equation represented Young and Machin's results for 285.8 K and 273.3 K with smaller residuals which also showed smaller variation with concentration than did the residuals calculated from the equation of Clarke and Glew.<sup>2</sup> Vaslow<sup>112</sup> also measured enthalpy changes for very short dilution chords for 298.15 K; his values showed a r.m.s. difference of 0.12 J·mol<sup>-1</sup> from the fitted equation. The enthalpy of mixing results obtained with a commercial mass-flow calorimeter,<sup>116</sup> for 298.15 K, agreed with the equation and the other experimental results with a r.m.s. difference of 2.3 J·mol<sup>-1</sup>. The 298.15 K enthalpy of dilution results of Millero *et al.*<sup>115</sup> were obtained with a commercial batch-mixing calorimeter. The r.m.s. difference of their results from the fitted equation, 14.4 J·mol<sup>-1</sup>, with individual residuals as large as 34 J·mol<sup>-1</sup>, was somewhat greater than the claimed accuracy of 4 J·mol<sup>-1</sup>. However, the subsequent measurements of Leung and Millero,<sup>117</sup> performed with the same calorimeter and for 303.15 K, agreed with the representation to 2.2 J·mol<sup>-1</sup> (r.m.s.). The agreement of the results of Leung and Millero suggested that the larger differences of the Millero *et al.* study were not representative of the calorimetric method, but instead probably resulted from other laboratory errors. The equation showed a r.m.s. difference from the results of Messikomer and Wood<sup>118</sup> of 7 J·mol<sup>-1</sup>, which was within their expected experimental uncertainties.

The enthalpy of dilution results of Mayrath and Wood<sup>123</sup> agreed with the fitted equation within the authors' estimated errors. The r.m.s. difference of the present equation from their results was about one half of that calculated from the equation of Pitzer *et al.*<sup>1</sup> The average difference of Mayrath and Wood's results from the fitted equation was small and positive, indicating a calculated value that was slightly more exothermic than their observed values. The enthalpies of dilution of Busey *et al.*<sup>114</sup> from 348 to 523 K were represented, for the most part, within their estimate of  $\pm 2$  per cent or 20 J·mol<sup>-1</sup>, whichever was larger. Their three measurements for 332 K did not agree well with the remainder of the fitted results (average deviation = 160 J·mol<sup>-1</sup>) and were not significantly weighted. Their dilutions of a 0.2 mol·kg<sup>-1</sup> solution, for 573 K, showed differences from the fitted equation of -8 to -10 per cent (approximately -1 kJ·mol<sup>-1</sup>). These were the principal results from Busey *et al.* that disagreed by significantly more than their estimated errors. For temperatures less than 570 K, the agreement of the fitted equation to the results for Busey *et al.* was comparable to that calculated from the equation of Pitzer *et al.* For the 573 K results, the r.m.s. difference from the present equation was a factor of 2.5 smaller than that reported by Pitzer *et al.* The average deviation of the Busey *et al.* results from the fitted equation was near zero for 373 K, and was positive for results from 423 to 523 K. For 573 K, the average deviation was negative, however, if exclusion of the 0.2 mol·kg<sup>-1</sup> dilu-

tions was made, then the average deviation was also positive for this temperature. The fitted equation agreed with the enthalpies of dilution from Archer,<sup>124</sup> for 398 to 498 K, approximately within stated errors. Disagreement with the 349 K results (r.m.s. difference = 16 J·mol<sup>-1</sup>) was slightly greater than the estimated uncertainties, but was not a serious discrepancy. The average difference for the results of Archer was negative for all of the experimental temperatures. The agreement of the fitted equation with all three sets of enthalpies of dilution for temperatures greater than 373 K was within approximately  $\pm 3$  per cent (r.m.s.), indicating a good degree of reliability of the three different high-temperature calorimeters. The only exception was the 573 K, low-molality, enthalpies of dilution; the difference for these results could result from either a model bias or an experimental problem (Busey *et al.* described leakage of their solution-containment vessels).

#### 4.2.4. Enthalpy of Solution Results

For near-ambient conditions, enthalpies of dilution can be determined with an accuracy of a few J·mol<sup>-1</sup> or better. In order to obtain the same degree of accuracy for the concentration dependence of the apparent molar enthalpy from enthalpies of solution, the enthalpies of solution must be measured with an accuracy of 0.02 per cent at 298.15 K and of 0.01 per cent at 273.15 K. The inaccuracy of the best enthalpies of solution is an order of magnitude greater than this at 298.15 K. Thus, the concentration dependence of the apparent molar enthalpy is determined primarily by enthalpy of dilution measurements.

Figure 10 shows the differences of experimental enthalpy of solution results from the fitted equation for 298.15 K. The recent results of Sanahuja and Cesari<sup>138</sup> and of Taniewska-Osinska and Logwinienko<sup>136</sup> exhibited differences from the fitted equation that varied remarkably with concentration. This indicated that their results agreed with neither the earlier enthalpies of solution nor the enthalpies of dilution, and were thus inconsistent with a large portion of the results included in the representation. The difference between the results of Davies and Benson<sup>141</sup> and the results of Benson and Benson,<sup>128</sup> approximately 20 J·mol<sup>-1</sup>, is seen in the figure. The minimum variance for the enthalpy of solution data sets was taken to be twice this reproducibility. Figure 11 shows the differences of enthalpy of solution results from the fitted equation for temperatures within a few degrees of the 0.1 MPa freezing point of water. Clearly, the agreement is poor. This is because of substantial disagreement of these enthalpy of solution results with the heat capacity results and with the enthalpy of dilution results. Craft and Van Hook<sup>129</sup> reported the enthalpy of solution of NaCl into water obtained with a calorimeter of their own construction and the enthalpy of solution of NaCl into NaCl(aq) obtained with a commercial batch calorimeter. They reported a greater precision was available with the commercial instrument. However, their results obtained

with the "home-made" calorimeter agreed significantly better with the fitted equation. Agreement of the results obtained with their "homemade" calorimeter was within  $\pm 50$  J·mol<sup>-1</sup> at each temperature from 278 to 348 K, whereas their results obtained with the commercial calorimeter showed a r.m.s. difference of 120 J·mol<sup>-1</sup>. The high-temperature enthalpy of solution results from Gardner and Mitchell<sup>132</sup> did not show a large systematic bias relative to the fitted equation.

The 298.15 K, 0.1 MPa standard-state enthalpy of solution calculated from the least-squares estimated parameters is 3853 J·mol<sup>-1</sup>. This is in reasonable agreement with the value obtained by Clarke and Glew,<sup>2</sup> 3858 J·mol<sup>-1</sup>. The difference occurred primarily because of differences in the fitted results, the weighting of results and model biases. The difference was acceptable when compared to the differences of the 298.15 K enthalpy of solution results amongst themselves and from the fitted equation.

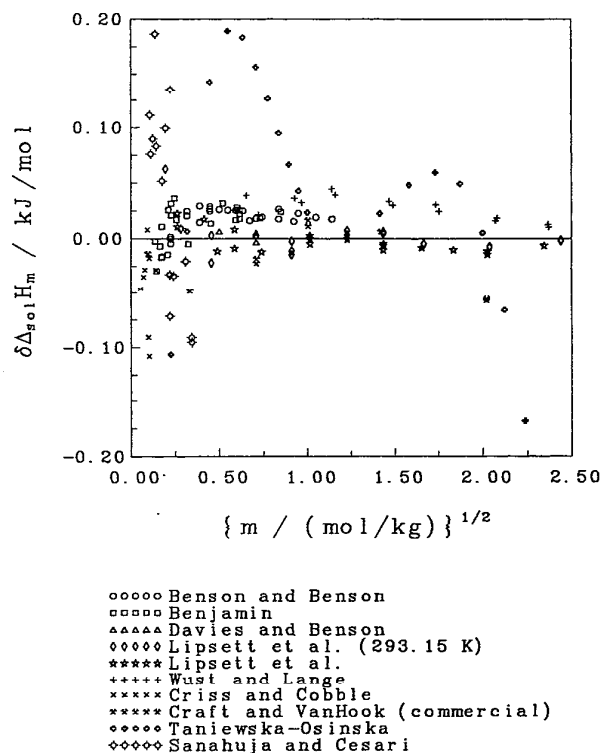


FIG. 10. Difference between experimental enthalpy of solution results for 298.15 K, 0.1 MPa and values calculated from the fitted equation. The experimental results are from: Benson and Benson,<sup>128</sup> Benjamin,<sup>134</sup> Davies and Benson,<sup>141</sup> Lipsett *et al.*,<sup>139,140</sup> Wst and Lange,<sup>130</sup> Criss and Cobble,<sup>133</sup> Craft and VanHook,<sup>129</sup> Taniewska-Osinska and Logwinienko,<sup>136</sup> and Sanahuja and Cesari.<sup>137</sup>

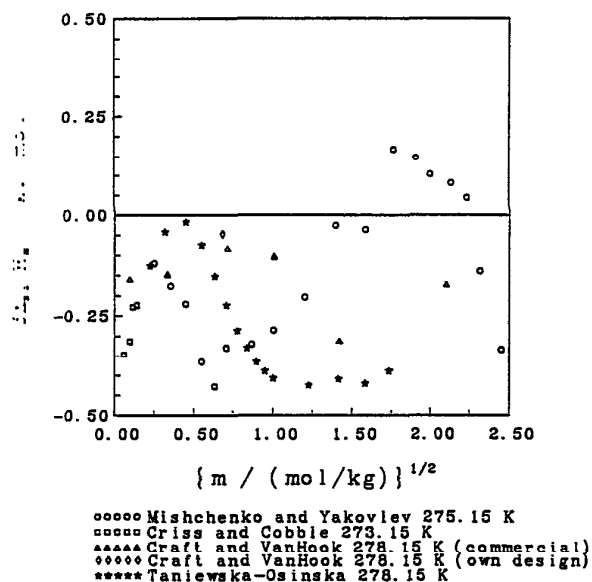


FIG. 11. Difference between experimental enthalpy of solution results for conditions near 275 K, 0.1 MPa and values calculated from the fitted equation. The experimental results are from: Mishchenko and Yakovlev,<sup>131</sup> Criss and Cobble,<sup>133</sup> Craft and VanHook,<sup>129</sup> and Taniewska-Osinska and Logwinienko.<sup>136</sup>

#### 4.2.5. Heat Capacity Results

For the sake of the current discussion, heat-capacity results will be divided into three categories. These categories are: 1) results obtained with calorimeters that performed measurements on static samples; 2) results obtained with mass-flow calorimeters, where the calorimeters were calibrated with an electrolyte solution (this solution usually has been NaCl(aq)); 3) results obtained with mass-flow calorimeters where the calibration was performed without the presumed knowledge of the heat capacity of a solution. The results of Simard *et al.*<sup>144</sup> were obtained with a commercial mass-flow enthalpy-of-mixing calorimeter and will be considered as members of the first group described above.

Mass-flow heat-capacity calorimeters that are designed for the measurement of the heat capacity of solutions usually measure the heat capacity of one fluid relative to another. These calorimeters possess, as do all calorimeters, the potential for systematic errors that arise from unaccounted heat-transfer within the calorimeter and to its surrounding environment. In the mass-flow heat-capacity calorimeters, heat-transfer from the calorimetric tubing and the heater, to the surroundings has been generally recognized as a principal source of systematic error in these measurements.<sup>147, 142, 150</sup> Attempts to correct for these heat losses have generally fallen into two categories, those involving adoption and application of a particular solution(s) as a chemical standard and those involving more fundamental methods.

In general, a chemical-standard approach has been used for the mass-flow calorimeters used at near-ambient conditions. This calibration method entails knowledge of the heat capacity of one or more compositions of a particular solute-solvent pair. Desnoyers *et al.*<sup>156</sup> recommended NaCl(aq) as the chemical standard for calibration of mass-flow heat-capacity calorimeters. They fitted an equation to three sets of experimental results for heat capacities at 298.15 K. These three sets of results were obtained in three different laboratories, but all were obtained with the same type of commercial instrument. The fitted equation was then used to "correct" their previous results for NaCl(aq),<sup>44, 151</sup> including those obtained for temperatures other than 298.15 K. Similar procedures were used by Allred and Woolley,<sup>47</sup> and Olofsson.<sup>24</sup> Such obtained results were not included in the data representation for a number of reasons: 1) The calibration method described by Desnoyers *et al.* only brings the NaCl(aq) calorimetric results into agreement with an average value obtained from a subset of the calorimeters. Systematic errors that might be present in the subset would then be perpetuated in the other "calibrated" calorimetric results. Heat capacity results obtained for NaCl(aq) and the Desnoyers *et al.* calibration method are thus not independent observations for NaCl(aq). An analogy to the inclusion of such-corrected results in the present representation, is to calibrate an enthalpy-of-combustion calorimeter with benzoic acid, use the so-calibrated calorimeter to combust benzoic acid, and then use the final result as an independent measurement for the enthalpy of combustion of benzoic acid; 2) The results of Allred and Woolley and those of Desnoyers and co-authors were obtained by assuming that the heat losses in their calorimeters were independent of temperature, or insignificantly dependent on temperature, over the small range of temperature available to the instrumentation. There is not an *a priori* reason to assume that the heat losses were independent of temperature; 3) Inclusion of these NaCl(aq) results would introduce correlated observations into the least-squares procedure and thus have an improper effect on the procedure.

Agreement of some of the near-ambient heat capacity results, from the first category, with the fitted equation is shown in Fig. 12. Above 1 mol·kg<sup>-1</sup>, all of these results agreed with the fitted equation within  $\pm 2$  J·K<sup>-1</sup>·mol<sup>-1</sup>; below 1 mol·kg<sup>-1</sup> the residuals appeared relatively random. Because of the relation between the temperature dependence of the relative apparent molar enthalpy and the concentration dependence of the apparent molar heat capacity, it is clear that there also existed agreement of the enthalpies of dilution with these heat capacity results. Figure 13 shows the agreement of some near-ambient mass-flow calorimetric results, for which calibrations were performed by flow-rate fluctuation methods. Agreement above 1 mol·kg<sup>-1</sup> for these results was within  $\pm 2$ –3 J·K<sup>-1</sup>·mol<sup>-1</sup>, with an apparently random distribution of residuals for lower molalities. Figure 14 shows the agreement of some of the heat-capacity results from the commercial mass-flow calorimeters, without the authors'

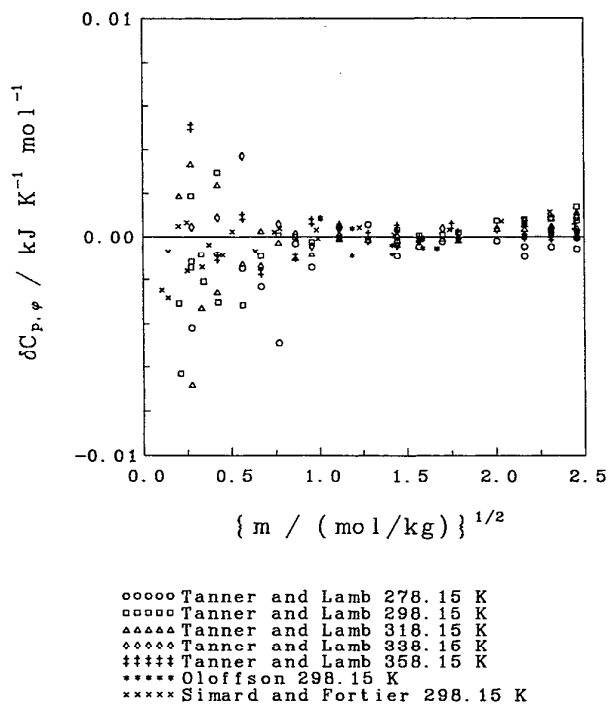


FIG. 12. Difference between experimental heat capacity results and values calculated from the fitted equation. The experimental results are from: Tanner and Lamb,<sup>143</sup> Oloffson,<sup>24</sup> and Simard and Fortier,<sup>144</sup>

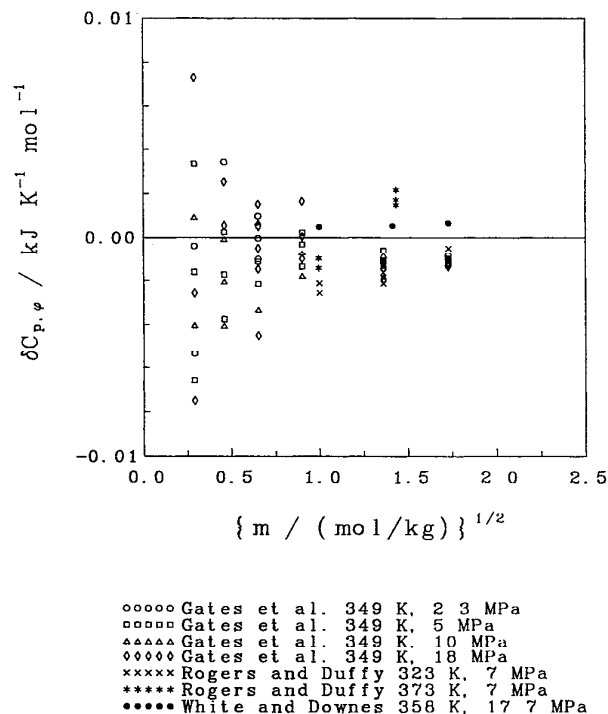


FIG. 13. Difference between experimental heat capacity results, obtained with mass-flow calorimeters for which calibrations were performed by means of a flow-rate variation method, and values calculated from the fitted equation. The experimental values are from: Gates *et al.*,<sup>146</sup> Rogers and Duffy,<sup>142</sup> and White and Downes.<sup>148</sup>

changes due to chemical-standard corrections. The difference of the results of Perron *et al.* from the fitted equation appeared to be somewhat dependent on temperature. Clearly, the temperature-independent correction of these results, as described by Desnoyers *et al.*,<sup>156</sup> would not improve the agreement of all of Perron *et al.*'s results with the remainder of the fitted experimental results. Rather, it would cause the 274.65 K and 278.15 K results to be in poorer agreement than would otherwise have been the case. From Fig. 14, it appears that the concentration dependence of the disagreement of the experimental heat-capacity results from the fitted equation, and thus also the remainder of the fitted results, varied from calorimeter to calorimeter. This was evident in the results of Alary *et al.*<sup>33</sup> and the more recent of the two commercial calorimeters used by Oloffson *et al.*<sup>24</sup> This variation in the concentration dependence of the systematic difference of calorimetric result and fitted equation suggests that the dependence of the "correction factor," described by Desnoyers *et al.*,<sup>156</sup> on  $c_{p,s}/c_{p,w}$  should also be investigated when a chemical-standard calibration of these instruments is performed.

The results of Gates *et al.*<sup>146</sup> to 573.4 K were represented with an r.m.s. error somewhat smaller than their stated accuracies with the exception of the results for 0.9911 mol·kg<sup>-1</sup> solutions. The pattern of residuals sug-

gested the concentration determination for this solution was in error and thus these results were not included in the representation. The measurements of Rogers and Duffy<sup>142</sup> to 573 K were fitted with a r.m.s. difference corresponding to 0.1% in the quantity  $c_{p,s}/c_{p,w}$ . Heat capacities near 597 K from both of these groups disagreed with each other. The results of Carter and Wood<sup>150</sup> were given the most significant weight in this region, due to their improved method of calibration of the calorimeter. The heat-capacity results of Puchkov *et al.*<sup>152</sup> were of significantly lower accuracy than the other results and were given no significant weight in the representation.

In an interesting experiment, Thurmond and Brass<sup>163</sup> measured heat flux through NaCl(aq) samples in a scanning calorimeter for temperatures from 298 K to approximately 233 K. The equation they used for treating their results:

$$\dot{Q} = c_p \dot{T} \quad (39)$$

where  $\dot{Q}$  was the observed heat flux and  $c_p$  was the calculated specific heat capacity of the sample, did not take into account changes in enthalpy due to changes in the vapor pressure of the solution (Ref. 164 describes treatment of the saturation heat capacity in scanning-

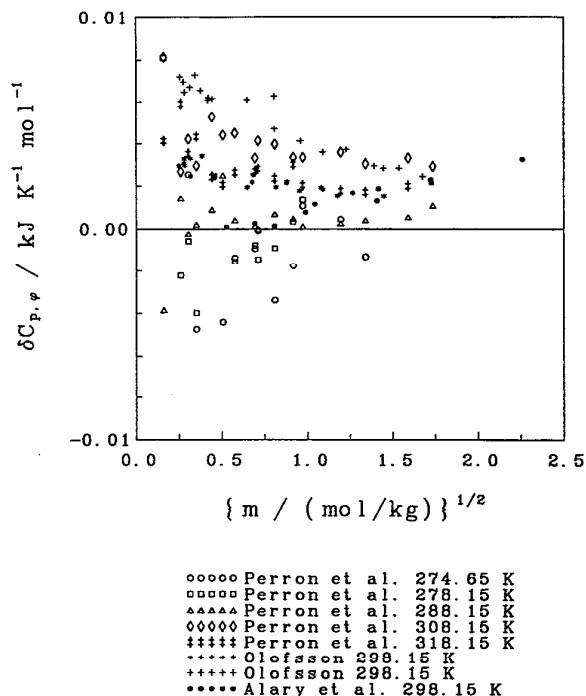


FIG. 14. Difference between experimental heat capacity results, obtained with commercial mass-flow calorimeters without chemical-standard calibrations, and values calculated from the fitted equation. Pressure is 0.1 MPa. The experimental results are from: Perron *et al.*,<sup>44</sup> Olofsson,<sup>24</sup> and Alary *et al.*<sup>33</sup>

calorimeter results.) Not including the vapor space contribution in Eq. (39) should lead to an observed heat capacity that is larger than the true heat capacity. This is indeed found; specific heat capacity values calculated from the equations given by Thurmond and Brass were systematically larger than those calculated from the measurements of Tanner and Lamb,<sup>143</sup> by amounts ranging from ~5 percent for 0.5 mol·kg<sup>-1</sup> to ~1 per cent for 6 mol·kg<sup>-1</sup> at both 298.15 K and 278.15 K. Because these uncertainties are large and because only fitted equations were given, a set of calculated results from 0.5 to 6 mol·kg<sup>-1</sup> and only for 248.15 K were included in the representation and were weighted according to the values given in Table 4. Values of the apparent molar heat capacity calculated from the equations of Thurmond and Brass are shown in Fig. 15. Error bars for the 248.15 K results were calculated assuming a ±3 per cent uncertainty in the specific heat capacity results, the size of the error bar is only weakly dependent on temperature. Also shown are values calculated from the fitted equation and the 278.15 K results of Tanner and Lamb.

## 5. Invariant and Univariant Equilibria

In the region of interest considered here there exist two invariant equilibria, NaCl(cr) + NaCl(aq) +

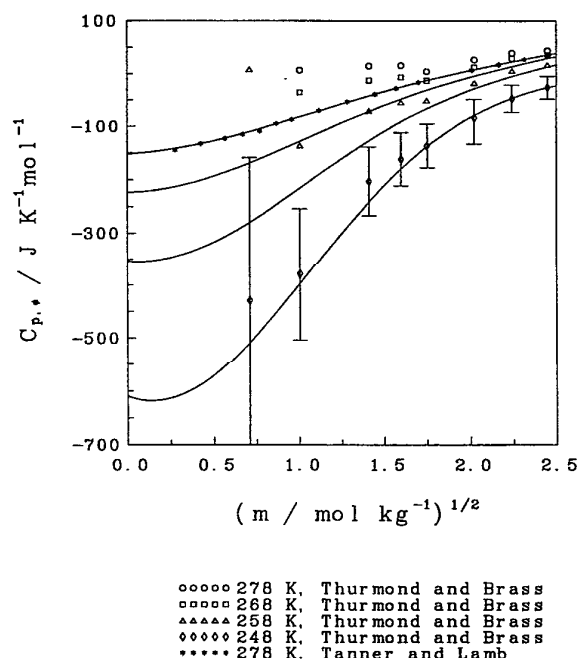


FIG. 15. Apparent molar heat capacities at low temperatures. The experimental results are from: Tanner and Lamb,<sup>143</sup> and Thurmond and Brass<sup>163</sup> Solid lines are values calculated from the fitted equation at each temperature. Error bars represent an uncertainty of ±3 per cent in the solution heat capacity.

NaCl·2H<sub>2</sub>O(cr) + H<sub>2</sub>O(g) and NaCl·2H<sub>2</sub>O(cr) + NaCl(aq) + H<sub>2</sub>O(g) + H<sub>2</sub>O(cr, I). Table 5 gives the positions of the two invariant equilibria calculated from the fitted equations for the chemical potential of NaCl(aq), NaCl(cr), NaCl·2H<sub>2</sub>O(cr), and H<sub>2</sub>O. Also given in the table are experimental values; the agreement was considered reasonable. The invariant equilibria, NaCl·2H<sub>2</sub>O(cr) + NaCl(aq) + NaCl(cr) + H<sub>2</sub>O(cr, VI), lies well outside of the experimental conditions considered here (approximately 1600 MPa<sup>156</sup>). There also exist other invariant equilibria, mostly involving two different phases of ice, dihydrate crystal, and aqueous solution.<sup>161</sup> The thermodynamic variables (*T*, *p*, *m*) that describe these equilibria are not well known.

There are seven univariant equilibria in the *T*, *p* region considered here. The NaCl(aq) + H<sub>2</sub>O(cr, I) + H<sub>2</sub>O(g) equilibrium is experimentally observed as solvent freezing-point depressions and was discussed above. The two equilibria, NaCl(cr) + NaCl(aq) + H<sub>2</sub>O(g) and NaCl·2H<sub>2</sub>O(cr) + NaCl(aq) + H<sub>2</sub>O(g) are characterized by solubility measurements performed at the vapor pressure of the solution. Figure 16 shows the difference of the fitted equation from some of the experimental results for these equilibria, also included are the results of Liu and Lindsay,<sup>83</sup> their solubilities corresponded to the saturation pressure of water, rather than solution. The solubilities given by Keevil,<sup>162</sup> from 456 to 600 K, were

TABLE 5. The invariant equilibria  $\text{NaCl}(\text{cr}) + \text{NaCl}(\text{aq}) + \text{NaCl}\cdot 2\text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g})$  and  $\text{NaCl}\cdot 2\text{H}_2\text{O}(\text{cr}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{cr}, \text{I})$ 

<i>T</i> /K	Calculated <i>p</i> /kPa	<i>m</i> /(mol kg <sup>-1</sup> )	<i>T</i> /K	Reported <i>p</i> /kPa	Reported <i>m</i> /(mol kg <sup>-1</sup> )	Ref.
$\text{NaCl}(\text{cr}) + \text{NaCl}(\text{aq}) + \text{NaCl}\cdot 2\text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g})$						
273.28	0.468	6.096	273.35	–	6.103	71
			273.20	–	–	7
			273.25	–	6.097	72
			273.30	–	6.097	159
			273.25	–	6.097	73
			273.35	–	5.89	158
			273.25	0.460	–	157
$\text{NaCl}\cdot 2\text{H}_2\text{O}(\text{cr}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{cr}, \text{I})$						
252.15	0.093	5.138	252.03	–	5.20	89
			251.55	–	5.08	71
			252.05	–	5.13	72
			251.85	–	5.26	159
			252.25	–	5.13	73
			251.95	–	5.17	158
			252.34	–	5.176	86

systematically 2 per cent larger than values calculated from the fitted equation. The values given by Keevil probably were not measured by him.<sup>172</sup>

The method for solubility measurement, for near ambient temperature to 373 K, described by Potter and Clynne<sup>86</sup> consisted of determining the temperature at which a known amount of solute completely dissolved. Their aqueous solubility values for NaCl, KCl, and the hydrates of CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub> were smaller than the results of others. They attributed the difference of their results from the others to errors in the other studies. They mentioned the possibility of fluid inclusions having occurred in the dried salt crystals (these affecting the determination of the concentration of the saturated solution for NaCl and KCl) or "small skeletal crystals" that remained suspended in the solution after equilibrium was reached (especially a problem in the concentrated and viscous solutions of CaCl<sub>2</sub>). Their conclusion, that the other methods possessed significant and inherent errors as compared to their results, if true, should have a significant impact on the present work. If their conclusion was correct, then the other solubility results should have been deweighted in the present representation. Fortunately, the accuracy of Potter and Clynne's solubility values can be checked by comparison with other thermodynamic measurements. The equation for the standard-state enthalpy change for solution can be written as:

$$\Delta_{\text{sol}}H_{\text{m}}^{\circ} = -2RT^2[m_s^{-1}(\partial m_s/\partial T)_p + \gamma_s^{-1}(\partial \gamma_s/\partial T)_p] \quad (40)$$

or 298 K and 0.1 MPa, values of  $\gamma$  and  $(\partial \gamma/\partial T)_{m,p}$  are essentially independent of solubility measurements and are

dependent primarily on osmotic coefficient, enthalpy of dilution, and heat capacity results. Evaluation of these quantities may thus be performed at a given molality and, in the case of  $(\partial \gamma/\partial T)_p$ , along a given  $(\partial m_s/\partial T)_p$  direction. The values of  $(\partial m_s/\partial T)_p$  and  $m_s$  that correspond to the solubility measurements from Potter and Clynne can be calculated from Potter and Clynne's fitted equation for the saturation weight fraction of NaCl(aq). From Potter and Clynne's 298.15 K  $(\partial m_s/\partial T)_p$  and  $m_s$ , the quantities  $\gamma_s$  and  $(\partial \gamma_s/\partial T)_p$  were calculated using the present equations. Placing the four quantities,  $m_s$ ,  $(\partial m_s/\partial T)_p$ ,  $\gamma_s$ , and  $(\partial \gamma_s/\partial T)_p$  in Eq. (40) allowed a comparison of standard-state enthalpy of solution values calculated from Potter and Clynne's solubilities to values obtained from experiment. The standard-state enthalpy change for solution calculated from Eq. (40) and the Potter and Clynne solubility results was approximately 4620 J·mol<sup>-1</sup> (298.15 K). This value was much larger than can be obtained from the observed enthalpies of solution. To accept that Potter and Clynne's method gave a more accurate solubility than did the other methods, at least for NaCl, one must dismiss not only the other solubility measurements but must also dismiss either the enthalpies of solution or the combination of osmotic coefficient and enthalpy of dilution results. Rejection of all of these measurements did not seem reasonable.

Adams and Gibson<sup>7</sup> measured the *T, p* locus of the univariant equilibria  $\text{NaCl}\cdot 2\text{H}_2\text{O}(\text{cr}) + \text{NaCl}(\text{cr}) + \text{NaCl}(\text{aq})$ . The pressure dependence of this equilibria depends on the density, and its pressure dependence, of each of the three substances. In order to represent the



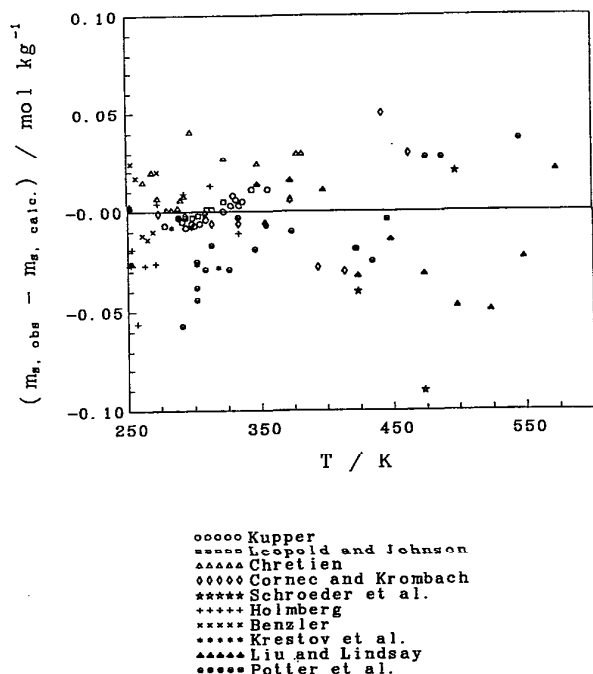


FIG. 16. Difference between experimental solubilities and values calculated from the fitted equations. The experimental results are from references 70, 71, 72, 73, 74, 75, 78, 81, 82, 83, 84, and 86.

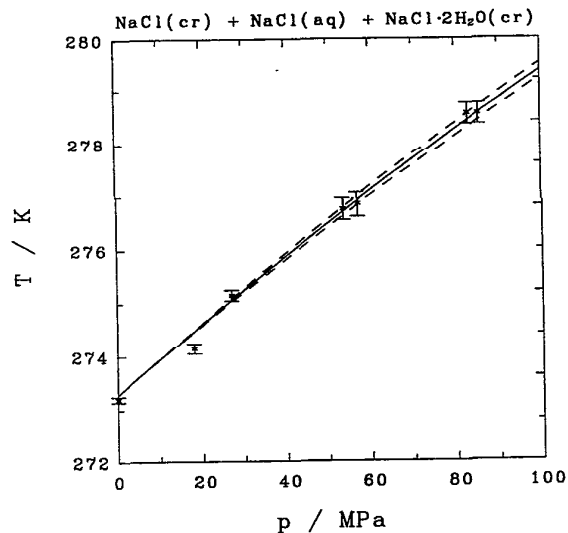


FIG. 17. Experimental values of the equilibrium  $\text{NaCl}(\text{cr}) + \text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr}) + \text{NaCl}(\text{aq})$  and values calculated from the fitted equations. The symbols are the experimental values and the stated uncertainties from Ref. 7. The solid line is calculated from the values given in the text. The dashed lines are the effect of an uncertainty of  $\pm 2 \text{ kg}\cdot\text{m}^{-3}$  in the density of  $\text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr})$  on the calculated values.

results of Adams and Gibson, the density of  $\text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr})$  was adjusted to give the agreement between experiment and calculation shown in Fig. 17. The error bars shown in the figure were the uncertainties given by Adams and Gibson. The optimized value for the 273 K density of  $\text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr})$  was  $1629 \text{ kg}\cdot\text{m}^{-3}$ . The effect of an uncertainty of  $\pm 2 \text{ kg}\cdot\text{m}^{-3}$  in the density of the dihydrate crystal is shown in the figure as dashed lines. Adams and Gibson gave a value of the density of  $\text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr})$  determined from the change of volume for the reaction  $\text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr}) = \text{NaCl}(\text{cr}) + \text{NaCl}(\text{aq}, \text{sat.})$ . The value they determined was  $1628 \text{ kg}\cdot\text{m}^{-3}$ , in excellent agreement with the present value. The equilibria  $\text{H}_2\text{O}(\text{g}) + \text{NaCl}(\text{cr}) + \text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr})$  is experimentally observed as the vapor pressure of water over the dihydrate. Figure 18 shows the calculated and experimental values for the vapor pressure of water over the dihydrate. The univariant equilibria,  $\text{H}_2\text{O}(\text{cr}, \text{I}) + \text{H}_2\text{O}(\text{g}) + \text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr})$  is simply the continuation of the  $T, p$  locus of the sublimation pressure of ice for temperature below that of the invariant equilibria  $\text{H}_2\text{O}(\text{cr}, \text{I}) + \text{H}_2\text{O}(\text{g}) + \text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr}) + \text{NaCl}(\text{aq})$ . This is because the sublimation pressure of ice is greater than the vapor pressure of water over the dihydrate. There does not appear to be experimental values with which to compare calculated values for the remaining univariant equilibria,  $\text{H}_2\text{O}(\text{cr}, \text{I}) + \text{NaCl}(\text{aq}) + \text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr})$ .

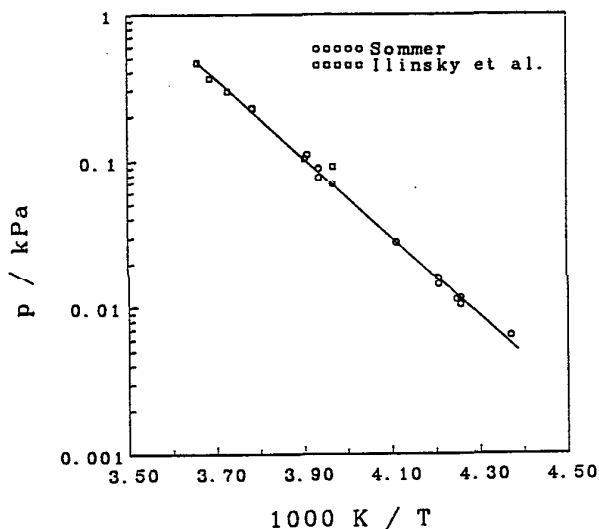


FIG. 18. Experimental values of the equilibrium  $\text{NaCl}(\text{cr}) + \text{NaCl} \cdot 2\text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{O}(\text{g})$  and values calculated from the fitted equations. The experimental results are from Illinsky *et al.*<sup>88</sup> and taken from a figure from Sommer.<sup>87</sup> The line is calculated from values given in the text.

## 6. Formation Properties

The 298.15 K, 0.1 MPa, standard-state Gibbs energy of solution, obtained from the present equation,  $-9.041 \text{ kJ}\cdot\text{mol}^{-1}$ , is in excellent agreement with the value obtained by Clarke and Glew,<sup>2</sup>  $-9.039 \text{ kJ}\cdot\text{mol}^{-1}$ . The differences in the standard-state enthalpy of solution and standard-state Gibbs energy of solution between the present work and that of Clarke and Glew can be taken to be representative of the uncertainties in these values, approximately  $10 \text{ J}\cdot\text{mol}^{-1}$ , because the differences are obtained from fitting two somewhat different databases for NaCl(aq) with two somewhat different models. The uncertainty given in Table 2 for the entropy of NaCl(aq) is not truly the uncertainty in this value. It is more properly considered as the uncertainty in the entropy of solution of NaCl(cr). This is because the entropy of NaCl(cr), taken from Ref. 4, appears in the calculations in combination with the entropy of NaCl(aq) to give  $\Delta_{\text{sol}}S_{\text{m}}^{\circ}$ . The true uncertainty for the standard-state entropy of NaCl(aq) must contain the uncertainty in the entropy of NaCl(cr). Because of the discrepancies in experimental results discussed in Ref. 4 the uncertainty in the entropy of NaCl(cr) is non-negligible. The presently obtained value for the standard-state entropy of NaCl(aq), for 298.15 K and 0.1 MPa,  $115.51 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  can be compared to the CODATA value of  $115.05 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The difference in these two values, after adjusting for differences in the entropy of NaCl(cr), corresponds to a difference in the quantity  $\Delta_{\text{sol}}G_{\text{m}}^{\circ} - \Delta_{\text{sol}}H_{\text{m}}^{\circ}$  of  $97 \text{ J}\cdot\text{mol}^{-1}$ . This difference is significantly larger than the uncertainty in this value.

The 298.15 K, 0.1 MPa, standard-state enthalpy and Gibbs energy of formation of NaCl(cr) and NaCl·2H<sub>2</sub>O(cr) can be calculated from the Gibbs energies of solution of NaCl(cr) and NaCl·2H<sub>2</sub>O(cr) and the entropies of NaCl(aq), NaCl·2H<sub>2</sub>O(cr), H<sub>2</sub>O(l),<sup>17</sup> and NaCl(cr),<sup>4</sup> and the enthalpies of formation of NaCl(aq)<sup>17</sup> and of H<sub>2</sub>O(aq).<sup>17</sup> The calculated enthalpies and Gibbs energies of formation are given in Table 6. The uncertainty in the formation property values listed in Table 6 for NaCl·2H<sub>2</sub>O(cr) is estimated to be 300 to 500  $\text{J}\cdot\text{mol}^{-1}$ , and for NaCl(cr) are estimated to be 100  $\text{J}\cdot\text{mol}^{-1}$ . The uncertainty in the values for NaCl(cr) arises primarily from uncertainty in the entropy of NaCl(cr). The uncertainty in the entropy of NaCl(cr) is described elsewhere.<sup>4</sup> Small round-off errors may occur using the values in Table 6. This type of round-off error may be minimized by using the equations given in Ref. 4 and in the present work.

The formation properties given in Table 6 for NaCl(cr) are not directly comparable to the values of Wagman *et al.*<sup>165</sup> because the values in Ref. 165 do not satisfy:

$$\Delta_{\text{sol}}G_{\text{m}}^{\circ} = \Delta_{\text{sol}}H_{\text{m}}^{\circ} - T\Delta_{\text{sol}}S_{\text{m}}^{\circ}. \quad (41)$$

Eq. (41) is out of balance by approximately  $50 \text{ J}\cdot\text{mol}^{-1}$  or  $0.17 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  in Ref. 165. This difference appears to be larger than the uncertainties in either the standard-state enthalpy of solution or the standard-state Gibbs energy of solution. The difference in the 298.15 K molar entropy of the dihydrate crystal from the anhydrous crystal, per mole of water, is calculated to be  $45.1 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . This value is in good agreement with values determined for other hydrates, for example, the corresponding value for NaBr was  $45.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .<sup>8</sup>

TABLE 6. The Gibbs energy of formation, the enthalpy of formation and the molar entropy of NaCl(cr) and NaCl·2H<sub>2</sub>O(cr) for 298.15 K and 0.1 MPa calculated from the least-squares estimated parameters.

Substance	$\Delta_{\text{f}}G_{\text{m}}^{\circ}$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{f}}H_{\text{m}}^{\circ}$ $\text{kJ}\cdot\text{mol}^{-1}$	$S_{\text{m}}^{\circ}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$C_{\text{p},\text{m}}^{\circ}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
NaCl(cr)	-384.28	-411.27	72.27	50.16
NaCl·2H <sub>2</sub> O(cr)	-858.75	-997.24	162.51	137.

TABLE 7. Calculated values of  $A_{\phi}$ ,  $\beta_{\text{Mx}}^{(0)}$ ,  $\beta_{\text{Mx}}^{(1)}$ ,  $C_{\text{Mx}}^{(0)}$ , and  $C_{\text{Mx}}^{(1)}$

$\frac{T}{\text{K}}$	$\frac{p}{\text{MPa}}$	$A_{\phi}$	$\beta_{\text{Mx}}^{(0)}$ $\text{kg}\cdot\text{mol}^{-1}$	$\beta_{\text{Mx}}^{(1)}$ $\text{kg}\cdot\text{mol}^{-1}$	$\frac{10^3 C_{\text{Mx}}^{(0)}}{\text{kg}^2\cdot\text{mol}^{-2}}$	$\frac{C_{\text{Mx}}^{(1)}}{\text{kg}^2\cdot\text{mol}^{-2}}$
273	0.1	0.3763	0.06542	0.2265	1.304	-0.06719
298	0.1	0.3914	0.08055	0.2630	0.2682	-0.01022
323	0.1	0.4102	0.09139	0.2826	-0.5856	0.00639
373	0.1	0.4597	0.1008	0.3218	-1.725	0.01267
473	1.55	0.6168	0.0892	0.4031	-1.441	0.04725
573	8.6	0.9563	0.0664	0.4073	-1.441	0.1642
598	12.	1.1329	0.0681	0.3862	-1.380	0.2216

TABLE 8. Calculated values of  $G_{m,2}^{\circ} - G_{m,2,T,P}^{\circ}$ ,  $H_{m,2}^{\circ} - H_{m,2,T,P}^{\circ}$ ,  $S_{m,2}^{\circ} - S_{m,2,T,P}^{\circ}$ ,  $C_p^{\circ}$ ,  $V_{\phi}^{\circ}$ 

$T$ K	$p$ MPa	$G_{m,2}^{\circ} - G_{m,2,T,P}^{\circ}$ kJ·mol <sup>-1</sup>	$H_{m,2}^{\circ} - H_{m,2,T,P}^{\circ}$ kJ·mol <sup>-1</sup>	$S_{m,2}^{\circ} - S_{m,2,T,P}^{\circ}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$C_p^{\circ}$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$V_{\phi}^{\circ}$ cm <sup>3</sup> ·mol <sup>-1</sup>
273	0.1	3.023	3.104	10.94	-182.6	12.9
298	0.1	0.017	0.013	0.04	-85.3	16.6
323	0.1	-2.796	-1.726	-5.57	-60.1	17.9
373	0.1	-8.071	-4.861	-14.57	-74.1	16.9
473	1.55	-16.766	-18.898	-47.21	-253	-0.4
573	8.6	-19.479	-81.27	-163.2	-1746	-114
598	12.	-17.754	-137.71	-258.5	-4538	-255

TABLE 9. Calculated values of the osmotic coefficient,  $\phi$ 

$T$ K	$p$ MPa	$m$ /mol·kg <sup>-1</sup>				
		0.1	0.5	1.0	3.0	6.0
273	0.1	0.9316	0.9108	0.9157	1.0107	1.2466
298	0.1	0.9322	0.9218	0.9371	1.0486	1.2694
323	0.1	0.9302	0.9234	0.9431	1.0609	1.2648
373	0.1	0.9219	0.9139	0.9340	1.0459	1.2111
473	1.55	0.8893	0.8606	0.8667	0.9294	1.0163
573	8.6	0.8105	0.7302	0.7110	0.7125	0.7444

Table 10. Calculated values of the stoichiometric activity coefficient,  $\gamma_{\pm}$ 

$T$ K	$p$ MPa	$m$ /mol·kg <sup>-1</sup>				
		0.1	0.5	1.0	3.0	6.0
273	0.1	0.7796	0.6706	0.6340	0.6585	0.8990
298	0.1	0.7771	0.6805	0.6572	0.7177	0.9885
323	0.1	0.7697	0.6755	0.6569	0.7299	0.9933
373	0.1	0.7459	0.6443	0.6228	0.6801	0.8727
473	1.55	0.6666	0.5269	0.4818	0.4551	0.4864
573	8.6	0.5129	0.3258	0.2631	0.1912	0.1632

## 7. Acknowledgment

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## 8. References

- K. S. Pitzer, J. C. Peiper, R. H. Busey, *J. Phys. Chem. Ref. Data* **13**, 1 (1984).
- C. W. Clarke, D. N. Glew, *J. Phys. Chem. Ref. Data* **14**, 489 (1985).
- P. G. Hill, *J. Phys. Chem. Ref. Data* **19**, 1233 (1990).
- D. G. Archer, *J. Phys. Chem. Ref. Data*, **21**, 1 (1992).
- J. O'M. Bockris, A. Pilla, J. L. Barton, *J. Phys. Chem.* **64**, 507 (1960).
- L. H. Adams, E. D. Williamson, J. Johnston, *J. Amer. Chem. Soc.* **41**, 12 (1919).
- L. H. Adams, R. E. Gibson, *J. Amer. Chem. Soc.* **52**, 4252 (1930).
- D. G. Archer, *J. Phys. Chem. Ref. Data* **20**, 509 (1991).
- K. S. Pitzer, *J. Phys. Chem.* **77**, 268 (1973).
- K. S. Pitzer in *Activity Coefficients in Electrolyte Solutions*, R. N. Pytkowicz, ed. (C.R.C. Press, Boca Raton, FL 1979).
- P. Lancaster, K. Salkauskas, *Curve and Surface Fitting* (Academic Press, New York 1986).
- J. A. Rard, D. G. Miller, *J. Chem. Eng. Data* **26**, 33 (1981).
- H. F. Holmes, R. E. Mesmer, *J. Solution Chem.* **15**, 495 (1986).
- D. G. Archer, P. Wang, *J. Phys. Chem. Ref. Data* **19**, 371 (1990).
- D. J. Bradley, K. S. Pitzer, *J. Phys. Chem.* **83**, 1599 (1979) and **87**, 3798 (1983).
- P. S. Z. Rogers, K. S. Pitzer, *J. Phys. Chem. Ref. Data* **11**, 15 (1982).
- J. D. Cox, D. D. Wagman, V. A. Medvedev, *CODATA Key Values for Thermodynamics*, (Hemisphere, Washington 1989).
- N. R. Draper, H. Smith, *Applied Regression Analysis*, (J. Wiley, New York 1981).
- I. W. Duedall, P. K. Weyl, *Rev. Sci. Instrum.* **12**, 66 (1967).
- F. Vaslow, *J. Phys. Chem.*, **73**, 3745 (1969).
- R. E. Hall, *J. Wash. Acad. Sci.* **14**, 167 (1924).
- A. Kruis, *Z. Phys. Chem.* **34**, 1 (1931).
- H. E. Wirth, *J. Amer. Chem. Soc.*, **62**, 1128 (1940).
- I. V. Olofsson, *J. Chem. Thermodynam.* **11**, 1005 (1979).
- F. Vaslow, *J. Phys. Chem.*, **70**, 2286 (1966).
- F. J. Millero, *Rev. Sci. Instrum.* **38**, 1441 (1967).
- Yu. A. Epikhin, M. S. Stakhanova, *Russ. J. Phys. Chem.* **41**, 1157 (1967).
- L. A. Dunn, *Trans Faraday Soc.* **64**, 2951 (1968).
- F. J. Millero, E. V. Hoff, L. Kahn, *J. Solution Chem.* **1**, 309 (1972).
- F. J. Millero, G. K. Ward, P. V. Chetirkin, *J. Acoust. Soc. Am.*, **61**, 1492 (1977).
- F. T. Gucker, D. Stubble, D. J. Hill, *J. Chem. Thermodynam.* **7**, 865 (1975).
- P. P. Singh, E. M. Woolley, K. G. McCurdy, L. G. Hepler, *Can. J. Chem.* **54**, 3315 (1976) and Depository of Unpublished Data, National Research Council of Canada.
- J. F. Alary, M. A. Simard, J. Dumont, C. Jolicœur, *J. Solution Chem.* **11**, 755 (1982).
- J. A. Gates, R. H. Wood, *J. Chem. Eng. Data* **30**, 44 (1985).
- A. K. Helmy, F. F. Assaad, M. N. Hassan, H. Sadek, *J. Phys. Chem.* **72**, 2358 (1968).
- M. K. Srinivasan, B. Prasad, *Trans. Faraday Soc.* **35**, 1462 (1930).

- <sup>37</sup>W. R. Bousfield, C. E. Bousfield, *Phil. Trans. Roy. Soc. London, Ser. A* **218**, 119 (1919).
- <sup>38</sup>G. P. Baxter, C. C. Wallace, *J. Amer. Chem. Soc.* **38**, 70 (1916).
- <sup>39</sup>G. Jones, S. M. Christian, *J. Amer. Chem. Soc.* **59**, 484 (1937).
- <sup>40</sup>L. A. Dunn, *Trans. Faraday Soc.* **64**, 1898 (1968).
- <sup>41</sup>F. J. Millero, *J. Phys. Chem.* **74**, 356 (1970).
- <sup>42</sup>F. J. Millero, G. K. Ward, F. K. Lepple, E. V. Hoff, *J. Phys. Chem.* **78**, 1636 (1974).
- <sup>43</sup>C.-T. A. Chen, J. H. Chen, F. J. Millero, *J. Chem. Eng. Data*, **25**, 307 (1980).
- <sup>44</sup>G. Perron, J.-L. Fortier, J. E. Desnoyers *J. Chem. Thermodynamics*, **7**, 1177 (1975).
- <sup>45</sup>J.-L. Fortier, M.-A. Simard, P. Picker, C. Jolicoeur, *Rev. Sci. Instrum.* **50** 1474 (1979).
- <sup>46</sup>G. Dessauges, N. Miljevic, W. A. Van Hook, *J. Phys. Chem.* **84**, 2587 (1980).
- <sup>47</sup>G. C. Allred, E. M. Woolley, *J. Chem. Thermodynamics* **13**, 147 (1981).
- <sup>48</sup>F. J. Millero, W. Drost-Hansen, *J. Chem. Eng. Data* **13**, 330 (1968).
- <sup>49</sup>R. T. Emmett, Ph. D. Dissertation, University of Miami (1973).
- <sup>50</sup>R. Hilbert, Ph.D. Dissertation, University of Karlsruhe (1979).
- <sup>51</sup>R. E. Gibson, O. H. Loeffler, *J. Amer. Chem. Soc.* **63**, 443 (1941).
- <sup>52</sup>R. E. Gibson, O. H. Loeffler, *Annal. N.Y. Acad. Sci.* **51**, 727 (1949).
- <sup>53</sup>V. Majer, J. A. Gates, A. Inglese, R. H. Wood, *J. Chem. Thermodynamics* **20**, 949 (1988).
- <sup>54</sup>A. J. Ellis, *J. Chem. Soc. A* 1579 (1966).
- <sup>55</sup>P. S. Z. Rogers, D. J. Bradley, K. S. Pitzer, *J. Chem. Eng. Data* **27**, 47 (1982).
- <sup>56</sup>D. F. Grant-Taylor, *J. Solution Chem.* **10**, 621 (1981).
- <sup>57</sup>M. Gehrig, H. Lentz, E. U. Franck *Ber. Bunsenges. Phys. Chem.* **87**, 597 (1983).
- <sup>58</sup>A. J. Ellis, R. M. Golding, *Amer. J. Sci.* **261**, 47 (1963).
- <sup>59</sup>V. Majer, L. Hui, R. Crovetto, R. H. Wood, *J. Chem. Thermodynamics* **23**, 213 (1991).
- <sup>60</sup>D. G. Archer, V. Majer, A. Inglese, R. H. Wood, *J. Colloid Interf. Sci.* **124**, 591 (1988).
- <sup>61</sup>H. E. Wirth, F. K. Bangert, *J. Phys. Chem.* **76**, 3488 (1972).
- <sup>62</sup>I. Kh. Khaibullin, N. M. Borisov, *Teplotfiz. Vysokikh Temperatur* **4**, 518 (1966).
- <sup>63</sup>B. M. Fabuss, A. Korosi, A. K. M. Hug, J. Shamsul, *J. Chem. Eng. Data* **11**, 325 (1966).
- <sup>64</sup>A. Korosi, B. M. Fabuss, *J. Chem. Eng. Data* **13**, 548 (1968).
- <sup>65</sup>V. I. Zarembo, M. K. Federov, *Zhurnal Prikladnai Khimii* **48**, 1949 (1975).
- <sup>66</sup>A. M. Rowe, J. C. S. Chou, *J. Chem. Eng. Data* **15**, 61 (1970).
- <sup>67</sup>H. E. Wirth, A. LoSurdo, *J. Chem. Eng. Data* **13**, 226 (1968).
- <sup>68</sup>I. G. Mikhailov, V. A. Shutilov, *Akust. Zhur.* **10**, 450 (1964).
- <sup>69</sup>M. Sakurai, T. Nakajima, T. Komatsu, T. Nakagawa, *Chem. Letters* 971 (1975).
- <sup>70</sup>E. Küpper, *Caliche* **8**, 467 (1927).
- <sup>71</sup>A. Chretien, *Ann. Chim. Paris* **12**, 9 (1929).
- <sup>72</sup>E. Cornec, H. Krombach, *Ann. Chim. Paris* **18**, 5 (1932).
- <sup>73</sup>H. Benzler, *Ktetechnik* **7**, 66 (1955).
- <sup>74</sup>K. E. Holmberg, *Ab. Atomenergi, Stockholm Rapp.* AE-340, (1968).
- <sup>75</sup>R. W. Potter, M. A. Clynne, D. L. Browne, *Econ. Geol.* **73**, 284 (1978).
- <sup>76</sup>Earl of Berkeley, *Phil. Proc. Royal Soc. London*, **203**, 189 (1904).
- <sup>77</sup>A. F. Scott, W. R. Frazier, *J. Phys. Chem.* **31**, 459 (1927).
- <sup>78</sup>H. G. Leopold, J. Johnston, *J. Amer. Chem. Soc.* **49**, 1974 (1927).
- <sup>79</sup>F. Flottmann, *Z. Anal. Chem.* **73**, 1 (1928).
- <sup>80</sup>E. Cornec, A. Neumeister, *Caliche* **10**, 492, (1929).
- <sup>81</sup>W. C. Schroeder, A. Gabriel, E. P. Partridge, *J. Amer. Chem. Soc.* **57**, 1539 (1935).
- <sup>82</sup>R. D. Eddy, A. W. C. Menzies, *J. Phys. Chem.* **44**, 207 (1940).
- <sup>83</sup>C.-T. Liu, W. T. Lindsay, *J. Solution Chem.* **1**, 45 (1972).
- <sup>84</sup>R. W. Potter, R. S. Babcock, D. L. Brown, *J. Res. U.S.G.S.* **5**, 389, (1977).
- <sup>85</sup>G. A. Krestov, V.D. Ovchinnikova, T.K. Vorontsova, *Zh. Neorg. Khim.* **22**, 2311 (1977).
- <sup>86</sup>R. W. Potter and M. A. Clynne, *J. Res. U.S. Geol. Survey* **6**, 701 (1978).
- <sup>87</sup>J. Sommer, *Z. Angew. Physik.* **10**, 517 (1958).
- <sup>88</sup>V. P. Ilinsky, V.F.Korolev, E. I. Akumov, *J. Appl. Chem. USSR* **25**, 569, (1952).
- <sup>89</sup>W. H. Rodebush, *J. Amer. Chem. Soc.* **40**, 1204 (1918).
- <sup>90</sup>G. Scatchard, S. S. Prentiss, *J. Amer. Chem. Soc.*, **55**, 4355, (1933).
- <sup>91</sup>F. Momicchioli, O. Devoto, G. Grandi, G. Cocco, *Ber. Bunsenges. Phys. Chem.*, **74**, 59 (1970).
- <sup>92</sup>H. F. Gibbard, A. F. Gossman, *J. Solution Chem.*, **3**, 385 (1974).
- <sup>93</sup>Q. D. Craft, W. A. VanHook, *J. Solution Chem.*, **4**, 923 (1975).
- <sup>94</sup>N. Miljevic, G. Dessauges, W. A. VanHook, *J. Solution Chem.*, **10**, 29 (1981).
- <sup>95</sup>R. P. Smith, *J. Amer. Chem. Soc.*, **61**, 500 (1939).
- <sup>96</sup>R. P. Smith, D. S. Hirtle, *J. Amer. Chem. Soc.*, **61**, 1123 (1939).
- <sup>97</sup>H. F. Gibbard, G. Scatchard, R. A. Rousseau, J. L. Creek, *J. Chem. Eng. Data*, **19**, 281 (1974).
- <sup>98</sup>P. Olynyk, A. R. Gordon, *J. Amer. Chem. Soc.*, **65**, 224 (1943).
- <sup>99</sup>R. H. Stokes, *J. Am. Chem. Soc.* **69**, 1291 (1947)
- <sup>100</sup>R. E. Gibson, L. H. Adams, *J. Amer. Chem. Soc.* **55**, 2679 (1933).
- <sup>101</sup>S. Shankman, A. R. Gordon *J. Amer. Chem. Soc.* **61**, 2370 (1939).
- <sup>102</sup>C. N. Pepela, P. J. Dunlop, *J. Chem. Thermodynamics* **4**, 255 (1972).
- <sup>103</sup>E. R. Gardner, P. J. Jones, H. J. de Nordwall, *Trans. Faraday Soc.* **59**, 1994 (1963).
- <sup>104</sup>E. R. Gardner, *Trans. Faraday Soc.* **65**, 91, (1969).
- <sup>105</sup>C.-T. Liu, W. T. Lindsay, *J. Phys. Chem.* **74**, 341 (1970).
- <sup>106</sup>V.P. Mashovets, V.I. Zarembo, M.K. Fedorov, *J. Appl. Chem. USSR* **46**, 684 (1973).
- <sup>107</sup>R. Caramazza *Gazz. Chim. Ital.* **90**, 1839 (1960).
- <sup>108</sup>A. H. Truesdell, *Science* **161**, 884 (1968).
- <sup>109</sup>T. Mussini, A. Pagella, *Chim. Ind.(Milan)*, **52**, 1187 (1970).
- <sup>110</sup>H. S. Harned, L. F. Nims, *J. Amer. Chem. Soc.*, **54**, 423, (1932).
- <sup>111</sup>D. W. Anderson, G. N. Malcolm, H. N. Parton, *J. Phys. Chem.* **64**, 494 (1960).
- <sup>112</sup>F. Vaslow, *J. Phys. Chem.* **75**, 3317 (1971).
- <sup>113</sup>F. J. Millero, L. D. Hansen, E. V. Hoff, *J. Marine Res.* **31**, 21 (1973).
- <sup>114</sup>R. H. Busey, H. F. Holmes, R. E. Mesmer, *J. Chem. Thermodynamics*, **16**, 343 (1984).
- <sup>115</sup>E. A. Gulbransen, A. L. Robinson, *J. Amer. Chem. Soc.*, **56**, 2637 (1934).
- <sup>116</sup>J.-L. Fortier, P.-A. Leduc, J. E. Desnoyers, *J. Solution Chem.*, **3**, 323, (1974).
- <sup>117</sup>W. H. Leung, F. J. Millero, *J. Solution Chem.* **4**, 145 (1975).
- <sup>118</sup>E. E. Messikomer, R. H. Wood, *J. Chem. Thermodynamics* **7**, 119, (1975).
- <sup>119</sup>A. L. Robinson, *J. Amer. Chem. Soc.* **54**, 1311, (1932).
- <sup>120</sup>T. F. Young, O. G. Vogel, *J. Amer. Chem. Soc.* **54**, 3036, (1932).
- <sup>121</sup>T. F. Young, J. S. Machin, *J. Amer. Chem. Soc.* **58**, 2254, (1936).
- <sup>122</sup>R. Bury, A. Mayaffre, M. Chemla, *J. Chim. Phys.* **73**, 935 (1976).
- <sup>123</sup>J. E. Mayrath, R. H. Wood, *J. Chem. Thermodynamics* **14**, 15 (1982).
- <sup>124</sup>D. G. Archer, *J. Solution Chem.* **15**, 727 (1986).
- <sup>125</sup>D. D. Ensor, H. L. Anderson, *J. Chem. Eng. Data* **18**, 205 (1973).
- <sup>126</sup>R. H. Wood, R. A. Rooney, J. N. Braddaock, *J. Phys. Chem.* **73**, 1673 (1969).
- <sup>127</sup>F. A. Askew, E. Bullock, H. T. Smith, R. K. Tinkler, O. Gatty, J. H. Wolfenden, *J. Chem. Soc.* **1368** (1934).
- <sup>128</sup>G. C. Benson, G. W. Benson, *Rev. Sci. Instrum.* **26**, 477 (1955).
- <sup>129</sup>Q. D. Craft, W. A. Van Hook, *J. Solution Chem.* **4**, 901 (1975).
- <sup>130</sup>J. Wst, E. Lange, *Z. Phys. Chem. (Leipzig)* **116**, 161 (1925).
- <sup>131</sup>K. P. Mishchenko, I. F. Yakovlev, *J. Gen. Chem. USSR*, **29**, 1735 (1959).
- <sup>132</sup>W. L. Gardner, R. E. Mitchell, J. W. Cobble, *J. Phys. Chem.* **73**, 2025 (1969).
- <sup>133</sup>C. M. Criss, J. W. Cobble *J. Amer. Chem. Soc.* **83**, 3223 (1961).
- <sup>134</sup>L. Benjamin, *Can. J. Chem.* **41**, 2210 (1963).
- <sup>135</sup>A. Dadgar, M. R. Taherian, *J. Chem. Thermodynamics* **9**, 711 (1977).
- <sup>136</sup>S. Taniowska-Osinska, R. Logwinienko *Acta Univ. Lodz Ser. 2* **69** (1976).
- <sup>137</sup>A. Sanahuja, E. Cesari, *J. Chem. Thermodynamics* **16**, 823 (1985).
- <sup>138</sup>A. Sanahuja, E. Cesari, *J. Chem. Thermodynamics* **16**, 1195 (1984).
- <sup>139</sup>S. G. Lipsett, F. M. G. Johnson, O. Maass *J. Amer. Chem. Soc.* **49**, 925 (1927).

- <sup>140</sup>S. G. Lipsett, F. M. G. Johnson, O. Maass *J. Amer. Chem. Soc.* **49**, 1940 (1927).
- <sup>141</sup>D. H. Davies, G. C. Benson, *Can. J. Chem.* **43**, 3100 (1965).
- <sup>142</sup>P. S. Z. Rogers, C. J. Duffy, *J. Chem. Thermodynamics* **21**, 595 (1989).
- <sup>143</sup>J. E. Tanner, F. W. Lamb, *J. Solution Chem.* **7**, 303 (1978).
- <sup>144</sup>M.-A. Simard, J.-L. Fortier, *Can. J. Chem.* **59**, 3208 (1981).
- <sup>145</sup>M. Randall, F. D. Rossini, *J. Amer. Chem. Soc.* **51**, 323, (1929).
- <sup>146</sup>J. A. Gates, D. M. Tillett, D. E. White, R. H. Wood, *J. Chem. Thermodynamics* **19**, 131 (1987).
- <sup>147</sup>D. E. White, R. H. Wood, *J. Solution Chem.* **11**, 223 (1982).
- <sup>148</sup>D. R. White, C. J. Downes, *J. Solution Chem.* **17**, 733 (1988).
- <sup>149</sup>S. Likke, L. A. Bromley, *J. Chem. Eng. Data* **18**, 189 (1973).
- <sup>150</sup>R. W. Carter, R. H. Wood, *J. Chem. Thermodynamics* **23**, 1037, (1991).
- <sup>151</sup>J.-L. Fortier, P.-A. Leduc, J. E. Desnoyers, *J. Solution Chem.* **3**, 323 (1974).
- <sup>152</sup>L. V. Puchkov, P. S. Styazhkin, M. K. Fedorov, *Zh. Prikl. Khim.* **49**, 1232 (1976).
- <sup>153</sup>G. Scatchard, B. Vonnegut, D. W. Beaumont, *J. Chem. Phys.* **33**, 1292 (1960).
- <sup>154</sup>J. A. Rard, R. F. Platford in *Activity Coefficients in Electrolyte Solutions* 2nd ed., K. S. Pitzer, ed. (C.R.C. Press, Boca Raton, FL 1991) in press.
- <sup>155</sup>W. J. Hamer, Y.-C. Wu, *J. Phys. Chem. Ref. Data* **1**, 1047 (1972).
- <sup>156</sup>J. E. Desnoyers, C. DeVisser, G. Perron, P. Picker, *J. Solution Chem.* **5**, 605 (1976).
- <sup>157</sup>E. I. Akhumov, B. B. Vasil'ev, *Zh. Obsch. Khim.* **2**, 282 (1932).
- <sup>158</sup>E. K. Akopov, *J. Appl. Chem. USSR* **36**, 1859 (1963).
- <sup>159</sup>N. N. Khitrova, *J. Appl. Chem. USSR* **27**, 1217 (1954).
- <sup>160</sup>E. Janecke, *Z. Elektrochem.* **53**, 250 (1949).
- <sup>161</sup>See, for example, the phase diagram shown on page 2 of Gmelin *Handbuch der Anorganischen Chemie* Num 21 (Verlag Chemie, Weinheim, 1973).
- <sup>162</sup>N. B. Keevil, *J. Amer. Chem. Soc.* **64**, 841 (1942).
- <sup>163</sup>V. L. Thurmond, G. W. Brass, *J. Chem. Eng. Data*, **33**, 411 (1988).
- <sup>164</sup>S. E. Knipmeyer, D. G. Archer, R. D. Chirico, B. E. Gammon, I. A. Hossenlopp, A. Nguyen, N. K. Smith, W. V. Steele, M. M. Strube, *Fluid Phase Equilib.* **52**, 185, (1989).
- <sup>165</sup>D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).
- <sup>166</sup>J. L. Oscarson, S. E. Gillespie, J. J. Christensen, R. M. Izzatt, and P. R. Brown, *J. Solution Chem.* **17**, 841, 865 (1988).
- <sup>167</sup>H. F. Holmes, R. H. Busey, J. M. Simonson, R. E. Mesmer, D. G. Archer, and R. H. Wood, *J. Chem. Thermodyn.* **19**, 863 (1987).
- <sup>168</sup>J. E. Mayrath, R. H. Wood, *J. Chem. Eng. Data* **28**, 56 (1983).
- <sup>169</sup>L. M. Connaughton, J. P. Hershey, F. J. Millero, *J. Solution Chem.* **15**, 989 (1986).
- <sup>170</sup>J. R. Quint, R. H. Wood, *J. Phys. Chem.* **89**, 380 (1985).
- <sup>171</sup>R. T. Pabalan, K. S. Pitzer, *Geochim. Cosmochim. Acta* **51**, 2429 (1987).
- <sup>172</sup>K. S. Pitzer, personal communication with indication that this subject will be examined in a paper to appear in *Geochim. Cosmochim. Acta*, coauthored by I.-Ming Chou.
- <sup>173</sup>R. M. Izzatt, J. L. Oscarson, X. Chen, S. E. Gillespie, *Electric Power Research Institute Topical Report NP-5078* (1992).
- <sup>174</sup>J. M. Simonson, R. E. Mesmer, P. S. Z. Rogers, *J. Chem. Thermodynam.* **21**, 561 (1989).

### Appendix 1. Unusual Results for Calculation of the Specific Compressibility for Temperatures Greater Than 530 K and for Pressures Less Than 30 MPa

The specific compressibility, when calculated from the equations given in the main body of the text, for high temperature and low pressure exhibits a maximum with respect to pressure at fixed concentration and fixed temperature, for concentrations smaller than the reference molality. An example for which this maximum is clearly visible is shown in Fig. A1-1 (unbroken curve). The maximum shown in Fig. A1-1 results from a calculated change in the difference of the compressibility of the solution from that of the solvent  $\{\beta - \beta^0\}$  that is much larger at lower pressure, for example 8 MPa, than at a larger pressure, for example 30 MPa. A large pressure dependence of the change in compressibility of the solvent resulting from the addition of ions to a solvent of high compressibility is considered reasonable, (see Ref. 170 as an example of the rationalization of such effects) however, it is possible that this effect is over-estimated in the above-described representation. Examination of several alternate representations as well as the experimental results in the region of representation suggested that the maximum in the compressibility shown in Fig. A1-1 resulted from the combination of the choice of fitting functions with the choice of a particular dielectric-constant representation (used for calculation of Debye-Hückel limiting-law values.) This can be demonstrated by repeating the least-squares representation of the experimental results with the functions described in the body of the text with the sole exception of a substitution of the dielectric-constant equation of Bradley and Pitzer<sup>15</sup> for that of Archer and Wang.<sup>14</sup> The so-obtained representation yields the monotonically changing compressibility shown in Fig. A1-1. The second representation of experimental results is summarized in Tables A1-1 and A1-2 which are analogous to Tables 3 and 4. Substitution of the Bradley and Pitzer equation results in representation of the most significant experimental results, for temperatures less than 400 K, almost as well as they were represented when the Archer and Wang equation was used. Significant differences exist between the two representations for temperatures above 400 K. Representation of the 604 K density difference results of Majer *et al.*<sup>59</sup> was significantly better with use of the Bradley and Pitzer equation ( $\sigma_{\text{fit}}$  was halved) with much of this improvement having

been obtained at the expense of the 597 K density difference results from Majer *et al.*<sup>53</sup> On the other hand, a significant bias from the 573 K enthalpy of dilution results from Busey *et al.*<sup>114</sup> ( $\delta_{\text{fit}}$  increased from  $-30 \text{ J}\cdot\text{mol}^{-1}$  to  $460 \text{ J}\cdot\text{mol}^{-1}$ ), significant increases in the r.m.s. differences of the 598 K heat capacity results from Gates *et al.*<sup>142</sup> and from Rogers and Duffy<sup>146</sup> and an approximate 50% increase in the r.m.s. differences of the enthalpies of dilution, for temperatures greater than 400K, from Mayrath and Wood<sup>123</sup> were observed with the representation obtained with use of the Bradley and Pitzer equation.

Estimated parameter values obtained from the representation obtained with use of the Bradley and Pitzer equation are given in Table A1-3.

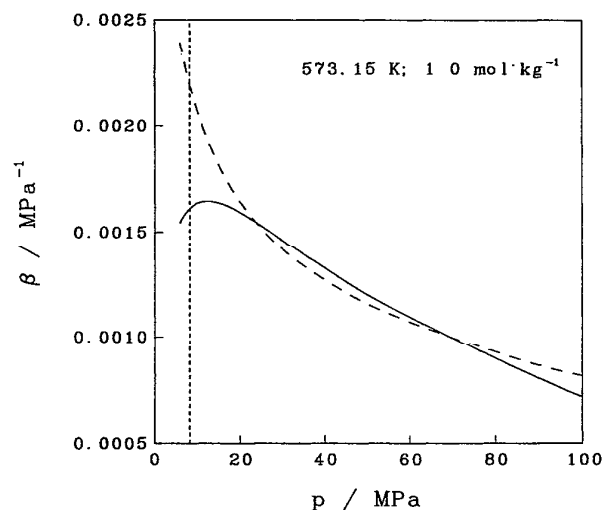


FIG. A1-1. Compressibility of  $1.0 \text{ mol}\cdot\text{kg}^{-1}$  NaCl(aq) against pressure for 573.15 K. The solid line is calculated from the representation that used the Archer and Wang dielectric-constant equation. The solid line is obtained from a representation that used the dielectric-constant equation from Bradley and Pitzer. The vertical line marks the saturation pressure of water for 573.15 K.

TABLE A1-1. Literature sources for the volumetric properties of NaCl(aq)

Reference	Temperature range (K)	Pressure range <sup>a</sup> (MPa)	Molality range (mol·kg <sup>-1</sup> )	n	type	$\sigma_{\text{est}}^b$	$\sigma_{\text{fit}}$	$\delta_{\text{fit}}$
19	273.95	0.1	0.015–0.126	11	$\rho_s^c$	$5 \times 10^{-6}$	$4 \times 10^{-6}$	$1.1 \times 10^{-6d}$
20	278.15	0.1	0.05–3.5	19	$V_\phi$	0.028	0.036	-0.021 <sup>e</sup>
21	298.15	0.1	0.17–5.86	13	$\rho_s/\rho_w$	$40 \times 10^{-6}$	$18 \times 10^{-6}$	$2 \times 10^{-6d}$
22	298.15	0.1	0.0026–0.75	15	$\rho_s/\rho_w$	$3 \times 10^{-6}$	$5 \times 10^{-6}$	$-3 \times 10^{-6d}$
23	298.15	0.1	0.04–6.14	11	$\rho_s/\rho_w$	$30 \times 10^{-6}$	$23 \times 10^{-6}$	$15 \times 10^{-6d}$
24(set 1)	298.15	0.1	0.06–2.1	21	$\rho_s-\rho_w$	U	$33 \times 10^{-6}$	$-28 \times 10^{-6d}$
24(set 2)	298.15	0.1	0.06–2.8	18	$\rho_s-\rho_w$	U	$54 \times 10^{-6}$	$40 \times 10^{-6d}$
25	298.15	0.1	0.05–3.5	19	$V_\phi$	0.017	0.016	-0.002 <sup>e</sup>
26	298.15	0.1	0.02–0.31	5	$\rho_s-\rho_w$	$5 \times 10^{-6}$	$4 \times 10^{-6}$	$0 \times 10^{-6d}$
27	298.15	0.1	1.0–6.0	7	$\rho_s/\rho_w$	U	$419 \times 10^{-6}$	$-233 \times 10^{-6d}$
28	298.15	0.1	0.21–0.82	2	$\rho_s/\rho_w$	$10 \times 10^{-6}$	$8 \times 10^{-6}$	$-1.0 \times 10^{-6d}$
28	298.15	0.1	0.004–0.82	1	$\Delta_{\text{dil}}V_\phi$	0.02	0.000	0.000 <sup>e</sup>
29	323.15	0.1	0.005–0.98	10	$\rho_s-\rho_w$	$20 \times 10^{-6}$	$25 \times 10^{-6}$	$13 \times 10^{-6d}$
30	298.15	0.1	0.01–1.0	12	$\rho_s-\rho_w$	$3 \times 10^{-6}$ ; 0.064%	$17 \times 10^{-6}$	$-13 \times 10^{-6d}$
31	298.15	0.1	0.17–5.0	9	$\rho_s/\rho_w$	U	$189 \times 10^{-6}$	$132 \times 10^{-6d}$
32	298.15	0.1	0.1–0.5	10	$\rho_s-\rho_w$	U	$79 \times 10^{-6}$	$44 \times 10^{-6d}$
33	298.15	0.1	0.28–5.10	10	$\rho_s-\rho_w$	U	$112 \times 10^{-6}$	$-78 \times 10^{-6d}$
34	298.15	0.1–40	0.06–5.0	40	$\rho_s-\rho_w$	$20 \times 10^{-6}$ ; 0.1%	$93 \times 10^{-6}$	$-15 \times 10^{-6d}$
33	298.15	0.1	0.28–5.10	10	$\alpha_s-\alpha_w$	$\sigma E_\phi = 2 \times 10^{-6}$ ; $m_L = 2.0$	$4.6 \times 10^{-6}$	$2.6 \times 10^{-6d}$
35	303.15	0.1	0.1–1.0	8	$V_\phi$	0.3	0.31	-0.29 <sup>e</sup>
36	308.15	0.1	0.002–1.08	13	$\rho_s/\rho_w$	$30 \times 10^{-6}$ ; 1.3%	$82 \times 10^{-6}$	$-52 \times 10^{-6d}$
37	280.15–306.19	0.1	0.25–5.7	21	$\rho_s/\rho_w$	$100 \times 10^{-6}$	$95 \times 10^{-6}$	$61 \times 10^{-6d}$
38	273.15–323.19	0.1	0.25–5.9	15	$\rho_s/\rho_w$	$100 \times 10^{-6}$	$95 \times 10^{-6}$	$-64 \times 10^{-6d}$
39	273.15–298.15	0.1	0.002–1.02	18	$\rho_s/\rho_w$	$15 \times 10^{-6}$	$18 \times 10^{-6}$	$4 \times 10^{-6d}$
40	273.2–338.15	0.1	0.23–0.9	27	$\Delta_{\text{dil}}V_\phi$	0.12	0.18	-0.11 <sup>e</sup>
40	273.2–338.15	0.1	0.21–1.0	17	$\rho_s/\rho_w$	$30 \times 10^{-6}$	$45 \times 10^{-6}$	$29 \times 10^{-6d}$
41	273.15–328.15	0.1	0.01–0.96	83	$\rho_s-\rho_w$	$5 \times 10^{-6}$ ; 0.14%	$22 \times 10^{-6}$	$-2 \times 10^{-6d}$
42	273.15–318.15	0.1	0.25–5.0	34	$\beta_s-\beta_w$	$0.6 \times 10^{-6}$	$0.59 \times 10^{-6}$	$0.01 \times 10^{-6d}$
43	273.15–308.15	0.1	0.01–1.5	47	$\rho_s-\rho_w$	$4 \times 10^{-6}$ ; 0.085%	$11 \times 10^{-6}$	$-3 \times 10^{-6d}$
44	274.65–318.15	0.1	0.03–3.0	58	$\rho_s-\rho_w$	$7.5 \times 10^{-6}$ ; 0.15%	$46 \times 10^{-6}$	$5 \times 10^{-6d}$
45	283.15–313.15	0.1	0.19–1.89	20	$\alpha_s-\alpha_w$	$\sigma E_\phi = 2 \times 10^{-6}$ ; $m_L = 2.0$	$1.8 \times 10^{-6}$	$-0.12 \times 10^{-6d}$
46	288.15–318.15	0.1	0.17–5.9	58	$\rho_s-\rho_w$	0.045%	$23 \times 10^{-6}$	$-0.4 \times 10^{-6d}$
47	288.15–313.15	0.1	0.06–2.9	55	$\rho_s-\rho_w$	U	$27 \times 10^{-6}$	$4 \times 10^{-6d}$
48	293.15–313.15	0.1	0.114	21	$V_\phi$	U	0.13	0.08 <sup>e</sup>
49	273.15–323.15	10–100	0.03–2.0	178	$\Delta\rho(P_2-P_1)$	$\sigma V_\phi = 0.1$ ; $m_L = 1.0$	0.44	0.2 <sup>e</sup>
50	293.15–571.65	10–100	0.017–5.7	216	$\rho_s$	$860 \times 10^{-6}$	$851 \times 10^{-6}$	$466 \times 10^{-6d}$
51, 52	298.15–358.15	0.1–100	0.89–5.68	104	$\rho_s/\rho_w$	$40 \times 10^{-6}$	$39 \times 10^{-6}$	$-1.1 \times 10^{-6d}$
53	323.16–548.05	***–40	0.056–5.0	250	$\rho_s-\rho_w$	$50 \times 10^{-6}$ ; 0.5%	$267 \times 10^{-6}$	$-105 \times 10^{-6d}$
53	321.6–549.7	***–32	0.01–3.09	163	$\rho_s-\rho_w$	$36 \times 10^{-6}$ ; 0.36%	$291 \times 10^{-6}$	$7 \times 10^{-6d}$
54	348.15–473.15	2.03	0.1–1.0	24	$\rho_s$	<sup>b</sup>	$164 \times 10^{-6}$	$-119 \times 10^{-6d}$
55	348.15–473.15	2.03	0.053–4.39	48	$\rho_s/\rho_w$	<sup>b</sup>	$183 \times 10^{-6}$	$-6 \times 10^{-6d}$
56	450–600	20.	0.1–4.0	59	$\rho_s$	U	0.016	0.0057 <sup>d</sup>
57	473.15–573.15	1.5–100	1.1–4.3	30	$\rho_s$	$3 \times 10^{-3}$	$4.2 \times 10^{-3}$	$2.6 \times 10^{-3d}$
58	448.15–573.15	$p_s$	0.5–3.0	24	$\rho_s$	$10 \times 10^{-3}$	$5.2 \times 10^{-3}$	$-4.2 \times 10^{-3d}$
53	597.45	21–39	0.01–5.05	30	$\rho_s-\rho_w$	$130 \times 10^{-6}$ ; 1.3%	$1.28 \times 10^{-3}$	$-0.66 \times 10^{-3d}$
59	604.4	27–38	0.01–3.1	87	$\rho_s-\rho_w$	$480 \times 10^{-6}$ ; 1.2%	$0.60 \times 10^{-3}$	$-0.19 \times 10^{-3d}$
169	308.15–368.15	0.101	0.26–6.2	141	$\rho_s-\rho_w$	$50 \times 10^{-6}$ ; 0.1%	$75 \times 10^{-6}$	$19 \times 10^{-6d}$

\*\*\* indicates that the lowest pressure for the data set changed with the experimental temperature

<sup>b</sup>The letter U indicates that these points were given an insignificant weight in the least-squares procedure. When two values are given the  $\sigma_{\text{exp}}$  was taken to be the larger of the two values given. In the cases where a value is given for  $m_L$ ; the expected square root of the variance is taken to be the first value for  $m > m_L$  and taken to be the first value divided by  $m_L$  for  $m < m_L$ .

<sup>c</sup>Values of density were calculated from the data given only as a figure.

<sup>d</sup>Units are  $\text{g cm}^{-3}$ .

<sup>e</sup>Units are  $\text{cm}^3 \text{mol}^{-1}$ .

<sup>f</sup>Units are  $\text{K}^{-1}$ .

<sup>g</sup>Units are  $\text{MPa}^{-1}$ .

<sup>h</sup>Values of  $\sigma_{\text{exp}}$  depended on temperature. Values were  $2 \times 10^{-4}$ ,  $2.8 \times 10^{-4}$ ,  $3.5 \times 10^{-4}$ ,  $4.2 \times 10^{-4}$ , and  $5 \times 10^{-4}$   $\text{g cm}^{-3}$ , for temperatures of 348.15 and 373.15, 398.15, 423.15, 448.15, and 473.15 K, respectively.

TABLE A1-2. Literature sources for the activity and thermal properties of NaCl(aq)

Reference	Temperature range (K)	Pressure range <sup>a</sup> (MPa)	Molality range (mol·kg <sup>-1</sup> )	<i>n</i>	Type <sup>b</sup>	$\sigma_{est}^c$	$\sigma_{fit}$	$\Delta_{fit}$
70	273.15	0.1	$m_s$	1	$m_s$ (NaCl·2H <sub>2</sub> O)	0.022	0.010	0.010 <sup>d</sup>
71	251.55–269.15	0.1	$m_s$	4	$m_s$ (NaCl·2H <sub>2</sub> O)	0.024	0.024	0.005 <sup>d</sup>
72	252.05–273.25	0.1	$m_s$	2	$m_s$ (NaCl·2H <sub>2</sub> O)	0.022	0.003	0.001 <sup>d</sup>
73	252.05–273.15	0.1	$m_s$	7	$m_s$ (NaCl·2H <sub>2</sub> O)	0.015	0.017	-0.004 <sup>d</sup>
74	252.15–271.15	0.1	$m_s$	5	$m_s$ (NaCl·2H <sub>2</sub> O)	0.040	0.036	0.033
75	252.34	0.1	$m_s$	1	$m_s$ (NaCl·2H <sub>2</sub> O)	0.3	0.04	-0.04 <sup>d</sup>
76	273.15–380.15	0.1, $p_s$	$m_s$	8	$m_s$ (NaCl)	0.040	0.036	-0.033 <sup>d</sup>
77	298.15	0.1	$m_s$	2	$m_s$ (NaCl)	0.010	0.013	0.013 <sup>d</sup>
70	278.15–356.15	0.1	$m_s$	16	$m_s$ (NaCl)	0.010	0.008	0.000 <sup>d</sup>
78	293.6–323.15	0.1	$m_s$	6	$m_s$ (NaCl)	0.010	0.003	-0.003 <sup>d</sup>
79	288.15–298.15	0.1	$m_s$	3	$m_s$ (NaCl)	0.020	0.011	-0.010 <sup>d</sup>
71	273.15–381.95	0.1, $p_s$	$m_s$	13	$m_s$ (NaCl)	0.030	0.026	-0.019 <sup>d</sup>
80	273.15–373.15	0.1	$m_s$	5	$m_s$ (NaCl)	0.063	0.061	-0.053 <sup>d</sup>
72	273.25–373.15	0.1	$m_s$	6	$m_s$ (NaCl)	0.010	0.009	0.006 <sup>d</sup>
72	393.15–462.55	$p_s$	$m_s$	4	$m_s$ (NaCl)	0.040	0.046	-0.005 <sup>d</sup>
81	423.15–573.15	$p_s$	$m_s$	6	$m_s$ (NaCl)	0.100	0.088	0.028 <sup>d</sup>
82	375.5–441.45	$p_s$	$m_s$	2	$m_s$ (NaCl)	0.050	0.048	-0.036 <sup>d</sup>
74	273.15–333.15	0.1	$m_s$	4	$m_s$ (NaCl)	0.025	0.015	-0.002 <sup>d</sup>
83	348.15–573.15	$p_w$	$m_s$	11	$m_s$ (NaCl)	0.030	0.023	0.014 <sup>d</sup>
84	422–603	$p_s$	$m_s$	13	$m_s$ (NaCl)	0.064	0.062	0.012 <sup>d</sup>
85	283.15–308.15	0.1	$m_s$	4	$m_s$ (NaCl)	0.010	0.008	0.007 <sup>d</sup>
86	290.8–373.14	0.1	$m_s$	12	$m_s$ (NaCl)	0.05	0.042	0.037 <sup>d</sup>
87	235–256			11	$p_{dec}$	6%	7%	-2%
88	251.95–273.3			5	$p_{dec}$	20	21	-3.8 <sup>e</sup>
89	$T_{fus}$	0.1	1.0–5.2	12	$\Delta_{fus}T$	U	0.011	-0.010 <sup>f</sup>
73	$T_{fus}$	0.1	3.26–5.13	4	$\Delta_{fus}T$	0.005	0.004	0.0035 <sup>f</sup>
90	$T_{fus}$	0.1	0.0008–1.3	28	$\Delta_{fus}T$	0.00075, $m_L=0.2$	0.0038	0.0018 <sup>f</sup>
74	$T_{fus}$	0.1	1.5–5.12	4	$\Delta_{fus}T$	0.005, $m_L=5.0$	0.012	-0.0059 <sup>f</sup>
91	$T_{fus}$	0.1	0.02–3.07	21	$\Delta_{fus}T$	0.0007, $m_L=1.0$	0.0057	0.001 <sup>f</sup>
92	$T_{fus}$	0.1	0.14–3.6	32	$\Delta_{fus}T$	0.002, $m_L=1.0$	0.0018	0.0013 <sup>f</sup>
93	$T_{fus}$	0.1	0.007–4.2	32	$\Delta_{fus}T$	0.0008, $m_L=0.2$	0.0025	-0.0014 <sup>f</sup>
94	373	0.1	0.07–2.8	15	$\Delta_{vap}T$	0.003	0.0033	-0.0022 <sup>f</sup>
95	333–343	0.1	0.05–1.0	24	$\Delta_{vap}T$	0.0006	0.00061	-0.00021 <sup>f</sup>
95	353–373	0.1	0.05–1.0	36	$\Delta_{vap}T$	0.00037	0.00037	0.00003 <sup>f</sup>
96	333.15	0.05	1.5–3.5	10	$\Delta_{vap}T$	0.005	0.0048	0.0038 <sup>f</sup>
96	343.15–373.15	0.07	1.5–3.5	43	$\Delta_{vap}T$	0.003	0.0023	-0.00009 <sup>f</sup>
97	298.15–373.15	0.1	1.0–6.1	56	$\phi$	0.0039	0.0044	-0.0032 <sup>f</sup>
98	293.15–303.15	0.1	2.4–6.1	36	$\phi$	0.0036	0.0035	-0.0024 <sup>f</sup>
99	298.15	$p_s$	4.0–5.9	9	$p_s-p_w$	0.0023	0.0022	0.0001 <sup>f</sup>
100	293.43	$p_s$	6.1	2	$p_s-p_w$	0.0020	0.0019	-0.0012 <sup>f</sup>
100	298.15	0.1	4.3–6.0	6	$p_s-p_w$	0.007	0.0055	0.0043 <sup>f</sup>
101	293.43–298.15	$p_s$	4.7–6.1	3	$p_s-p_w$	0.002	0.0025	0.00036 <sup>f</sup>
102	298.15	$p_s$	0.76–5.9	12	$p_s-p_w$	0.0046	0.0043	-0.0027 <sup>f</sup>
83	348.15–423.15	$p_s$	3.8–7.2	20	$p_s-p_w$	0.0075	0.0057	0.0046 <sup>f</sup>
83	448.15–498.15	$p_s$	3.9–8.4	18	$p_s-p_w$	0.005	0.0031	0.0028 <sup>f</sup>
83	523.15–573.15	$p_s$	4.1–10.4	18	$p_s-p_w$	0.003	0.0018	0.0006 <sup>f</sup>
103	422–541	$p_s$	1.0–3.0	22	$p_s-p_w$	0.01	0.0098	-0.0031 <sup>f</sup>
104	440–512.4	$p_s$	0.5–1.0	7	$p_s-p_w$	U	0.024	0.012 <sup>f</sup>
105	398.15–573.15	$p_s$	0.25–1.0	38	$p_s-p_w$	U	0.013	-0.0073 <sup>f</sup>
106	423.15–573.15	$p_s$	1.2–5.55	20	$p_s-p_w$	U	0.030	-0.010 <sup>f</sup>
107	273.15–323.15	0.1	0.001–4.0	60	$\ln(\gamma_2/\gamma_1)$	0.005	0.0043	0.00025
108	288.15–323.15	0.1	0.02–1.0	32	$\ln(\gamma_2/\gamma_1)$	U	0.0041	0.0010
109	298.15–343.15	0.1	0.03–5.0	48	$\ln(\gamma_{\pm})$	U	0.019	-0.00056
110	273.45–313.15	0.1	0.05–4.0	76	$\ln(\gamma_2/\gamma_1)$	0.005	0.0048	-0.0012
111	298.15	0.1	0.03–2.97	4	$\Delta_{dil}L_{\phi}$	80	50	-20 <sup>g</sup>
112	298.15	0.1	0.4–1.23	66	$\Delta_{dil}L_{\phi}$	0.09, $m_L=0.8$	0.13	0.016 <sup>g</sup>
113	298.15	0.1	0.1–0.83	21	$\Delta_{dil}L_{\phi}$	15	14	-7.8 <sup>g</sup>
114	348.35–372.85	6.6–41.	0.03–5.2	33	$\Delta_{dil}L_{\phi}$	2%, 20.	24	-4.0 <sup>g</sup>
114	423.25–473.05	6.6–41.6	0.03–5.2	47	$\Delta_{dil}L_{\phi}$	2%, 20.	61	29 <sup>g</sup>
114	523.45	6.6–41.7	0.03–5.2	31	$\Delta_{dil}L_{\phi}$	2%	153	-19 <sup>g</sup>
114	572.85	10.5–41.7	0.03–5.2	24	$\Delta_{dil}L_{\phi}$	2%	657	-460 <sup>g</sup>
115	283.15–298.15	0.1	0.0003–0.40	56	$\Delta_{dil}L_{\phi}$	8.0	8.0	-2.8 <sup>g</sup>
116	298.15	0.1	0.005–1.0	23	$\Delta_{dil}L_{\phi}$	2.5	2.4	1.5 <sup>g</sup>
117	303.15	0.1	0.2–1.0	7	$\Delta_{dil}L_{\phi}$	3.0	2.7	-2.5 <sup>g</sup>



TABLE A1-2. Literature sources for the activity and thermal properties of NaCl(aq) – Continued

Reference	Temperature range (K)	Pressure range <sup>a</sup> (MPa)	Molality range (mol·kg <sup>-1</sup> )	<i>n</i>	Type <sup>b</sup>	$\sigma_{est}^c$	$\sigma_{fit}$	$\Delta_{fit}$
118	298.15	0.1	0.04–5.0	19	$\Delta_{dil}L_\phi$	6.0	6.1	-3.4 <sup>d</sup>
118	323.15	0.1	0.04–5.0	23	$\Delta_{dil}L_\phi$	10	9.7	-3.7 <sup>d</sup>
118	348.15	0.1	0.04–5.0	18	$\Delta_{dil}L_\phi$	10	6.3	1.4 <sup>d</sup>
119	298.15	0.1	0.0008–0.1	24	$\Delta_{dil}L_\phi$	5	4.7	-0.4 <sup>d</sup>
120	298.08	0.1	0.046–0.45	2	$\Delta_{dil}L_\phi$	12	12.9	12.0 <sup>d</sup>
120	298	0.1	0.44–6.14	17	$\Delta_{dil}L_\phi$	1	0.89	0.58 <sup>d</sup>
121	273.4	0.1	0.09–6.1	21	$\Delta_{dil}L_\phi$	0.5, $m_L=0.5$	0.88	-0.35 <sup>d</sup>
121	285.8	0.1	0.2–6.1	18	$\Delta_{dil}L_\phi$	0.5, $m_L=0.5$	0.53	-0.35 <sup>d</sup>
121	298.2	0.1	0.19–6.1	17	$\Delta_{dil}L_\phi$	0.3, $m_L=0.5$	0.30	0.093 <sup>d</sup>
122	298.15	0.1	0.00025–1.0	7	$\Delta_{dil}L_\phi$	2.5	2.7	1.2 <sup>d</sup>
123	348.15	0.1	0.035–6.0	21	$\Delta_{dil}L_\phi$	5.0, $m_L=0.3$	5.8	-2.5 <sup>d</sup>
123	373.15	0.11	0.009–6.0	28	$\Delta_{dil}L_\phi$	10.0	7.5	5.5 <sup>d</sup>
123	423.65	0.5	0.007–6.0	46	$\Delta_{dil}L_\phi$	<sup>h</sup>	28	24 <sup>d</sup>
123	450.95	0.9	0.04–6.0	25	$\Delta_{dil}L_\phi$	<sup>h</sup>	26	21 <sup>d</sup>
123	472.95	1.55	0.20–6.0	11	$\Delta_{dil}L_\phi$	30	39	31 <sup>d</sup>
124	349.2	1.03	0.03–3.0	18	$\Delta_{dil}L_\phi$	20	20	-14 <sup>d</sup>
124	398.3	1.03	0.03–3.0	19	$\Delta_{dil}L_\phi$	<sup>h</sup>	27	-14 <sup>d</sup>
124	448.3	1.03	0.01–3.0	22	$\Delta_{dil}L_\phi$	<sup>h</sup>	76	-25 <sup>d</sup>
124	498.3	3.35	0.01–3.0	21	$\Delta_{dil}L_\phi$	<sup>h</sup>	80	-31 <sup>d</sup>
125	313.15	0.1	0.005–6.0	42	$\Delta_{dil}L_\phi$	20	15	9 <sup>d</sup>
125	323.15	0.1	0.004–5.7	31	$\Delta_{dil}L_\phi$	20	22	6 <sup>d</sup>
125	333.15	0.1	0.008–5.7	32	$\Delta_{dil}L_\phi$	20	16	2 <sup>d</sup>
125	343.15	0.1	0.007–5.7	32	$\Delta_{dil}L_\phi$	20	20	-7 <sup>d</sup>
125	353.15	0.1	0.007–5.7	29	$\Delta_{dil}L_\phi$	U	62	25 <sup>d</sup>
126	298.15	0.1	0.27–3.0	6	$\Delta_{dil}L_\phi$	20	15	-4 <sup>d</sup>
127	293.15	0.1	0.02–0.04	9	$\Delta_{sol}H_m$	250	168	-46 <sup>d</sup>
128	298.15	0.1	0.05–1.3	24	$\Delta_{sol}H_m$	40	23	21 <sup>d</sup>
129	278.15–348.15	0.1	0.46	5	$\Delta_{sol}H_m$	40	46	-45 <sup>d</sup>
130	298.15	0.1	0.5–5.6	14	$\Delta_{sol}H_m$	40	30	28 <sup>d</sup>
129	278.15–313.15	0.1	0.0003–4.1	41	$\Delta_{sol}H_m(m_2-m_1)$	120	128	-99 <sup>d</sup>
131	275.15	0.1	0.06–6.0	18	$\Delta_{sol}H_m$	230	235	-142 <sup>d</sup>
132	387.4–472.65	$p_s$	0.01–0.04	17	$\Delta_{sol}H_m$	300	282	-24 <sup>d</sup>
133	273.2–368.3	0.1	0.003–0.02	58	$\Delta_{sol}H_m$	150	156	-109 <sup>d</sup>
134	298.15	0.1	0.02–0.72	23	$\Delta_{sol}H_m$	40	23	14 <sup>d</sup>
135	298.15	0.1	0.01–0.03	5	$\Delta_{sol}H_m$	40	25	-21 <sup>d</sup>
136	278.15–298.15	0.1	0.05–5.0	88	$\Delta_{sol}H_m$	170	171	-81 <sup>d</sup>
137	303–313	0.1	0.006–0.12	48	$\Delta_{sol}H_m$	190	181	141 <sup>d</sup>
138	298.15	0.1	0.01–0.12	16	$\Delta_{sol}H_m$	100	102	21 <sup>d</sup>
139	293.15–298.15	0.1	0.8–5.9	17	$\Delta_{sol}H_m$	40	18	0.7 <sup>d</sup>
140	298.15	0.1	0.07–5.5	20	$\Delta_{sol}H_m$	40	11	-2 <sup>d</sup>
141	298	0.1	0.25–0.5	4	$\Delta_{sol}H_m$	40	6	4 <sup>d</sup>
142	323.14–573.15	7–36	1.0–6.0	127	$c_{p,s}/c_{p,w}$	0.00125	3.5	-0.4 <sup>h</sup>
142	598.01	20.1	1.0–6.0	24	$c_{p,s}/c_{p,w}$	0.005	31.2	19.0 <sup>h</sup>
146	349–573	***-17.9	0.08–5.0	402	$c_{p,s}/c_{p,w}$	*	12.8	-2.2 <sup>i</sup>
146	597.8	17.9	0.085–3.0	18	$c_{p,s}/c_{p,w}$	*	111	71 <sup>i</sup>
147	348.2–598.6	17.7	3.0	7	$c_{p,s}/c_{p,w}$	*	3.2	-2.2 <sup>i</sup>
148	358.3, 573.95	17.7	1.0–3.0	6	$c_{p,s}/c_{p,w}$	*	5.8	4.2 <sup>i</sup>
150	598.11	17.7	1.0–3.0	6	$c_{p,s}/c_{p,w}$	*	7.1	-5.1 <sup>i</sup>
149	353.15–473.15	***	0.35–2.13	35	$c_{p,s}$	0.012	5.4	0.2 <sup>i</sup>
143	278.15	0.1	0.076–6.0	20	$C_{p,\phi}$	0.5, $m_L=1.5$	1.2	-0.6 <sup>k</sup>
143	298.15	0.1	0.04–6.0	30	$C_{p,\phi}$	0.5, $m_L=1.5$	1.9	-0.4 <sup>k</sup>
143	318.15	0.1	0.04–6.0	26	$C_{p,\phi}$	0.5, $m_L=1.5$	2.0	-0.5 <sup>k</sup>
143	338.15	0.1	0.08–6.0	22	$C_{p,\phi}$	0.5, $m_L=1.5$	0.9	0.1 <sup>k</sup>
143	358.15	0.1	0.08–6.0	17	$C_{p,\phi}$	0.5, $m_L=1.5$	1.5	0.3 <sup>k</sup>
24	298.15	0.1	1.0–3.2	13	$C_{p,\phi}$	0.4, $m_L=2.5$	0.5	0.04 <sup>k</sup>
144	298.15	0.1	0.011–5.32	22	$C_{p,\phi}$	0.75, $m_L=0.1$	1.1	-0.4 <sup>k</sup>
145	298.15	0.1	0.05–2.5	11	$C_{p,\phi}$	1.0, $m_L=0.6$	3.6	-1.9 <sup>k</sup>
27	298.15	0.1	1.0–6.0	8	$c_{p,s}/c_{p,w}$	U	1.1	0.7 <sup>k</sup>
115	298.15	0.1	0.01–3.0	22	$C_{p,\phi}$	U	2.7	2.3 <sup>k</sup>
44	274.65	0.1	0.07–1.8	12	$C_{p,\phi}$	U	3.9	-0.6 <sup>k</sup>
44	278.15	0.1	0.03–1.0	11	$C_{p,\phi}$	U	3.7	1.1 <sup>k</sup>
44	288.15	0.1	0.03–3.0	16	$C_{p,\phi}$	U	1.3	0.6 <sup>k</sup>
44	308.15	0.1	0.03–3.0	16	$C_{p,\phi}$	U	3.8	3.7 <sup>k</sup>

TABLE A1-2. Literature sources for the activity and thermal properties of NaCl(aq) – Continued

Reference	Temperature range (K)	Pressure range <sup>a</sup> (MPa)	Molality range (mol·kg <sup>-1</sup> )	<i>n</i>	Type <sup>b</sup>	$\sigma_{\text{est}}^c$	$\sigma_{\text{fit}}$	$\Delta_{\text{fit}}$
44	318.15	0.1	0.03–2.5	15	$C_{p,\phi}$	U	2.7	2.5 <sup>k</sup>
32	298.15	0.1	0.08–0.5	10	$C_{p,\phi}$	U	0.6	–0.4 <sup>k</sup>
24	298.15	0.1	0.06–2.1	21	$C_{p,\phi}$	U	2.3	2.2 <sup>k</sup>
24	298.15	0.1	0.07–2.8	19	$C_{p,\phi}$	U	5.3	5.1 <sup>k</sup>
47	283.15–313.15	0.1	0.04–2.9	53	$C_{p,\phi}$	U	0.9	0.0 <sup>k</sup>
33	298.15	0.1	0.28–5.1	10	$C_{p,\phi}$	U	1.8	1.4 <sup>k</sup>
152	423.15–573.15	$p_s$	0.4–6.04	24	$c_{p,s}/c_{p,w}$	U	70	37 <sup>k</sup>
163	248.15	0.1	2.0–6.0	6	$c_{p,s}$	10, $m_L = 6.0$	16	–5 <sup>k</sup>

<sup>a</sup> \*\* indicates that the lowest pressure for the data set changed with the experimental temperature

<sup>b</sup> Type  $m_s$  refers to solubility of the indicated substance;  $p_{\text{dec}}$  refers to the vapor pressure of water in equilibrium with the dihydrate; The symbol  $p_s - p_w$  refers to the difference in vapor pressure between solution and solvent.

<sup>c</sup> The letter U indicates that these points were given an insignificant weight in the least-squares procedure. When two values are given the  $\sigma_{\text{exp}}$  was taken to be the larger of the two values given. In the cases where a value is given for  $m_L$ , the expected square root of the variance is taken to be the first value for  $m > m_L$  and taken to be the first value divided by  $m_L$  for  $m < m_L$ .

<sup>d</sup> Units are kJ·mol<sup>-3</sup>.

<sup>e</sup> Units are Pa.

<sup>f</sup> Values given in terms of the osmotic coefficient.

<sup>g</sup> Units are J·mol<sup>-1</sup>.

<sup>h</sup> Values of  $\sigma_{\text{exp}}$  were unitless, other values given in terms of  $C_{p,\phi}$ , units are J·K<sup>-1</sup>·mol<sup>-1</sup>.

<sup>i</sup> Values of  $\sigma_{\text{exp}}$  were unitless and were those given in the cited reference, other values given in terms of  $C_{p,\phi}$ , units are J·K<sup>-1</sup>·mol<sup>-1</sup>.

<sup>j</sup> Values of  $\sigma_{\text{exp}}$  had units of J·K<sup>-1</sup>·g<sup>-1</sup>, other values given in terms of  $C_{p,\phi}$ , units are J·K<sup>-1</sup>·mol<sup>-1</sup>.

<sup>k</sup> Units are J·K<sup>-1</sup>·mol<sup>-1</sup>.

Table A1-3. Least-squares estimated parameters for Eqs. (3-37) with use of the dielectric-constant equation of Bradley and Pitzer <sup>a</sup>

Parameter	Value	Parameter	Value	Parameter	Value
$b_{1,1}$	0.242651052883794	$b_{2,1}$	-1.94792794517029	$b_{3,1}$	
$b_{1,2}$		$b_{2,2}$	5.53477399563770	$b_{3,2}$	-0.0476961507576975
$b_{1,3}$	-0.160578547305475	$b_{2,3}$		$b_{3,3}$	0.0248453996970447
$b_{1,4}$	1.22249898267412	$b_{2,4}$	-40.9575943938422	$b_{3,4}$	-0.583285519436642
$b_{1,5}$		$b_{2,5}$		$b_{3,5}$	
$b_{1,6}$		$b_{2,6}$		$b_{3,6}$	0.0966416317519622
$b_{1,7}$	-65.8299103364965	$b_{2,7}$	495.488959381070	$b_{3,7}$	5.17677315192276
$b_{1,8}$		$b_{2,8}$	-0.647069267974439	$b_{3,8}$	-0.00530484869542637
$b_{1,9}$	0.592206494036454	$b_{2,9}$		$b_{3,9}$	
$b_{1,10}$	-21.6059704995988	$b_{2,10}$		$b_{3,10}$	1.49331442521389
$b_{1,11}$	79.9242989836885	$b_{2,11}$	263.514104240237	$b_{3,11}$	-3.57598920090558
$b_{1,12}$	-1.37402918488118	$b_{2,12}$		$b_{3,12}$	0.0846547308275376
$b_{1,13}$		$b_{2,13}$	-110.865524218289	$b_{3,13}$	
$b_{1,14}$		$b_{2,14}$		$b_{3,14}$	-19.6647827776674
$b_{1,15}$	35.9009013869343	$b_{2,15}$		$b_{3,15}$	-3.16551434879799
$b_{1,16}$	-49.4314672615553	$b_{2,16}$	-54.9466586142382	$b_{3,16}$	3.62129862281871
$b_{1,17}$	1.04390658682638	$b_{2,17}$		$b_{3,17}$	
$b_{1,18}$	-41.9541567430562	$b_{2,18}$		$b_{3,18}$	3.67884876799807
$b_{1,19}$		$b_{2,19}$		$b_{3,19}$	
$b_{1,20}$		$b_{2,20}$		$b_{3,20}$	
$b_{1,21}$	33.2379600367917	$b_{2,21}$		$b_{3,21}$	
$b_{1,22}$	2.03031549012081	$b_{2,22}$		$b_{3,22}$	
$b_{1,23}$	-0.187396334924425	$b_{2,23}$		$b_{3,23}$	
$b_{1,24}$	8.81256035834609	$b_{2,24}$		$b_{3,24}$	-0.564064305163377
$b_{4,1}$	0.738770355969160	$b_{6,1}$	1.65044633819023	$\Delta_{\text{sol}}G_{\text{anhydrous},T_r,P_r}^{\circ}$	-9.036665 ± 0.0065 kJ·mol <sup>-1</sup>
$b_{4,2}$	-3.48181614204602	$b_{6,2}$	-0.786584166653199	$\Delta_{\text{sol}}G_{\text{dihydrate},T_r,P_r}^{\circ}$	-8.944448 ± 0.044 kJ·mol <sup>-1</sup>
$b_{4,3}$	1.08380749393807	$b_{6,3}$	0.216559238906270	$S_{\text{m,cr,dihydrate},T_r,P_r}^{\circ}$	162.7623 ± 1.2 J·K <sup>-1</sup> ·mol <sup>-1</sup>
$b_{4,4}$		$b_{6,4}$	-1.02990273530200	$S_{\text{m,NaCl(aq)},T_r,P_r}^{\circ}$	115.4905 ± 0.030 J·K <sup>-1</sup> ·mol <sup>-1</sup>
$b_{4,5}$					
$b_{4,6}$	-9.76294707814877	$b_{5,1}$	1.73824910134822		
$b_{4,7}$		$b_{5,2}$	0.949889120761842		
$b_{4,8}$		$b_{5,3}$	4.94057353407296		
$b_{4,9}$		$b_{5,4}$	5.33065983741207		
$b_{4,10}$		$b_{5,5}$	-11.8258826797546		
$b_{4,11}$		$b_{5,6}$	0.146278779523558		
$b_{4,12}$		$b_{5,7}$	-8.31379076485402		
$b_{4,13}$		$b_{5,8}$	0.237944972833914		
$b_{4,14}$					
$b_{4,15}$					
$b_{4,16}$					
$b_{4,17}$					
$b_{4,18}$					
$b_{4,19}$					
$b_{4,20}$					
$b_{4,21}$					
$b_{4,22}$					
$b_{4,23}$					
$b_{4,24}$	28.1027292775539				

<sup>a</sup> The ± values are 95% confidence intervals within the global data representation.

## Appendix 2. Comparison of Enthalpies of Dilution from Different Calorimeters

Fig. A2-1 shows differences of enthalpy of dilution results from different calorimeters for  $\text{Na}_2\text{SO}_4(\text{aq})$  and  $\text{HCl}(\text{aq})$ . All are shown against the observed heat flux in one of the calorimeters. Calculation of the differences shown in Fig. A2-1 is described below.

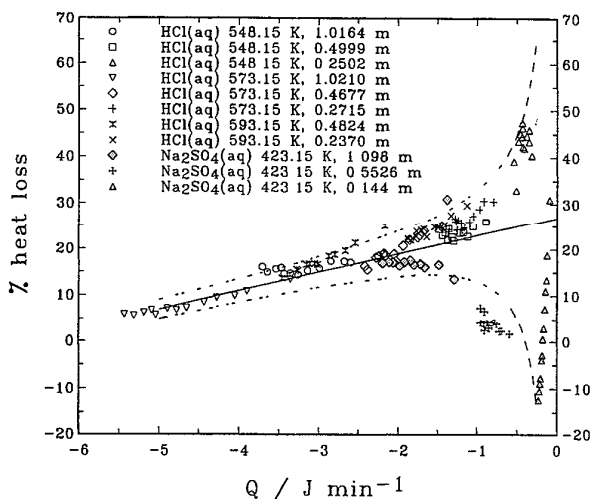


FIG. A2-1. Differences of enthalpies of dilution from different calorimeters.

The first comparison to be described is for  $\text{HCl}(\text{aq})$  from 548.15 K to 593.15 K. Oscarson *et al.*<sup>166</sup> presented their results in a manner somewhat different than that normally encountered in the description of enthalpy of dilution results. Because of this difference the calculation of  $\Delta L_\phi$  from the flow rates and observed enthalpies is briefly described. The flow rate of water (in  $\text{g H}_2\text{O}\cdot\text{min}^{-1}$ ) in each of the calorimetric flow streams is obtained from multiplication of the value in the column labeled "Flow of Stream" and the number associated with the lower case letter above the appropriate "Heat of Dilution" column. The flow rate of solute ( $\text{mol}\cdot\text{min}^{-1}$ ) is obtained by multiplying the flow rate of water ( $\text{g}\cdot\text{min}^{-1}$ ) in the appropriate column by the molality of solute and dividing by  $1000 \text{ g}\cdot\text{kg}^{-1}$ . The molar enthalpy of dilution,  $\Delta L_\phi$ , is obtained by dividing the reported enthalpy flux ( $\text{J}\cdot\text{min}^{-1}$ ) by the solute flow rate. The final molality for the dilution is obtained by dividing the solute flow rate by the sum of the two water flow rates and multiplying by  $1000 \text{ g}\cdot\text{kg}^{-1}$ .

The values of  $\Delta L_\phi$  for  $\text{HCl}(\text{aq})$  calculated in this way are referred to as  $\Delta L_{\phi, \text{HCl}(\text{aq}), \text{O}}$ . Values for comparison were calculated from the equation for  $\text{HCl}(\text{aq})$  given by Holmes *et al.*<sup>167</sup> (their Model III). These values are referred to as  $\Delta L_{\phi, \text{HCl}(\text{aq}), \text{H}}$ . All of the  $\Delta L_{\phi, \text{HCl}(\text{aq}), \text{O}}$  were smaller in magnitude than the corresponding

$\Delta L_{\phi, \text{HCl}(\text{aq}), \text{H}}$ . The percentage difference of these two values was termed a "% heat loss" and evaluated for each observation as:

$$\% \text{ heat loss} = 100 \frac{\Delta L_{\phi, \text{HCl}(\text{aq}), \text{H}} - \Delta L_{\phi, \text{HCl}(\text{aq}), \text{O}}}{\Delta L_{\phi, \text{HCl}(\text{aq}), \text{H}}} \quad (\text{A2-1})$$

These calculated values of % heat loss, against the observed enthalpy flux,  $Q$ , are shown in Fig. A2-1.

The second comparison is for  $\text{Na}_2\text{SO}_4(\text{aq})$  for 423.15 K. Values of  $\Delta L_\phi$  for  $\text{Na}_2\text{SO}_4(\text{aq})$  for 423.15 K were calculated from the enthalpy of dilution results given by Mayrath and Wood<sup>168</sup> in the following manner. Pitzer's ion-interaction equation for the apparent molar enthalpy:

$$L_\phi = \nu |z_{\text{M}^+} z_{\text{X}^-}| A_H \ln(1 + bI^{1/2})/2b - 2\nu_{\text{M}^+} \nu_{\text{X}^-} RT^2 (m B_{\text{MX}}^L + m^2 \nu_{\text{M}^+} z_{\text{M}^+} C_{\text{MX}}^L) \quad (\text{A2-2})$$

where:

$$B_{\text{MX}}^L = \left( \frac{\partial \beta_{\text{MX}}^{(0)}}{\partial T} \right)_p + 2 \left( \frac{\partial \beta_{\text{MX}}^{(1)}}{\partial T} \right)_p [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] / \alpha^2 I \quad (\text{A2-3})$$

$$C_{\text{MX}}^L = 0.5 |z_{\text{M}^+} z_{\text{X}^-}|^{-1/2} \left( \frac{\partial C_{\text{MX}}^\phi}{\partial T} \right)_p \quad (\text{A2-4})$$

and where  $A_H$  is the Debye-Hückel coefficient for apparent molar enthalpy,  $\alpha = 1.4 (\text{kg}\cdot\text{mol}^{-1})^{1/2}$ ,  $b = 1.2 (\text{kg}\cdot\text{mol}^{-1})^{1/2}$ , was fitted to Mayrath and Wood's experimental enthalpies of dilution for 423.65 K and 373.15 K. These two fitted equations were used to both calculate  $\Delta L_\phi$  and to interpolate for the 0.5 K difference in temperature between Mayrath and Wood's results and the results of Oscarson *et al.* The values of  $\Delta L_\phi$  that corresponded to the conditions given by Oscarson *et al.* and that were calculated from Mayrath and Wood's results are referred to as  $\Delta L_{\phi, \text{Na}_2\text{SO}_4(\text{aq}), \text{M}}$ . The  $\Delta L_{\phi, \text{Na}_2\text{SO}_4(\text{aq}), \text{M}}$  were larger in magnitude than the values of  $\Delta L_{\phi, \text{Na}_2\text{SO}_4(\text{aq}), \text{O}}$  calculated from the flow rates and enthalpy flux given by Oscarson *et al.*, except for the very lowest molalities. The values of % heat loss for the  $\text{Na}_2\text{SO}_4(\text{aq})$  results, calculated as in Eq. (A2-1), are also shown in Fig. A2-1.

Recently, Izzatt *et al.*<sup>173</sup> reported enthalpy of dilution values for  $\text{NaOH}(\text{aq})$ . They presented a table that compared their enthalpies of dilution for a nominal 1.9  $\text{mol}\cdot\text{kg}^{-1}$  solution, for 523.15 K, to values they obtained "by interpolation" from information given by Simonson *et al.*<sup>174</sup> The differences of the enthalpy of dilution, reported in the Izzatt *et al.* table, were generally only a few tenths of a per cent, with the r.m.s. difference being about 0.5 per cent. These differences indicate a remark

able agreement between the two calorimeters; an agreement that is almost an order of magnitude better than that found for different calorimeters for NaCl(aq), when comparing individual dilution measurements. Such an agreement, if generally correct, would indicate an accuracy of Busey's calorimeter<sup>114</sup> that would be about an order of magnitude more accurate than reported and would indicate an incorrect weighting of the Busey *et al.*<sup>114</sup> results in the present work. Because of the significance of the Busey *et al.* results to the present work, other enthalpy of dilution results for NaOH(aq) given by Izzatt *et al.* were examined.

One test of the accuracy of an enthalpy of dilution calorimeter is how well dilutions with different initial molalities, i.e. overlapping dilution chords, agree with each other. Examination of overlapping dilution chords can be considered a test of the internal accuracy of the calorimeter. Figure A2-2 shows values given by Izzatt *et al.*<sup>173</sup> for the enthalpy of dilution, as  $\Delta L_{\phi}$ , of the nominal 1.9 mol·kg<sup>-1</sup> solutions and also a 9.82 mol·kg<sup>-1</sup> solution for 523.15 K. The enthalpy of dilution for the 1.9 mol·kg<sup>-1</sup> solutions is about 10 per cent larger than the corresponding enthalpy of dilution obtained from the 9.82 mol·kg<sup>-1</sup> dilutions (or about 3 per cent of the enthalpy of dilution of the 9.82 mol·kg<sup>-1</sup> solution). Thus, the internal accuracy of the enthalpy of dilution for NaOH(aq), for 523.15 K, does not appear to be better than 3 to 10 per cent. Because the internal accuracy of the calorimetric results is approximately an order of magnitude less accurate than what might be inferred from Izzatt *et al.*'s comparison of

the 1.9 mol·kg<sup>-1</sup> dilutions, the weighting of the Busey *et al.*<sup>114</sup> results in the present work was considered appropriate and changes were not warranted by the Izzatt *et al.* work.

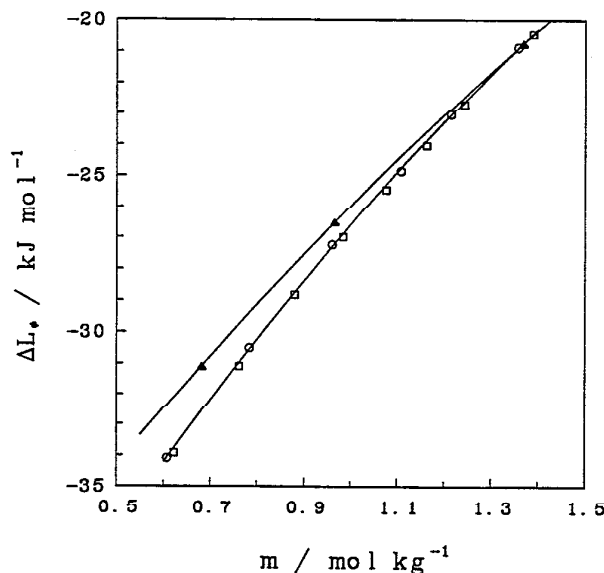


FIG. A2-2. Enthalpy of dilution of NaOH(aq), for 523.15 K and 4.5 MPa, from Izzatt *et al.*<sup>173</sup> The squares are dilutions from 1.93 mol·kg<sup>-1</sup>; the circles are dilutions from 1.84 mol·kg<sup>-1</sup>. The triangles are dilutions from 9.82 mol·kg<sup>-1</sup>.