

# Thermodynamic Properties of the $\text{KCl}+\text{H}_2\text{O}$ System

Cite as: Journal of Physical and Chemical Reference Data **28**, 1 (1999); <https://doi.org/10.1063/1.556034>  
Submitted: 22 May 1998 . Published Online: 25 March 1999

Donald G. Archer



View Online



Export Citation

## ARTICLES YOU MAY BE INTERESTED IN

Thermodynamic Properties of the  $\text{NaCl}+\text{H}_2\text{O}$  System. II. Thermodynamic Properties of  $\text{NaCl}(\text{aq})$ ,  $\text{NaCl}\cdot 2\text{H}_2(\text{cr})$ , and Phase Equilibria

Journal of Physical and Chemical Reference Data **21**, 793 (1992); <https://doi.org/10.1063/1.555915>

Thermodynamic Properties of Aqueous Sodium Chloride Solutions

Journal of Physical and Chemical Reference Data **13**, 1 (1984); <https://doi.org/10.1063/1.555709>

Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at  $25^\circ\text{C}$

Journal of Physical and Chemical Reference Data **1**, 1047 (1972); <https://doi.org/10.1063/1.3253108>

Where in the **world** is AIP Publishing?  
*Find out where we are exhibiting next*



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

Donald G. Archer<sup>a)</sup>

Physical and Chemical Properties Division, Chemical Science and Technology Laboratory,  
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received May 22, 1998; final revision received September 24, 1998

The thermodynamic properties of the KCl+H<sub>2</sub>O system were examined in order to provide: (1) an improved equation for the osmotic coefficient as a function of molality and temperature for purposes of isopiestic measurements, (2) a determination of the thermodynamic properties of the standard-state solution process, and (3) a test of the accuracy of the enthalpy of solution values for KCl(cr), a calorimetric standard. New equations that describe the thermodynamic properties of the KCl+H<sub>2</sub>O system were obtained from previously published measurements for this system. The measured values included in the fitted equations spanned the range of temperature from approximately 260 to 420 K for KCl(aq) and 1.5 K to 1033.7 K for KCl(cr). New equations and/or values for the following properties are given in the present work: (1) thermal properties of KCl(cr) from 0 K to the melting point, 1045 K, (2) the change in chemical potential for both KCl and H<sub>2</sub>O in KCl(aq) as a function of temperature, and molality, valid from 260 to 420 K, and (3) standard-state properties for the aqueous solution process. The effect of heat treatment on the determination of enthalpy of solution values was also examined. This examination indicated that the NIST recommendation of heating Standard Reference Material 1655, potassium chloride, at 800 K for a minimum of 4 h prior to its use in calorimeter calibration, should probably not be followed. The heat treatment recommended by the NIST certificate appears, at this point, to have a higher probability of corrupting the sample than improving the accuracy of the measurement. © 1999 American Institute of Physics and American Chemical Society. [S0047-2689(99)00101-4]

Key words: activity coefficient, aqueous, enthalpy, Gibbs energy, heat capacity, osmotic coefficient, potassium chloride, solubility, thermodynamics, vapor pressure.

## Contents

1. Introduction. . . . .	2	2. Thermodynamic properties of KCl(cr) calculated from Eqs. (1), (2). . . . .	4
2. Thermodynamic Properties of Potassium Chloride(cr). . . . .	2	3. Literature sources for the activity and thermal properties of KCl(aq). . . . .	6
3. Thermodynamic Properties of Potassium Chloride(aq). . . . .	3	4. Least-squares estimated parameters for the model of thermodynamic properties of KCl(aq)... . . . .	8
3.1. Treatment of the Thermodynamic Data. . . . .	3	5. Calculated values of $A_\phi$ , $\beta_{MX}^{(0)}$ , $\beta_{MX}^{(1)}$ , and $C_{MX}$ .. . . .	8
3.2. Agreement with the Experimental Results for Potassium Chloride(aq). . . . .	8	6. Calculated values of $G_{m,2}^\circ - G_{m,2,T_r}^\circ$ , $H_{m,2}^\circ - H_{m,2,T_r}^\circ$ , $S_{m,2}^\circ - S_{m,2,T_r}^\circ$ , and $C_{p,\phi}$ . . . . .	8
3.2.1. Activity Results. . . . .	8	7. Calculated values of the osmotic coefficient $\phi$ ... . . . .	9
3.2.2. Enthalpy of Dilution Results. . . . .	10		
3.2.3. Enthalpy of Solution Results. . . . .	10		
3.2.4. Heat Capacity Results. . . . .	14		
4. Phase Equilibria and Thermodynamic Properties of the Solution Process for 298.15 K. . . . .	15		
5. References. . . . .	15		

## List of Tables

1. Least-squares estimated knot positions for KCl(cr). . . . .	3
--	---

## List of Figures

1. Comparison of measurements for potassium chloride to fitted equation for temperatures less than 50 K. . . . .	4
2. Comparison of measurements for potassium chloride to fitted equation for temperatures from 50 to 450 K. . . . .	4
3. Differences of measured osmotic coefficients obtained from solvent activity determinations from those calculated from the model for near ambient temperatures. . . . .	9
4. Differences of measured osmotic coefficients obtained from solvent activity determinations from those calculated from the model for	

<sup>a)</sup>Electronic mail: donald.archer@nist.gov

©1999 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. This copyright is assigned to the American Institute of Physics and the American Chemical Society.  
Reprints available from ACS; see Reprints List at back of issue.

temperatures other than 298.15 K. . . . .	9
5. Differences of solute activity coefficients obtained from electrochemical concentration cell measurements from the model. . . . .	9
6. Differences of measured enthalpies of dilution from the model for temperatures near 298.15 K. . . . .	10
7. Differences of measured enthalpies of solution from the model. . . . .	12
8. Differences of measured enthalpies of solution from the model against temperature. . . . .	14
9. Values of the solubility calculated from the model compared to measured values. . . . .	15

## 1. Introduction

The isopiestic method of determination of vapor pressures is a relative method in which the vapor pressure for an unknown solution with involatile solutes is determined by its equilibration with a solution of an involatile solute, a common solvent and known vapor pressure.<sup>1</sup> Application of the method to aqueous solutions therefore requires the knowledge of accurate vapor pressure relations for aqueous solutions of the reference solutes. Two common standards are NaCl(aq) and KCl(aq). In the past, the equations often used for the osmotic coefficients of these two reference electrolytes at 298.15 K have been those given by Hamer and Wu.<sup>2</sup> Clarke and Glew<sup>3</sup> noted previously a small bias of Hamer and Wu's equation for NaCl(aq) from their model<sup>3</sup> of the thermodynamic properties of NaCl(aq) and observed that this bias was due in part to a lack of inclusion of highly accurate freezing-point depressions and changes in boiling temperatures. These measurements were obtained at temperatures other than 298.15 K, whereas Hamer and Wu considered measurements for 298.15 K only. Archer<sup>4</sup> generated an equation for the thermodynamic properties of NaCl(aq) that utilized a different model basis from that used by Clarke and Glew. Archer found essentially the same effect reported by Clarke and Glew. Those two equations for NaCl(aq)<sup>3,4</sup> are now being utilized in the treatment of isopiestic molality ratios relative to NaCl(aq). However, many isopiestic studies have used KCl(aq) as a reference electrolyte. Hamer and Wu's representations of thermodynamic measurements for NaCl(aq) and KCl(aq) maintained agreement with reported isopiestic ratios for the two electrolytes. Thus, the possibility existed that the small bias found in the equation for NaCl(aq) would also exist in Hamer and Wu's equation for KCl(aq). Elimination of this bias and generation of a better set of properties for KCl(aq) as an isopiestic standard is one goal of the current report.

A second purpose of the current article is to determine the standard-state thermodynamic properties for the solution of potassium chloride in water. These are required in a continuing analysis of the CODATA Key Values for Thermodynamics.<sup>5</sup>

The third item of interest deals with the use of potassium chloride for testing and calibration of solution calorimeters, particularly calorimeters used for measurements of enthalpies of solution and enthalpies of reaction for near ambient conditions. In this regard, the National Institute of Standards and Technology supplies potassium chloride as Standard Reference Material 1655. The present work invalidates earlier claims regarding the lack of suitability of potassium chloride as a calibrant and also casts doubt upon certain pre-

scribed methods for handling potassium chloride samples prior to measurement of an enthalpy of solution. Some of the previously recommended procedures for handling SRM-1655 prior to measurement may introduce an error in the measurement of the enthalpy of the solution.

In 1988, Pabalan and Pitzer<sup>6</sup> published an equation for the thermodynamic properties of KCl(aq), which was valid to approximately 600 K and 50 MPa. The present contribution is not meant as a replacement of the equation provided by Pabalan and Pitzer. Instead, it establishes baseline parameters, which they accepted as known, that can be used in conjunction with their equation. The present equation examines a larger base of near-ambient data, includes phase equilibria data, considers only measurements within a few tenths of a megapascal from atmospheric pressure, and does not include pressure dependence of the thermodynamic properties. It seemed little improvement of the latter (pressure dependence) from that given by Pabalan and Pitzer would have been achieved.

## 2. Thermodynamic Properties of Potassium Chloride(cr)

In this section, a model for the thermodynamic properties of crystalline potassium chloride is developed. Such an equation is required for inclusion of enthalpies of solution as a function of temperature and for the treatment of the phase-equilibria data for KCl(cr) and KCl(aq).

Several sets of measurements of the thermal properties of potassium chloride have been published in the past. Unfortunately, the measurements below 300 K from these different sources are generally disparate. To obtain thermodynamic properties for the full range of temperature, some of the previous measurements were selected and included in a least-squares representation. All of the selected enthalpy increments and heat capacities were fitted simultaneously by means of a cubic-spline method described previously.<sup>7</sup>

Briefly, a function  $f(T)$  was used, where:

$$f(T) = [T \cdot (C_{p,m}^{\circ} / C_p^{\circ})^{-1/3} - bT] / T^{\circ}, \quad (1)$$

where  $b$  was a constant arbitrarily chosen to be 0.25 for the present case, and where  $C_p^{\circ}$  was  $1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  and  $T^{\circ}$  was 1 K. The function  $f(T)$  of Eq. (1) was fitted with a cubic spline using polynomials of the form:

$$f(T) = a_i(T - T_i)^3 + b_i(T - T_i)^2 + c_i(T - T_i) + d_i, \quad (2)$$

where the subscript  $i$  referred to the polynomial that contained the specified value of  $T$  and spanned the temperature range  $T_i$  to  $T_{i+1}$ , and  $a_i$ ,  $b_i$ ,  $c_i$ , and  $d_i$  are the coefficients of the  $i$ th polynomial. A particular  $(T_i, d_i)$  pair is referred to as a "knot." A "natural spline" end condition (i.e., second

derivative equal to 0) was imposed at the highest temperature knot. The end condition imposed at the lowest temperature knot was a value of  $-b$ ,  $-0.25$ , for the first derivative. This was equivalent to assuming that the Debye temperature was independent of temperature near 0 K. (For the purpose of calculation:  $T_{i+1} > T > T_i$ .) The calculated heat capacity was thus:

$$C_{p,m}^{\circ}/C_p^{\circ} = \left( \frac{T}{T^{\circ}f(T) + bT} \right)^3. \quad (3)$$

Equation (3) was integrated numerically to obtain the enthalpy. The model was fitted to the experimental values with a nonlinear least-squares program. The vector of residuals was calculated using Eq. (3) for the heat capacity or numerical integrations of Eq. (3) to obtain the enthalpy increments.

The following assumed uncertainties [in terms of square root of variance (srv)] were assigned for the purpose of the least-squares calculation. The heat capacity measurements from Leadbetter and Settattree<sup>8</sup> spanned the range of temperature from 304 to 641 K. They were corrected for a small systematic bias<sup>9</sup> and assigned a srv of  $\pm 0.3\%$  in the representation. Enthalpy increments from Douglas and Harman<sup>10</sup> spanned the temperature range from 273.16 to 1033.74 K for the crystal phase. The upper temperatures of these enthalpy increments were changed from an IPTS-68 temperature basis to that of the ITS-90 by using published values of such differences.<sup>11,12</sup> These measured values were assigned a srv of  $\pm 20 \text{ J} \cdot \text{mol}^{-1}$  in the representation.

The measurements from Webb and Wilks<sup>13</sup> and from Keesom and Pearlman<sup>14</sup> were for temperatures below the normal boiling point of helium and were assigned srvs of  $\pm 5\%$ . The measurements from Berg and Morrison<sup>15</sup> were assigned a srv of  $\pm 0.5\%$  from 25 to 271 K,  $\pm 1\%$  from 10 to 25 K,  $\pm 2\%$  from 5 to 10 K and  $\pm 5\%$  below 5 K and the lowest temperature measurement (2.82 K) was given no weight in the representation. Kirkham and Yates<sup>16</sup> gave a table of "smoothed" heat capacity values from 25 to 300 K. Those values were assigned a srv of  $\pm 0.25\%$ . The measurements from Southard and Nelson<sup>17</sup> were assigned a srv of  $\pm 0.5\%$ . Measurements from Telea *et al.*,<sup>18</sup> from Strelkov *et al.*,<sup>19</sup> from Clusius *et al.*,<sup>20</sup> and from Feodos'ev<sup>21</sup> were given no weight in the representation.

Representation of the experimental results over the full range of temperature required 11 variable values for the knot positions. The final knot positions are given in Table 1. The number of digits given in Table 1 should be sufficient for calculation of thermodynamic properties and was not meant to be representative of any statistical assessment. The Debye temperature calculated from the 0 K knot was 235.1 K. Calculated thermodynamic properties of potassium chloride are given in Table 2.

Agreement of the least-squares determined model with measured values, for temperatures less than 50 and 450 K, respectively, is shown in Figs. 1 and 2. Of particular note is the poor agreement of the measurements among themselves for temperatures from 4 to 300 K. Because of these systematic differences between the different sets of measurements,

TABLE 1. Least-squares estimated knot positions for KCl(cr)

$T_i$ (K)	$d_i$
0	14.9521
7	12.9400
15	10.1587
30	7.2736
60	5.1115
90	4.4994
190	4.7481
400	6.3371
600	6.7672
800	4.0478
1200	-14.2204

the 298.15 K entropy cannot be considered to be any better determined than at least  $\pm 0.5\%$ . This minimum uncertainty is twice the value CODATA<sup>5</sup> assigned to the entropy value in their determination of the "key" thermodynamic properties of aqueous ions. There existed other measurements for temperatures greater than 300 K. However, the established extremely high accuracy of the enthalpy-increment calorimeter of Douglas and Harman<sup>10</sup> and the agreement of their measurements with those of Leadbetter and Settattree,<sup>8</sup> within Leadbetter and Settattree's claimed uncertainties, essentially obviated inclusion of these other measurements. For example, the enthalpy-increment measurements from Thompson and Flengas<sup>22</sup> showed root-mean-square (rms) and average differences of 1.2% and 0.15% from the representation. These can be compared to the values 0.067% and 0.002% for the Douglas and Harman results. Those interested in the other measurements above 300 K are referred to the Douglas and Harman article.

### 3. Thermodynamic Properties of Potassium Chloride(aq)

#### 3.1. Treatment of the Thermodynamic Data

Because the model used here is similar to that used previously for NaCl(aq),<sup>4</sup> only a brief description is given here. The model is based on Pitzer's ion-interaction model.<sup>23,24</sup> The fitted equation for the excess Gibbs energy  $G^E$  for a 1-1 valence electrolyte is:

$$\frac{G^E}{n_w RT} = -4IA\phi \ln(1 + bI^{1/2})/b + 2\nu_M\nu_X(m^2B_{MX} + m^3\nu_Mz_M C_{MX}), \quad (4)$$

where

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

where  $\beta_{MX}^{(0)}$ ,  $\beta_{MX}^{(1)}$ , and  $C_{MX}$  are adjustable parameters (ion-interaction parameters) that are dependent on temperature and pressure;  $\alpha$  and  $b$  were chosen to be constants with the values 2.0 and  $1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ , respectively;  $\nu_M$  and  $\nu_X$  are the stoichiometric numbers of cations and anions formed upon dissociation,  $I$  is the ionic strength, and  $n_w$  is the num-

TABLE 2. Thermodynamic properties of KCl(cr) calculated from Eqs. (1), (2)

$T$ (K)	$C_{p,m}$ ( $J \cdot K^{-1} \cdot mol^{-1}$ )	$H_m(T) - H_m(0 K)$ ( $kJ \cdot mol^{-1}$ )	$S_m$ ( $J \cdot K^{-1} \cdot mol^{-1}$ )
5	0.038	0.0000	0.0126
10	0.336	0.0008	0.1067
15	1.254	0.0044	0.390
20	3.010	0.015	0.971
25	5.469	0.036	1.897
30	8.37	0.070	3.145
35	11.56	0.120	4.67
40	14.86	0.186	6.43
50	21.17	0.367	10.44
60	26.55	0.606	14.79
80	34.32	1.221	23.58
100	39.25	1.960	31.81
120	42.58	2.781	39.28
140	44.85	3.656	46.02
160	46.44	4.570	52.12
180	47.61	5.511	57.66
200	48.53	6.473	62.73
220	49.30	7.452	67.39
240	49.96	8.444	71.71
260	50.53	9.449	75.73
280	51.03	10.465	79.49
298.15	51.44	11.395	82.71
300	51.48	11.490	83.03
320	51.88	12.524	86.37
340	52.26	13.566	89.52
360	52.60	14.614	92.52
380	52.92	15.669	95.37
400	53.23	16.731	98.10
420	53.52	17.799	100.70
440	53.81	18.872	103.20
460	54.09	19.951	105.60
480	54.36	21.035	107.90
500	54.64	22.125	110.13
520	54.92	23.221	112.28
540	55.21	24.322	114.35
560	55.50	25.429	116.37
580	55.79	26.542	118.32
600	56.10	27.661	120.22
620	56.42	28.786	122.06
640	56.75	29.918	123.86
660	57.09	31.056	125.61
680	57.46	32.202	127.32
700	57.85	33.355	128.99
720	58.26	34.516	130.62
740	58.70	35.685	132.23
760	59.16	36.864	133.80
780	59.66	38.052	135.34
800	60.19	39.250	136.86
820	60.76	40.460	138.35
840	61.36	41.681	139.82
860	61.99	42.914	141.27
880	62.64	44.160	142.71
900	63.31	45.420	144.12
920	64.01	46.693	145.52
940	64.72	47.980	146.91
960	65.45	49.282	148.28
980	66.19	50.598	149.63
1000	66.93	51.930	150.98
1020	67.69	53.276	152.31
1040	68.45	54.637	153.63
1045	68.64	54.980	153.96

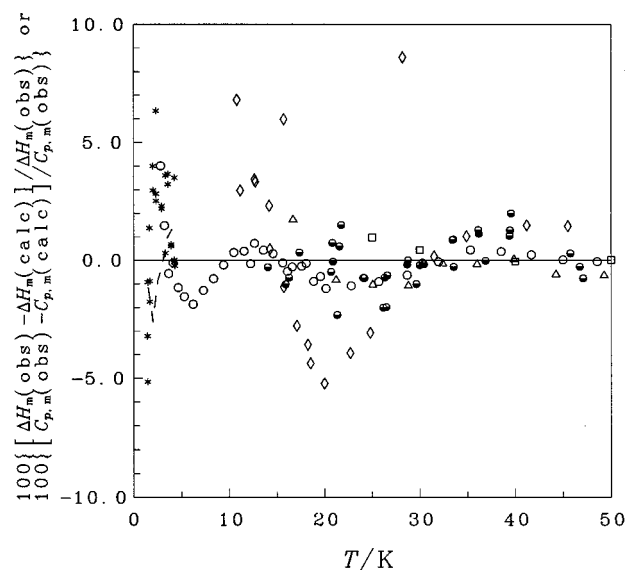


FIG. 1. Comparison of measurements for potassium chloride to fitted equation for temperatures less than 50 K. The symbols are: (○) Berg and Morrison (Ref. 15); (△) Southard and Nelson (Ref. 17); (◇) Clusius *et al.* (Ref. 20); (□) Kirkham and Yates (Ref. 16); (\*) Keesom and Pearlman (Ref. 14); (●) Strelkov *et al.* (Ref. 19); (--) Webb and Wilks (Ref. 13).

ber of kg of water.  $A_\phi$  is the Debye–Hückel coefficient for the osmotic coefficient. The Debye–Hückel coefficients used in the present work were calculated from the equation of state for water from Hill<sup>25</sup> and the dielectric-constant equation from Archer and Wang.<sup>26</sup>

The excess Gibbs energy is related to the Gibbs energy of the solution  $G$  for a 1-1 electrolyte as:

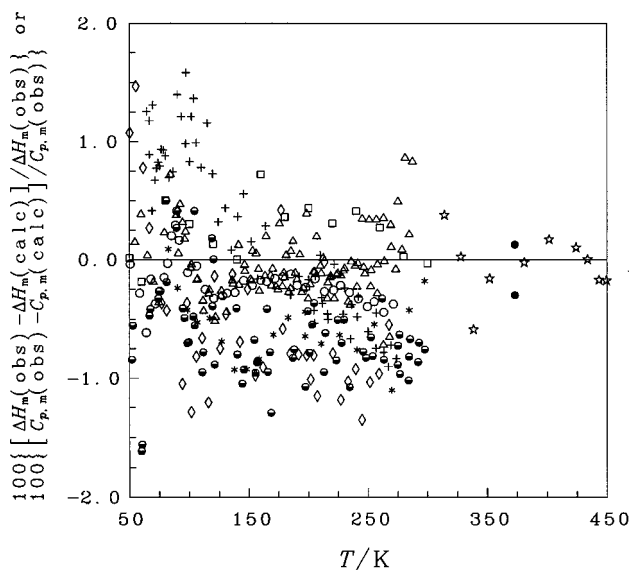


FIG. 2. Comparison of measurements for potassium chloride to fitted equation for temperatures from 50 to 450 K. The symbols are: (○) Berg and Morrison (Ref. 15); (◇) Clusius *et al.* (Ref. 20); (△) Southard and Nelson (Ref. 17); (□) Kirkham and Yates (Ref. 16); (●) Strelkov *et al.* (Ref. 19); (+) Telea *et al.* (Ref. 18); (\*) Feodos'ev (Ref. 21); (●) Douglas and Harman (Ref. 10); (☆) Leadbetter and Sattaree (Ref. 8).

$$G^E = G - n_1 G_{m,1}^\circ - n_2 G_{m,2}^\circ + RT \nu n_2 [1 - \ln(m/m^\circ)], \quad (5)$$

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 ( $\nu=2$ , for the present case) and  $m^\circ$  is  $1.0 \text{ mol} \cdot \text{kg}^{-1}$ . The standard-state molar Gibbs energies 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.

Appropriate differentiation of Eq. (4) leads to the osmotic coefficient  $\phi$  and the stoichiometric activity coefficient  $\gamma_\pm$ :

$$\begin{aligned} \phi - 1 = & -|z_M z_X| A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} + m \frac{2\nu_M \nu_X}{\nu} (\beta_{MX}^{(0)}) \\ & + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2}) + m^2 \frac{4\nu_M^2 \nu_X z_M}{\nu} C_{MX}, \end{aligned} \quad (6)$$

$$\begin{aligned} \ln \gamma_\pm = & -|z_M z_X| A_\phi \left( \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right) + m \frac{2\nu_M \nu_X}{\nu} \\ & \times \left\{ 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{\alpha^2 I} \left[ 1 - \left( 1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2} \right) \right] \right. \\ & \left. \times \exp(-\alpha I^{1/2}) \right\} + m^2 \frac{2\nu_M^2 \nu_X z_M}{\nu} \cdot 3C_{MX}, \end{aligned} \quad (7)$$

where  $z_M$  and  $z_X$  are the charges of the cation and the anion, respectively. 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 in kilograms. The relative apparent molar enthalpy  $L_\phi$  is:

$$\begin{aligned} L_\phi = & \nu |z_M z_X| A_H \ln(1 + bI^{1/2})/2b \\ & - 2\nu_M \nu_X RT^2 (mB_{MX}^L + m^2 \nu_M z_M C_{MX}^L), \end{aligned} \quad (8)$$

where

$$\begin{aligned} B_{MX}^L = & \left( \frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_p + 2 \left( \frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_p \\ & \times [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] / \alpha^2 I \end{aligned} \quad (9)$$

and

$$C_{MX}^L = \left( \frac{\partial C_{MX}}{\partial T} \right)_p, \quad (10)$$

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

$$\begin{aligned} C_{p,\phi} = & C_{p,m,2}^\circ + \nu |z_M z_X| A_C \ln(1 + bI^{1/2})/2b \\ & - 2\nu_M \nu_X RT^2 (mB_{MX}^C + m^2 \nu_M z_M C_{MX}^C), \end{aligned} \quad (11)$$

where

$$\begin{aligned} B_{MX}^C = & \left( \frac{\partial^2 \beta_{MX}^{(0)}}{\partial T^2} \right)_p + \frac{2}{T} \left( \frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_p \\ & + 2 \left[ \left( \frac{\partial^2 \beta_{MX}^{(1)}}{\partial T^2} \right)_p + \frac{2}{T} \left( \frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_p \right] [1 - (1 + \alpha I^{1/2}) \\ & \times \exp(-\alpha I^{1/2})] / \alpha^2 I, \end{aligned} \quad (12)$$

$$C_{MX}^C = \left( \frac{\partial^2 C_{MX}}{\partial T^2} \right)_p + \frac{2}{T} \left( \frac{\partial C_{MX}}{\partial T} \right)_p \quad (13)$$

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. As before,<sup>4</sup> a reference molality  $m_r$  was used in the formation of the model to avoid representation of the extreme temperature and pressure dependences of the usual ideal-solution standard state. In these terms, the apparent molar heat capacity is represented with the equation:

$$\begin{aligned} C_{p,\phi} + c_{p,w}/n_r = & C_p(m_r)/n_r + \nu |z_M z_X| A_C \ln[(1 + bI^{1/2})/ \\ & (1 + bI_r^{1/2})] / 2b - 2\nu_M \nu_X RT^2 \\ & \times [(m - m_r) B_{MX}^C + (m^2 - m_r^2) \nu_M z_M C_{MX}^C], \end{aligned} \quad (14)$$

where  $C_p(m_r)$  is the heat capacity of a quantity of solution containing 1 kg of solvent at the desired temperature and pressure,  $c_{p,w}$  is the heat capacity of 1 kg of water, and  $n_r$  is the number of moles of solute in this quantity of solution. The value of  $m_r$  was chosen to be  $5 \text{ mol} \cdot \text{kg}^{-1}$ .

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

$$\begin{aligned} G_{m,2,T}^\circ = & G_{m,2,T_r}^\circ + \frac{n_1 G_{m,1,T_r}^\circ - n_1 G_{m,1,T}^\circ}{n_r} + \frac{G_{T_r,m_r}^E - G_{T,m_r}^E}{n_r} \\ & - (T - T_r) \left( S_{2,m,T_r}^\circ + \frac{n_1 S_{1,m,T_r}^\circ}{n_r} + \frac{S_{T_r,m_r}^E}{n_r} \right) \\ & - T \int_{T_r}^T \frac{1}{T^2} \int [C_p(m_r)/n_r] dT dT, \end{aligned} \quad (15)$$

where

$$S_{T_r}^E = - \left( \frac{\partial G_{T_r}^E}{\partial T} \right)_p. \quad (16)$$

$T_r$  was chosen to be 298.15 K.

The equation describing the solubility of the anhydrous solid phase is:

$$\Delta_{\text{sol}} G_m^\circ = G_{m,2}^\circ - G_{m,\text{cr}}^\circ = -2 RT \ln(m_s \gamma_{\pm,s} / m^\circ), \quad (17)$$

where  $G_{m,2}^\circ$  and  $G_{m,\text{cr}}^\circ$  are the standard-state molar Gibbs energies for the solute and the crystal phase at a given  $T$  and  $p$ , respectively,  $\Delta_{\text{sol}} G_m^\circ$  is the standard-state molar Gibbs energy for the solution process of the crystal phase and  $m_s$  and  $\gamma_{\pm,s}$  are the saturation molality and the mean stoichiometric

TABLE 3. Literature sources for the activity and thermal properties of KCl(aq)

Reference	Temperature range (K)	Molality range (mol·kg <sup>-1</sup> )	n <sup>a</sup>	Type	$\sigma_{\text{est}}^{\text{b}}$	$\sigma_{\text{fit}}^{\text{c}}$	$\delta_{\text{fit}}^{\text{d}}$
27	298.15	0.11–4.8	35	$\phi$	0.003	0.0015	–0.0006
28	298.15	0.11–4.75	18	$\phi$	<sup>e</sup>	0.0023	0.0012
29	298.15	0.11–4.8	79	$\phi$	<sup>e</sup>	0.0006	–0.0002
30	298.15	4.3–4.9	2	$\phi$	0.0011	0.0012	0.0012
31	298.15	0.1–4.8	25	$\phi$	<sup>f</sup>	0.0025	–0.0012
32	298.15	2.2–4.6	6	$\phi$	0.002	0.0012	–0.0012
33	298.15	1.9–4.2	5	$\phi$	U	0.0044	0.0026
34	298.15	0.03–0.10	14	$\phi$	0.005	0.0023	0.0000
35	288.15	0.1–4.0	16	$\phi$	0.003	0.0016	0.0010
36	318.15	0.52–5.2	18	$\phi$	0.003	0.0014	–0.0009
37	318.15	0.5–3.5	15	$\phi$	0.003	0.0038	–0.0036
38	273.15	0.4–3.8	10	$\phi$	0.003	0.0016	0.0005
39	333.15	1.0–6.4	22	$\phi$	0.004	0.0028	–0.0018
40	353.15	0.8–6.76	56	$\phi$	0.004	0.0018	–0.0010
41	382.0	1.2–7.1	21	$\phi$	0.003	0.0035	0.0029
41	413.8	1.2–6.65	20	$\phi$	0.003	0.0047	0.0021
42	$T_{\text{fus}}$	0.0014–1.25	26	$\Delta_{\text{fus}}T$	<sup>g</sup>	0.0020	0.0013
43	$T_{\text{fus}}$	0.006–2.23	17	$\Delta_{\text{fus}}T$	<sup>g</sup>	0.0020	–0.0006
44	$T_{\text{fus}}$	0.1–1.82	26	$\Delta_{\text{fus}}T$	<sup>g</sup>	0.0015	0.0005
45	$T_{\text{fus}}$	2.4–3.0	4	$\Delta_{\text{fus}}T$	<sup>g</sup>	0.0014	0.0018
46	$T_{\text{fus}}$	0.95–1.9	2	$\Delta_{\text{fus}}T$	<sup>h</sup>	0.027	–0.026
47	$T_{\text{fus}}$	0.71–3.3	6	$\Delta_{\text{fus}}T$	<sup>h</sup>	0.008	–0.007
137	$T_{\text{fus}}$	0.44–3.3	12	$\Delta_{\text{fus}}T$	<sup>h</sup>	0.0044	0.0029
48	$T_{\text{fus}}$	0.71–3.3	6	$\Delta_{\text{fus}}T$	U	0.014	–0.010
49	323.15,343.15	0.7–3.2	10	$p_s-p_w$	<sup>i</sup>	0.0029	0.0003
50	293.15	0.3–4.0	16	$p_s-p_w$	<sup>j</sup>	0.0081	–0.0066
51	298.15	0.12–3.0	7	$\Delta_{\text{dil}}L_\phi$	0.010	0.0090	0.0026 <sup>k</sup>
52	303.15	0.2–1.1	8	$\Delta_{\text{dil}}L_\phi$	0.010	0.0064	0.0001 <sup>k</sup>
53	373.15,423.65	0.02–4.5	19	$\Delta_{\text{dil}}L_\phi$	0.050	0.020	–0.012 <sup>k</sup>
54	293.15	0.14–2.2	4	$\Delta_{\text{dil}}L_\phi$	0.030	0.029	0.018 <sup>k</sup>
55	285.38,290.93	0.007–0.34	4	$\Delta_{\text{dil}}L_\phi$	0.020	0.020	0.007 <sup>k</sup>
56	313.15–353.15	0.12–4.4	23	$\Delta_{\text{dil}}L_\phi$	0.040–0.050	0.035	0.003 <sup>k</sup>
57	285.65,298.15	0.0002–0.51	20	$\Delta_{\text{dil}}L_\phi$	0.010	0.0075	–0.0042 <sup>k</sup>
58	298.15	0.57–4.82	1	$\Delta_{\text{dil}}L_\phi$	0.060	0.007	0.007 <sup>k</sup>
58	298.15	4.07–4.82	3	$\Delta_{\text{dil}}L_\phi$	0.002	0.0021	0.0012 <sup>k</sup>
59	298.15	0.05–2.1	24	$C_{p,\phi}$	0.004	0.0022	0.0020 <sup>l</sup>
60	298.15	0.05–2.5	11	$C_{p,\phi}$	U	0.0024	0.0019 <sup>l</sup>
61	298.15	0.023–1.0	12	$C_{p,\phi}$	0.006	0.0058	0.0056 <sup>l</sup>
62	278.15–358.15	0.1–4.7	39	$C_{p,\phi}$	0.004–0.002	0.0023	0.0005 <sup>l</sup>
63	298.15–373.15	0.01–2.0	29	$c_{p,s}/c_{p,w}$	<sup>l</sup>	0.0050	0.0006 <sup>l</sup>
64	288.15–318.15	0.01–1.0	28	$c_{p,s}/c_{p,w}$	<sup>m</sup>	0.017	0.003 <sup>l</sup>
65	298.15–348.15	0.1–4.6	13	$c_{p,s}/c_{p,w}$	U	0.025	–0.016 <sup>l</sup>
66	303.15–403.15	0.5–1.8	44	$c_{p,s}$	0.004	0.0019	–0.0006 <sup>l</sup>
67	296.6–358.9	0.11	13	$\Delta_{\text{sol}}H_m$	0.0125–0.05	<sup>o</sup>	<sup>o</sup>
68	289.3–358.4	$m_s$	16	$m_s$	0.05 <sup>p</sup>	0.035	0.016 <sup>k</sup>
46	263.15–333.15	$m_s$	9	$m_s$	0.05 <sup>p</sup>	0.039	–0.009 <sup>k</sup>

TABLE 3. Literature sources for the activity and thermal properties of KCl(aq)—Continued

Reference	Temperature range (K)	Molality range (mol·kg <sup>-1</sup> )	n <sup>a</sup>	Type	$\sigma_{\text{est}}^{\text{b}}$	$\sigma_{\text{fit}}^{\text{c}}$	$\delta_{\text{fit}}^{\text{d}}$
69	280.65–448.8	$m_{\text{s}}$	10	$m_{\text{s}}$	0.05 <sup>P</sup>	0.043	–0.013 <sup>k</sup>
70	373.15–442.65	$m_{\text{s}}$	4	$m_{\text{s}}$	0.05 <sup>P</sup>	0.029	–0.014 <sup>k</sup>
71	298.57–366.55	$m_{\text{s}}$	11	$m_{\text{s}}$	0.05 <sup>P</sup>	0.040	0.029 <sup>k</sup>
72	298.15	$m_{\text{s}}$	1	$m_{\text{s}}$	0.05 <sup>P</sup>	0.000	0.000 <sup>k</sup>
73	373.15–443.15	$m_{\text{s}}$	4	$m_{\text{s}}$	0.1 <sup>P</sup>	0.054	–0.016 <sup>k</sup>
74	383.15–434.15	$m_{\text{s}}$	4	$m_{\text{s}}$	0.2 <sup>P</sup>	0.093	0.089 <sup>k</sup>
48	266.15–296.15	$m_{\text{s}}$	14	$m_{\text{s}}$	U	0.060	0.014 <sup>k</sup>

<sup>a</sup>n is the number of observations.

<sup>b</sup> $\sigma_{\text{est}}$  is an estimated square root of variance used for weighting the measurements. The letter U indicates that these points were given an insignificant weight in the least-squares procedure.

<sup>c</sup> $\sigma_{\text{fit}}$  is the rms deviation of the measurements from the model.

<sup>d</sup> $\delta_{\text{fit}}$  is the average deviation of the measurements from the model.

<sup>e</sup>Values of  $\sigma_{\text{exp}}$  were assumed as 0.0028 for  $m < 0.25$  mol·kg<sup>-1</sup>; and 0.0011 for all other molalities.

<sup>f</sup>Values of  $\sigma_{\text{exp}}$  were assumed as 0.0056 for  $m < 0.15$  mol·kg<sup>-1</sup>; 0.0028 for  $m < 0.25$  mol·kg<sup>-1</sup>; and 0.0011 for all other molalities.

<sup>g</sup>Values of  $\sigma_{\text{exp}}$  were calculated as the uncertainty in osmotic coefficient due to an uncertainty of 0.003 K or 0.003, whichever was larger.  $\sigma_{\text{fit}}$  and  $\delta_{\text{fit}}$  given in terms of osmotic coefficient.

<sup>h</sup>For Ref. 46, values of  $\sigma_{\text{exp}}$  were calculated as the uncertainty in osmotic coefficient due to an uncertainty of 0.1 K for  $m/m^{\circ} = 0.948$  and 1.89, and 1 K for  $m/m^{\circ} = 3.185$ . For Ref. 47, values of  $\sigma_{\text{exp}}$  were calculated as the uncertainty in osmotic coefficient due to an uncertainty of 0.5 K. For Ref. 137, values of  $\sigma_{\text{exp}}$  were calculated as the uncertainty in osmotic coefficient due to an uncertainty of 0.05 K.  $\sigma_{\text{fit}}$  and  $\delta_{\text{fit}}$  given in terms of osmotic coefficient.

<sup>i</sup>Values of  $\sigma_{\text{exp}}$  were calculated as the uncertainty in osmotic coefficient due to an uncertainty of  $4 \times 10^{-6}$  MPa or 0.005, whichever was larger.  $\sigma_{\text{fit}}$  and  $\delta_{\text{fit}}$  given in terms of osmotic coefficient.

<sup>j</sup>Values of  $\sigma_{\text{exp}}$  were calculated as the uncertainty in osmotic coefficient due to an uncertainty of  $4 \times 10^{-5}$  MPa or 0.005, whichever was larger.  $\sigma_{\text{fit}}$  and  $\delta_{\text{fit}}$  given in terms of osmotic coefficient.

<sup>k</sup>Units are kJ·mol<sup>-1</sup> for enthalpies of dilution, enthalpies of solution, and Gibbs energies of solution.

<sup>l</sup>Units are kJ·K<sup>-1</sup>·mol<sup>-1</sup>.

<sup>m</sup> $\sigma_{\text{est}}$  was calculated on the basis of [0.0002 or 1% of  $(1 - c_{p,s}/c_{p,w})$ ].

<sup>n</sup> $\sigma_{\text{est}}$  was calculated on the basis of [0.0006 of  $(c_{p,s}/c_{p,w})$ ].

<sup>o</sup>See text for discussion of these values.

<sup>p</sup> $\sigma_{\text{est}}$  in mol·kg<sup>-1</sup>.

activity coefficient for the solute at saturation, respectively. Of course,  $G_{m,2}^{\circ}$  and  $G_{m,\text{cr}}^{\circ}$  cannot be evaluated and so Eq. (17) was rewritten as:

$$\Delta_{\text{sol}} G_{m,T}^{\circ} = \Delta_{\text{sol}} G_{m,T_r}^{\circ} + \{G_{m,2,T}^{\circ} - G_{m,2,T_r}^{\circ}\} - \{G_{m,\text{cr},T}^{\circ} - G_{m,\text{cr},T_r}^{\circ}\} \\ = -2 RT \ln(m_{\text{s}} \gamma_{\pm,s} / m^{\circ}). \quad (18)$$

The first braced term of Eq. (18) was obtained from Eq. (15). The second braced term was obtained from the model of the crystalline properties given in Sec. 2. Hydrate phases, if they exist for potassium chloride, have not been quantified and so are not included here.

Solubility measurements were included in the global data fit. The Gibbs energy of solution at the reference temperature  $T_r$  was treated as an adjustable parameter, as was  $S_{m,2,T_r}^{\circ}$ . 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. (18).

The adjustable parameters  $\beta_{\text{MX}}^{(0)}$ ,  $\beta_{\text{MX}}^{(1)}$  and  $C_{\text{MX}}$  were assumed to be linear combinations of functions of temperature as:

$$\beta_{\text{MX}}^{(0)} = f(1, T) / m^{\circ}, \quad (19)$$

$$\beta_{\text{MX}}^{(1)} = f(2, T) / m^{\circ}, \quad (20)$$

$$C_{\text{MX}} = f(3, T) / m^{\circ 2}, \quad (21)$$

where

$$f(i, T) = \{b_{i,1} + 10^{-2} b_{i,2} (T - T_r) / T^{\circ} + 10^{-5} b_{i,3} [(T - T_r) / T^{\circ}]^2 \\ + 10^2 b_{i,4} T^{\circ} / (T - 225 \text{ K}) + 10^3 b_{i,5} (T^{\circ} / T) \\ + 10^6 b_{i,6} [T^{\circ} / (T - 225 \text{ K})]^3\}. \quad (22)$$

$C_p(m_r) / n_r$  was given by:

$$C_p(m_r) / n_r = [b_{4,1} + 10^{-2} b_{4,2} T / T^{\circ} + 10^{-5} b_{4,3} (T / T^{\circ})^2] C_p^{\circ'} \quad (23)$$

where  $C_p^{\circ'}$  is 1.0 kJ·mol<sup>-1</sup>·K<sup>-1</sup>. The weighting factors for the experimental results were calculated from an estimated square root of variance for each data set given in Table 3. The least-squares estimated parameters are given in Table 4. Note that not all of the  $b_{i,j}$  parameters were required to represent accurately the available experimental data. Selected calculated values, against which to compare computations with the model, are given in Tables 5–7.



TABLE 4. Least-squares estimated parameters for the model of thermodynamic properties of KCl(aq)

Parameter	Value	Parameter	Value	Parameter	Value <sup>a</sup>
$b_{1,1}$	0.413 229 483 398 493	$b_{3,1}$	-0.001 335 159 349 944 78	$\Delta_{\text{sol}}G_{T_r, p_r}^0$	-5.181 81 ± 0.0105 kJ·mol <sup>-1</sup>
$b_{1,2}$	-0.087 012 147 611 402 7	$b_{3,2}$		$S_{\text{m,KCl(aq)}, T_r, p_r}^0$	157.9349 ± 0.042 J·K <sup>-1</sup> ·mol <sup>-1</sup>
$b_{1,3}$	0.101 413 736 179 231	$b_{3,3}$			
$b_{1,4}$	-0.019 982 253 852 280 1	$b_{3,4}$	0.002 341 176 938 342 28		
$b_{1,5}$	-0.099 812 058 168 081 6	$b_{3,5}$	-0.000 758 965 835 467 07		
$b_{1,6}$		$b_{3,6}$			
$b_{2,1}$	0.206 691 413 598 171	$b_{4,1}$	0.392 752 231 164 169		
$b_{2,2}$	0.102 544 606 022 162	$b_{4,2}$	0.238 245 380 035 212		
$b_{2,3}$		$b_{4,3}$	-0.332 010 848 757 757		
$b_{2,4}$					
$b_{2,5}$					
$b_{2,6}$	-0.001 883 496 080 009 03				

<sup>a</sup>The ± values are 95% confidence intervals within the global data representation. The listed uncertainty for  $S_{\text{m,KCl(aq)}, T_r, p_r}^0$  does not include the uncertainty in  $S_{\text{m,KCl(cr)}, T_r, p_r}^0$ . See text for details.  $p_r = 0.1$  MPa.

### 3.2. Agreement with the Experimental Results for Potassium Chloride(aq)

#### 3.2.1. Activity Results

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

$$\phi = \frac{(G_{\text{m},1,1}^{\circ} - G_{\text{m},1,g}^{\circ})}{RT \nu m M_1}, \quad (24)$$

where the difference in chemical potential for the vapor and the liquid at the temperature and pressure of the solution,  $G_{\text{m},1,g}^{\circ} - G_{\text{m},1,1}^{\circ}$ , was calculated from the equation of state for water. Osmotic coefficients were also calculated from measured differences of the freezing temperatures of water in a potassium chloride solution from that of pure water by means of the equation given by Scatchard *et al.*<sup>75</sup> Osmotic coefficients were determined from measured isopiestic ratios by means of the reference equation for NaCl(aq) given by Archer.<sup>4</sup>

Figure 3 shows differences of the osmotic coefficients for KCl(aq), obtained from measured properties of the solvent in the solution, from the present fitted equation for temperatures near 300 K. Agreement of all of the measurements can be considered excellent with the exception of those from Shult's *et al.*<sup>33</sup>

Figure 4 shows differences from the model of osmotic coefficients obtained from isopiestic molality determinations for temperatures more removed from 300 K. Also shown in

this figure are the differences of osmotic coefficients calculated from Herrington and Jackson's<sup>49</sup> measurements of vapor pressures. They are in very good agreement with the model.

Vapor pressure measurements from Petit<sup>76</sup> and from Harrison and Perman<sup>77</sup> were not of sufficient accuracy to be useful for the present purposes.

Solute activity coefficients have been determined with various electrochemical combinations, most of which involved a potassium amalgam. These measurements showed a general agreement with the model to approximately 1 mol·kg<sup>-1</sup>. Above this concentration, there were systematic biases that were temperature dependent and smallest for temperatures near ambient. The differences of activity coefficients determined from the concentration-cell measurements from Harned and Cook,<sup>78</sup> Smith,<sup>79</sup> and Caramazza<sup>80</sup> are compared with the present equation for KCl(aq) in Fig. 5. Three curves representing the trends of Harned and Cook's values for 273.15, 293.15, and 313.15 K are shown in Fig. 5 as an aid in visualizing trends of the residuals. The sign of the residuals for the larger concentrations changes as temperature passes through approximately 300 K. The higher concentration measurements are therefore not in good agreement with solvent activity measurements, except for the temperatures where the two (through the Gibbs–Duhem relation) are crossing. Because the residuals for the concentration cells show a definite temperature dependence to their systematic bias, the temperature dependence of the activity coefficients

TABLE 5. Calculated values of  $A_{\phi}$ ,  $\beta_{\text{MX}}^{(0)}$ ,  $\beta_{\text{MX}}^{(1)}$ , and  $C_{\text{MX}}$ 

$T$ (K)	$A_{\phi}$ (kg <sup>1/2</sup> ·mol <sup>-1/2</sup> )	$\beta_{\text{MX}}^{(0)}$ (kg·mol <sup>-1</sup> )	$\beta_{\text{MX}}^{(1)}$ (kg·mol <sup>-1</sup> )	$10^3 C_{\text{MX}}$ (kg <sup>2</sup> ·mol <sup>-2</sup> )
273.15	0.376 422	0.028 7052	0.164 183	0.748 53
298.15	0.391 476	0.051 1414	0.201 879	-0.680 23
323.15	0.410 277	0.062 8792	0.230 356	-1.298 50
348.15	0.433 068	0.069 3401	0.256 955	-1.614 08
373.15	0.459 887	0.072 7020	0.283 021	-1.788 83

TABLE 6. Calculated values of  $G_{\text{m},2}^0 - G_{\text{m},2,T_r}^0$ ,  $H_{\text{m},2}^0 - H_{\text{m},2,T_r}^0$ ,  $S_{\text{m},2}^0 - S_{\text{m},2,T_r}^0$ , and  $C_{p,\phi}^0$ 

$T$ (K)	$G_{\text{m},2}^0 - G_{\text{m},2,T_r}^0$ (kJ·mol <sup>-1</sup> )	$H_{\text{m},2}^0 - H_{\text{m},2,T_r}^0$ (kJ·mol <sup>-1</sup> )	$S_{\text{m},2}^0 - S_{\text{m},2,T_r}^0$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$C_{p,\phi}^0$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
273.15	4.094	3.739	13.156	-210.0
298.15	0.000	0.000	0.00	-116.2
323.15	-3.839	-2.607	-8.406	-96.9
348.15	-7.487	-4.999	-15.537	-96.7
373.15	-10.959	-7.539	-22.578	-108.4

TABLE 7. Calculated values of the osmotic coefficient  $\phi$ 

T (K)	(m/mol·kg <sup>-1</sup> )					
	0.1	0.5	1.0	2.0	4.0	6.0
273.15	0.9253	0.8907	0.8813	0.8854	0.9294	
298.15	0.9261	0.9000	0.8992	0.9154	0.9673	
323.15	0.9244	0.9018	0.9049	0.9275	0.9855	1.0390
348.15	0.9213	0.8994	0.9040	0.9291	0.9898	1.0420
373.15	0.9168	0.8939	0.8984	0.9234	0.9838	1.0341

from the concentration cells are also not in agreement with calorimetric determinations of apparent molar enthalpies. This discrepancy with apparent molar enthalpies was noted by Harned and Cook.<sup>78</sup> Because all of these concentration-cell results were in good agreement with each other, but not with other types of measurements, for concentrations greater than 1 mol·kg<sup>-1</sup>, an inherent problem in the method might be suspected for KCl(aq). Harned's concentration cell measurements, obtained at 298.15 K only, were in agreement with the Harned and Cook<sup>78</sup> measurements for the same temperature.

Hornbrook *et al.*<sup>82</sup> measured the emf of transference cells using silver-silver chloride electrodes in dilute solution (0.01–0.1 mol·kg<sup>-1</sup>) and for temperatures from 288.15 to 318.15 K. Values of the ratio of their activity coefficients [ $\gamma_{\pm}(0.01 \text{ mol}\cdot\text{kg}^{-1})/\gamma_{\pm}(m \text{ mol}\cdot\text{kg}^{-1})$ ] showed a rms deviation and an average deviation of 0.0011 and -0.0010 from the model. The very slight biasing of these values could be attributed to the cation transference number used to extract the activity coefficient ratio from the measured quantities.

More recent measurements of an electrochemical cell formed from a potassium-amalgam electrode and a silver-silver chloride electrode in a dilute potassium chloride solution were made by Giordano *et al.*<sup>83</sup> for concentrations of (0.05–0.7) mol·kg<sup>-1</sup>. Their values of solute activity coeffi-

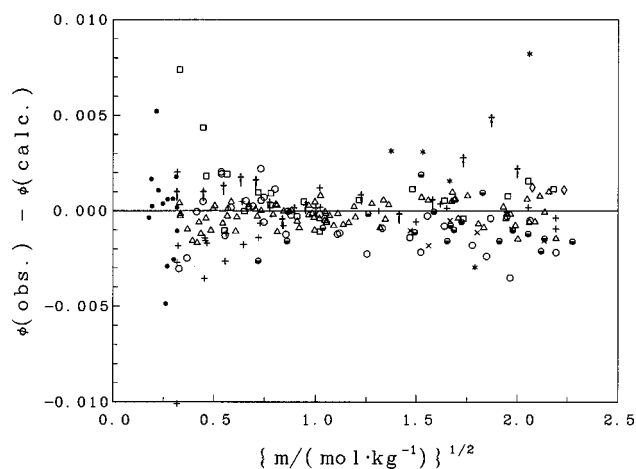


FIG. 3. Differences of osmotic coefficients obtained from solvent activity determinations from those calculated from the model for near ambient temperatures. The symbols are: (○) Robinson and Sinclair (Ref. 27); (□) Janis and Ferguson (Ref. 28); (△) Robinson (Ref. 26); (◇) Rard and Miller (Ref. 30); (+) Scatchard *et al.* (Ref. 31); ×, Kigintsev and Luk'yanov (Ref. 32); (\*) Shult's *et al.* (Ref. 33); (●) Gordon (Ref. 34); (◐) Davis *et al.* (Ref. 36); (†) Childs and Platford (Ref. 35).

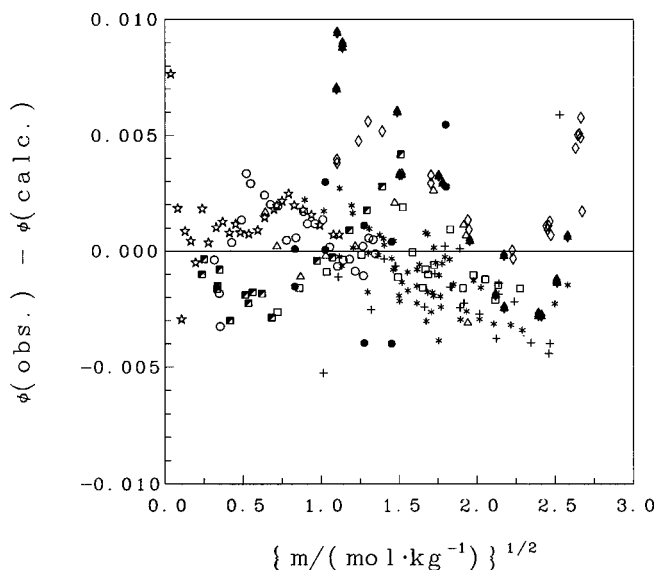


FIG. 4. Differences of osmotic coefficients obtained from solvent activity determinations from those calculated from the model for temperatures other than 298.15 K. The symbols are: (□) Davis *et al.* (Ref. 36); (●) Herrington *et al.* (Ref. 49); (△) Platford (Ref. 38); (+) Humphries *et al.* (Ref. 39); (\*) Moore *et al.* (Ref. 40); (◇) Holmes *et al.* (Ref. 41) (382 K); (▲) Holmes *et al.* (Ref. 41) (414 K); (☆) Scatchard and Prentiss (Ref. 42); (◐) Damkohler *et al.* (Ref. 43); (○) Jones and Bury (Ref. 44).

ents showed large divergences from the model and from other solute activity coefficient measurements. For example, their values of  $\gamma_{\pm}$  for a 0.5 mol·kg<sup>-1</sup> solution differed from the model by +0.003, -0.007, -0.014, -0.018, and -0.022 for temperatures of 283.15, 298.15, 313.15, 328.15,

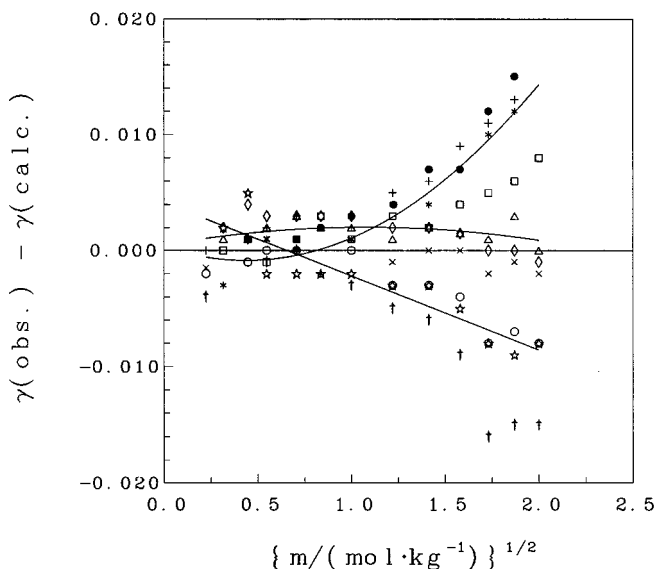


FIG. 5. Differences of solute activity coefficients obtained from electrochemical concentration cell measurements from the model. The symbols are: (\*) Harned and Cook (Ref. 78), 273.15 K; (□) Harned and Cook (Ref. 78), 283.15 K; (△) Harned and Cook (Ref. 78), 293.15 K; (◇) Harned and Cook (Ref. 78), 298.15 K; (☆) Harned and Cook (Ref. 78), 313.15 K; (●) Smith (Ref. 79), 273.15 K; (+) Caramazza (Ref. 80), 273.15 K; (×) Caramazza (Ref. 80), 298.15 K; (○) Caramazza (Ref. 80), 308.15 K; (†) Caramazza (Ref. 80), 323.15 K. The lines are representations of the differences of Harned and Cook's measurements for 273.15, 293.15 and 313.15 K.

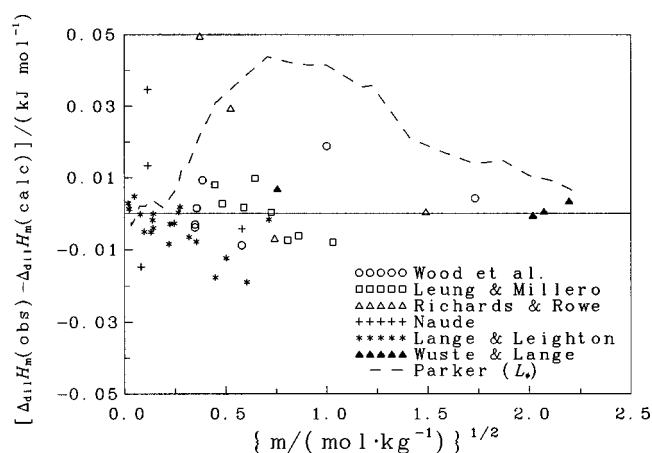


Fig. 6. Differences of measured enthalpies of dilution from the model for temperatures near 298.15 K. The symbols are: (○) Wood *et al.* (Ref. 51); (□) Leung and Millero (Ref. 52); (△) Richards and Rowe (Ref. 54); (+) Naude (Ref. 55); (\*) Lange and Leighton (Ref. 57); (△) Wustle and Lange (Ref. 58). The dashed line is the difference of Parker's (Ref. 84) values of relative apparent molar enthalpy from the model.

and 343.15 K, respectively. Giordano's measurements showed remarkable disagreement not only with the model and its inherent suite of measurements, but also with the electrochemical concentration-cell measurements for  $0.5 \text{ mol} \cdot \text{kg}^{-1}$ , measured by Harned and Cook.<sup>78</sup> For  $0.1 \text{ mol} \cdot \text{kg}^{-1}$ , their value of the activity coefficient was 0.007 smaller than that obtained by Hornibrook *et al.*<sup>82</sup>

### 3.2.2. Enthalpy of Dilution Results

Agreement of the model with the enthalpy of dilution measurements, tabulated in Table 3, was generally good, with none of the measurements deviating by substantially more than expected uncertainties.

Figure 6 shows differences of measured enthalpies of dilution from the fitted model for temperatures near ambient. Also shown are differences of Parker's<sup>84</sup> 298.15 K relative apparent molar enthalpies from the fitted model (they were not included in the data representation). There existed a systematic bias in Ref. 84's values from the present values and also from some of the measured values. As an example of the latter, Lange and Leighton<sup>57</sup> gave a value of  $-7.5 \text{ J} \cdot \text{mol}^{-1}$  for the 298.15 K enthalpy change for the dilution of  $0.5086 \text{ mol} \cdot \text{kg}^{-1}$  KCl(aq) to  $0.01374 \text{ mol} \cdot \text{kg}^{-1}$ , whereas interpolation of Parker's tabulated values gave this enthalpy of dilution as  $-46 \text{ J} \cdot \text{mol}^{-1}$ . This difference is indicative of the differences of the  $L_\phi$  values shown in Fig. 6.

Notes and large graphs in NIST files indicated that the Lange and Leighton values were quite significant in Parker's evaluation and thus, at first glance, the differences might appear to be inconsequential.

Parker<sup>84</sup> used the "chord-area plot" method<sup>85</sup> of determining apparent molar enthalpies from measured enthalpies of dilution and, in some cases, from the concentration dependence of measured enthalpies of solution. Parker's method involved determining the quantity  $(\Delta_{\text{dil}} H_m) / \Delta(m^{1/2})$  for the

measured enthalpies of dilution, plotting these "chords," drawing a continuous curve through some point in each member of the set of chords, and then integrating the resultant curve. This method is predicated on the assumption that the quantity  $(\Delta_{\text{dil}} H_m) / \Delta(m^{1/2})$  is a good measure of the derivative  $d(H_m) / d(m^{1/2})$ ; this assumption will be true if either the change in molality for the dilution is very small or if higher derivatives are known to be nearly zero. Young,<sup>85</sup> who developed the method with Vogel, was aware of these limitations. Young and co-authors' measurements for NaCl(aq)<sup>85,86</sup> consisted of extremely short dilution chords, obtained by adding small amounts of water to a much larger sample of concentrated solution. In Young and Groenier's<sup>87</sup> examination of Gulbransen and Robinson's<sup>88</sup> enthalpies of dilution for NaCl(aq), which were not particularly short dilution chords, they stated:

"When the chords had been plotted (as illustrated in Young and Vogel's second figure) it proved to be difficult to draw the derivative curves through them with the desired precision; the graphical method proved to be not well suited to these data.

Those chords which were obtained by dilution of the more concentrated solutions were very long because the experiments of Gulbransen and Robinson had been designed for another method of treatment. Because of the extremely small thermal effects involved, the chords obtained from dilution of the very dilute solutions were burdened with unavoidable experimental errors. Consequently, considerable personal judgement was required for drawing of the derivative curve on the chord-area plot and it was desirable to introduce the method of least-squares."

Lange and Leighton<sup>57</sup> measured long dilution chords (dilution by factors of 10–30 in molality) as did Richards and Rowe<sup>54</sup> (dilution ratios of 2:1 to 16:1) and Naude<sup>55</sup> (dilution ratios of 25:1 and 50:1). The unsuitability of the chord-area plot method for long dilution chords may indeed be the source of discrepancies of Parker's relative apparent molar enthalpy values from some of the measured enthalpies of dilution upon which her values were based.

The matter of Parker's relative apparent molar enthalpies for KCl(aq) is specifically important for understanding subsequent issues discussed in this article. Additionally, the method of treatment used by Parker is important for other aqueous electrolytes because of the use of values so obtained in other undertakings such as the development of the CODATA Key Values for Thermodynamics.<sup>5</sup>

### 3.2.3. Enthalpy of Solution Results

Prior to 1975 commentary and disagreement regarding the use of potassium chloride as a calibrant of solution calorimeters appeared in the literature. Predominantly, many of the entries into the literature consisted of a report of a measured

enthalpy(ies) of solution of crystalline potassium chloride into water, comparison to some other value, and in some cases where disagreement existed, unsubstantial commentary regarding the unsuitability of potassium chloride as a calibrant or as a check on the satisfactory operation of a calorimeter. A more recent (1977) and seemingly more substantial article by Montgomery *et al.*<sup>89</sup> examined the use of KCl(aq) as a calibrant. They discussed, among other things, a portion of the previous enthalpy of solution debate and made specific recommendations regarding a reference value for the enthalpy of solution of potassium chloride and regarding procedures for handling samples of crystalline potassium chloride prior to measurement of an enthalpy of solution. That article appeared to have been the final word in the debate and the conclusions and results therein have been cited by others as though they were definitive. However, there were serious flaws in the methodology described in that article that have not been commented upon subsequently. Further, the work conducted for the present article casts doubt on some of the conclusions and recommendations of that article and derivatively also on the recommended handling procedures for SRM-1655. Hence, the basis and methodology of the Montgomery *et al.* conclusions regarding the enthalpy of solution of potassium chloride and its use as a calibrant are examined in some detail here.

Montgomery *et al.*<sup>89</sup> observed a difference between Gunn's<sup>90</sup> enthalpy of solution measurements for samples of KCl(cr) which had received different heat treatments and hypothesized that previously reported discrepancies of enthalpy of solution measurements were due to insufficient drying of the samples. Specifically, Montgomery *et al.* proposed that significant amounts of water existed in occlusions and could only be removed by drying at temperatures above 600 K. To buttress this proposition, Montgomery *et al.* collected a large sample of previously reported enthalpies of solution for 298.15 K and segregated them into one of two groups according to whether the report indicated the sample of KCl had been heated above 600 K. They then plotted the enthalpies of solution, against year of measurement, in two figures—one for each of the two groups. However, the enthalpy of solution is a function of concentration and so to aid their comparison and the construction of their figures, Montgomery *et al.* adjusted all measured enthalpies of solution from the concentration of the measurement to a concentration of 0.05 mol·kg<sup>-1</sup>. Each plotted value was accompanied by an error bar that represented "uncertainty." To Montgomery *et al.*, uncertainty was essentially synonymous with reproducibility or precision, whether or not multiplied uniformly by some integer. Montgomery *et al.* then calculated a "weighted mean" for the two groups. (Apparently, "weighted" corresponded to their "uncertainty" which was a measure of precision.) From this procedure Montgomery *et al.* obtained two values for the enthalpy of solution of potassium chloride, the first ( $17.4992 \pm 0.0059$  kJ·mol<sup>-1</sup>) for samples not heated above 600 K, and the second ( $17.5360 \pm 0.0034$  kJ·mol<sup>-1</sup>) for samples heated above 600 K. In Montgomery's *et al.* words:

"These two values differ by  $0.0368 \pm 0.0068$  kJ·mol<sup>-1</sup>. It appears that this difference, which is 0.21 per cent of the measured value, essentially represents the effect of occluded water in the potassium chloride not heated above 600 K. The uncertainties given here are twice the s.d.m. overall."

Since the time of Montgomery's *et al.* article, the need for drying samples of potassium chloride at temperatures above 600 K prior to use in calibrating a calorimeter has been accepted as indubitable. However, there were flaws in Montgomery's *et al.* statistical analysis and they offered no supporting evidence of the requisite amount of occluded water. Thus, it might be of some benefit to question the indubitable.

Montgomery's *et al.* statistical analysis is considered here. An inherent assumption of their analysis was that either no systematic biases occurred with all of the different calorimeters (which will be referred to here as the "all calorimeters are created equal" assumption) or there was such a large source of *independent* systematic errors for all the calorimeters that the central limit theory would predict an unbiased normal probability distribution for the random variable. (The word "independent" has a definite meaning in statistics. For observations of a random variable to be independent there can be no correlation among them, among other things.) Neither of these assumptions was actually stated, but one of the two was essential to a rational use of the statistical methods chosen by Montgomery *et al.*; this will be shown below. Both of the assumptions are, of course, unreasonable. If all calorimeters were indeed created equal, then we could do all calorimetry with nothing more elaborate than a coffee cup and garden thermometer. The second assumption is untenable because the design of any particular calorimeter usually follows one of only a few general patterns. The inherent flaws, or biases, of that particular design pattern could dominate all, or most, of the calorimeters that imitated that pattern. Additionally, the repeated appearance of any particular calorimeter in the averaging process lopsides the combination of individual biased or non-normal distributions to the particular biased or non-normal distribution characteristics of that particular multiply included calorimeter, thus invalidating one of the central limit theory's premises, namely, that the observations were independent of each other. In other words, averaging ten values from one calorimeter that has a systematic bias 1% small with ten other values, one each from ten different calorimeters that all possess different systematic biases not greatly exceeding  $\pm 1\%$ , but randomly distributed, does not give an unbiased average value. Such an average will be biased because it is obtained from a biased distribution that is also most likely non-normal. (It has been argued that it is impossible to determine that the enthalpy of solution values are not normally distributed. Such an argument is not correct. In the present case, the measured enthalpies of solution form a platykurtic distribution, which by definition cannot also be a normal distribution. That the sample of enthalpies of solution are platykurtically distributed is obvious from Fig. 7, discussed later.)

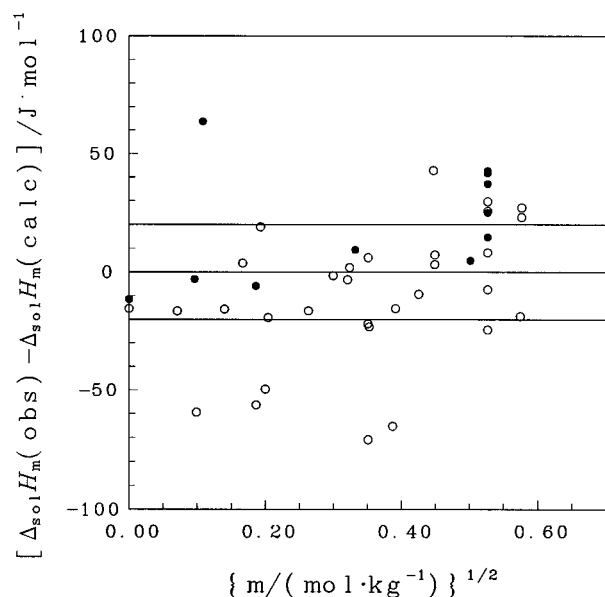


FIG. 7. Differences of measured enthalpies of solution from the model. The filled circles are for potassium chloride samples heated above 600 K, with increasing concentration they correspond to references: 92 (no concentration for the measurement was given, no description of values used to adjust to zero molality was given), 93, 94, 95, 96, 90 (four entries, all same concentration), 97. The empty circles are for potassium chloride samples not heated above 600 K, with increasing concentration they correspond to references: 98 (no concentration for the measurement was given, no description of values used to adjust to zero molality was given), 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 90, 123, 124, 102, 125, 126, and 127.

The first statistical error to be considered was the weighting of the enthalpy of solution values by their precisions. Rather than discuss this error in mathematical terms, an analogy is drawn here. Webster<sup>91</sup> gave an excellent heuristic example of a broken digital clock as an instrument that is extremely precise (no matter how many times it is sampled it gives the exact same time value) but not particularly accurate (in fact, accurate only twice a day for a 12 h clock). The broken digital clock also has a systematic bias that changes sign dependent upon the true value of the sampled variable (time). Now consider three analog clocks that possess only hour hands; they are not nearly so precise as the broken digital clock, but significantly more accurate. Next, consider sampling the four clocks at a particular instant and averaging the four values, *weighting each value by its precision*. Of course, the average value will always be the time of the broken digital clock, it has zero imprecision, and thus the precision-weighted average is not a good measure of the true time in this case. Obviously, the weighting of the components of the average by the precision of the sampled values assumes either: (1) there are no systematic biases in any of the clocks (calorimeters) or (2) in a very large sample of clocks (calorimeters) the systematic errors of all the clocks (calorimeters) taken together results in a normal distribution or, at the very least, some unbiased symmetrical unimodal distribution. Thus, an underlying assumption of Montgomery's *et al.* procedure, perhaps unrecognized by them, was

one of the two assumptions described in the preceding paragraph. But neither of these assumptions is correct and so the weighting of the averages by precision was incorrect. [The "all calorimeters are created equal" principle must also refer to all other aspects of the measurements. This includes: (1) all calorimetrists took equal care in their measurements and (2) all sources of crystalline potassium chloride contain nearly identical amounts of impurities, e.g., sodium or hydroxide. In fact, several of Montgomery's *et al.* references did not describe the source of their potassium chloride samples or their handling. This is particularly true of most of the reports emanating from the former Soviet Union.]

The second statistical error resulted from insufficient control of confounding variables. To statistically identify the dependence of a random variable on one quantity X, there must be sufficient control of all other possible influencing, or confounding, variables. Montgomery's *et al.* segregation of measured values by the criterion of heating the sample above 600 K also segregated samples, unintentionally so, by the concentration for the measurement (thus, concentration was a confounding variable). Of the ten observations involving samples heated above 600 K shown in their Fig. 3, six were for concentrations greater than  $0.25 \text{ mol} \cdot \text{kg}^{-1}$ , one was for an unreported concentration, and the remaining three were for concentrations about, or less than,  $0.1 \text{ mol} \cdot \text{kg}^{-1}$ . Of these ten samples, four samples, all from Gunn,<sup>90</sup> were extremely highly weighted. These four values were so highly weighted they essentially determined the average value; all four were determined for a concentration of  $0.2775 \text{ mol} \cdot \text{kg}^{-1}$ . On the other hand, the sampled enthalpies of solution, where the sample had not been heated above 600 K, were somewhat evenly distributed over the concentration range  $0.01\text{--}0.30 \text{ mol} \cdot \text{kg}^{-1}$ . The resultant average of these samples roughly corresponded to an average concentration of  $0.13 \text{ mol} \cdot \text{kg}^{-1}$ . Thus, Montgomery's *et al.* two averages corresponded not just to differences of heat treatment but also to differences in composition:  $\sim 0.13$  vs  $\sim 0.28 \text{ mol} \cdot \text{kg}^{-1}$ . Montgomery *et al.* attempted to negate the confounding effect of concentration on the measured enthalpies of solution by adjusting all of the sampled enthalpies of solution from the concentration that corresponded to the measurement to an arbitrarily chosen  $0.05 \text{ mol} \cdot \text{kg}^{-1}$ . By back-calculating values from their figures, one finds that they most likely made this adjustment with apparent molar enthalpy values equivalent to those given by Parker.<sup>84</sup> Figure 6 and Sec. 3.2.3 indicated that Parker's values of  $L_\phi$  were systematically biased and that this bias might have been expected as a natural consequence of the graphical chord-area method used in Ref. 84 for the large dilution ratios reported for KCl(aq). In fact, Fig. 6 indicates the magnitude of possible systematic error for adjusting a measured enthalpy of solution from  $0.2775$  to  $0.05 \text{ mol} \cdot \text{kg}^{-1}$  was about  $30\text{--}40 \text{ J} \cdot \text{mol}^{-1}$  for potassium chloride, if one uses NBS values<sup>84</sup> for such an adjustment as apparently did Montgomery *et al.* In other words, the possible error *introduced* by adjustment of the enthalpies determined at different compositions of solution to a common composition should have been expected to have been of the

same size as the effect due to sample treatment being sought, because of the mathematical weaknesses of the chord-area plot method for the types of measurements that existed for KCl(aq). Thus, because of the two statistical flaws, the  $37 \pm 7 \text{ J} \cdot \text{mol}^{-1}$  difference between the averages of the samples shown in Montgomery's *et al.* Figs. 2 and 3 had no real statistical significance.

Because the statistical flaws in Montgomery's *et al.* analysis could have affected their conclusions, the type of comparison they suggested was reconsidered here. Only the enthalpies of solution determined by Kilday<sup>67</sup> were included in the data representation described in Sec. 3.1. This decision was based on the present author's lack of subscription to the "all calorimeters are created equal" principle, with its attendant corollaries. Kilday's calorimeter was exceptional in design, care of construction, and determination of potential biases. The enthalpy of solution is also partly determined in the data representation by the solid-solution equilibrium line. The temperature dependence of the enthalpy of solution must also be in agreement with the differences of heat capacities of solution and crystal. Kilday dried her sample of SRM-1655 at a temperature greater than 600 K.

For each member of the sample of measured enthalpies of solution, a difference of the measured value from that calculated from the present representation of the properties of the KCl+H<sub>2</sub>O system was calculated. If Montgomery's *et al.* hypothesis were indeed correct, then these differences, when plotted against concentration, should show two bands of residuals, one separated from the other by 30–45 J·mol<sup>-1</sup>, with one band comprised primarily of measurements for KCl(cr) where the solid had been heated to greater than 600 K. The calculated differences are shown in Fig. 7. The differences of enthalpies of solution of KCl(cr) samples heated above 600 K are shown as solid circles, those not so heat treated are shown as empty circles. It is seen that most of the measurements fall within 20 J·mol<sup>-1</sup> (about 0.1%) of the values calculated from the data representation. Additionally, if one excludes the values from Gunn's<sup>90</sup> calorimeter (the four solid circles that fall outside the  $\pm 20 \text{ J} \cdot \text{mol}^{-1}$  band, near 0.28 mol·kg<sup>-1</sup>) there appears to be little, if any, systematic bias based on heat treatment. Six of eight *different* calorimetric determinations using material heated above 600 K, showed differences less than 0.05% from the average of most of the measurements made with material not heated above 600 K. Figure 7 shows two things. The first is that there is, in general, very good agreement of many of the previously measured enthalpies of solution with only a few outliers, as one might expect with any random variable. The second is that there is not convincing evidence that any discrepancies in heat of solution measurements for KCl arose from insufficient drying, i.e., not heating a sample of KCl(cr) above 600 K prior to measurement of an enthalpy of solution.

There exists an outlier band of residuals centered about  $-60 \text{ J} \cdot \text{mol}^{-1}$ . Some of these values were obtained with not particularly accurate calorimeters and may represent the limitations of some facets of isoperibol calorimeter design

(see for example Kilday<sup>128</sup>) or sample compositions (impurities).

Figure 7 shows quite good ( $\pm 0.1\%$ ) agreement of most measured enthalpies of solution across many laboratories. Thus, a question to pose is what provoked the belief that there existed significant discrepancies in measured values of the heat of solution of potassium chloride? Many of the differences in values since 1940 arose from adjustment of values from the measured concentration to some other value of concentration by the original authors or by others. Consider the hypothetical case of two investigators who each measured the enthalpy of solution of KCl(aq) at 0.30 mol·kg<sup>-1</sup> and obtained exactly the same value. The first adjusts his enthalpy of solution value from 0.30 mol·kg<sup>-1</sup> to another concentration, say 0.1 mol·kg<sup>-1</sup>, where some "best" evaluated value exists, using Parker's  $L_\phi$  values. The second does the same thing, except he uses Lange and Leighton's values of  $L_\phi$  for the adjustment. The two values, originally identical at 0.30 mol·kg<sup>-1</sup>, would then show disagreement at 0.1 mol·kg<sup>-1</sup>. This was a significant part of the misunderstanding regarding the accuracy of the various measured values for potassium chloride.

One final point remains to be made. Montgomery's *et al.* hypothesis contains the assumption that occluded water is common in samples of KCl(cr); if it was not, then there would have been no point in performing the average of the values shown in their Fig. 2. From values of the saturation molality of KCl(aq), the enthalpy of solution, and the enthalpy of dilution from saturation to the molality of the enthalpy of solution measurement, the amount of occluded water necessary to create a 0.21% error in a measurement of the enthalpy of solution can be calculated. It is approximately a mass fraction of 0.16%. This amount of occluded water could be determined through gravimetric analysis by silver chloride precipitation (capable of 0.02% accuracy). Although this would have been an obvious and simple test of their hypothesis, Montgomery *et al.* did not describe any such attempt to determine the amount of water present in different samples of potassium chloride as a function of the drying procedure.

All of the above does not mean that water-containing occlusions do not occur in some samples of crystalline potassium chloride. Rather, it means the test proposed by Montgomery *et al.*, when concentration dependence is handled properly, does not indicate that such occlusions commonly occur in sufficient quantity to rival the inaccuracies of the calorimetric measurements themselves or that those occlusions that do occur are not removed by drying at more moderate temperatures than those in excess of 600 K. Rard has carefully analyzed drying temperatures and times for crystalline salts (see Ref. 129 for an example). His experience has been that significantly less water is found in potassium chloride samples than in sodium chloride samples, in which moisture may be found at mass fractions of 0.1%–0.15%.<sup>130</sup> Rard<sup>131</sup> recrystallized potassium chloride from water and examined the dehydration behavior. Samples dried at 473, 573, and 673 K showed no differences beyond 0.01%, indicating

occlusions were removed to this level by drying at 473 K, or did not occur beyond this level in crystals grown in aqueous solutions. Heating crystalline potassium chloride much above 700 K in air caused small amounts of decomposition of the crystalline material itself. If that decomposition resulted in the introduction of potassium hydroxide into the sample material, then a 0.01% mass change of the sample would yield a change of  $-30 \text{ J}\cdot\text{mol}^{-1}$  (0.17%) in the heat of solution at 298.15 K. (This calculation is only one possible effect that could occur from decomposition in air at high temperature. Formation of some type of oxy-chloride material is a possibility and could give entirely different results.)

The Gunn study,<sup>90</sup> cited by Montgomery *et al.* as seminal to their analysis, is considered now. Gunn heated two samples of KCl(cr) in air at nearly 1000 K for 18 h and fused a third sample in air in a muffle furnace. The enthalpies of solution for these three samples showed the largest positive deviations of his measurements from the model. Gunn heated a fourth sample in air at 378 K for 18 h. The enthalpy of solution for this fourth sample was different from that calculated from the model by only  $8 \text{ J}\cdot\text{mol}^{-1}$  ( $\sim 0.05\%$ ). The agreement of the moderately heated sample with most other measurements and also the model would seem to indicate a lack of any significant systematic bias in Gunn's calorimeter for endothermic enthalpies of solution. Thus, one could surmise that the larger residuals observed for the samples heated in air to nearly 1000 K and above may have been due to the sort of decomposition Rard observed for KCl heated above 700 K in air. Other empirical evidence regarding this supposition is lacking. All of the observations in this and the previous paragraph further support the above conclusions regarding the lack of evidence requiring drying of KCl(cr) at temperatures in excess of 600 K and the lack of real and significant disagreement of previously measured enthalpies of solution for potassium chloride.

The NIST SRM-1655 certificate<sup>132</sup> states that the sample of KCl(cr) "should be heated for at least 4 h at  $800 \pm 10 \text{ K}$  to remove occluded water and then cooled in a desiccator" prior to measurement of an enthalpy of solution. The certificate does not specify that this heat treatment should be performed in vacuum or under an inert gas. Rard's study indicated decomposition of KCl heated at this temperature in air and the present results indicated the existence of insignificant, if any, dependence of measured enthalpy of solution on heat treatment for temperatures from 380 K to somewhat above 600 K. Therefore, the heat treatment recommended by the NIST certificate appears, at this point, to have a higher probability of corrupting the sample than improving the accuracy of the measurement.

More recent measurements have done little to improve upon the situation and, in fact, are often greatly less accurate than the earlier measurements. As examples, the enthalpy of solution measurements from Dadgar and Taherian,<sup>133</sup> Sanahuja and Cesari,<sup>134</sup> and Sanahuja<sup>135</sup> show rms deviations from the model of  $466 \text{ J}\cdot\text{mol}^{-1}$  ( $\sim 2.7\%$ ),  $95 \text{ J}\cdot\text{mol}^{-1}$  ( $\sim 0.5\%$ ), and  $150 \text{ J}\cdot\text{mol}^{-1}$  ( $\sim 0.9\%$ ), respectively.

Three sets of measured enthalpies of solution span a sig-

nificant temperature range. These are the measurements from Kilday,<sup>67</sup> Oloffson *et al.*,<sup>111</sup> and Vasilev and Lobanov.<sup>114</sup> The differences of these measurements from the fitted model are shown in Fig. 8, with the exception of the highest temperature measurement (390 K) from Oloffson *et al.* which was discordant by about  $300 \text{ J}\cdot\text{mol}^{-1}$ . For temperatures less than 330 K, the rms differences of both Oloffson's *et al.* and Vasilev and Lobanov's measured values from the fitted model are significantly greater than the differences of their 298.15 K values from the model. It could be argued that the rms of their near ambient values might be a better measure of the uncertainty of their measurements than consideration of only the 298.15 K value. The rms difference of the three measurements nearest to ambient conditions was  $40 \text{ J}\cdot\text{mol}^{-1}$  for Oloffson *et al.* and  $78 \text{ J}\cdot\text{mol}^{-1}$  for Vasilev and Lobanov.

### 3.2.4. Heat Capacity Results

Measurements of the heat capacity of aqueous potassium chloride from Tanner and Lamb,<sup>62</sup> (278.15–358.15 K), Ruterjans *et al.*,<sup>66</sup> (303.15–403.15 K), Saluja *et al.*<sup>63</sup> (298.15–373.15 K), Hess and Gramke<sup>64</sup> (288.15–318.15 K), Randall and Rossini<sup>60</sup> (298.15 K), and Oloffson<sup>59</sup> (298.15 K) were all fitted within expected limits. Saluja's *et al.* measurements were obtained for a pressure of 0.6 MPa. Pabalan and Pitzer's<sup>6</sup> heat capacity measurements for 17 MPa indicated the adjustment of Saluja's *et al.* measurements to 0.1 MPa from 0.6 MPa would have been  $\leq 1.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , less than the expected uncertainties due to heat-loss correction factors of 1%, a representative value described by Saluja *et al.*

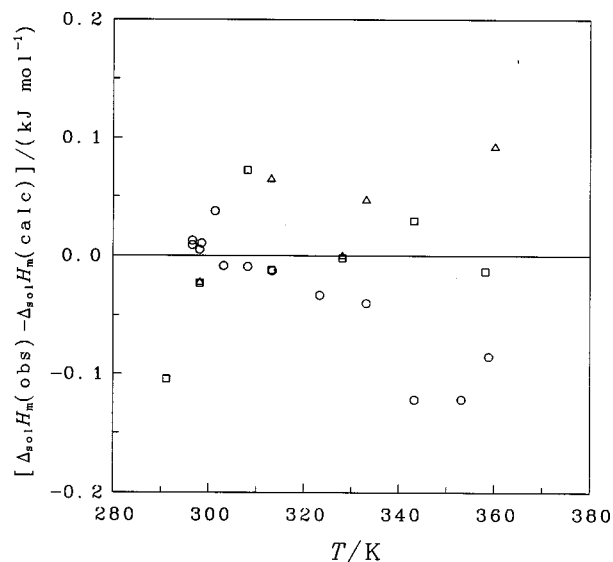


Fig. 8. Differences of measured enthalpies of solution from the model against temperature. The symbols are: (○) Kilday (Ref. 67); (△) Oloffson *et al.* (Ref. 111); (□) Vasilev and Lobanov (Ref. 114).

#### 4. Phase Equilibria and Thermodynamic Properties of the Solution Process for 298.15 K

Measurements of the solubility of potassium chloride in water are shown in Fig. 9. Also shown are values calculated from the model. Agreement is generally good, with the exception of Shul'gina *et al.*<sup>48</sup> values, which diverged at the lowest temperatures. Shul'gina also reported that a hydrate of unknown composition formed between 266.55 and 262.55 K. There appeared to be no other supporting information for the existence of this hydrate in the literature. The invariant equilibrium  $\text{KCl(aq)} + \text{KCl(cr)} + \text{H}_2\text{O(cr)} + \text{H}_2\text{O(g)}$  is calculated to exist at 262.575 K, and  $3.238 \text{ mol}\cdot\text{kg}^{-1}$ , in the absence of hydrate formation. These values are different from those given by Linke,<sup>136</sup> 262.35 K and  $3.327 \text{ mol}\cdot\text{kg}^{-1}$ . The difference can be ascribed to the more recent measurements and also to the required thermodynamic consistency maintained within the present model.

The calculated values of the ice freezing line are in good agreement with values reported by Scatchard and Prentiss,<sup>42</sup> Damköhler and Weinzierl,<sup>43</sup> Jones and Bury,<sup>44</sup> and Momicchioli *et al.*<sup>45</sup> Recently Hall *et al.*<sup>137</sup> measured the ice freezing line from 0.4 to  $3.3 \text{ mol}\cdot\text{kg}^{-1}$ . They listed their uncertainty in temperature measurement as  $\pm 0.05 \text{ K}$ . The rms difference of their measurements corresponded to approximately half this uncertainty.

The standard-state properties for the solution process at  $T_r = 298.15 \text{ K}$  and  $p_r = 0.1 \text{ MPa}$  were calculated to be  $\Delta_{\text{sol}}G_m^\circ = -5.1841 \pm 0.0085 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{sol}}S_m^\circ = 75.23 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The latter value was calculated from the values given in Tables 2 and 4 for  $S_{\text{m,KCl(cr)},T_r}^\circ$  and

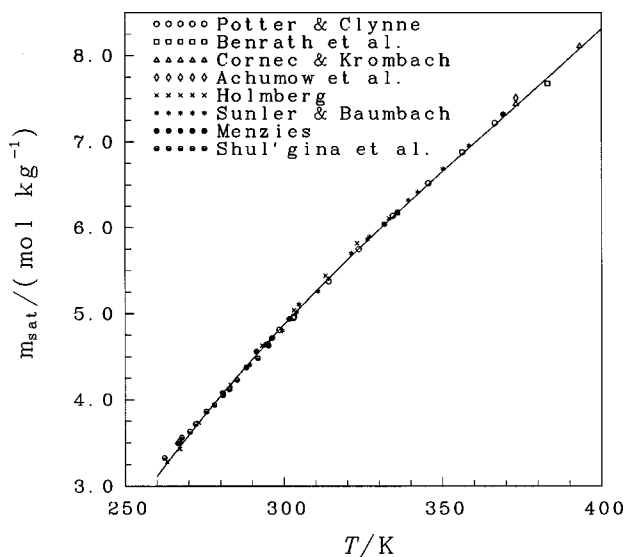


FIG. 9. Values of the solubility calculated from the model compared to measured values. The symbols are: (○) Potter and Clynne (Ref. 71); (□) Benrath *et al.* (Ref. 74); (△) Cornec and Krombach (Ref. 70); (◇) Achumow *et al.* (Ref. 73); (×) Holmberg (Ref. 46); (●) Shearman and Menzies (Ref. 69); (●) Shul'gina *et al.* (Ref. 48); (\*) Sunlar and Baumbach (Ref. 68).

$S_{\text{m,KCl(aq)},T_r}^\circ$ , respectively. The uncertainty given in Table 4 for the entropy of  $\text{KCl(aq)}$  is not truly the uncertainty in this value. It is more properly considered as the uncertainty in the entropy of solution of  $\text{KCl(cr)}$ . This is because the entropy of  $\text{KCl(cr)}$ , taken from Sec. 2, appears in the calculations in combination with the entropy of  $\text{KCl(aq)}$  to give  $\Delta_{\text{sol}}S_m^\circ$ . The true uncertainty for the standard-state entropy of  $\text{KCl(aq)}$  must contain the uncertainty in the entropy of  $\text{KCl(cr)}$ . Because of the discrepancies in experimental results discussed in Sec. 2, the uncertainty in the entropy of  $\text{KCl(cr)}$  is non-negligible. From  $\Delta_{\text{sol}}G_m^\circ$  and  $\Delta_{\text{sol}}S_m^\circ$ ,  $\Delta_{\text{sol}}H_m^\circ$  can be calculated to be  $17.247 \text{ kJ}\cdot\text{mol}^{-1}$  for 298.15 K and 0.1 MPa. These three values can be compared to values given by Wagman *et al.*<sup>138</sup> Wagman's *et al.* values of the enthalpies of formation and entropies can be used to calculate  $\Delta_{\text{sol}}H_m^\circ$  and  $\Delta_{\text{sol}}S_m^\circ$  as  $17.217 \text{ kJ}\cdot\text{mol}^{-1}$  and  $76.41 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , respectively. Appropriate combination of these two values gives  $\Delta_{\text{sol}}G_m^\circ = -5.56 \text{ kJ}\cdot\text{mol}^{-1}$ , whereas the value obtained from the differences of the  $\Delta_rG_m^\circ$  values given by Wagman *et al.* is  $-5.35 \text{ kJ}\cdot\text{mol}^{-1}$ , thus there is an imbalance in the thermodynamic consistency of about  $200 \text{ J}\cdot\text{mol}^{-1}$  in Wagman *et al.* values for potassium chloride.

#### 5. References

- J. A. Rard and R. F. Platford, in *Activity Coefficients in Electrolyte Solutions*, edited by K. S. Pitzer (Chemical Rubber Corp., Boca Raton, FL, 1991).
- W. J. Hamer and Y. C. Wu, *J. Phys. Chem. Ref. Data* **1**, 1047 (1972).
- E. C. W. Clarke and D. N. Glew, *J. Phys. Chem. Ref. Data* **14**, 489 (1985).
- D. G. Archer, *J. Phys. Chem. Ref. Data* **21**, 793 (1992).
- J. D. Cox, D. D. Wagman, and V. A. Medvedev, *CODATA Key Values for Thermodynamics* (Hemisphere, Washington, DC, 1989).
- R. T. Pabalan and K. S. Pitzer, *J. Chem. Eng. Data* **33**, 354 (1988).
- D. G. Archer, *J. Phys. Chem. Ref. Data* **21**, 1 (1992).
- A. J. Leadbetter and G. R. Settatree, *J. Phys. C* **2**, 385 (1969).
- D. G. Archer, *J. Chem. Eng. Data* **42**, 281 (1997).
- T. B. Douglas and A. W. Harman, *J. Res. Natl. Bur. Stand.* **78A**, 515 (1974).
- H. Preston-Thomas, *Metrologia* **27**, 3 (1990).
- G. W. Burns, G. F. Strouse, B. W. Magnum, M. C. Croarkin, W. F. Guthrie, P. Marcarino, M. Battuello, H. K. Lee, J. C. Kim, K. S. Gam, C. Rhee, M. Chattle, M. Arai, H. Sakurai, A. I. Pokhodun, N. P. Moiseeva, S. A. Perevalova, M. J. deGroot, J. Zhang, K. Fan, and S. Wu, *Temperature, Its Measurement and Control in Science and Industry* (American Institute of Physics, New York, 1992), Vol. 6.
- F. J. Webb and J. Wilks, *Proc. R. Soc. London Sect. A* **230**, 549 (1955).
- P. H. Keesom and N. Pearlman, *Phys. Rev.* **91**, 1354 (1953).
- W. T. Berg and J. A. Morrison, *Proc. R. Soc. London Sect. A* **242**, 467 (1957).
- A. J. Kirkham and B. Yates, *Cryogenics* **8**, 381 (1968).
- J. C. Southard and R. A. Nelson, *J. Am. Chem. Soc.* **55**, 4865 (1933).
- C. Telea, P. Ferloni, and P. Franzosini, *Gazz. Chim. Ital.* **102**, 546 (1972).
- P. G. Strelkov, E. S. Itskevich, V. N. Kostryukov, and G. G. Mirskaya, *Z. Fiz. Khim.* **28**, 645 (1954).
- K. Clusius, J. Goldman, and A. Perlick, *Z. Naturforsch.* **49**, 424 (1949).
- N. Feodos'ev, *Zh. Fiz. Khim.* **12**, 291 (1938).
- W. T. Thompson and S. N. Flengas, *Can. J. Chem.* **49**, 1550 (1971).
- K. S. Pitzer, in *Activity Coefficients in Electrolyte Solutions*, edited by K. S. Pitzer (Chemical Rubber Corp., Boca Raton, FL, 1991).
- K. S. Pitzer, *Thermodynamics*, 3rd ed. (McGraw Hill, New York, 1995).
- P. G. Hill, *J. Phys. Chem. Ref. Data* **19**, 1223 (1990).
- D. G. Archer and P. Wang, *J. Phys. Chem. Ref. Data* **19**, 371 (1990).
- R. A. Robinson and D. A. Sinclair, *J. Am. Chem. Soc.* **56**, 1830 (1934).
- A. A. Janis and J. B. Ferguson, *Can. J. Res.* **17B**, 215 (1939).



- <sup>29</sup>R. A. Robinson, *Trans. R. Soc. New Zealand* **75**, 203 (1945).
- <sup>30</sup>J. A. Rard and D. G. Miller, *J. Chem. Eng. Data* **26**, 38 (1981).
- <sup>31</sup>G. Scatchard, W. J. Hamer, and S. E. Wood, *J. Am. Chem. Soc.* **60**, 3061 (1938).
- <sup>32</sup>A. N. Kirgintsev and A. V. Luk'yanov, *Russ. J. Phys. Chem.* **37**, 1501 (1963).
- <sup>33</sup>M. M. Shult's, L. L. Makarov, and S. Yu-Jeng, *Russ. J. Phys. Chem.* **36**, 1181 (1962).
- <sup>34</sup>A. R. Gordon, *J. Am. Chem. Soc.* **65**, 221 (1943).
- <sup>35</sup>C. W. Childs and R. F. Platford, *Aust. J. Chem.* **24**, 2487 (1971).
- <sup>36</sup>T. M. Davis, L. M. Duckett, J. F. Owen, C. S. Patterson, and R. Saleeby, *J. Chem. Eng. Data* **30**, 432 (1985).
- <sup>37</sup>K. L. Hellams, C. S. Patterson, B. H. Prentice, and M. J. Taylor, *J. Chem. Eng. Data* **10**, 323 (1965).
- <sup>38</sup>R. F. Platford, *J. Chem. Eng. Data* **18**, 215 (1973).
- <sup>39</sup>W. T. Humphries, C. F. Kohrt, and C. S. Patterson, *J. Chem. Eng. Data* **13**, 327 (1968).
- <sup>40</sup>J. T. Moore, W. T. Humphries, and C. S. Patterson, *J. Chem. Eng. Data* **17**, 180 (1972).
- <sup>41</sup>H. F. Holmes, C. F. Baes, and R. E. Mesmer, *J. Chem. Thermodyn.* **10**, 983 (1978).
- <sup>42</sup>G. S. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.* **55**, 4355 (1933).
- <sup>43</sup>G. Damköhler and J. Weinziel, *Z. Phys. Chem. Abt. A* **167**, 71 (1933).
- <sup>44</sup>E. R. Jones and C. R. Bury, *Philos. Mag.* **3**, 1032 (1927).
- <sup>45</sup>F. Momicchioli, O. Devoto, G. Grandi, and G. Cocco, *Ber. Bunsenges. Phys. Chem.* **74**, 59 (1970).
- <sup>46</sup>K. E. Holmberg, *Ab. Atomenergi, Stockholm Rapp. AE-340* (1968).
- <sup>47</sup>W. H. Rodebush, *J. Am. Chem. Soc.* **40**, 1204 (1918).
- <sup>48</sup>M. P. Shul'gina, O. S. Kkarchuk, and O. K. Yanateva, *Izv. Sektora Fiz.-Khim. Analiza., Inst. Obshch. Neorgan. Khim., Akad. Nauk SSSR* **26**, 198 (1955).
- <sup>49</sup>T. M. Herrington and R. T. Jackson, *Trans. Faraday Soc.* **69**, 1635 (1973).
- <sup>50</sup>B. F. Lovelace, J. C. W. Frazer, and V. B. Sease, *J. Am. Chem. Soc.* **43**, 102 (1921).
- <sup>51</sup>R. H. Wood, R. A. Rooney, and J. N. Braddock, *J. Phys. Chem.* **73**, 1673 (1969).
- <sup>52</sup>W. H. Leung and F. J. Millero, *J. Solution Chem.* **4**, 145 (1975).
- <sup>53</sup>J. E. Mayrath and R. H. Wood, *J. Chem. Thermodyn.* **14**, 563 (1982).
- <sup>54</sup>T. W. Richards and A. W. Rowe, *J. Am. Chem. Soc.* **43**, 770 (1921).
- <sup>55</sup>S. M. Naude, *Z. Phys. Chem.* **135**, 209 (1928).
- <sup>56</sup>H. P. Snipes, C. Manly, and D. D. Ensor, *J. Chem. Eng. Data* **20**, 287 (1975).
- <sup>57</sup>E. Lange and P. A. Leighton, *Z. Elektrochem.* **34**, 566 (1928).
- <sup>58</sup>J. Wust and E. Lange, *Z. Phys. Chem.* **116**, 161 (1925).
- <sup>59</sup>I. V. Olofsson, *J. Chem. Thermodyn.* **11**, 1005 (1979).
- <sup>60</sup>M. Randall and F. D. Rossini, *J. Am. Chem. Soc.* **51**, 323 (1929).
- <sup>61</sup>J.-L. Fortier, P.-A. Leduc, and J. E. Desnoyers, *J. Solution Chem.* **3**, 323 (1974).
- <sup>62</sup>J. E. Tanner and F. W. Lamb, *J. Solution Chem.* **7**, 303 (1978).
- <sup>63</sup>P. P. S. Saluja, R. J. Lemire, and J. C. LeBlanc, *J. Chem. Thermodyn.* **24**, 181 (1992).
- <sup>64</sup>C. D. Hess and B. E. Gramkee, *J. Phys. Chem.* **44**, 483 (1940).
- <sup>65</sup>A. P. Rutskov, *Zh. Prikl. Khim.* **21**, 820 (1948).
- <sup>66</sup>H. Ruterjans, F. Shreiner, U. Sage, and Th. Ackermann, *J. Phys. Chem.* **73**, 986 (1969).
- <sup>67</sup>M. V. Kilday, *J. Res. Natl. Bur. Stand.* **85**, 467 (1980).
- <sup>68</sup>A. A. Sunler and J. Baumbach, *J. Chem. Eng. Data* **21**, 335 (1976).
- <sup>69</sup>R. W. Shearman and A. W. C. Menzies, *J. Am. Chem. Soc.* **59**, 185 (1937).
- <sup>70</sup>E. Cornec and H. Krombach, *Ann. Chim. Paris* **18**, 5 (1932).
- <sup>71</sup>R. W. Potter, M. A. Clynne, and D. L. Browne, *Econ. Geol.* **73**, 284 (1978).
- <sup>72</sup>G. S. Durham, E. J. Rock, and J. S. Frayn, *J. Am. Chem. Soc.* **75**, 5792 (1953).
- <sup>73</sup>E. I. Achumow and J. B. Wasseljew, *Zh. Obshch. Khim.* **2**, 271 (1932).
- <sup>74</sup>A. Benrath, F. Gjedebo, B. Schiffers, and H. Wunderlich, *Z. Anorg. Allg. Chem.* **231**, 285 (1937).
- <sup>75</sup>G. Scatchard, B. Vonnegut, and D. W. Beaumont, *J. Chem. Phys.* **33**, 1292 (1960).
- <sup>76</sup>M. Petit, *J. Chim. Phys.* **62**, 1119 (1965).
- <sup>77</sup>W. R. Harrison and E. P. Perman, *Trans. Faraday Soc.* **23**, 1 (1927).
- <sup>78</sup>H. S. Harned and M. A. Cook, *J. Am. Chem. Soc.* **59**, 1290 (1937).
- <sup>79</sup>R. P. Smith, *J. Am. Chem. Soc.* **55**, 3279 (1933).
- <sup>80</sup>R. Caramazza, *Gazz. Chim. Ital.* **90**, 1721 (1960).
- <sup>81</sup>H. S. Harned, *J. Am. Chem. Soc.* **51**, 416 (1929).
- <sup>82</sup>W. J. Hornibrook, G. J. Janz, and A. R. Gordon, *J. Am. Chem. Soc.* **64**, 513 (1942).
- <sup>83</sup>G. M. Giordano, P. Longhi, T. Mussini, and S. Rondinini, *J. Chem. Thermodyn.* **9**, 997 (1977).
- <sup>84</sup>V. B. Parker, *Natl. Stand. Ref. Data Ser.* **2**, (1965).
- <sup>85</sup>T. F. Young and O. G. Vogel, *J. Am. Chem. Soc.* **54**, 3036 (1932).
- <sup>86</sup>T. F. Young and J. S. Machin, *J. Am. Chem. Soc.* **58**, 2254 (1936).
- <sup>87</sup>T. F. Young and W. L. Groenier, *J. Am. Chem. Soc.* **58**, 187 (1936).
- <sup>88</sup>E. A. Gulbransen and A. L. Robinson, *J. Am. Chem. Soc.* **56**, 2637 (1934).
- <sup>89</sup>R. L. Montgomery, R. A. Melaugh, C.-C. Lau, G. H. Meier, H. H. Chan, and F. D. Rossini, *J. Chem. Thermodyn.* **9**, 915 (1977).
- <sup>90</sup>S. R. Gunn, *J. Phys. Chem.* **69**, 2902 (1965).
- <sup>91</sup>J. G. Webster, *Medical Instrumentation* (Houghton Mifflin, New York, 1978).
- <sup>92</sup>G. K. Johnson and K. H. Gayer, *J. Chem. Thermodyn.* **11**, 41 (1979).
- <sup>93</sup>D. F. Evans and R. E. Richards, *J. Chem. Soc.* 3932 (1952).
- <sup>94</sup>T. L. Higgins and E. F. Westrum, *J. Phys. Chem.* **65**, 830 (1961).
- <sup>95</sup>N. Fontell, *Soc. Sci. Fennica Commentationes Phys.-Math.* **1**, 10 (1938).
- <sup>96</sup>K. P. Mischenko, *Z. Elektrochem.* **36**, 777 (1930).
- <sup>97</sup>J. Hietala, *Ann. Acad. Sci. Fennicae* **AV163**, 1 (1960).
- <sup>98</sup>C. C. Stephenson, P. G. Abojian, R. Provost, and C. Wulff, *J. Chem. Eng. Data* **13**, 191 (1968).
- <sup>99</sup>G. R. Argue, E. E. Mercer, and J. W. Cobble, *J. Phys. Chem.* **65**, 2041 (1961).
- <sup>100</sup>G. Somsen, J. Coops, and M. W. Tolk, *Rec. Trav. Chim.* **82**, 231 (1963).
- <sup>101</sup>V. A. Palkin, V. E. Gorbunov, and T. A. Kapitonova, *Russ. J. Phys. Chem.* **43**, 914 (1969).
- <sup>102</sup>E. Hutchinson, K. E. Manchester, and L. Winslow, *J. Phys. Chem.* **58**, 1124 (1954).
- <sup>103</sup>V. A. Medvedev and M. E. Efimov, *Russ. J. Phys. Chem.* **49**, 780 (1975).
- <sup>104</sup>E. S. Newman, *J. Res. Natl. Bur. Stand.* **66A**, 381 (1962).
- <sup>105</sup>V. K. Abrosimov and G. A. Krestov, *Russ. J. Phys. Chem.* **41**, 1699 (1967).
- <sup>106</sup>V. A. Zverev and G. A. Krestov, *Russ. J. Phys. Chem.* **42**, 286 (1968).
- <sup>107</sup>P. Paoletti, *Trans. Faraday Soc.* **61**, 219 (1965).
- <sup>108</sup>B. B. Letson and G. R. Taylor, *U.S. Bur. Mines, Rept. Invest.* 6583 (1965).
- <sup>109</sup>R. H. Busey, H. H. Dearman, and R. B. Bevan, *J. Phys. Chem.* **66**, 82 (1962).
- <sup>110</sup>P. K. Gallagher and E. L. King, *J. Am. Chem. Soc.* **82**, 3511 (1960).
- <sup>111</sup>G. Olofsson, S. Sunner, M. Efimov, and J. Laynez, *J. Chem. Thermodyn.* **5**, 199 (1973).
- <sup>112</sup>N. N. Greenwood and D. J. Prince, *J. Chem. Soc.* 2876 (1969).
- <sup>113</sup>S. Sunner and I. Wadso, *Acta Chem. Scand.* **13**, 97 (1959).
- <sup>114</sup>V. P. Vasilev and G. A. Lobanov, *Russ. J. Inorg. Chem.* **11**, 383 (1966).
- <sup>115</sup>V. M. Gurevich and V. A. Sokolov, *Russ. J. Phys. Chem.* **46**, 1074 (1972).
- <sup>116</sup>N. A. Reshetnikov, *Zh. Neorg. Khim.* **6**, 682 (1961).
- <sup>117</sup>R. E. Barieau and W. F. Giauque, *J. Am. Chem. Soc.* **72**, 5676 (1950).
- <sup>118</sup>P. Balk and G. C. Benson, *J. Phys. Chem.* **63**, 1009 (1959).
- <sup>119</sup>P. Gerding, J. Leden, and S. Sunner, *Acta. Chem. Scand.* **17**, 2190 (1963).
- <sup>120</sup>G. W. Richards and A. A. Woolf, *J. Chem. Soc.* 470 (1969).
- <sup>121</sup>M. N. Papadopoulos and W. F. Giauque, *J. Phys. Chem.* **77**, 2740 (1955).
- <sup>122</sup>J. L. Bills and F. A. Cotton, *J. Phys. Chem.* **64**, 1477 (1960).
- <sup>123</sup>J. H. Stern and C. W. Anderson, *J. Phys. Chem.* **68**, 2528 (1964).
- <sup>124</sup>L. T. Eremenko, Yu. R. Kolesov, and L. V. Kustova, *Russ. J. Phys. Chem.* **38**, 1259 (1964).
- <sup>125</sup>T. Davies, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.* 2304 (1954).
- <sup>126</sup>M. Ciampolini and P. Paoletti, *J. Phys. Chem.* **65**, 1224 (1961).
- <sup>127</sup>L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.* **82**, 3828 (1960).
- <sup>128</sup>M. V. Kilday, *J. Res. Natl. Bur. Stand.* **85**, 449 (1980).
- <sup>129</sup>J. A. Rard and D. G. Archer, *J. Chem. Eng. Data* **40**, 170 (1995).
- <sup>130</sup>J. A. Rard (personal communication).
- <sup>131</sup>J. A. Rard, *J. Chem. Thermodyn.* **28**, 83 (1996).

- <sup>132</sup>G. A. Uriano, *Standard Reference Material 1655. Potassium Chloride, KCl(cr) for Solution Calorimetry* (National Institute of Standards and Technology, USDOC, Washington, D.C.).
- <sup>133</sup>A. Dadgar and M. R. Taherian, *J. Chem. Thermodyn.* **9**, 711 (1977).
- <sup>134</sup>A. Sanahuja and E. Cesari, *J. Chem. Thermodyn.* **16**, 1195 (1984).
- <sup>135</sup>A. Sanahuja, *J. Chem. Thermodyn.* **17**, 1063 (1985).
- <sup>136</sup>W. F. Linke, *Solubilities* (American Chemical Society, Washington, D.C., 1965), Vol. II.
- <sup>137</sup>D. L. Hall, S. M. Sterner, and R. J. Bodnar, *Econ. Geol.* **83**, 197 (1988).
- <sup>138</sup>D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2 (1982).