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Enthalpies of Solution of Sodium Chloride and Potassium Sulfate in Water. Thermodynamic Properties of the Potassium Sulfate + Water System[†]

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An adiabatic calorimeter was used to measure enthalpies of solution into water of sodium chloride (∼0.13 mol·kg^{-1}) at nominal temperatures of 298.15 K, 303.15 K, and 308.15 K and of potassium sulfate (∼0.039 mol·kg^{-1}) at nominal temperatures of 298.15 K and 303.15 K. The results for sodium chloride were compared to a previous equation of state so as to validate the use of values from that equation of state for calibration of, or checks on the accuracy of, solution calorimeters. Thermodynamic properties from the literature for the potassium sulfate + water system and the present measurements were used to generate equations that represented the thermodynamic properties of this system from the freezing point of the aqueous solution to 500 K. The measured values included in the fitted equations spanned the range of temperature of approximately 271 K to 530 K for K_2SO_4(aq) and 13 K to 854 K for K_2SO_4(cr). New equations and/or values for the following properties are given in the present work: (1) thermal properties of K_2SO_4(cr) from 0 K to near the orthorhombic to hexagonal transition at 857 K, (2) the change in chemical potential for both K_2SO_4 and H_2O in K_2SO_4(aq) as a function of temperature and molality, valid from 271 K to 500 K, from 0 mol·kg^{-1} to the saturation molality, and to pressures of 40 MPa, and (3) standard-state properties for the aqueous solution process.

Introduction

This contribution is part of a program of determination of the thermodynamic properties of materials that may serve as calorimetric standards or that are important for use in groundwater simulation programs. In this article, we report new accurate enthalpies of solution for a substance from each category.

The first substance is sodium chloride. In 1992, Archer published a comprehensive equation that represented the properties of the sodium chloride + water system valid for a wide range of temperature and pressure.[1] That equation is sufficient for use for calibration of instruments that measure volumetric properties and for calibration of calorimeters that measure enthalpies of mixing, enthalpies of dilution, and heat capacities. The equation has also served as a source of reference values for NaCl(aq) when it has been used as the reference electrolyte in isopiestic vapor pressure measurements. The usefulness of the sodium chloride + water system for all of these calibration or standards purposes arises, in part, because of the large body of highly accurate measurements of many different thermodynamic properties for the system. The better-determined of these properties are generally of sufficient accuracy that they satisfy thermodynamic relationships that interrelate different types of thermodynamic properties.

Previously determined enthalpies of solution for sodium chloride in water scatter quite a bit when comparisons are made on an interlaboratory basis. Even the more probable of those measurements disagreed by approximately 20 J·mol^{-1} on an interlaboratory basis. This corresponded roughly to 0.5% of the measured enthalpy of solution for molalities < 0.5 mol·kg^{-1}. Some of the more recently reported measurements were much less accurate and showed deviations from the earlier measurements of a few hundred J·mol^{-1}, or about 5%. If viewed solely on this basis, it would appear that the enthalpy of solution of sodium chloride was not sufficiently well-known to serve as a calorimetric standard. However, the standard-state enthalpy of solution of sodium chloride calculated from Archer's 1992 equation[1] was (3853 ± 8) J·mol^{-1}, where ±8 J·mol^{-1} was a 95% confidence interval. This means that enthalpies of solution calculated from the Archer equation for dilute concentrations should be accurate to approximately ±0.1%, at the usual 1 σ level. This significant improvement of the accuracy of the calculated enthalpy of solution over the values measured previously can be attributed to the fact that Archer's equation gave an accurate representation of the NaCl(aq) = NaCl(cr) equilibrium line and that this equilibrium line was so well determined over an extensive temperature region that it significantly improved the accuracy of the calculated enthalpy of solution over values obtained from the previous calorimetric determinations. However, this point is not accepted by all. Some argue that it is simply not possible to determine an enthalpy of a reaction from measurements of the Gibbs energy of the reaction over a wide temperature range such that this enthalpy of reaction can be more accurately determined than that obtained from any calorimetric measurements. This same rationale has also sometimes been used to argue that it is not possible to determine heat capacity from measurements of enthalpy

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[†] Certain commercial materials and suppliers are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by either the U.S. Government or the National Institute of Standards and Technology, nor does it imply that the equipment or materials identified are necessarily the best available for the purpose.

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increments over a range of temperature more accurately than what can be obtained from any "direct" heat capacity measurements. While these arguments have been made, and often have been accepted, as though they were universally correct, they are not. Whether a calorimetrically determined enthalpy of reaction is more accurate than one determined from measurements of the Gibbs energy of reaction as a function of temperature depends on the accuracies of the two respective types of measurements, the range of temperature over which the Gibbs energy was determined, and whether systematic bias was introduced as an artifact in the mathematical process of obtaining the required derivatives from the Gibbs energy as a function of temperature.

We have measured, and report here, the enthalpy of solution of NaCl(aq) with a highly accurate adiabatic calorimeter as a function of temperature from 298.15 K to 308.15 K. These measurements show agreement with the Archer (1992) equation, within its uncertainties, and establish that the enthalpy of solution of sodium chloride can be used as a standard with an uncertainty of approximately ±0.1% for near ambient temperatures and dilute solution conditions.

Potassium sulfate is the second substance for which we report here enthalpy of solution measurements. Pabalan and Pitzer[2] calculated the solubility of arcanite (K_2SO_4(cr)) using values of $\Delta_f G_m°$ for K_2SO_4(cr) and K_2SO_4(aq) taken from Harvie and Weare[3] and $\Delta_f H_m°$ and $S_m°$ for K_2SO_4(cr) and K_2SO_4(aq) taken from ref 4. The calculated solubility was reasonably correct for 298.15 K but diverged from measured values as temperature increased. However, this disagreement between measured and calculated solubilities was not larger than 8% from 273 K to 485 K. Because the misrepresentation of the measured values was a function of temperature, there were at least three possible causes of it, namely, errors in the assumed $\Delta_f H$ and $S_m°$ for K_2SO_4(cr) and/or K_2SO_4(aq), error in the equation used for the chemical potential of K_2SO_4(aq), and error in the measured values of the solubility as a function of temperature. New, accurate, measurements for the enthalpy of solution of K_2SO_4(cr) are necessary to explore the first of these possibilities. We also present here new equations for the properties of the $K_2SO_4 + H_2O$ system. This new formulation eliminates the systematic misrepresentations of solubility observed previously.

Experimental Section

Calorimeter. Measurements were made with an adiabatic calorimeter. The mechanical parts of the calorimeter were those described by Prosen and Kilday.[5] In short, the calorimeter vessel was made of a platinum−iridium alloy (Pt−Ir) and had an internal volume of approximately 330 cm^3. This vessel was plated with approximately 3.2 mm of silver to reduce thermal gradients about the vessel. A similarly constructed lid permitted entry of a stirrer, entry of vessels that contained a resistance heater and a resistance thermometer, and suspension of a sample cell. All of these components were also made of Pt−Ir alloy, and their entry points into the vessel were sealed at the lid with O-rings, so as to prevent atmospheric contact with the internal contents of the calorimeter vessel. The unique sample-containing device[5] introduced solute into the calorimeter without a measurable enthalpy change associated with the opening of the device. The adiabatic shield comprises two parts, a lower shield and a lid that together surrounded completely the calorimeter vessel. Both parts of the shield were gold-plated copper and had heater wire attached to all of their external surfaces. The lower shield was cast as a single piece to eliminate seams that could result in thermal gradients. External to the adiabatic shield was a guard system that utilized cooling from a refrigerated bath and resistive heating. The guard system also served as the vacuum chamber for maintaining the nearly adiabatic conditions. The vacuum chamber was evacuated with a roughing pump and a diffusion pump.

A 25 Ω capsule platinum thermometer (Leeds and Northrup) was used for measurement of the temperature of the calorimeter. This thermometer was calibrated at the National Institute of Standards and Technology on the International Temperature Scale of 1990 (ITS-90) for temperatures from the triple point of water to the freezing temperature of indium.

The instrument control and data acquisition methods were somewhat similar to those described previously for our adiabatic enthalpy-increment calorimeters;[6] however, there are some differences because of the nature of the measurement and the construction of the enthalpy of solution calorimeter. The resistance of the thermometer was measured with a self-balancing ac bridge (ASL Co.). The calorimeter was calibrated electrically both before and after the solution measurement. Power to the calorimeter heater and an in-series standard resistor was supplied by a general-purpose-interface-bus (GPIB) programmed, regulated, power supply. The output of this power supply was switched between a "dummy" resistor and the calorimeter circuit by a high-speed mercury-wetted relay. This relay was controlled by a separate multiplexor. The multiplexor also performed the switching necessary to measure voltages across the standard resistor and the calorimeter heater with a separate card. Voltages were measured with a $7^1/_2$-digit voltmeter with internal calibration. Time was measured with a 10 MHz frequency counter. A latching flip-flop circuit was fabricated and installed to prevent premature triggering of the counter's internal gates caused by switch bounce of the relays. A computer was used for data acquisition and control of the calorimeter measurement circuitry.

Temperature control of the adiabatic shields was performed with a second computer. This computer used the thermoelectric voltages of the shield thermocouples to control the temperatures of the individual shields. The two parts of the adiabatic shield were controlled individually. The thermopile voltages for the two parts of the adiabatic shield were measured with nanovoltmeters, the outputs of which were obtained by the computer over a GPIB. A thermocouple for the less-critical guard system was measured with a microvoltmeter that did not have a GPIB interface. The chart-recorder output from this microvoltmeter was digitized by a 12-bit analog-to-digital converter installed in the computer.

The digitized thermocouple voltages were used in algorithms that utilized proportional, integral, and derivative (PID) control actions. The algorithm outputs were converted to analog voltage signals by buffered, latching, 12-bit, digital-to-analog converters. The outputs from these converters drove voltage-programmed dc power supplies that were connected to the shield heaters. It was found that significantly better control of the shields was obtained by feeding the square root of the PID output to the power supplies.

Power to computers, measurement instruments, and power supplies was supplied with an uninterruptible, isolated power supply in order to overcome the short-term random power outages in the laboratory.

The enthalpies of solution of sodium chloride and potassium sulfate are endothermic, and the adiabatic shields do not lose heat to the surroundings rapidly enough to follow closely a rapidly dropping temperature of the calorimeter vessel occurring from the endothermic solution enthalpy. Therefore, electrical energy was superimposed over the dissolution process so that the final temperature after mixing was approximately the same as, or slightly warmer than, the temperature prior to the mixing. The small out-of-balance thermopotential of the adiabatic shield's thermopile was fed to a chart recorder. This out-of-balance signal was used to calculate the small enthalpy adjustments due to the small mismatches of the shield and vessel temperatures. This adjustment was always very small compared to the enthalpy of solution. Corrections to the observed enthalpy change were also made for evaporation of solvent into the void volume of the sample cell, for changes in solvent activity due to the dissolution, and for expansion of the vapor-space volume due to the change of volume upon mixing of the two condensed phases.

Materials. The sodium chloride used for the present measurements was taken from two different sources. Some of the samples were taken from optical crystals obtained from Solon Technologies Inc. The optical crystals (<50 ppm impurities) were used as received except for cutting and then grinding into smaller-sized crystals. These samples were from the same optical crystals from which Archer[7] took samples for enthalpy-increment measurements. Some of the sodium chloride samples were from Mallinckrodt. The Mallinckrodt samples of NaCl were dried at 773 K for 24 h prior to use and stored in a desiccator. Potassium sulfate was from Aldrich, 99.99% pure. It was dried at 773 K to constant weight. The dried sample was sieved with a 125 micron sieve, and the particles larger than the sieve dimension were used for the enthalpy of solution measurements.

Although neither sodium chloride nor potassium sulfate is hygroscopic, they were stored in desiccators except during the weighing and calorimetric procedures. Special precautions for weighing and handling the samples were not required to prevent exposure to room humidity. The samples were loaded into the tared sample cell and weighed, and the weights were converted to mass, correcting for buoyancy.

Results

Measured values for the enthalpy of solution of sodium chloride obtained with this calorimeter are given in Table 1, as are the differences of these values from the Archer (1992) equation of state.[1] A subset of these values had been published previously.[9] Since submission of that manuscript, additional measurements were made and the complete set of measured values is given in Table 1. The differences of the measured values from those calculated were used to calculate standard deviations of the populations. These standard deviations of the populations can be considered to represent the random deviations associated with the individual measurements. They correspond to an imprecision of approximately (80−100) μK in the measured temperature change for the dissolution measurement. The uncertainty associated with the determination of the temperature change for the mixing reaction is the largest source of random imprecision in the measurements.

Occasionally, a measured enthalpy change for dissolution of sodium chloride was observed to be much too small in magnitude, that is, more than 1% too small. These values arose from cell leakage prior to the opening of the cell. We did not observe any enthalpies that fell between 0.1% and 1.0% smaller than the mean value, other than the single value identified in Table 1. This observation implied that the cell was either sealed successfully or very poorly; however, this observation could not define that conclusion as a certainty. Therefore, there remained a possibility that an occasional very small leakage of the cell could have caused the population of measured values to be skewed to smaller absolute values, that is, values smaller in magnitude. Relating this possibility to the meaning of probabilistic uncertainty of a measurement indicates that the measurements determined with this instrument may be characterized by a non-normal distribution that is skewed slightly to values smaller in magnitude than the true value.

Table 1. Enthalpy of Solution of NaCl in H_2O

T(ITS-90) K	m mol·kg^{-1}	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$(obs) J·mol^{-1}	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$(obs) − $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$(calc)^{a} J·mol^{-1}
		Mallinckrodt	
298.1584	0.145 60	4221.3	−2.2
298.2805	0.136 91	4205.0	−1.8
298.2909	0.133 80	4196.3	−8.3
298.1546	0.130 02	4212.7	−7.5
298.1170	0.127 00	4225.3	+1.5
298.1765	0.129 05	4217.4	+0.2
298.1208	0.135 78	4224.9	−1.0
298.0623	0.125 74	4233.4	+3.3
298.1084	0.136 19	4220.6	−6.9
298.1243	0.136 76	4221.9	−3.8
298.1197	0.137 01	4227.5	+1.2
298.1244	0.137 14	4220.5	−5.3
			average = −2.6 J·mol^{-1}
			s.d. population^{c} = 3.8 J·mol^{-1}
		Optical Crystal	
298.3366	0.131 24	4190.3	−8.0
298.1641	0.135 61	4220.8	+0.2
298.1654	0.135 74	4226.1	+5.3
298.3866	0.131 24	4190.4	−1.3
298.1641	0.135 61	4221.0	+0.5
298.1654	0.135 74	4225.20	+4.8
			average = 0.25 J·mol^{-1}
			s.d. population^{c} = 4.8 J·mol^{-1}
		Mallinckrodt	
303.1363	0.123 10	3623.8	−3.8
303.1214	0.127 84	3628.4	−2.3
303.1396	0.141 46	3614.1	−23.3^{b}
303.1447	0.137 19	3624.9	−9.8
303.1581	0.138 57	3627.0	−6.9
303.1414	0.136 40	3621.8	−12.9
			average = −7.1 J·mol^{-1}
			s.d. population^{c} = 4.3 J·mol^{-1}
		Optical Crystal	
303.3100	0.136 59	3604.9	−10.7
		Mallinckrodt	
308.1444	0.130 20	3068.2	−7.1
308.1556	0.151 41	3081.6	−8.1
308.1467	0.141 84	3086.7	+2.7
308.1529	0.136 97	3075.6	−4.2
308.1474	0.139 58	3072.4	−10.0
308.1621	0.136 71	3074.9	−3.6
			average = −5.3 J·mol^{-1}
			s.d. population^{c} = 4.5 J·mol^{-1}

[a] Difference of the measured value from that calculated from the Archer (1992) equation of state for NaCl(aq)[1] and the Archer equation for NaCl(cr).[8] [b] This measurement was excluded from the statistical calculations. [c] Unbiased.

The 1992 equation for NaCl(aq)[1] was found to be in excellent agreement with the measured values. For temperatures near 298.15 K, the mean difference of the measured values from those calculated from the equation of state was −2.6 J·mol^{-1}. The standard deviation of this

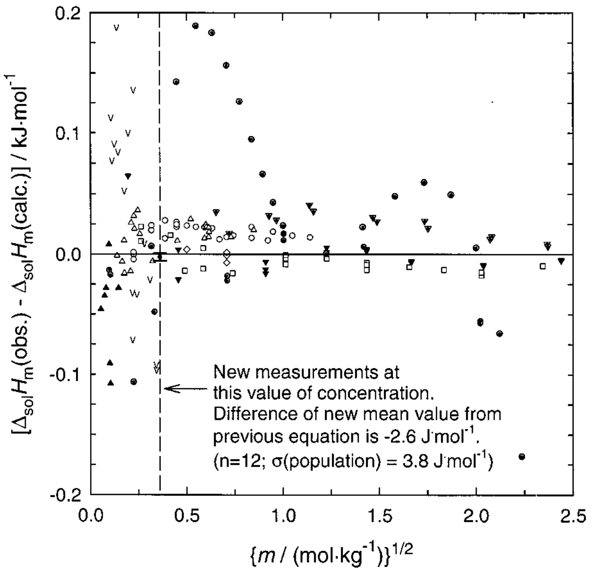

Figure 1. Comparison of measured enthalpies of solution to values calculated from the equations given by Archer.[1] The differences of the new measurements are shown as a solid circle with an associated error bar. That error bar is 1 standard deviation of the population.

Table 2. Enthalpy of Solution of K_2SO_4 in H_2O

T(ITS-90)	m	$\Delta_{sol}H_m$(obs)	T(ITS-90)	m	$\Delta_{sol}H_m$(obs)
K	mol·kg^{-1}	J·mol^{-1}	K	mol·kg^{-1}	J·mol^{-1}
298.1503	0.038 72	24773.4	303.1594	0.038 32	23093.1
298.1663	0.038 42	24737.6	303.1334	0.038 46	23056.4
298.1578	0.039 40	24770.4	303.1376	0.038 17	23109.2
298.2248	0.039 78	24758.0	303.1426	0.038 22	23087.7
298.1807	0.038 62	24788.1	303.1579	0.038 99	23076.1
298.1766	0.040 24	24798.6	303.1592	0.038 66	23092.3
298.1682	0.039 59	24773.9	303.1599	0.039 05	23005.9[a]
298.1681	0.039 18	24734.5	303.1514	0.039 01	23071.9

[a] This measurement was excluded from the calculations.

mean value was 1.6 J·mol^{-1}. These measurements therefore establish that values of the enthalpy of solution calculated from this equation of state at 298.15 K were accurate to within 3−4 J·mol^{-1} or about 0.075% to 0.1% of the measured value. Figure 1 shows differences of enthalpy of solution values reported previously in the literature by others, as well as the mean difference of the values reported here. The error bar associated with the present values is the standard deviation of the population. The improvement of the present measurements over those published previously is obvious from the figure.

Measured values of the enthalpy of solution for 303 K and for 308 K were slightly smaller, (−7 and −5) J·mol^{-1}, respectively, than values calculated from the equation of state. These differences were not statistically significant when compared to the standard deviation of the means at a $p = 0.1$ level. If the differences are, in fact, real, then the −6 J·mol^{-1} difference would be consistent with a bias of only −0.5 J·K^{-1}·mol^{-1} in the calculated values of $C_{p,\phi}$, for a nominal concentration of 0.13 mol·kg^{-1}. This bias is well below that expected from the uncertainties of individual measurements of the heat capacity of a solution of sodium chloride for this composition (see, for example, Figure 12 of Archer[1]).

No statistically significant difference was found for sodium chloride samples taken from the sample of optical crystals when compared to that from the Mallinckrodt sample ($p = 0.1$; t-test).

The subset of enthalpy of solution measurements that had been published previously,[9] as well as other recently determined thermodynamic properties, was included in a revision to the 1992 equations for the NaCl + H_2O system that was published elsewhere by Archer and Carter.[10]

The measured enthalpies of solution for potassium sulfate at nominal temperatures of 298.15 K and 303.15 K are given in Table 2. On the basis of the temperature uncertainty discussed above, these measurements are expected to be precise to ±0.1%, or better, and their mean value will be more accurate than this. The uncertainty of these measurements is discussed further below.

Treatment of the Thermodynamic Data for the K_2SO_4 + H_2O System

K_2SO_4(cr). A model for the thermodynamic properties of crystalline potassium sulfate is developed here, valid for temperatures from 0 K to ≈857 K. Such an equation was required for inclusion of enthalpies of solution as a function of temperature and for the treatment of the phase-equilibria data for $K_2SO_4(cr) = K_2SO_4(aq)$. A solid−solid-phase transition for K_2SO_4(cr) occurs at 857 K. We have not attempted to model the properties of the hexagonal solid phase that exists between 857 K and the melting temperature, as these temperatures are far outside the range of interest here.

To obtain thermodynamic properties for the range of temperature considered here, previous thermodynamic 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.[8]

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

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

where b was a constant, arbitrarily chosen to be 0.2 for the present case, and where $C_p°$ was 1 J·K^{-1}·mol^{-1} and $T°$ was 1 K. The function $f(T)$ of eq 1 was fitted with a cubic spline using polynomials of the form

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

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 ith 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 $-b$ (−0.2) 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

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

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 integration of eq 3 to obtain enthalpy increments.

Several sets of measurements of the thermal properties of potassium sulfate have been published. These are listed in Table 3. The subambient heat capacity measurements

Table 3. Sources of Literature Data for K_2SO_4(cr)

ref	type	temp range	n^a	$\sigma_{fit}{}^b$	$\delta_{fit}{}^c$
11	C_p	52.7−295.4 K	29	0.37	−0.26
12	C_p	12.5−299.5 K	78	0.50	0.11
13	$H_T - H_{T_r}$	462−809 K	5	0.81	0.80
14	C_p	298.5−773.7 K	30	0.41	0.25
15	$H_T - H_{T_r}$	394−814 K	5	0.40	−0.23
16	$H_T - H_{T_r}$	457−852 K	21	0.49	−0.26
17	$H_T - H_{T_r}$	774.4−853.8 K	21	0.40	0.24

[a] Number of measurements in the data set. [b] The root-mean-square percentage deviation from the fitted equation for the data set. [c] The average percentage deviation from the fitted equation for the data set.

Table 4. Least-Squares Estimated Knot Positions for K_2SO_4(cr)

T_i, K	d_i	T_i, K	d_i
0	19.4108	200	1.6726
10	12.2271	300	−0.9805
20	7.9149	500	−7.8908
30	6.0854	700	−17.3781
50	4.4507	950	−42.4474
100	3.3082		

from Moore and Kelley[11] and from Paukov[12] were both weighted as though they had square roots of the variance (srv's) of ±1%. The high-temperature enthalpy increment measurements from Shomate and Naylor,[13] Dworkin and Bredig,[16] and Rubinchik et al.[17] were weighted as though they had srv's of ±400 J·mol^{-1}. The enthalpy increment measurements from Denielou et al.[15] were obtained with a Bunsen ice calorimeter. They gave values of the enthalpy relative to 0 K presumably calculated from their measurements and a value of $H_{T=274K} - H_{T=0K}$ taken from elsewhere. We calculated the differences of their tabulated values to obtain $H_T - H_{T=274K}$, supposing that these calculated values would be more representative of the quantities that they actually measured. We assigned to these values a weighting factor calculated as though their measurements were characterized by a srv of ±100 J·mol^{-1}. The high temperature heat capacity measurements from Shmidt[14] were assumed to be consistent with a srv of ±0.5%. The representation of the measured values required 12 variable knots. The optimized knot positions are given in Table 4. Calculated thermodynamic properties for K_2SO_4(cr) are given in Table 5.

Table 5. Calculated Thermodynamic Properties of K_2SO_4(cr)

T	$C_{p,m}$	$H_m(T) - H_m(0\ K)$	S_m
K	J·K^{-1}·mol^{-1}	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
5	0.023	0.000	0.007
10	0.347	0.001	0.087
15	1.758	0.005	0.445
20	4.73	0.021	1.320
25	9.34	0.055	2.840
30	15.30	0.117	5.053
35	22.01	0.210	7.910
40	28.84	0.337	11.296
45	35.36	0.497	15.07
50	41.42	0.690	19.12
55	47.05	0.911	23.33
60	52.23	1.159	27.65
65	56.93	1.432	32.02
70	61.15	1.728	36.40
75	64.93	2.043	40.75
80	68.32	2.377	45.05
85	71.36	2.726	49.28
90	74.11	3.090	53.44
95	76.64	3.467	57.52
100	78.99	3.856	61.51
110	83.32	4.668	69.24
120	87.26	5.521	76.66
130	90.86	6.412	83.79
140	94.19	7.337	90.65
150	97.29	8.295	97.26
160	100.20	9.282	103.63
170	102.95	10.298	109.79
180	105.57	11.341	115.75
190	108.09	12.409	121.52
200	110.51	13.502	127.13
220	115.15	15.760	137.88
240	119.53	18.107	148.09
260	123.69	20.539	157.82
280	127.62	23.053	167.13
298.15	131.00	25.400	175.26
300	131.33	25.643	176.07
350	139.76	32.425	196.96
400	147.21	39.602	216.12
450	153.92	47.133	233.85
500	160.07	54.985	250.39
550	165.88	63.135	265.92
600	171.56	71.571	280.60
650	177.50	80.294	294.56
700	185.06	89.348	307.97
800	210.83	109.001	334.18
850	229.34	119.994	347.50

The root-mean-square (rms) percentage deviation and the average percentage deviation from the fitted equation for each data set are given in Table 3. Figure 2 shows the percentage deviations of the measured values from the fitted equation, where they can be seen to be distributed evenly about the equation. The *NIST Chemistry WebBook*[18] gave equations for the thermodynamic properties of K_2SO_4(cr) valid for $T \geq 300$ K. We calculated differences of the measured values from the relevant equation given in the *NIST Chemistry WebBook* and show these in Figure 3, where open circles represent heat capacity measurements and filled circles represent enthalpy increment measurements relative to either (298 or 273) K. It can be seen that there are significant systematic biases of the *WebBook* equation from the measurements. These biases become particularly severe for heat capacities above 700 K and for enthalpies above 750 K. The heat capacities calculated from the present equation are shown in Figure 4. Also shown in that figure are some measured values of heat capacity and values calculated from the *NIST Chemistry WebBook* equation. The present equation depends also on the representation of enthalpy increments to the solid−solid-phase transition that cannot be shown in Figure 4. The enthalpy increment measurements are also consistent with the nonlinear behavior of the heat capacity observed above 700

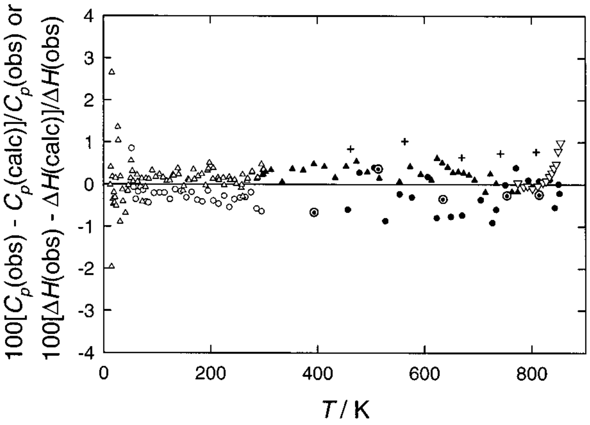

Figure 2. Differences of measured enthalpy increments or heat capacities from the fitted equation. The symbols are as follows: ○, Moore and Kelley;[11] △, Paukov;[12] +, Shomate and Naylor;[13] ▲, Shmidt;[14] ●, Dworkin and Bredig;[16] ▽, Rubinchik et al.;[17] ⊙, Denielou et al.[15]

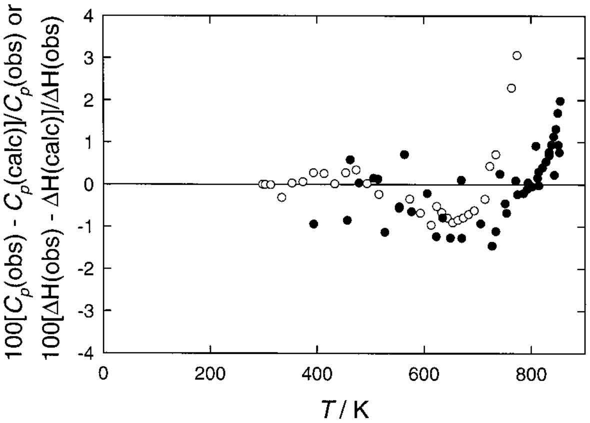

Figure 3. Differences of the measured values from the equation given in the *NIST Chemistry WebBook*.[18] Heat capacity values are shown as open circles. Enthalpy increments relative to 298 K are shown as solid circles.

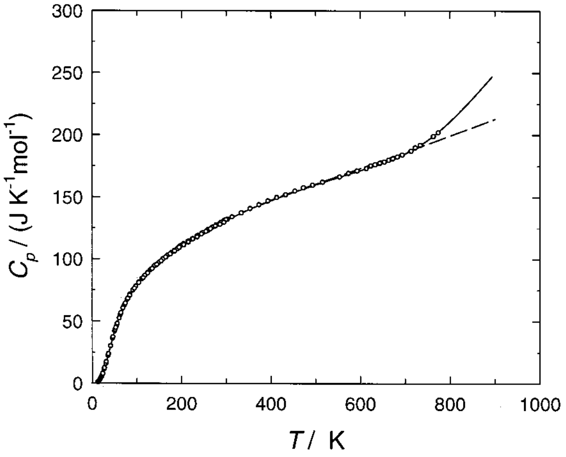

Figure 4. Calculated and measured values of the heat capacity of orthorhombic K_2SO_4(cr). The solid line was calculated from the new equation given here. The dashed line was calculated from the equation given in the *NIST Chemistry WebBook*.[18]

K. Figure 4 shows the source of the misrepresentation of the measured values by the *WebBook* equation. The measured heat capacity and enthalpy increments show an increasing positive curvature over the temperature range 700 K to 857 K as the solid−solid-phase transition is approached, but the *WebBook* equation remains nearly linear in this region. Similar behavior was observed for the tabulated values for K_2SO_4(cr) given by Chase et al.[19]

K_2SO_4(aq) and Phase Equilibria. Because the model is essentially that used previously,[1,10] only a brief description is given here. We have used Archer's extension of Pitzer's ion-interaction model; that is, there is an inclusion of the ionic strength dependence of the third virial coefficient to Pitzer's equation so as to improve representation of the experimental results. The fitted equation for the excess Gibbs energy is

$$\frac{G^{\mathrm{ex}}}{n_{\mathrm{w}}RT} = -4|z_{\mathrm{M}}z_{\mathrm{X}}|A_{\phi}\ln\{1 + b(I/m°)^{1/2}\} + 2\nu_{\mathrm{M}}\nu_{\mathrm{X}}\{(m/m°)^2B_{\mathrm{MX}} + (m/m°)^3\nu_{\mathrm{M}}z_{\mathrm{M}}C_{\mathrm{MX}}\} \quad (4)$$

where

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + 2\beta^{(1)}_{\mathrm{MX}}[1 - \{1 + \alpha(I/m°)^{1/2}\} \times \exp\{-\alpha(I/m°)^{1/2}\}]/\{\alpha^2(I/m°)\} \quad (4a)$$

and

$$C_{\mathrm{MX}} = C^{(0)}_{\mathrm{MX}} + 4C^{(1)}_{\mathrm{MX}}[6 - \{6 + 6\alpha_2(I/m°)^{1/2} + 3\alpha_2^{\,2}(I/m°) + \alpha_2^{\,3}(I/m°)^{3/2}\}\exp\{-\alpha_2(I/m°)^{1/2}\}]/\{\alpha_2^{\,4}(I/m°)^2\} \quad (4b)$$

where $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $C^{(0)}_{\mathrm{MX}}$, and $C^{(1)}_{\mathrm{MX}}$ are adjustable parameters (ion-interaction parameters) that are dependent on temperature and pressure; z_{M} and z_{X} are the charges of the cation and the anion, respectively; b was chosen to be a constant, 1.2 $\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$; ν_{M} and ν_{X} are the stoichiometric numbers of cations and anions formed upon dissociation, respectively; α_1 and α_2 were taken to be 2.0 $\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$ and 2.5 $\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$, respectively; and n_{w} is the number of kilograms of water. A_{ϕ} 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[20] and the dielectric-constant equation from Archer and Wang.[21] Appropriate derivatives of eq 4 give other thermodynamic properties. These additional equations can be found elsewhere[1,10] and are not reproduced here. The adjustable parameters $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $C^{(0)}_{\mathrm{MX}}$, and $C^{(1)}_{\mathrm{MX}}$ were assumed to be linear combinations of functions of temperature as

$$\beta^{(0)}_{\mathrm{MX}} = f(1,p,T)/m° \quad (5)$$

$$\beta^{(1)}_{\mathrm{MX}} = f(2,p,T)/m° \quad (6)$$

$$C^{(0)}_{\mathrm{MX}} = f(3,p,T)/m^{\circ 2} \quad (7)$$

$$C^{(1)}_{\mathrm{MX}} = f(4,p,T)/m^{\circ 2} \quad (8)$$

where

$$f(i,p,T) = [b_{i,1} + b_{i,2}T/(1000\ \mathrm{K}) + b_{i,3}\{T/(500\ \mathrm{K})\}^2 + b_{i,4}T°/(T - 215\ \mathrm{K}) + b_{i,5}200(T°/T)^2 + b_{i,6}\{T/(500\ \mathrm{K})\}^3 + b_{i,7}(1 \times 10^{-5})(p/p°) + b_{i,8}(2 \times 10^{-4})(p/p°)\{T°/(T - 225\ \mathrm{K})\} + b_{i,9}(1 \times 10^{-5})(p/p°)\{T/(500\ \mathrm{K})\} + b_{i,10}(2 \times 10^{-4})(p/p°)\{T°/(650\ \mathrm{K} - T)\} + b_{i,11}(1 \times 10^{-7})(p/p°)^2 + b_{i,12}(2 \times 10^{-6})(p/p°)^2\{T°/(T - 225\ \mathrm{K})\} + b_{i,13}(4 \times 10^{-2})(p/p°)\{T°/(T - 225\ \mathrm{K})\}^2 + b_{i,14}(1 \times 10^{-5})(p/p°)\{T/(500\ \mathrm{K})\}^2 + b_{i,15}(2 \times 10^{-8})(p/p°)^3\{T°/(T - 225\ \mathrm{K})\}] \quad (9)$$

The functional forms for the apparent molar heat capacity and volume of the solute, $C_{\mathrm{p},\phi}°$ and $V_{\phi}°$, respectively, were

$$C_{\mathrm{p},\phi}°/C_{\mathrm{p}}° = c_1 + c_2T°/(T - 228\ \mathrm{K}) + c_3(T/300\ \mathrm{K}) + c_4(T/300\ \mathrm{K})^2 + c_5[T°/(647\ \mathrm{K} - T)]^2 \quad (10)$$

$$V_{\phi}°/V° = d_1 + d_2(p/p°) + d_3T°/(647\ \mathrm{K} - T) + d_4(p/p°)(T/T°)/(3 \times 10^5) + d_5(p/p°)T°/(647\ \mathrm{K} - T) + d_6(100\ \mathrm{K}/T) \quad (11)$$

where $C_{\mathrm{p}}°$ and $V°$ were 1 $\mathrm{kJ}\cdot\mathrm{mol}^{-1}\cdot\mathrm{k}^{-1}$ and 1 $\mathrm{dm}^3\cdot\mathrm{mol}^{-1}$. Literature sources of measured properties of K_2SO_4(aq) and measured solubilities are given in Table 6. Included in Table 6 for each set of measurements are the type of measurement, the concentration and temperature ranges for the data set, the number of observations, the expected

Table 6. Literature Sources for the Thermodynamic Properties of K_2SO_4(aq)

ref	temp range, K	molality range, mol·kg^{-1}	n[a]	type	σ_{est}[b]	σ_{fit}[c]	δ_{fit}[d]
22	298.15	0.54	1	ϕ	U	0.008	0.008[e]
23	298.15	0.22−0.48	10	ϕ	U	0.068	0.067[e]
24	383−498	0.56−2.36	56	ϕ	0.004	0.0052	0.0005[e]
25	298.15	0.07−0.62	7	ϕ	U	0.024	0.015[e]
26	298.15	0.433−0.62	3	ϕ	U	0.008	0.000[e]
27	298.15	0.1−0.69	21	ϕ	0.002	0.0024	0.0010[e]
28	298.15−308.15	0.25−0.59	4	p_s	U	0.047	−0.0099[e]
29	298.15	0.1−0.69	5	$p_s - p_w$	U	0.020	−0.016[e]
30	292−325	m_{sat}	9	p_{sat}	U	0.154	0.150[e]
31	T_{fus}	0.28−0.40	2	$\Delta_{fus}T$	0.5 K	0.049	−0.002[f]
32	T_{fus}	0.1−0.45	6	$\Delta_{fus}T$	U	0.061	0.054[f]
33	T_{fus}	0.003−0.41	25	$\Delta_{fus}T$	0.002 K	0.0097	−0.0058[f]
34	T_{fus}	0.001−0.01	7	$\Delta_{fus}T$	0.001 K	0.014	−0.009[f]
35	T_{fus}	0.003−0.12	8	$\Delta_{fus}T$	0.001 K	0.0052	0.0012[f]
36	T_{fus}	0.05−0.32	5	$\Delta_{fus}T$	0.01 K	0.010	0.009[f]
37	T_{fus}	0.025−0.35	15	$\Delta_{fus}T$	0.003 K	0.0024	−0.0008[f]
38	T_{fus}	0.001−0.011	12	$\Delta_{fus}T$	0.001 K	0.0051	0.0026[f]
39	T_{fus}	0.001−0.09	20	$\Delta_{fus}T$	U	0.015	0.012[f]
40	298.15	0.06−0.65	9	ΔL_ϕ	U	0.119	−0.089[g]
41	373.15	0.0025−0.66	8	ΔL_ϕ	*h*	0.067	−0.035[g]
41	423.65	0.007−0.66	11	ΔL_ϕ	*h*	0.095	−0.051[g]
42	303.15	0.12−0.56	4	ΔL_ϕ	0.01	0.032	0.002[g]
43	298.15	0.02−0.94	22	ΔL_ϕ	0.1	0.130	−0.102[g]
43	323.15	0.01−1.16	23	ΔL_ϕ	U	1.70	1.68[g]
44	298.15	0.67−0.08	3	ΔL_ϕ	0.1	0.108	0.108[g]
45	298.15	1.7×10^{-4} to 0.1	59	ΔL_ϕ	0.02	0.020	0.004[g]
46	273−294	5×10^{-4} to 0.5	18	ΔL_ϕ	0.1	0.112	0.055[g]
present work	298.15	0.039	8	$\Delta_{sol}H_m$	0.01	0.022	−0.006[g]
present work	303.15	0.039	7	$\Delta_{sol}H_m$	0.01	0.019	0.007[g]
47	298.15	0	1	$\Delta_{sol}H_m$	U	8.9	8.9[g]
43	298.15	0.02−0.12	5	$\Delta_{sol}H_m$	U	0.061	0.033[g]
43	323.15	0.03−0.1	5	$\Delta_{sol}H_m$	U	5.1	5.1[g]
48	298.15	0.11	1	$\Delta_{sol}H_m$	U	0.048	0.048[g]
49	298.15	∼0.07	3	$\Delta_{sol}H_m$	U	0.11	−0.011[g]
50	298.15	∼0.07	1	$\Delta_{sol}H_m$	U	0.36	0.36[g]
51	298.15	∼0.14	1	$\Delta_{sol}H_m$	U	0.026	0.026[g]
44	293.15−298.15	0.07−0.52	31	$\Delta_{sol}H_m$	0.1	0.082	0.036[g]
52	293.15	0.14	1	$\Delta_{sol}H_m$	U	0.083	−0.083[g]
additivity	398.15−498.15	0	5	$C_{p,\phi}$	0.05	0.022	0.004[i]
53	298.15−373.15	0.03−0.4	22	$C_{p,\phi}$	$0.004 m_L = 0.05$	0.0071	−0.0013[i]
54	298.15	0.04−0.5	8	$C_{p,\phi}$	0.004	0.0008	0.0005[i]
55, 56	298.15	0.013−0.33	8	$C_{p,\phi}$	$0.004 m_L = 0.05$	0.006	−0.002[i]
57	298.15	0.05−0.65	6	$C_{p,\phi}$	$0.002 m_L = 0.4$	0.0027	−0.0018[i]
58	299−366	m_s	7	m_s	U	0.079	0.076[j]
59	273.6−374.3	m_s	8	m_s	0.01	0.037	−0.002[j]
60	298.15	m_s	1	m_s	0.005	0.009	0.009[j]
61	298.15−323.15	m_s	2	m_s	0.005	0.024	0.024[j]
62	298.15	m_s	1	m_s	0.005	0.047	0.047[j]
63	298.15	m_s	1	m_s	0.005	0.012	0.012[j]
64	358.15−373.15	m_s	3	m_s	0.005	0.029	0.027[j]
65	348.15	m_s	1	m_s	0.005	0.024	0.024[j]
66	273.2−348.2	m_s	4	m_s	0.005	0.019	0.008[j]
67	298.15	m_s	1	m_s	0.005	0.027	0.027[j]
68	452−562	m_s	7	m_s	0.005	0.099	−0.038[j]
69	298.15	m_s	1	m_s	0.005	0.003	0.003[j]
32	284.75−308.2	m_s	8	m_s	U	0.25	0.23[j]
31	271.6−333.2	m_s	9	m_s	0.0025	0.031	0.020[j]
70	283.7−323.2	m_s	13	m_s	0.0025	0.024	−0.008[j]
71	298.15	0.015−0.34	10	$\rho_s - \rho_w$	20×10^{-6}	25×10^{-6}	-17×10^{-6} [k]
72	298.15	5×10^{-4} to 0.5	11	ρ_s/ρ_w	20×10^{-6}	14×10^{-6}	12×10^{-6} [k]
72	273.15	5×10^{-4} to 0.3	10	ρ_s/ρ_w	50×10^{-6}	165×10^{-6}	105×10^{-6} [k]
73	285.65−315.65	0.0025−0.09	42	ρ_s/ρ_w	U	107×10^{-6}	34×10^{-6} [k]
74	298.15	0.21−0.51	3	ρ_s/ρ_w	20×10^{-6}	9×10^{-6}	1×10^{-6} [k]
74	298.15	0.001−0.009	4	V_ϕ	0.05	0.06	−0.004[l]
75	303−523	0.066−0.41	180	ρ_s	$(1-2) \times 10^{-3}$[l]	0.97×10^{-3}	0.41×10^{-3} [k]
76	323.15−473.15	0.05−0.5	28	ρ_s	1×10^{-3}	3.7×10^{-4}	1.6×10^{-4} [k]
70	303−333	0.71−1.02	6	ρ_s	5×10^{-4}	2.66×10^{-4}	1.19×10^{-4} [k]
53	297−373	0.03−0.4	23	$\rho_s - \rho_w$	1×10^{-4}	2.07×10^{-4}	-1.59×10^{-4} [k]
54	298.15	0.04−0.5	9	V_ϕ	0.4	0.07	−0.03[l]
77	278−368	0.01−0.65	86	$\rho_s - \rho_w$	50×10^{-6} or 0.1%[m]	69×10^{-6}	-5.8×10^{-6} [k]
78	298−517	0.005−0.5	99	$\rho_s - \rho_w$	1×10^{-4}	1.62×10^{-4}	-0.48×10^{-4} [k]
79	298.15	1×10^{-4} to 0.5	12	ρ_s/ρ_w	20×10^{-6}	14×10^{-6}	-11×10^{-6} [k]
80	298.15	0.03−0.64	8	ρ_s/ρ_w	20×10^{-6}	16×10^{-6}	2.3×10^{-6} [k]
75	298.15	0.005−0.33	15	$\rho_s - \rho_w$	50×10^{-6}	21×10^{-6}	2.5×10^{-6} [k]

[a] n is the number of observations. [b] σ_{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. In the cases where a value is given for m_L, the expected square root of the variance is taken to be the first of the two given values for $m > m_L$ and taken to be the first value multiplied by (m_L/m) for $m < m_L$. [c] σ_{fit} is the rms deviation of the measurements from the model. [d] δ_{fit} is the average deviation of the measurements from the model. [e] Values of σ_{est}, σ_{fit}, δ_{fit} are given in terms of the osmotic coefficient. [f] Values of σ_{est} used in the program were calculated as the uncertainty in osmotic coefficient due to the value of σ_{est} given in K. σ_{fit} and δ_{fit} are given in terms of osmotic coefficient. [g] Values of σ_{est}, σ_{fit}, and δ_{fit} are given in kJ·mol^{-1}. [h] Values of σ_{est} were taken to be those given in ref 41 or 0.03 kJ·mol^{-1}, whichever was larger. [i] Values of σ_{est}, σ_{fit}, and δ_{fit} are given in kJ·K^{-1}·mol^{-1}. [j] σ_{est} was calculated on the basis of the tabulated value for solubility in mol·kg^{-1}. σ_{fit} and δ_{fit} are given in terms of the Gibbs energy of solution and have units of kJ·mol^{-1}. [k] Values of σ_{est}, σ_{fit}, and δ_{fit} are given in g·cm^{-3}. [l] Values of σ_{est}, σ_{fit}, and δ_{fit} are given in cm^3·mol^{-1}. [m] Values of σ_{est} were calculated from either 50×10^{-6} g·cm^{-3} or 0.1% of $\rho_s - \rho_w$, whichever was larger. σ_{fit} and δ_{fit} are given in g·cm^{-3}.

Table 7. Least-Squares Estimated Parameters for Eqs 4−11[a]

parameter	value	parameter	value	parameter	value
$b_{1,1}$	−5.283 835 383 801 49	$b_{2,1}$	13.776 547 872 443 4	$b_{3,1}$	$9.495\ 875\ 471\ 816\ 362 \times 10^{-2}$
$b_{1,2}$	25.577 355 440 560 5	$b_{2,2}$	−46.423 797 918 140 3	$b_{3,2}$	−0.420 385 295 650 703
$b_{1,3}$	−11.203 499 241 484 7	$b_{2,3}$	12.244 340 593 950 8	$b_{3,3}$	0.108 976 551 235 173
$b_{1,4}$	−20.562 653 212 511 6	$b_{2,4}$		$b_{3,4}$	
$b_{1,5}$	507.480 290 994 979	$b_{2,5}$	−1576.094 447 795 65	$b_{3,5}$	
$b_{1,6}$	3.505 640 464 703 90	$b_{2,6}$		$b_{3,6}$	
$b_{1,7}$	−3573.674 567 645 65	$b_{2,7}$		$b_{3,7}$	104.278 445 868 054
$b_{1,8}$	8796.579 055 713 49	$b_{2,8}$		$b_{3,8}$	−771.946 818 023 454
$b_{1,9}$	5491.037 299 094 07	$b_{2,9}$		$b_{3,9}$	
$b_{1,10}$		$b_{2,10}$		$b_{3,10}$	
$b_{1,11}$	141.848 167 150 139	$b_{2,11}$		$b_{3,11}$	
$b_{1,12}$	−611.369 490 639 860	$b_{2,12}$		$b_{3,12}$	
$b_{1,13}$	−1070.675 463 179 36	$b_{2,13}$		$b_{3,13}$	
$b_{1,14}$	−2737.674 906 382 54	$b_{2,14}$		$b_{3,14}$	
$b_{4,1}$		c_1	7.111 809 993 395 58	$\Delta_{\mathrm{sol}}GT_{\mathrm{r}},p_{\mathrm{r}}{}^{\circ}$	10.1717 ± 0.0327 $\mathrm{kJ{\cdot}mol^{-1}}$
$b_{4,2}$	1.442 290 864 222 74	c_2	−76.827 505 556 371 8	$S_{\mathrm{MgK_2SO_4(aq)},T_{\mathrm{r}},p_{\mathrm{r}}}{}^{\circ}$	220.82 ± 0.11 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$
$b_{4,3}$		c_3	−9.795 784 395 271 77		
$b_{4,4}$		c_4	3.793 578 946 437 26		
$b_{4,5}$		c_5	−35 202.713 791 727		
$b_{4,6}$					
$b_{4,7}$	18 299.331 461 325 3	d_1	0.235 843 914 353 712		
$b_{4,8}$	−106 325.081 936 061	d_2	$2.595\ 182\ 668\ 934\ 208 \times 10^{-4}$		
$b_{4,9}$		d_3	−30.509 553 088 250 9		
$b_{4,10}$		d_4	−1.279 265 877 959 52		
$b_{4,11}$		d_5	0.390 129 931 240 221		
$b_{4,12}$		d_6	−0.346 851 747 681 157		
$b_{4,13}$					
$b_{4,14}$					
$b_{4,15}$					

[a] The volume of the crystal phase was taken to be 65.46 $\mathrm{cm^3\ mol^{-1}}$. The ± values are 95% confidence intervals within the global data representation.

Table 8. Calculated Values of A_{ϕ}, $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $C^{(0)}_{\mathrm{MX}}$ and $C^{(1)}_{\mathrm{MX}}$

T, K	p, MPa	A_{ϕ}, $\mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$	$\beta^{(0)}_{\mathrm{MX}}$, $\mathrm{kg{\cdot}mol^{-1}}$	$\beta^{(1)}_{\mathrm{MX}}$, $\mathrm{kg{\cdot}mol^{-1}}$	$10^2C^{(0)}_{\mathrm{MX}}$, $\mathrm{kg^2{\cdot}mol^{-2}}$	$C^{(1)}_{\mathrm{MX}}$, $\mathrm{kg^2{\cdot}mol^{-2}}$
273.15	0.1	0.376 422	−0.062 343 8	0.525 298	1.249 27	0.375 692
298.15	0.1	0.391 476	−0.003 620 3	0.743 026	0.828 868	0.422 744
323.15	0.1	0.410 277	0.030 037 9	0.870 62	0.459 268	0.464 713
348.15	0.1	0.433 068	0.055 493 1	0.949 936	0.142 544	0.504 462
373.15	0.1	0.459 887	0.076 418 9	1.009 32	-0.120 538	0.543 044
423.15	0.5	0.526 809	0.107 220	1.141 56	−0.472 516	0.650 721
473.15	1.6	0.617 107	0.126 556	1.367 70	−0.564 827	0.843 410
498.15	2.6	0.675 215	0.133 535	1.534 18	−0.499 079	0.999 000

Table 9. Calculated Values of $G_{m,2}{}^{\circ} - G_{m,2,T_2}{}^{\circ}$, $C_{p,\phi}{}^{\circ}$, and $V_{\phi}{}^{\circ}$

T, K	p, MPa	$G_{m,2}{}^{\circ} - G_{m,2,T_{\mathrm{r}}}{}^{\circ}$, $\mathrm{kJ{\cdot}mol^{-1}}$	$C_{p,\phi}{}^{\circ}$, $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$	$V_{\phi}{}^{\circ}$, $\mathrm{cm^3{\cdot}mol^{-1}}$
273.15	0.1	5.890	−615.8	27.3
298.15	0.1	0.000	−261.1	32.1
323.15	0.1	−5.293	−181.3	34.3
348.15	0.1	−10.221	−180.7	34.1
373.15	0.1	−14.822	−202.1	31.5
423.15	0.5	−22.984	−252.9	17.7
473.15	1.6	−29.654	−371.0	−12.2
498.15	2.6	−32.332	−545	−36.8

Table 10. Calculated Values of the Osmotic Coefficient, ϕ

		ϕ at the following $m/\mathrm{mol{\cdot}kg^{-1}}$					
T, K	p, MPa	0.1	0.5	1.0	1.5	2.0	2.5
273.15	0.1	0.7721	0.6554	0.6082			
298.15	0.1	0.7801	0.6895	0.6596			
323.15	0.1	0.7782	0.6983	0.6718	0.6770		
348.15	0.1	0.7704	0.6955	0.6693	0.6673		
373.15	0.1	0.7585	0.6852	0.6582	0.6495	0.6516	
423.15	0.5	0.7256	0.6490	0.6184	0.5991	0.5832	0.5659
473.15	1.6	0.6811	0.5961	0.5605	0.5366	0.5162	0.4940
498.15	2.6	0.6532	0.5633	0.5258	0.5030	0.4871	0.4727

uncertainties used to calculate weighting factors, and the rms and average differences of the data set relative to the equation. The least-squares determined parameters are given in Table 7. Tabulated properties for the purpose of testing program code are given in Tables 8−10.

The uncertainty listed in Table 7 for $S_{\mathrm{m},T_{\mathrm{r}},p_{\mathrm{r}}}{}^{\circ}(\mathrm{K_2SO_4(aq)})$ is not truly the uncertainty in that quantity. It is more properly considered as the uncertainty in the entropy of solution of K_2SO_4. This is because the entropy of K_2SO_4(cr) taken from the representation of the properties of the crystal phase, discussed above, appeared in the calculations in combination with the entropy of K_2SO_4(aq) to give $\Delta_{\mathrm{sol}}S_{\mathrm{m}}{}^{\circ}$. The true uncertainty for the standard-state entropy of K_2SO_4(aq) must contain the uncertainty in the entropy of K_2SO_4(cr). Because of the discrepancies in experimental results discussed above, the uncertainty in the entropy of K_2SO_4(cr) is non-negligible.

The upper range of temperature considered for the present representation was limited to 530 K, because of the scarcity of thermodynamic measurements above this temperature and because of additional chemical reactions that will become more significant above 500 K. These additional reactions include the formation of bisulfate in the solution and a significantly increasing extent of ion association.

Agreement of the Representation with the Measured Values. Isopiestic molalities relative to KCl(aq) and NaCl(aq) were converted to osmotic coefficients using consistent reference equations from Archer.[10,81] Freezing-point depressions were converted to osmotic coefficients using the

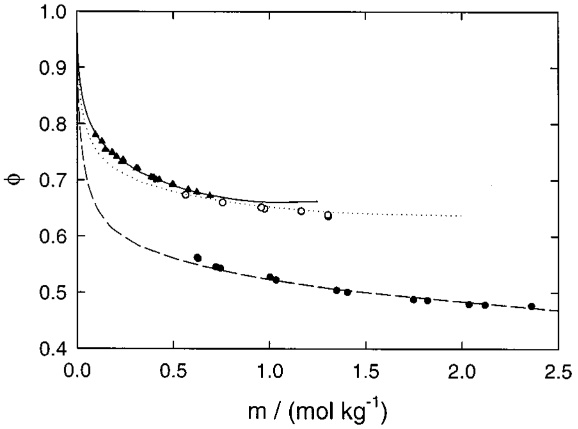

Figure 5. Values of the osmotic coefficient calculated from the present equation, showing extrapolation into the supersaturation region and values obtained from isopiestic vapor pressure measurements. The solid, dotted, and dashed lines are for 298.15 K, 383.14 K, and 498.19 K, respectively. The symbols are as follows: ▲, Robinson and Wilson;[27] ○, 383.14 K, Holmes and Mesmer;[24] ●, 498.19 K, Holmes and Mesmer.[24]

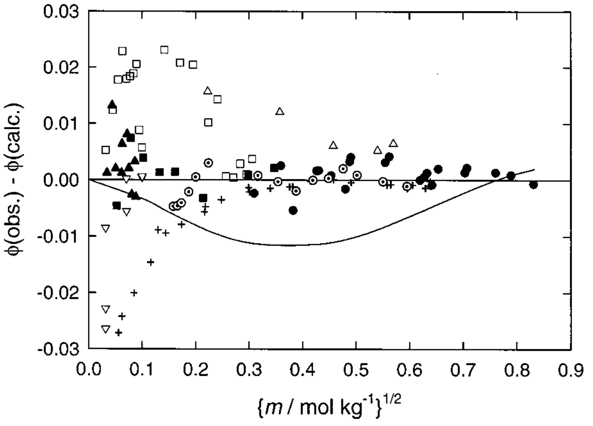

Figure 6. Differences of osmotic coefficient values calculated from measurements from values calculated from the present equation. The symbols are as follows: ●, Robinson and Wilson;[27] ■, Hall and Harkin;[35] △, Rivett;[36] ▽, Hovorka and Rodebush;[34] +, Indelli;[33] ⊙, Archibald;[37] ▲, Osaka;[38] □, Jones.[39] Also shown are calculated differences of the equation from Goldberg[90] from the present equation, shown as a solid line.

equation given by Craft and Van Hook.[82] Osmotic coefficients were calculated from vapor pressure measurements using the equation of state of water.[20] The fitted equation agreed with most of the osmotic coefficients obtained for temperatures from the freezing point of the solution to near 500 K within expected uncertainties. Calculated and observed osmotic coefficient values are shown at three temperatures in Figure 5. Agreement of the osmotic coefficient values for temperatures below 300 K is shown in Figure 6. Figure 6 includes isopiestic determinations at 298.15 K and the results from several freezing-point studies. These are seen to be in good agreement. The recent isopiestic vapor pressure study reported by Todorovic and Ninkovic[23] disagreed quite significantly from the fitted equation and was not included in the fitted database. Their values showed an average deviation of 0.067, in ϕ, from the fitted equation with differences increasing from 0.046 for 0.216 mol·kg^{-1} to 0.089 for 0.48 mol·kg^{-1}. These differences are 20 to 30 times the accepted uncertainty of the method. The measurements of vapor pressure from Fillippov et al.,[28] Pearce and Eckstrom,[29] and Leopold and Johnston[30] and the freezing-point depressions from Jones[39] were not of sufficient accuracy for inclusion in the fitted database. Recent freezing-point depressions from Sirbu[83] were much too large and were considered no further.

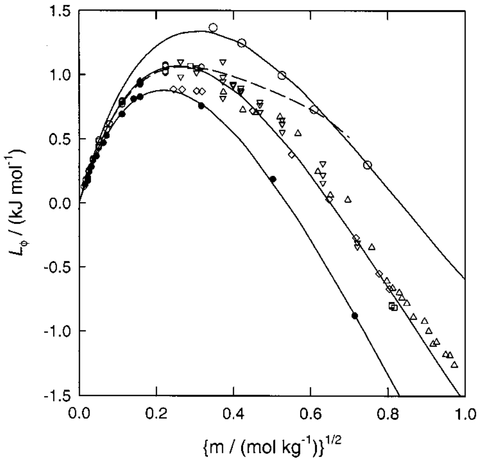

Figure 7. Values of the relative apparent molar enthalpy calculated from the present equations for 294 K, 298.15 K, and 303.15 K. The symbols are for measurements of enthalpies of dilution or of differences in the enthalpy of solution as a function of concentration. The symbols are as follows: ●, 294 K, Plake;[46] ○, Lange and Streeck;[45] □, $\Delta_{dil}H_m$, Mishchenko and Promina (1936); ▽, ($\Delta_{sol}H_m - \Delta_{sol}H_m°$), Mishchenko and Promina;[44] △, Gritsus et al.;[43] ◇, Li et al.;[40] ○, 303.15 K, Leung and Millero.[42] The dashed line was calculated from the equation given by Goldberg.[91]

There is one set of electromotive force measurements, which involved a potassium amalgam electrode.[84] Potassium amalgam electrode cells, measured by several authors, were found to give systematically erroneous values for the activity coefficient of KCl(aq).[81] Therefore, we did not include the values from Åkerlöf[84] in the fitted database because all of their statistical degrees of freedom would have been consumed just in determining whether they possessed systematic bias.

Measured enthalpies of dilution agreed with the fitted equation reasonably well. In accord with Holmes and Mesmer,[85] we rejected the enthalpies of dilution for 323.15 K from Gritsus et al.[43] while accepting their 298.15 K values. Their 298.15 K values extend into the supersaturation region and are in reasonable agreement with the fitted equation, although they are slightly biased from earlier measurements from Mishchenko and Promina[44] and those from Plake[46] and Leung and Millero.[42] Agreement of the measurements and the fitted equation for near-ambient conditions is shown in Figure 7. The recent enthalpies of dilution for 298.15 K from Li et al.[40] showed a systematic bias from the fitted equation and were not included in the fitted database. At higher temperatures, there is some negative bias to the lower molality enthalpy of dilution measurements from Mayrath and Wood,[41] at 423.65 K. This means that the observed values are somewhat more exothermic than those calculated. However, this bias is only about twice the uncertainty given by Mayrath and Wood for these dilutions and so we have not taken the bias as being measurably indicative of unaccounted reactions occurring in the solution at this temperature.

Figure 8 shows calculated and observed heat capacity values for 298.15 K. The observed values are from Randall and Rossini;[57] Perron et al.,[55] corrected according to the information in Desnoyers et al.;[56] and Hovey et al.[54] Olofsson et al.[86] reported having made heat capacity measurements for 298.15 K; but their article did not contain the measured values, only fitted parameters. Their

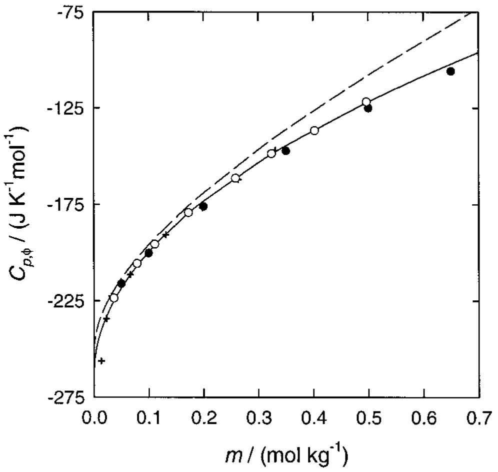

Figure 8. Values of the apparent molar enthalpy calculated from the present equation for 298.15 K, solid line, and values measured. The symbols are as follows: ●, Randall and Rossini;[57] +, Perron et al.,[55] corrected by means of the information given by Desnoyers et al.;[56] ○, Hovey et al.[54] The dashed line was calculated from the equation given by Goldberg.[90]

fitted $C_{p,\phi}°$ was 3 to 4 J·K^{-1}·mol^{-1} more positive than those obtained by Hovey et al.[54] and Desnoyers et al.[56] Saluja et al.[53] reported heat capacity values for temperatures from 298 K to 373 K. The fitted equation showed a rms difference of 7.1 J·K^{-1}·mol^{-1} for the results from Saluja et al., which was considered reasonable. The pattern of residuals for the Saluja heat capacity and density measurements, against molality, showed systematic deviations for the 0.2956 mol·kg^{-1} solution. These errors did not appear to correspond directly to an error in molality determination. We gave the measurements for that composition no weight in the fitting procedure but included them in the calculated statistics for the data sets. Above 373 K, there are no measured values of the heat capacity. We have included in the fitted database values of $C_{p,\phi}°$ calculated at the saturation pressure from

$$C_{p,\phi}°(K_2SO_4) = C_{p,\phi}°(Na_2SO_4) + 2C_{p,\phi}°(KCl) - 2C_{p,\phi}°(NaCl) \quad (12)$$

for the temperatures (398.15, 423.15, 448.15, 473.15, and 498.15) K. To calculate values from eq 12, we used $C_{p,\phi}°$ for NaCl(aq), KCl(aq), and Na_2SO_4(aq) from Archer and Carter,[10] Pabalan and Pitzer,[87] and Pabalan and Pitzer,[88] respectively. There are not heat capacity measurements for either K_2SO_4(aq) or Na_2SO_4(aq) below 298 K. Values of $C_{p,\phi}°(K_2SO_4)$ for temperatures ranging from <298 K to the freezing temperatures of the solutions are therefore extrapolations of the higher temperature behavior.

Several sets of density or apparent molar volume results appear in the literature. We found that representation of room-temperature density results, within the global representation, required inclusion of the pressure derivatives of $\beta^{(0)}_{MX}$, $C^{(0)}_{MX}$, and $C^{(1)}_{MX}$. This was due, in some part, to inclusion of density measurements for concentrations as large as 1.1 mol·kg^{-1} near 333 K. Figure 9 shows differences of measured densities from the fitted equation for several sets of measurements at room temperature. One consideration here is representation of the solid−solution solubility. At higher temperatures, volumetric properties affect the location of this equilibrium, which occurs for concentrations from (1.4 to >2) mol·kg^{-1} for temperatures above 373 K. Therefore, functions were chosen so as not to diverge wildly outside the region of measurements, which extends only to 0.5 mol·kg^{-1} for temperatures above 373 K.

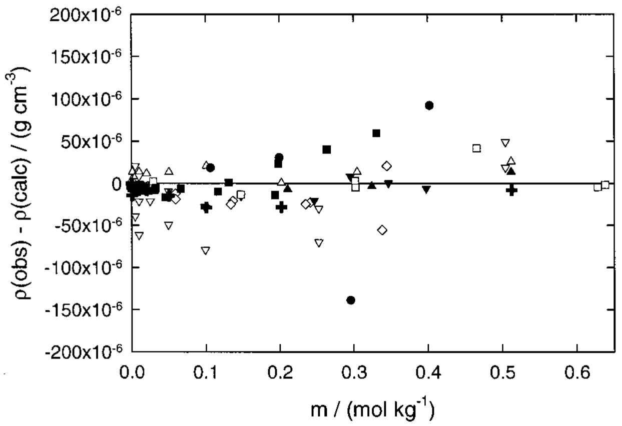

Figure 9. Differences of measured density values from the fitted equation for temperatures near 298.15 K. The symbols are as follows: □, Adams;[80] ◇, Wirth;[71] +, Jones and Ray;[79] △, Jones and Colvin;[72] ▲, Dunn;[74] ■, Perron et al.;[55] ▼, Dedick et al.;[77] ●, Saluja et al.;[53] ▽, 10 MPa, Obsil et al.[78]

We rejected several measurements from the density data set reported by Dedick et al.[77] These included all of the measurements reported for 328.15 K and also several of the lower molality points at various concentrations. The recent measurements over wide ranges of temperature and pressure from Obsil et al.[78] and from Azizov[75] are systematically biased from each other at high temperatures. In the Obsil et al. data set, we deweighted the two measurements reported for 450.07 K, 10 MPa, and 0.5 mol·kg^{-1}, because these two observations showed deviations about 5 to 10 times that for the other observations.

The principal enthalpies of solution that were given weight in the least-squares procedure were the presently reported values. We also gave some weight to the enthalpies of solution reported by Mishchenko and Promina[44] only because they were determined over a significant concentration range at 298.15 K and therefore helped define the relative apparent molar enthalpy at 298.15 K. Other values were not included because the high degree of accuracy of the present measurements precludes the inclusion of values that may possess significant systematic biases. Comparison of measured enthalpies of solution to the fitted equation, for the present measurements and others reported previously, is shown in Figure 10. The significant improvement in precision of the present measurements compared to the earlier values is quite evident. The rms difference of the present measurements from the fitted equation was 20 J·mol^{-1} or approximately 0.08% of the measured quantity. The values for 298 K and 303 K are biased by (−6 and +7) J·mol^{-1}, respectively (approximately 0.03% of the measured values). This biasing corresponds to an uncertainty of 2.6 J·K^{-1}·mol^{-1} in the quantity $C_{p,\phi}$(0.039 mol·kg^{-1}) − $C_{p,m}$(crystal). From the examination of the crystal property data, the minimum uncertainty in $C_{p,m}$(crystal) at 298.15 K is ±0.8 J·K^{-1}·mol^{-1}. The minimum uncertainty in $C_{p,\phi}$(0.039 mol·kg^{-1}) is on the order of ±(2 to 3) J·K^{-1}·mol^{-1}, based upon the present work and upon previous examinations of the uncertainties obtained from calorimetry of the types that were used previously for K_2SO_4(aq), for example, that found in ref 1. The combination of these two latter minimum uncertainties, (2.8 to 3.8) J·K^{-1}·mol^{-1}, is comparable to the small biasing of the present measured enthalpies of solution.

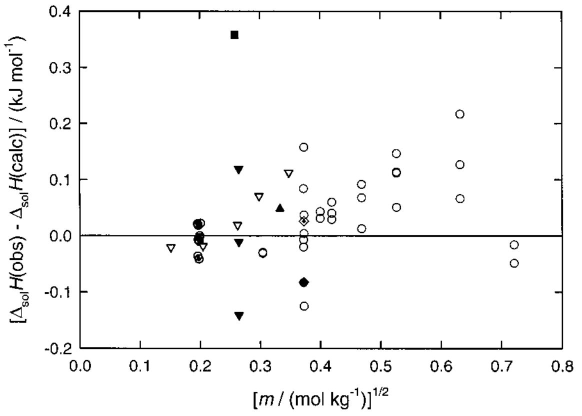

Figure 10. Differences of measured enthalpies of solution from the fitted equation. The symbols are as follows: ⊙, present work, nominal temperatures 298.15 K and 303.15 K; ◆, Cohen and Kooy,[52] 293.15 K; ○, Mishchenko and Promina,[44] 293.15 K and 298.15 K; plus in a diamond, Colomina Barbera,[51] 293.15 K; ▼, Romanova and Samoilov,[49] 298.15 K; ▲, Tsvetkov and Rabinovich,[48] 298.15 K; ▽, Gritsus et al.,[43] 298.15 K; □, Kapustinskii and Samoilov,[50] 298.15 K.

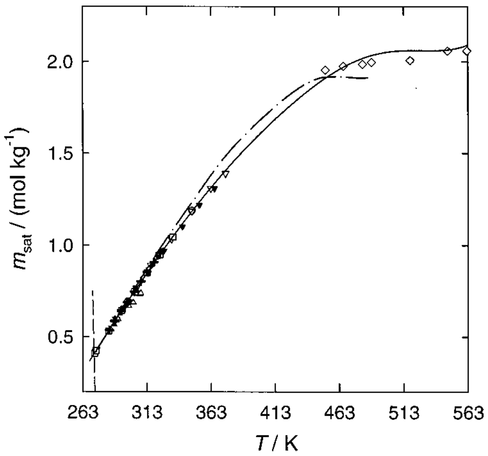

Figure 11. Solubility of potassium sulfate against temperature. The solid line represents potassium sulfate solubility calculated from the present equation. The dashed line is the ice freezing line. The dash−dot line represents values that Pabalan and Pitzer[2] calculated from previously tabulated thermodynamic properties. The symbols are measured solubility values from the following references: ▽, Berkeley;[59] ●, Leopold and Johnston;[30] ○, Schroeder and Schlackman;[66] ◇, Benrath et al.;[68] △, Shul'gina et al.;[32] □, Holmberg;[31] +, Ishii and Fujita;[70] ▼, Potter and Clynne.[58]

Comparison of calculated and measured solubility values is shown in Figure 11. Agreement is very reasonable for the entire fitted region, <500 K, and also for extrapolation to about 563 K. The invariant equilibrium $K_2SO_4(cr) + K_2SO_4(aq) + H_2O(cr) + H_2O(g)$ was calculated to exist at 271.64 K and 0.405 mol·kg^{-1}. This compares well with the values given by Holmberg,[31] namely, 271.56 K and 0.3976 mol·kg^{-1}. The values tabulated by Linke,[89] 271.25 K and 0.451 mol·kg^{-1}, were essentially the values reported by Shul'gina et al.[32] as a metastable equilibrium. We did not include Shul'gina et al.'s solubility determinations in the fitted database because they disagreed with all of the other solubility measurements and the other thermodynamic measurements, including the enthalpy of solution. Shul'gina et al. asserted that the invariant equilibrium involving K_2SO_4(cr) was a metastable one because they believed they had identified a monohydrate phase as the stable phase below 282.85 K. However, Holmberg,[31] Schroeder and Schlackman,[66] and Berkeley[59] did not observe the formation of a monohydrate in their solubility measurements for temperatures below 282 K. If a monohydrate phase does exist at these temperatures, the solubility measurements from Shul'gina et al. are too inaccurate, as evidenced by his solubility determinations for the anhydrous crystal, to define its thermodynamic properties with any degree of certainty.

Comparison with Previous Evaluations. Pabalan and Pitzer[2] collected thermodynamic properties from several different sources and combined them to show that reasonable predictions of mineral solubility could be obtained over wide ranges of temperature when using ion-interaction equations for calculation of the activity coefficients of the components in the aqueous phase. For comparison purposes, we show their calculated values in Figure 11. The entropy values used by Pabalan and Pitzer (taken from Wagman et al.[4]) for K_2SO_4(cr) and K_2SO_4(aq) resulted in $\Delta_{sol}S_m^\circ = 49.5$ J·K^{-1}·mol^{-1}. The value obtained here for $\Delta_{sol}S_m^\circ$ was (45.60 ± 0.10) J·K^{-1}·mol^{-1}, where the uncertainty is a 95% confidence interval within the global representation. The difference, 3.9 J·K^{-1}·mol^{-1}, leads to errors in the Gibbs energies of solution of (−290 and −780) J·mol^{-1} at 373 K and 500 K, respectively. This error accounts for solubilities greater than those observed for $310\ K < T < 375\ K$. However, it does not correspond to the observation that the calculated solubilities were less than those measured for $T > 450$ K. Counteracting the error in the entropy of solution taken from Wagman et al.[4] were systematic errors in the assumed heat capacities of the crystal and aqueous phases. At 500 K, the differences in the standard-state heat capacities of the solution used by Pabalan and Pitzer[2] and that calculated here led to an error of +2.54 kJ·mol^{-1} in $\Delta_{sol}G_m^\circ$ at 500 K. We conclude that the degree of agreement between the solubility of arcanite calculated by Pabalan and Pitzer and that measured for temperatures somewhat greater than room temperature could be considered somewhat fortuitous, as the agreement resulted partly due to the compensation of errors in the previously tabulated thermodynamic property values.

Holmes and Mesmer[85] gave an equation that represented excess thermodynamic properties from near the freezing point of the solutions to 500 K. The present equation is based on a larger set of measurements, including new measurements not available to Holmes and Mesmer, and includes volumetric properties and the phase equilibria between the solute and the aqueous solution. Differences in osmotic and activity coefficients from their equation and the present one are acceptable considering the differences in the fitted databases. We believe the inclusion of the more recent heat capacity results, valid to 373 K, and the inclusion of additional results for near and below ambient conditions should make the present equation somewhat more accurate than that given by Holmes and Mesmer.

Goldberg[90] gave an equation for the 298.15 K osmotic and activity coefficients of K_2SO_4(aq). His equation was based primarily on isopiestic determinations from Robinson and Wilson[27] and freezing-point depressions that were adjusted to 298.15 K. The differences of his "recommended" osmotic coefficients from the present equation are shown in Figure 6. His calculated values diverged from the present equation and from all of the reliable measurements for concentrations of (0.05 to 0.5) mol·kg^{-1}.

A residual plot of osmotic coefficients for K_2SO_4(aq) given in Goldberg[90] showed systematic differences of the osmotic coefficients obtained from the isopiestic measurements from Robinson and Wilson,[27] on one hand, from those obtained from Indelli's[33] freezing-point depressions, on the other hand. These differences ranged from 0.01 to 0.026 for concentrations ranging from 0.1 mol·kg^{-1} to 0.4 mol·kg^{-1}. Additionally, values given in the tables in Goldberg[90] are consistent with differences of about −0.3 to −0.4 for the osmotic coefficients that Goldberg obtained from Archibald's[37] freezing temperatures versus his "recommended" osmotic coefficient values. Because of the importance of the solute activity coefficient in determination of the standard-state Gibbs energy of solution, and its dependence on the osmotic coefficient, we examined in some detail the basis of the difference of Goldberg's recommended values from the equation presented here. We found that Goldberg[90] calculated molality incorrectly from the normality values ("gramme-equivalents per litre") given by Archibald,[37] which resulted in calculated molalities that were twice the real values and which extended to nearly twice the known solubility at the invariant freezing temperature. In Goldberg's method, the quantity $\phi(T{=}298.15\text{K}) - \phi(T_{\text{fus}})$ was required for use of the freezing-point determinations in calculation of osmotic coefficients at 298 K. This quantity depended on integration of a molality derivative of the relative apparent molar enthalpy and heat capacity. Goldberg[90] gave polynomial coefficients for these properties at 298.15 K. Properties calculated from his equations are shown in Figures 7 and 8. The values of $(\partial L_\phi/\partial m)_{T,p}$ and $(\partial C_{p,\phi}/\partial m)_{T,p}$ from the Goldberg equations[90] diverged from those calculated from reasonable representations of the then-available measured values for concentrations above 0.1 mol·kg^{-1} and 0.3 mol·kg^{-1}, respectively. Some of this misrepresentation arose because Goldberg apparently considered enthalpy measurements only to 0.1 mol·kg^{-1} and heat capacity measurements only to 0.3 mol·kg^{-1}, and neglected all of the published values for greater concentrations. This might have yielded reasonably accurate $\phi(T{=}298.15\text{K}) - \phi(T_{\text{fus}})$ to 0.1 mol·kg^{-1}; however, Goldberg used extrapolations of the relative apparent molar enthalpy polynomial to more than 7 times the fitted region of composition. The misrepresentations of enthalpy and heat capacity behavior, due to the extreme extrapolations of the two polynomials, resulted concomitantly in values of $\phi(T{=}298.15\text{K}) - \phi(T_{\text{fus}})$ that were very inaccurate. We therefore conclude that the misrepresentation of the measured osmotic coefficients, and the necessary concomitant error in the calculated solute activity coefficient, by Goldberg's recommended values,[90] resulted from a series of calculational errors.

Comparison of the presently determined thermodynamic property values for the solution process with those given by Wagman et al.[4] would not be useful or relevant because the thermodynamic properties given by Wagman et al.[4] for K_2SO_4(cr) did not satisfy the thermodynamic relation $G = H - TS$. Comparison with the *CODATA Key Values for Thermodynamics*[91] was not possible because Cox et al.[91] did not give their optimized properties of the potassium sulfate crystal phase.

Conclusion

We described here a revised enthalpy of solution calorimeter, and we have reported new enthalpy of solution measurements for sodium chloride and potassium sulfate obtained with it. These new enthalpy of solution values were compared with values given previously in the literature and found to be more accurate. The new measurements for sodium chloride confirm that it can be used as a calibration standard for, or as a check on the accuracy of, solution calorimeters. We also generated new equations and thermodynamic properties for the potassium sulfate + water system. These new equations spanned the range of temperature from the freezing point of the solutions to 500 K and from the saturation pressure to 40 MPa. These new equations are an improvement over previously reported assessments of the thermodynamic properties of the potassium sulfate + water system, some of which contained significant systematic bias.

Acknowledgment

The authors wish to thank Joseph Rard for bringing several references to our attention.

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