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Isopiestic Determination of the Osmotic and Activity Coefficients of K_2SO_4(aq) at the Temperatures 298.15 and 323.15 K, and Revision of the Thermodynamic Properties of the $K_2SO_4 + H_2O$ System

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Isopiestic vapor-pressure measurements were made for K_2SO_4(aq) from (0.228 to 0.740) mol·kg^{-1} at 298.15 K and from (0.200 to 0.957) mol·kg^{-1} at 323.15 K, using NaCl(aq) as the isopiestic reference standard. These isopiestic measurements extend to saturation at 323.15 K and to slightly above saturation at 298.15 K. There are no previous isopiestic studies for K_2SO_4(aq) at 323.15 K. Thermodynamic properties from the literature for the potassium sulfate + water system and the present measurements were used to generate equations that represent the thermodynamic properties of this system from the freezing point of the aqueous solution to 500 K. The measured values included for least-squares estimation of the model parameters spanned the temperature range approximately 271 K to 530 K for K_2SO_4(aq).

Introduction

Potassium sulfate is an important constituent in groundwater, surface water, and ocean water. Additionally, potassium sulfate is important for the establishment of the thermodynamic properties of substances considered “key” in the subsequent determination of thermodynamically consistent sets of thermodynamic properties. Potassium sulfate is also used as a reference substance in certain types of electrochemical cells. As a reference substance or as a “key” substance, thermodynamic properties of the highest accuracy are desirable.

Previously, Archer and Kirklin[1] reported new enthalpy of solution values for K_2SO_4(cr) dissolving in water and generated an equation of state for the $K_2SO_4 + H_2O$ system. Their equation of state resolved problems in the solubility of potassium sulfate calculated from earlier sets of thermodynamic properties for the system. However, their analysis indicated some shortcomings in the apparent molar enthalpy at 298.15 K that resulted from an absence of high-quality measurements for the enthalpy of dilution in the vicinity of 298.15 K. The uncertainty in this property could introduce a concomitant small uncertainty in the temperature dependence of the activity coefficient of K_2SO_4(aq) at the saturation molality. New measurements of the isopiestic vapor pressure of K_2SO_4(aq) are reported here for 298.15 K and 323.15 K. There are no previous isopiestic measurements between the temperatures 298.15 K and 383.14 K, and the new measurements at 323.15 K help bridge this temperature gap. These new measurements, which lead to the activity of water in the solution, when incorporated into the fitted database, will improve the accuracy of the calculated temperature dependence of the solute activity coefficient.

Experimental Section

The isopiestic experiments were performed at Oak Ridge National Laboratory (ORNL), at both temperatures of $(298.15 \pm 0.00_3)$ K and $(323.15 \pm 0.00_3)$ K, using a slightly modified version of the apparatus described by Rush and Johnson.[2] This apparatus, its operation, and the experimental conditions and techniques are essentially identical to those described by Clegg et al.[3] and by Rard et al.[4] Rard and Platford[5] give a detailed general description of the isopiestic method.

Five different stock solutions of NaCl(aq) and four of K_2SO_4(aq) were used for the isopiestic measurements. Molalities of all but one of the NaCl(aq) stock solutions and of all four K_2SO_4(aq) stock solutions were determined by passing a known mass of solution through a cation exchange column, which replaces the Na^+ or K^+ originally present in the solution (and any cationic impurities) with an equivalent amount of H^+, followed by potentiometric-pH mass titration of the eluted H^+ with standardized NaOH(aq).[4] Assumed molar masses are 58.4428 g·mol^{-1}

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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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Table 1. Molalities of NaCl(aq) and K_2SO_4(aq) Stock Solutions

series[a]	m(NaCl) mol·kg^{-1}	m(NaCl) mol·kg^{-1}	m(K_2SO_4) mol·kg^{-1}	m(K_2SO_4) mol·kg^{-1}
1, 2	0.9748[b]		0.51635[c]	
11, 12	0.19580[c]		0.51835[c]	
13	0.91218[c]		0.51835[c,d]	
14−18	0.56386[c]	0.99769[c]	0.37558[c]	0.22952[c]

[a] The numbering of the various series of experiments corresponds to the numbering system used by Palmer et al.[7] The K_2SO_4(aq) stock solutions with $m = 0.516\,35$ and $0.518\,35$ mol·kg^{-1} were prepared from Aldrich "Gold Label" lot 0405BL, the K_2SO_4(aq) stock solution with $m = 0.375\,58$ mol·kg^{-1} was prepared from Aldrich "Gold Label" lot 04503JP, and the K_2SO_4(aq) stock solution with $m = 0.229\,52$ mol·kg^{-1} was prepared from Alfa "Ultrapure" lot 060779. [b] Molality as calculated from the masses of NaCl(cr) and H_2O(l) used to prepare the solution. [c] Molality obtained by cation exchange chromatography followed by mass titration of the eluted H^+ with NaOH(aq). [d] Same solution as the one given immediately above.

Table 2. Isopiestic Molalities and Osmotic Coefficients of NaCl(aq) and K_2SO_4(aq) at 298.15 K[a]

m(NaCl) mol·kg^{-1}	m(K_2SO_4) mol·kg^{-1}	ϕ(K_2SO_4)
	Series 1	
0.3776 ± 0.0003	0.32492 ± 0.00001	0.7132
0.2731 ± 0.0001	0.22829 ± 0.00012	0.7347
	Series 2	
0.6304 ± 0.0004	0.57116 ± 0.00042	0.6804
0.6150 ± 0.0004	0.55565 ± 0.00048	0.6820
0.5942 ± 0.0001	0.53401 ± 0.00020	0.6853
0.4630 ± 0.0001	0.40546 ± 0.00009	0.7014
0.3913 ± 0.0003	0.33678 ± 0.00002	0.7131
	Series 13	
0.6316 ± 0.0016*	0.62177 ± 0.00385**	0.6262 ($w = 0$)
0.6185 ± 0.0001	0.55897 ± 0.00011	0.6818
	Series 14	
0.7926 ± 0.0000[b]	0.74051 ± 0.00017	0.6631
0.7921 ± 0.0001	0.73994 ± 0.00000	0.6636
0.6981 ± 0.0000[b]	0.64199 ± 0.00001	0.6716
0.6980 ± 0.0000	0.64146 ± 0.00005	0.6722
0.5480 ± 0.0001[b]	0.49004 ± 0.00008	0.6877
0.5477 ± 0.0001	0.48979 ± 0.00013	0.6881
	Series 15	
0.6037 ± 0.0001[b]	0.54685 ± 0.00003	0.6799
0.6035 ± 0.0000	0.54675 ± 0.00013	0.6800
0.5760 ± 0.0006[b]	0.51920 ± 0.00033	0.6822
0.5748 ± 0.0001	0.51967 ± 0.00033	0.6815
0.5502 ± 0.0001[b]	0.49354 ± 0.00015	0.6854
0.5496 ± 0.0001	0.49350 ± 0.00001	0.6855
0.5210 ± 0.0004[b]	0.46510 ± 0.00033	0.6885
0.5207± 0.0009*	0.46505 ± 0.00055	0.6886

[a] Osmotic coefficients of the reference standard NaCl(aq) were calculated with Archer's equation and parameters.[8] Molalities without asterisks are from higher-quality experiments for which the uncertainty of the average molalities is $\leq 0.001m$ for $m > 0.5$ mol·kg^{-1} and $\leq 0.002m$ for $m < 0.5$ mol·kg^{-1}. Equilibrium molalities are followed by a single asterisk when the scatter of the isopiestic molalities slightly exceeds that typically obtained for such experiments by up to a factor of 2, and by two asterisks for those experiments with larger scatter. The value of ϕ given zero weight in the model parameter evaluations is identified with ($w = 0$). [b] Duplicate samples of two different NaCl(aq) reference standard stock solutions and of two different K_2SO_4(aq) solutions were used in these experiments. Each reported average molality is for one of these pairs of solutions, and the average molality of the corresponding second pair is given immediately below. The values of ϕ(K_2SO_4) were calculated separately for each K_2SO_4(aq) molality pair, using the average of the product of the molality and osmotic coefficients of the two NaCl(aq) pairs.

for NaCl, 174.260 g·mol^{-1} for K_2SO_4, and 18.0153 g·mol^{-1} for H_2O. All apparent masses were converted to masses using buoyancy corrections. Stock solution molality determinations were made in duplicate and were reproducible to ≤0.1%. However, because the molalities of the K_2SO_4(aq) stock solutions and of all but one of the NaCl(aq) stock solutions were determined in an identical manner, any systematic errors in their determinations, if present, will partially cancel when osmotic coefficients are calculated from the isopiestic molality ratios.

Table 1 contains a summary of the stock solution molalities obtained from these analyses, and it identifies which stock solutions were used for each series of experiments. Ten different series of isopiestic experiments were performed. The source materials for the K_2SO_4(aq) stock solutions were from two lots (0405BL and 04503JP) of Aldrich "Gold Label" K_2SO_4(cr) and Alfa "Ultrapure" lot 060779. The purity of the second lot of Aldrich "Gold Label" K_2SO_4(cr), as reported by the supplier, is 99.999%, presumably as mass percent.

The amounts of metallic cation impurities in lot 04503JP of Aldrich "Gold Label" K_2SO_4(cr) and the Alfa "Ultrapure" lot 060779 were determined in triplicate, at ORNL, using ion chromatography (IC). Solutions of NaCl(aq) and LiCl(aq) were also eluted through this IC system, to calibrate the retention times and peak areas for Na^+ and Li^+ ions, which were potential cationic impurities in the K_2SO_4(s) samples. No distinct IC impurity peaks were observed for either of these alkali metal cations in solutions prepared from either K_2SO_4(cr) sample, and if either of these impurities were present, their concentrations were comparable to or less than background levels. If either of the heavier alkali metal ions Rb^+ or Cs^+ were present, their peaks would overlap the tail of the intense K^+ major component peak. The K^+ peaks exhibited no anomalies at the retention times expected for Rb^+ and Cs^+. On the basis of these IC experiments, the Aldrich "Gold Label" K_2SO_4(s) had no detectable impurities, and the Alfa "Ultrapure" K_2SO_4(cr) had <0.01 mol % sodium or lithium, which is consistent with the purity claimed by the supplier.

The isopiestic experiments were performed at various times between 1985 and 1988 and during 1996 and 1997. Tables 2 and 3 list the results for the experiments at 298.15 K and 323.15 K, respectively. Reported are the average equilibrium molalities for duplicate samples located on opposite sides of the circular gold-plated copper block, along with the deviations of individual molalities from their corresponding averages. By comparison to the aqueous solubilities of K_2SO_4(cr) tabulated by Linke,[6] the two highest pairs of equilibrium molalities of K_2SO_4(aq) at 298.15 K, which are reported as the first experiment of series 14 in Table 2, extend about 0.05 mol·kg^{-1} above the solubility limit with K_2SO_4(cr) as the solid phase. At 323.15 K the solubility tabulated by Linke is within 0.01 mol·kg^{-1} of our highest experimental molality. No precipitation occurred during these two isopiestic experiments.

Each series of experiments represents two or more sequential equilibrations using the same pair of duplicate samples of NaCl(aq) and of K_2SO_4(aq), where NaCl(aq) is the reference standard. However, in series 14−18 duplicate samples of two different NaCl(aq) stock solutions and two different K_2SO_4(aq) stock solutions were used, and the reported averages of the equilibrium molalities for each pair of solutions from the same stock solution are in excellent agreement. The molalities of the pairs of NaCl(aq) solutions from the two different stock solutions are also in excellent agreement for series 14−18, except for the

Table 3. Isopiestic Molalities and Osmotic Coefficients of NaCl(aq) and K_2SO_4(aq) at 323.15 K[a]

m(NaCl)/mol·kg^{-1}	m(K_2SO_4)/mol·kg^{-1}	ϕ(K_2SO_4)
	Series 11	
0.9010 ± 0.0018*	0.83563 ± 0.00024	0.6746
0.6667 ± 0.0011*	0.59615 ± 0.00035	0.6925
0.4959 ± 0.0005	0.43133 ± 0.00037	0.7077
0.3691 ± 0.0004	0.31291 ± 0.00020	0.7241
0.2775 ± 0.0002	0.23197 ± 0.00026	0.7341
0.2653 ± 0.0001	0.21939 ± 0.00010	0.7422
	Series 12	
0.4486 ± 0.0002	0.38310 ± 0.00031	0.7198 (w = 0)
0.4218 ± 0.0001	0.36045 ± 0.00008	0.7190
	Series 13	
1.0187 ± 0.0022**	0.95747 ± 0.00138*	0.6696
0.6175 ± 0.0002	0.55043 ± 0.00026	0.6933
0.4603 ± 0.0001	0.39878 ± 0.00017	0.7098
0.2429 ± 0.0000	0.20004 ± 0.00028	0.7455
	Series 15	
0.6432 ± 0.0002[b]	0.57849 ± 0.00005	0.6878
0.6432 ± 0.0000	0.57742 ± 0.00029	0.6890
0.4449 ± 0.0001[b]	0.38624 ± 0.00008	0.7080
0.4447 ± 0.0001	0.38597 ± 0.00017	0.7085
	Series 16	
0.5338 ± 0.0001[b]	0.47115 ± 0.00002	0.6980
0.5336 ± 0.0001	0.47059 ± 0.00028	0.6989
0.3854 ± 0.0000[b]	0.33040 ± 0.00011	0.7162
0.3906 ± 0.0038** [c]	0.33010 ± 0.00001	0.7168
	Series 17	
0.7812 ± 0.0001[b]	0.71601 ± 0.00002	0.6784
0.7803 ± 0.0001	0.71408 ± 0.00013	0.6803
0.7492 ± 0.0001[b]	0.68359 ± 0.00014	0.6805
0.7483 ± 0.0002	0.68151 ± 0.00021	0.6826
0.7169 ± 0.0001[b]	0.65179 ± 0.00008	0.6823
0.7166 ± 0.0004	0.65005 ± 0.00006	0.6841
	Series 18	
0.9977 ± 0.0001[b]	0.93865 ± 0.00033	0.6677
0.9962 ± 0.0001	0.93488 ± 0.00024	0.6704
0.8668 ± 0.0000[b]	0.80324 ± 0.00031	0.6737
0.8657 ± 0.0000	0.80065 ± 0.00027	0.6758

[a] See footnote *a* of Table 2. [b] See footnote *b* of Table 2. [c] This NaCl(aq) molality from Series 16 was not used for calculating the reported values of $\phi(K_2SO_4)$ for that experiment, since the other NaCl(aq) molality pair is known more precisely.

second experiment of series 16 at 323.15 K, where the two NaCl(aq) molalities differ by 1.9%. The average molalities of each pair of K_2SO_4(aq) solutions from different stock solutions are usually in good agreement, except for series 17 and 18, where the pairs of average values differ systematically by 0.3 to 0.4%.

The equilibrium molalities in Tables 2 and 3 for each series are listed from the highest to the lowest molality studied, rather than in the actual order of their determination. Series 13 and 15 involved measurements at both temperatures, whereas the other eight series of measurements were each made at a single temperature.

Solutions of one or more of Na_2SO_4(aq), Rb_2SO_4(aq), Cs_2SO_4(aq), or $(NH_4)_2SO_4$(aq) were also present during many of the isopiestic equilibrations, and those results were reported previously.[3,4,7] The numerical designators assigned to the different series of isopiestic measurements are the same as the ones used for the Rb_2SO_4(aq) and Cs_2SO_4(aq) study.[7]

Values of the osmotic coefficients ϕ were calculated from the reported isopiestic molalities, with the osmotic coefficients of the NaCl(aq) reference standard calculated using the equation and parameters of Archer.[8] The calculated ϕ values for K_2SO_4(aq) from the various series of experiments are generally quite consistent. However, values of ϕ from the series 15 experiments are consistently slightly lower than those from the other series of experiments by $\Delta\phi =$ (0.002 to 0.004). These same solutions were also equilibrated with Rb_2SO_4(aq) samples, and the derived values of ϕ for Rb_2SO_4(aq) at 298.15 K are also slightly low.[7] Pairs of two different NaCl(aq) reference standards were used in these equilibrations, and because the molalities of both pairs were always in excellent agreement, the noted minor discrepancies in ϕ cannot have resulted from an error in a NaCl(aq) stock solution molality or from failure to have reached isopiestic equilibrium. The two different pairs of K_2SO_4(aq) solutions for series 17 and 18 yield values of ϕ that differ typically by $\Delta\phi \approx 0.002$; however, the average values of ϕ from these experiments agree well with those from series 11 and 13, which are probably the most reliable experiments at 323.15 K.

In addition, the molalities of the duplicate samples for the first experiment of series 13 at 298.15 K are fairly scattered and the calculated osmotic coefficient is considerably low by $\Delta\phi \approx 0.05$. This experiment also involved samples of Cs_2SO_4(aq), whose isopiestic molalities are similarly scattered but whose ϕ is too high. This experiment at 298.15 K was the first equilibrium at this temperature following two previous equilibrations of these samples at 323.15 K. The observed scatter and discrepancies for this individual experiment clearly imply that these samples were not given sufficient time to reach thermodynamic equilibrium after the temperature change.

Results

Representation of the Thermodynamic Properties of K_2SO_4(aq) and Phase Equilibria. Because the model is essentially that used previously,[1,9] 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, G^E, is

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

where

$$B_{MX} = \beta^{(0)}_{MX} + 2\beta^{(1)}_{MX}[1 - \{1 + \alpha_1(I/m°)^{1/2}\} \times \exp\{-\alpha_1(I/m°)^{1/2}\}]/\{\alpha_1{}^2(I/m°)\} \quad (1a)$$

and

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

where $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $C^{(0)}_{MX}$, and $C^{(1)}_{MX}$ 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; 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 and 2.5, 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[10] and the dielectric-constant equation from Archer and Wang.[11] Appropriate derivatives of eq 1 give other thermodynamic properties. These additional equations can be found elsewhere[8,9] 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 and pressure as

$$\beta^{(0)}_{\mathrm{MX}} = f(1,p,T)/m^\circ \tag{2}$$

$$\beta^{(1)}_{\mathrm{MX}} = f(2,p,T)/m^\circ \tag{3}$$

$$C^{(0)}_{\mathrm{MX}} = f(3,p,T)/m^{\circ 2} \tag{4}$$

$$C^{(1)}_{\mathrm{MX}} = f(4,p,T)/m^{\circ 2} \tag{5}$$

where

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

The functional forms for the apparent molar heat capacity and volume of the solute, $C^\circ_{p,\phi}$ and V°_ϕ, respectively, are

$$C^\circ_{p,\phi} = c_1 + c_2T^\circ/(T - 228\ \mathrm{K}) + c_3(T/300\ \mathrm{K}) + c_4(T/300\ \mathrm{K})^2 + c_5[T^\circ/(647\ \mathrm{K} - T)]^2 \tag{7}$$

$$V^\circ_\phi = d_1 + d_2(p/p^\circ) + d_3T^\circ/(647\ \mathrm{K} - T) + d_4(p/p^\circ)(T/T^\circ)/(3 \times 10^5) + d_5(p/p^\circ)T^\circ/(647\ \mathrm{K} - T) + d_6(100\ \mathrm{K}/T) \tag{8}$$

In the above equations, T° is 1 K, p° is 1 MPa, and m° is 1 mol·kg^{-1}. Solubility measurements, which are cited in ref 1, were included in the global data fit. The Gibbs energy of solution at the reference temperature, $T_\mathrm{r} = 298.15$ K, and the reference pressure, $p_\mathrm{r} = 0.1$ MPa, was treated as an adjustable parameter, as was $S^\circ_{2,m,T_\mathrm{r},p_\mathrm{r}}$. Thermodynamic properties for the crystal phase were taken from Archer and Kirklin.[1]

Above 373 K, there are no measured values of the heat capacity for K_2SO_4(aq). To help guide the least-squares process, values of $C^\circ_{p,\phi}$ were calculated at the saturation pressure from

$$C^\circ_{p,\phi}(\mathrm{K_2SO_4}) = C^\circ_{p,\phi}(\mathrm{Na_2SO_4}) + 2C^\circ_{p,\phi}(\mathrm{KCl}) - 2C^\circ_{p,\phi}(\mathrm{NaCl}) \tag{9}$$

for the temperatures (398.15, 423.15, 448.15, 473.15, and 498.15) K and included in the fitted database. Values of $C^\circ_{p,\phi}(\mathrm{K_2SO_4})$ from eq 9 were calculated using $C^\circ_{p,\phi}$ for NaCl(aq), KCl(aq), and Na_2SO_4(aq) from Archer and Carter,[12] and Pabalan and Pitzer,[13,14] respectively. There are no heat capacity measurements for either K_2SO_4(aq) or Na_2SO_4(aq) below 298 K. Values of $C^\circ_{p,\phi}(\mathrm{K_2SO_4})$ for temperatures ranging from <298 K to the freezing temperatures of the solutions are therefore extrapolations of the higher temperature behavior.

The least-squares optimized parameters are given in Table 4. The absence of a value for a particular parameter indicates that parameter was not included in the global representation. The uncertainty listed in Table 4 for $S^\circ_{m,\mathrm{K_2SO_4(aq)},T_\mathrm{r},p_\mathrm{r}}$ is not truly the uncertainty in that quantity. It is more properly considered as being the uncertainty in the entropy of a solution of K_2SO_4, because the entropy of K_2SO_4(cr), taken from the representation of the properties of the crystal phase,[1] appeared in the calculations in combination with the entropy of K_2SO_4(aq) to give $\Delta_\mathrm{sol}S^\circ_\mathrm{m}$. The true uncertainty for the standard-state entropy of K_2SO_4(aq) must also contain the uncertainty in the entropy of K_2SO_4(cr). Because of the discrepancies in experimental results, discussed by Archer and Kirklin,[1] the uncertainty in the entropy of K_2SO_4(cr) is nonnegligible. Some calculated values, against which to test program execution, are given in Tables 5−8.

The upper range of temperature considered for the present representation was limited to 530 K, due to scarcity of thermodynamic measurements above this temperature and due to 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.

The present least-squares estimated model parameters represent all of the results that had been fitted previously[1] with approximately the same root-mean-square (rms) deviations as before. None of the weighting factors of the earlier data sets needed to be changed to accomplish an adequate representation of the complete database, that is, the previously considered measurements and the new ones reported here. Therefore, to conserve space, discussed here are only the new measurements that have been incorporated into the fitted data set and any changes in the quality of representations of earlier data sets that are significant. The interested reader is referred to the earlier publication of Archer and Kirklin[1] for additional details related to the representation of the other literature measurements.

A uniform weighting of the present measurements was calculated on the basis of an assumed square root of variance, $\sigma = 0.002$, for the present measurements. The present osmotic coefficients showed a rms deviation of 0.0022 from the final model and an average difference of -5.0×10^{-4}, for 51 of the 53 values tabulated in Tables 2 and 3, with the other two values having been given no weight in the representation. Figure 1 shows differences of various literature values from the least-squares estimated model for temperatures from the freezing temperatures to 323.15 K. The present ϕ values at 298.15 K are slightly smaller than those from Robinson et al.[15] for most of the composition range. The bias between the two sets is about 0.001 at 0.2 mol·kg^{-1} and about 0.003 at 0.65 mol·kg^{-1}. Differences of other osmotic coefficients from refs 15−22 are shown in the figure as are those taken from the evaluation of Goldberg.[23]

The only other significant change in the fitted database involved the apparent molar heat capacity values calculated from the additivity relations. Figure 2 shows the values calculated with eq 9 from the previous equations for potassium chloride, sodium chloride, and sodium sulfate. Also shown in the figure are values calculated from the least-squares estimated equations from the present work and from Archer and Kirklin.[1] The present model represents the values at the highest temperatures slightly better, although both models agree with the values within

Table 4. Least-Squares Estimated Parameters for Eqs 1−8[a]

parameter	value	parameter	value	parameter	value
$b_{1,1}$	−5.881 279 589 064 43	$b_{2,1}$	15.330 879 444 531 1	$b_{3,1}$	9.630 482 620 195 835 × 10^{-2}
$b_{1,2}$	28.672 184 275 448 7	$b_{2,2}$	−52.183 444 120 499 2	$b_{3,2}$	−0.428 770 918 245 846
$b_{1,3}$	−12.648 624 634 261 1	$b_{2,3}$	13.722 137 434 908 3	$b_{3,3}$	0.111 439 502 177 859
$b_{1,4}$	−19.960 058 535 073 6	$b_{2,4}$		$b_{3,4}$	
$b_{1,5}$	543.465 303 917 881	$b_{2,5}$	−1723.149 582 946 67	$b_{3,5}$	
$b_{1,6}$	3.974 056 983 512 13	$b_{2,6}$		$b_{3,6}$	
$b_{1,7}$	−3576.469 548 430 53	$b_{2,7}$		$b_{3,7}$	103.772 690 190 293
$b_{1,8}$	8777.076 117 508 11	$b_{2,8}$		$b_{3,8}$	−769.814 632 260 706
$b_{1,9}$	5509.217 613 452 86	$b_{2,9}$		$b_{3,9}$	
$b_{1,10}$	142.457 209 376 567	$b_{2,10}$		$b_{3,10}$	
$b_{1,11}$	−614.710 169 341 095	$b_{2,11}$		$b_{3,11}$	
$b_{1,12}$	−1072.570 693 254 60	$b_{2,12}$		$b_{3,12}$	
$b_{1,13}$	−2746.765 483 927 32	$b_{2,13}$		$b_{3,13}$	
$b_{4,1}$		c_1	6.953 519 709 783 90	$\Delta_{\mathrm{sol}}G^\circ_{T_r,p_r}$	10.188 ± 0.026 kJ·mol^{-1}
$b_{4,2}$	1.311 339 814 870 73	c_2	−75.371 653 168 014 7	$S^\circ_{m,\mathrm{K_2SO_4(aq)},T_r,p_r}$	220.76 ± 0.091 J·K^{-1}·mol^{-1}
$b_{4,3}$		c_3	−9.583 044 934 237 48		
$b_{4,4}$		c_4	3.707 353 922 774 02		
$b_{4,5}$		c_5	−33847.709 476 210 2		
$b_{4,6}$					
$b_{4,7}$	17 756.827 882 468 7	d_1	0.235 789 988 090 218		
$b_{4,8}$	−103 746.327 894 688	d_2	2.613 326 711 738 626 × 10^{-4}		
$b_{4,9}$		d_3	−30.507 714 025 468 3		
$b_{4,10}$		d_4	−1.281 467 852 581 54		
$b_{4,11}$		d_5	0.390 318 636 982 863		
$b_{4,12}$		d_6	−0.346 704 459 312 392		
$b_{4,13}$					

[a] The volume of the crystal phase was taken to be 65.46 cm^3 mol^{-1}, for the range of temperature and pressure. The ± values are 95% confidence intervals within the global data representation. The $b_{i,j}$, c_i, and d_i coefficients in this table are generally given to 15 figures. Significantly fewer figures than this will obviously be needed for calculation of reliable values of the temperature and pressure derivatives. Without knowing in advance which property is to be calculated, and at what molality, temperature, and pressure, it is not possible to recommend the number of figures to which to truncate individual coefficient values. There is also the likelihood that rounding off some of the coefficient values will result in unintended minor changes in calculated values of thermodynamic properties of K_2SO_4(aq) solutions. To ensure that thermodynamic properties calculated with our model are reliable, we report the coefficients to 15 figures, even though this may be more than the minimum number required for certain applications.

Table 5. 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	$\beta^{(0)}_{\mathrm{MX}}$	$\beta^{(1)}_{\mathrm{MX}}$	100 $C^{(0)}_{\mathrm{MX}}$	$C^{(1)}_{\mathrm{MX}}$
273.15	0.1	0.376 422	−0.062 534 9	0.553 229	1.228 349	0.340 267
298.15	0.1	0.391 476	-0.004 663 9	0.774 728	0.801 034	0.383 779
323.15	0.1	0.410 277	0.030 000 5	0.899 354	0.425 761	0.422 331
348.15	0.1	0.433 068	0.056 905 6	0.972 884	0.104 600	0.458 716
373.15	0.1	0.459 887	0.079 131 3	1.026 30	−0.161 687	0.493 963
423.15	0.5	0.526 809	0.111 404	1.152 87	−0.516 495	0.593 836
473.15	1.6	0.617 107	0.130 835	1.388 82	−0.606 977	0.775 967
498.15	2.6	0.675 215	0.137 821	1.567 70	−0.538 669	0.924 393

Table 6. Calculated Values of $G^\circ_{m,2} - G^\circ_{m,2,T_r}$, $C^\circ_{p,\phi}$, and V°_ϕ

T/K	p/MPa	$G^\circ_{m,2} - G^\circ_{m,2,T_r,p_r}$/ kJ·mol^{-1}	$C^\circ_{p,\phi}$/J·K^{-1}·mol^{-1}	V°_ϕ/cm^3·mol^{-1}
273.15	0.1	5.888	−609.9	27.3
298.15	0.1	0.000	−261.2	32.1
323.15	0.1	−5.292	−182.3	34.3
348.15	0.1	−10.219	−181.0	34.1
373.15	0.1	−14.817	−201.1	31.5
423.15	0.5	−22.981	−248.2	17.7
473.15	1.6	−29.683	−357.4	−12.2
498.15	2.6	−32.401	−520.3	−36.8

Table 7. Calculated Values of the Osmotic Coefficient, ϕ

		ϕ at the following values of m/mol·kg^{-1}					
T/K	p/MPa	0.1	0.5	1.0	1.5	2.0	2.5
273.15	0.1	0.7728	0.6544	0.6055			
298.15	0.1	0.7808	0.6878	0.6553			
323.15	0.1	0.7789	0.6969	0.6682	0.6712		
348.15	0.1	0.7710	0.6944	0.6669	0.6635		
373.15	0.1	0.7589	0.6844	0.6569	0.6475	0.6481	
423.15	0.5	0.7258	0.6483	0.6180	0.5990	0.5824	0.5631
473.15	1.6	0.6817	0.5954	0.5601	0.5366	0.5158	0.4921
498.15	2.6	0.6542	0.5629	0.5256	0.5033	0.4873	0.4716

their expected uncertainties. Also shown in the figure for comparison purposes are values calculated from the equation used by Pabalan and Pitzer[24] for calculation of mineral-solution properties over wide ranges of temperature. Their equation was based on earlier data that have been superseded in the literature. However, a comparison to show the resulting improvement is instructive.

Comparison with Previous Evaluations. Holmes and Mesmer[25] 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 also 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 equation are acceptable considering the differences in the fitted databases. We believe the inclusion of the present osmotic coefficients and the more recent heat capacity results, the latter 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.

Table 8. Calculated Values of the Stoichiometric Activity Coefficient, $\gamma_\pm$

		$\gamma_\pm$ at the following values of m/mol·kg^{-1}					
T/K	p/MPa	0.1	0.5	1.0	1.5	2.0	2.5
273.15	0.1	0.4364	0.2455	0.1806			
298.15	0.1	0.4388	0.2610	0.2009			
323.15	0.1	0.4299	0.2597	0.2023	0.1773		
348.15	0.1	0.4141	0.2492	0.1942	0.1688		
373.15	0.1	0.3937	0.2330	0.1803	0.1551	0.1402	
423.15	0.5	0.3449	0.1922	0.1446	0.1211	0.1059	0.0944
473.15	1.6	0.2892	0.1477	0.1064	0.0866	0.0740	0.0647
498.15	2.6	0.2588	0.1253	0.0880	0.0707	0.0602	0.0527

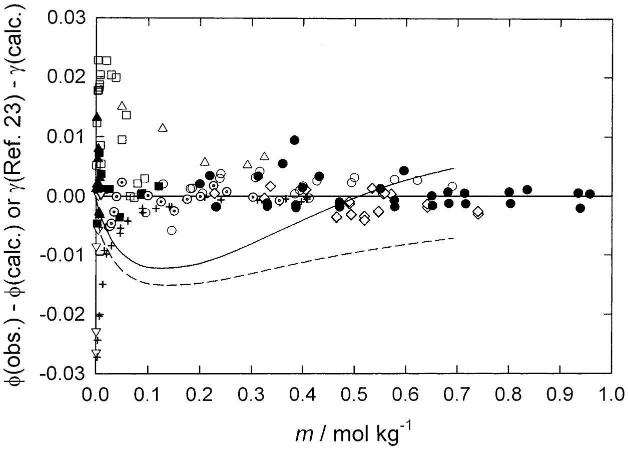

Figure 1. Differences of osmotic coefficient values calculated from measurements from values calculated from the present equation. Symbols: ○, Robinson et al.;[15] ■, Hall and Harkins;[16] △, Rivett;[17] ▽, Hovorka and Rodebush;[18] +, Indelli;[19] ⊙, Archibald;[20] ▲, Osaka;[21] □, Jones;[22] ◇, present results, 298.15 K; ●, present results, 323.15 K. The solid and dashed lines show calculated differences of Goldberg's[23] recommended values for the osmotic coefficient and the solute activity coefficient from the present equation, respectively.

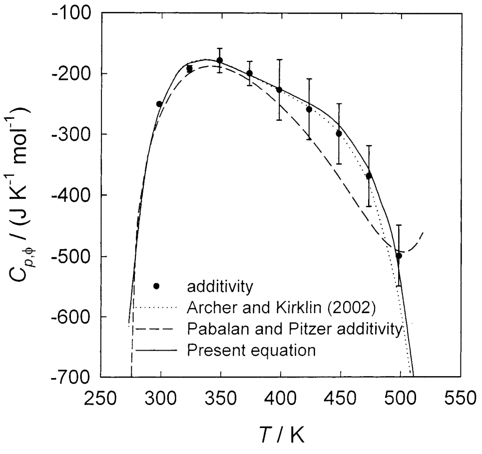

Figure 2. Values of the apparent molar heat capacity of K_2SO_4(aq) at infinite dilution. The symbols are individual values calculated from the sources identified in the text. The solid line was calculated from the present model, and the dotted line was calculated from the model of ref 1. The dashed line was calculated from the additivity relation from Pabalan and Pitzer,[24] which has been superseded by newer measurements and relations.

Comparison of the present model with osmotic coefficient values and solute activity coefficient values at 298.15 K recommended by Goldberg[23] is shown in Figure 1. His recommended values show systematic biases from all of the reliable measured values, including those measurements upon which they were based. The biased values result from a series of calculational errors that have been described elsewhere.[1] The errors in ref 23's recommended values are unfortunate, as these recommended values have been incorporated directly and indirectly into other derived databases and thermodynamic models. Kim and Frederick[26] incorporated into their large database a truncated, two-parameter version of the ion-interaction equation that they obtained from fitting activity coefficients calculated from Goldberg's empirical equation. They gave a standard deviation for the representation of those values of 0.0014, showing a close reproduction of the erroneous activity coefficients from Goldberg. More recently, Marion and Farren[27] described the generation of revised parameters for the FREZCHEM model, which is used to predict mineral-solution behavior in cold environments. They initially calculated new ion-interaction parameters for the binary K_2SO_4 system by fitting to Goldberg's[23] recommended activity coefficients and to data for arcanite solubility in the (K−Cl−SO_4−H_2O) system, but they found that these two properties were somewhat inconsistent. They also noted that an attempt to improve the representation of those activity coefficient values resulted in a less accurate representation of the solubility data. They[27] chose a model that gave a reasonable representation of the solubility data, but which then showed some differences from the recommended activity coefficient data. However, the differences of their fitted model from the solute activity coefficients for K_2SO_4(aq) given by Goldberg[23] are not as large as those shown in Figure 1, which indicates that some portion of the error in the solute activity coefficient may still reside in their model.

Rodil and Vera[28] have recently reported "ionic" activity coefficients of the potassium ion in K_2SO_4(aq) solutions at 298.15 K based on emf measurements with a cell containing a K^+ "ion selective" electrode. They combined their "ionic" activity coefficients with the mean activity of the total solute to derive the "ionic" activity coefficients of the sulfate ion, and they maintained that their "ionic" activity coefficients are reliable quantities. Their cell contained a liquid junction for which there is a liquid junction potential E_{lj}, whose values vary with the molality of the investigated solution. Rodil and Vera calculated these E_{lj} values using a modified version of Henderson's equation described by Bates,[29] which is based on ratios of limiting ionic electrical conductances, but with a constant added to the numerator and another constant subtracted from the denominator. The quantitative adequacy of this approximate expression at higher molalities is highly questionable. Malatesta[30] has discussed many of the conceptual problems with this method of determining "ionic" activity coefficients, and we refer the interested readers to his article for more information.

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