J. Chem. Eng. Data **1998,** *43,* 791−806

Isopiestic Investigation of the Osmotic and Activity Coefficients of Aqueous $MgSO_4$ and the Solubility of $MgSO_4 \cdot 7H_2O(cr)$ at 298.15 K: Thermodynamic Properties of the $MgSO_4 + H_2O$ System to 440 K[†]

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Isopiestic determinations of the osmotic coefficient of $MgSO_4$(aq) against NaCl(aq) and KCl(aq) reference standards were performed with long equilibration times ranging to 98 days. A value of the 298.15 K solubility of epsomite, $MgSO_4 \cdot 7H_2O$(cr), was also determined. The new measurements were combined with previous thermodynamic measurements to determine the thermodynamic properties of the $MgSO_4$ + H_2O system from the ice-freezing line to 440 K. The thermodynamic measurements were fitted with two different models, an ion-interaction model and a chemical-equilibrium model. The ability of the two models to represent this system was examined.

Introduction

We report some new isopiestic measurements for aqueous magnesium sulfate for 298.15 K and a new determination of the 298.15 K solubility. These measurements were combined with other thermodynamic measurements in an effort to characterize the magnesium sulfate + water system over a significant range of temperature.

Magnesium and sulfate ions are among the most common of the ions found in natural groundwaters and aquatic environments. Beyond its environmental presence, magnesium sulfate, in various forms, is found in a multitude of practical uses. Difficulties arise in creating a comprehensive model of the thermodynamic properties of the $MgSO_4$ + H_2O system. The complicating factors are the existence of a large number of crystalline hydrates and the existence of behavior of the aqueous ions that can be described as more strongly associative than that of some other systems, e.g., aqueous alkali halides. These same complicating factors are found also for many of the aqueous divalent transition-metal species. The importance of aqueous transition-metal systems in the environmental arena prompts a renewed look at the aqueous magnesium sulfate system as a probe of the ability of selected methods of representation of the thermodynamic properties to deal with these complicating factors.

Comprehensive models for aqueous magnesium sulfate have been created previously. Archer and Wood (1985) created a multiple equilibrium model that they fitted to selected thermodynamic measurements that spanned temperatures from the freezing point of the solution to 423 K. Subsequent to that work, Phutela and Pitzer (1986a) published apparent molar heat capacities that spanned the temperature range 348.15 K to 473.15 K. Their measurements did not extend to low enough concentration to provide independent measures of the ion-association and the standard-state properties. Rather, they obtained the standard-state heat capacity for $MgSO_4$(aq) from an algebraic combination of standard-state heat capacity values for other electrolytes as

$$C^{\circ}_{p,\phi}(\mathrm{MgSO_4}) = C^{\circ}_{p,\phi}(\mathrm{MgCl_2}) + C^{\circ}_{p,\phi}(\mathrm{Na_2SO_4}) - 2C^{\circ}_{p,\phi}(\mathrm{NaCl}) \quad (1)$$

They provided an ion-interaction model representation of those new measurements and selected measurements from the literature. Their model incorporated the $\beta^{(2)}_{MX}$ term for ion-association. Because of the use of eq 1, the quantity actually represented by Phutela and Pitzer was $(C_{p,\phi} - C^{\circ}_{p,\phi})$. In their analysis and discussion they compared their measured values of $C_{p,\phi}$ to values of $(C_{p,\phi} - C^{\circ}_{p,\phi})$ calculated by Archer and Wood, to which Phutela and Pitzer had added $C^{\circ}_{p,\phi}(\mathrm{MgSO_4})$ obtained by means of eq 1. They noted a 40 $J \cdot K^{-1} \cdot mol^{-1}$ difference in the so-obtained values at 373 K, which was larger than the expected errors in their measurements. However, in this comparison Phutela and Pitzer did not include an uncertainty in their calculated values of $C^{\circ}_{p,\phi}(\mathrm{MgSO_4})$, which, by examination of eq 1, might be expected to be not insignificant, particularly at temperatures removed somewhat from ambient. Phutela and Pitzer also noted differences of their model-calculated enthalpy of dilution values from those measured by Mayrath and Wood (1983) for low concentrations near 423 K. These differences approached 2 $kJ \cdot mol^{-1}$ for $m < 0.01$ $mol \cdot kg^{-1}$.

Pabalan and Pitzer (1987) calculated phase behavior in the system Na−K−Mg−Cl−SO_4−OH−H_2O using excess

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S0021-9568(98)00047-8 CCC: \$15.00

Gibbs energy models from a number of sources and tabulated values of standard-state properties. They found that some of the tabulated standard-state properties had to be adjusted to bring agreement between calculated and observed phase behaviors. This was particularly true for the $MgSO_4 + H_2O$ portion of the system for which they adjusted the standard-state chemical potentials of epsomite, hexahydrite, and kieserite crystal phases to agree with the lowest temperature solubilites for each of the respective phases. For $MgSO_4$(aq), they used the Phutela and Pitzer (1986a) equation for excess Gibbs energy. The possibility that Pabalan and Pitzer's changes in the standard-state properties might have been compensatory for inaccuracies in the excess properties was not discussed.

The present article examines these issues through comparison of the abilities of the multiple equilibrium model and the ion-interaction model to represent the solution property measurements and the phase behavior with similar measurement bases. Such a comparison might be enlightening because it could give useful information on the range of ion-association for which the ion-interaction equation is sufficient and for which it is not.

Experimental Section

Preparation of Stock Solutions, Impurity Analysis, and Molality Analyses. Water used in the experiments was purified first by ion exchange and then by distillation with a Barnstead still. Assumed molar masses were 74.551 $g \cdot mol^{-1}$ for KCl, 58.443 $g \cdot mol^{-1}$ for NaCl, and 120.364 $g \cdot mol^{-1}$ for $MgSO_4$. Weights in air were converted to masses using 1.984 $g \cdot cm^{-3}$ for the density of KCl(cr), 2.165 $g \cdot cm^{-3}$ for NaCl(cr), and 2.66 $g \cdot cm^{-3}$ for $MgSO_4$(cr).

A stock solution of KCl(aq) had been prepared by mass from KCl(cr) and purified water. This KCl was commercial material that had been purified by recrystallization and then fused in a platinum crucible under vacuum conditions. The molality of this solution was determined to be $(0.769\,52 \pm 0.000\,09)\ mol \cdot kg^{-1}$ by mass titration of four samples with $AgNO_3$(aq) using dichlorofluorescein as the end point indicator and to be $(0.769\,72 \pm 0.000\,18)\ mol \cdot kg^{-1}$ by dehydration of samples at (573, 623, and 673) K. See Rard (1996) for more details. The average of these two analysis results was accepted for molality calculations.

The NaCl(aq) stock solution was the same one described by Rard and Archer (1995). Its molality was determined to be $(2.9243 \pm 0.0008)\ mol \cdot kg^{-1}$ from dehydration of three samples at 773 K; this temperature has been found to be optimum for complete removal of residual water (Rard, 1996). See Rard and Archer (1995) for a detailed analysis of the purity of this NaCl(cr).

The $MgSO_4$(aq) stock solution was prepared from recrystallized Mallinckrodt Analytical Reagent $MgSO_4 \cdot xH_2O$(s) and purified water and was then filtered through a prewashed 0.2 μm polycarbonate membrane filtering unit. A sample of this solution was evaporated to dryness, and the anhydrous residue was analyzed for impurities using direct current arc optical emission spectroscopy. Impurities detected, in mass fractions, were 30×10^{-6} Ca, 10×10^{-6} each of Na and Al, 5×10^{-6} B, 3×10^{-6} each of Cu and Fe, and $\leq 5 \times 10^{-6}$ Si. Twenty-seven other elements were analyzed for but were not detected. Each of the observed impurities was assumed to be present as its sulfate, except for B, which was assumed to be present as B_2O_3. Thus the purity of the $MgSO_4$ was 99.977 mass % or 99.982_5 mol %. On a molar basis, 52% of the impurities were present as $CaSO_4$. These impurity concentrations are so low that the isopiestic behavior of its solutions should differ insignificantly from those of pure $MgSO_4$(aq).

The molality of the $MgSO_4$(aq) stock solution was determined in triplicate by dehydration analysis of acidified samples at (773, 823, and 848) K. The three sample crucibles and the tare crucible were weighed a total of 24 times on separate days, after being removed from the furnace and allowed to cool to room temperature in a desiccator. Stock solution molalities calculated from the individual weighings were highly consistent, with only two of the weighings yielding slightly discrepant results. The average of the mean molalities from the 22 most consistent weighings is $(0.450\,43_1 \pm 0.000\,07_8)\ mol \cdot kg^{-1}$, where this uncertainty is 1 "$n - 1$" standard deviation. See Rard (1997) for more details.

The partial pressure of H_2O in the laboratory varied from $p(H_2O, g) = (1.1$ to $1.5)$ kPa during the 24 days on which the crucibles were weighed. There was no significant variation of the calculated molalities of the stock solution with these $p(H_2O, g)$, indicating that (1) either the absorption of moisture by the anhydrous $MgSO_4$(s) was insignificant during the time it took to weigh the crucibles or (2) that it was quite small and essentially independent of $p(H_2O, g)$. The tare crucible was always weighed last, and the three sample crucibles were weighed in a certain order during 12 of the weighings (four times at each temperature) and in their reverse order during the remaining weighings. Calculated molalities from the weights for any particular crucible were consistently higher when that crucible was weighed third than when it was weighed first, which indicates that the second possibility was correct. These molality differences indicate that moisture absorption caused the calculated stock solution molality to be too high by $(0.000\,23_7 \pm 0.000\,12_7)\ mol \cdot kg^{-1}$. The corrected molality of the $MgSO_4$(aq) stock solution is then $\{(0.450\,43_1 \pm 0.000\,07_8) - (0.000\,23_7 \pm 0.000\,12_7)\}\ mol \cdot kg^{-1} = (0.450\,19 \pm 0.000\,15)\ mol \cdot kg^{-1}$.

Isopiestic Equilibrations. Water vapor pressure measurements were made for aqueous solutions of $MgSO_4$ at $(298.15 \pm 0.00_5)$ K (IPTS-68) at low to moderate molalities using KCl(aq) as the isopiestic reference standard and at higher molalities using NaCl(aq) as reference standard. These measurements were performed using the isopiestic method (Rard and Platford, 1991), with one of the stainless steel isopiestic chambers that were described elsewhere (Rard, 1985, 1996). A vapor-stirring "fan" was added to the copper heat-transfer block of the isopiestic chamber after the third equilibration of series 1. The "fan" provides some stirring of the vapor phase and enhances the rate at which solvent is exchanged between the isopiestic samples. This vapor stirring is especially important at lower molalities where the rate of attainment of isopiestic equilibrium becomes limited by mass transport of the solvent (Rard, 1996, 1997).

In most cases air was removed from the chambers in several stages using a vacuum pump (Rard, 1996). However, for the two highest molality isopiestic experiments, one of which involved a simultaneous determination of the solubility and water activity of a $MgSO_4$(aq) solution, removal of air from the isopiestic chamber was much less complete since it was done using a laboratory vacuum line. This was necessary since our vacuum pump was not working at the time.

Solution samples were equilibrated in sample cups made of tantalum metal, which is completely resistant to corrosion by most nonalkaline aqueous electrolytes including

Table 1. Isopiestic Molalities *m* and Osmotic Coefficients ϕ of $MgSO_4$(aq) and *m and ϕ^* of the KCl(aq) and NaCl(aq) Isopiestic Reference Standard Solutions at 298.15 K, and the Equilibration Times *t***

$m^*/(\mathrm{mol \cdot kg^{-1}})$	$m(MgSO_4)/(\mathrm{mol \cdot kg^{-1}})$	ϕ^* [a]	$\phi(MgSO_4)$	t/d
Series 1, KCl(aq) as Reference Standard				
0.544 95 ± 0.000 32	0.932 98 ± 0.000 00	0.8994	0.5253	72
0.581 17 ± 0.000 37	0.987 55 ± 0.000 14	0.8989	0.5290	86
0.679 03 ± 0.000 25	1.128 6 ± 0.000 3[b]	0.8983	0.5405	91
0.737 46 ± 0.000 42	1.209 1 ± 0.000 1	0.8981	0.5478	90
0.812 30 ± 0.000 22	1.308 0 ± 0.000 4	0.8982	0.5578	91
0.515 50 ± 0.000 13	0.884 99 ± 0.000 05	0.8998	0.5241	97
0.411 39 ± 0.000 14	0.715 41 ± 0.000 02	0.9020	0.5187	98
0.301 11 ± 0.000 14	0.525 02 ± 0.000 21	0.9060	0.5196	98
Series 2, NaCl(aq) as Reference Standard				
2.718 0 ± 0.000 6	3.018 5 ± 0.000 7[c]	1.0304	0.9278	30
3.525 1 ± 0.000 3	3.485 0 ± 0.001 5	1.0842	1.0967	20

[a] Osmotic coefficients for the reference standard solutions of KCl(aq) and NaCl(aq) were calculated from the equations given by Archer (1992a, 1997). [b] A fanlike device was added to the chamber after it was opened for this experiment; it provided some stirring of the vapor phase as the chamber was rocked back-and-forth during the equilibrations, which aided in the transport of water between the different sample cups. [c] Saturated solution of $MgSO_4$(aq) equilibrated with a reservoir solution containing excess $MgSO_4 \cdot 7H_2O$(cr).

KCl(aq), NaCl(aq), and $MgSO_4$(aq). Buoyancy corrections were made for all weights.

Samples of $MgSO_4$(aq) and KCl(aq) for the series 1 experiments were simultaneously equilibrated with solutions of H_2SO_4(aq) and $Lu_2(SO_4)_3$(aq) (Rard, 1996). However, the samples of $MgSO_4$(aq) were not present during the initial two equilibrations but were added later. The results for $MgSO_4$(aq) are reported separately because a more complicated data analysis is required and a review of thermodynamic properties of $MgSO_4$(aq) is included.

Duplicate samples of both electrolytes were used for these equilibrations. The isopiestic equilibrium molalities and their uncertainties are listed in Table 1 as are the equilibration times *t*. These uncertainties are based on the agreement between the molalities of the duplicate samples and do not include the ~0.03% uncertainties from the molality analyses of the stock solutions. Molality-based ("practical") osmotic coefficients ϕ^* of the NaCl(aq) and KCl(aq) reference standard solutions and ϕ of the $MgSO_4$ solutions are also given in this table. Values of ϕ^* of NaCl(aq) and KCl(aq) were calculated with the equations of Archer (1992a, 1997), and those of $MgSO_4$ were calculated using the fundamental equation for isopiestic equilibrium

$$\phi = \nu^* m^* \phi^* / \nu m = m^* \phi^* / m \tag{2}$$

where m^* is the equilibrium molality of KCl(aq) or NaCl(aq), m is the equilibrium molality of $MgSO_4$(aq) and ν^* and ν are the corresponding stoichiometric ionization numbers for these electrolytes. For this system, $\nu^* = \nu = 2$.

Times allowed for the solutions to equilibrate ranged from (72 to 98) d for the lower molality measurements (series 1) and (20 to 30) d for the saturated and supersaturated solution measurements (series 2), which are considerably longer than are normally used for this method (Rard and Platford, 1991). By way of contrast, Rard and Miller (1981) used (4 to 28) d equilibrations in their isopiestic investigation of the $MgSO_4$(aq) system, except for the lowest molality experiment, which was given 56 d. A plot of the values of ϕ of $MgSO_4$ from series 1 of Table 1 as a function of molality showed a maximum difference of about 0.0007 (0.13%) for one of the points from a smoothed curve drawn through all of the others, and an internal consistency of about 0.0002 to 0.0003 for the remaining points. This unusually good precision for ϕ of $MgSO_4$(aq) undoubtedly resulted from the exceptionally long equilibration times used in the present study. Such long equilibration times are unnecessary at higher molalities (Rard and Platford, 1991).

A comparison of the present values of ϕ of $MgSO_4$ with those from Rard and Miller (1981) indicates consistency at the higher molalities. However, values of ϕ of $MgSO_4$ from (0.925 38 to 1.1702) mol·kg^{-1} from the earlier study, in which (10 to 20) d equilibrations were used, respectively, are higher than the present results by about 0.001 to 0.002 (0.2 to 0.4)%, with the difference increasing as the molality is decreased. Since both of these studies involved the use of the same reference standard in this molality region, KCl(aq), uncertainties in the osmotic coefficients of the reference standard cannot be the cause of this discrepancy. In addition, the good agreement for the saturated solution indicates that neither the solution molality analyses nor differences in sample purity are significant contributing factors. The present experimental results should be significantly more accurate than the earlier results in this lower molality region because of the presence of the vapor-stirring "fan."

A simultaneous determination was made of the solubility of epsomite, $MgSO_4 \cdot 7H_2O$(cr), and the water activity of its saturated solution at 298.15 K by using the isopiestic method. In this experiment two samples of $MgSO_4$(aq) and two samples of the NaCl(aq) reference standard were equilibrated in the presence of a reservoir of saturated $MgSO_4$(aq) solution in contact with excess $MgSO_4 \cdot 7H_2O$(cr). The resulting solubility of (3.0185 ± 0.0007) mol·kg^{-1} from this 30 d equilibration is in excellent agreement (0.086%) with the previous value of (3.0211 ± 0.0022) mol·kg^{-1} (Rard and Miller, 1981), which is an average from (6 to 15) d isopiestic equilibrations. These uncertainties are statistical only and do not include the uncertainties in molalities of the respective stock solutions. The osmotic coefficient of the saturated solution from the present study, $\phi = 0.9278$, is likewise in excellent agreement (0.075%) with the value of $\phi = 0.9285$, from the earlier study after adjustment of the osmotic coefficient of the KCl(aq) reference standard to the most recent evaluation (Archer, 1997). These minor differences in ϕ between these two determinations are less than the uncertainties of the osmotic coefficients of the NaCl(aq) and KCl(aq) reference standards.

Treatment of the Thermodynamic Data

Description of Data Representation. As mentioned previously, two different models were used in the current

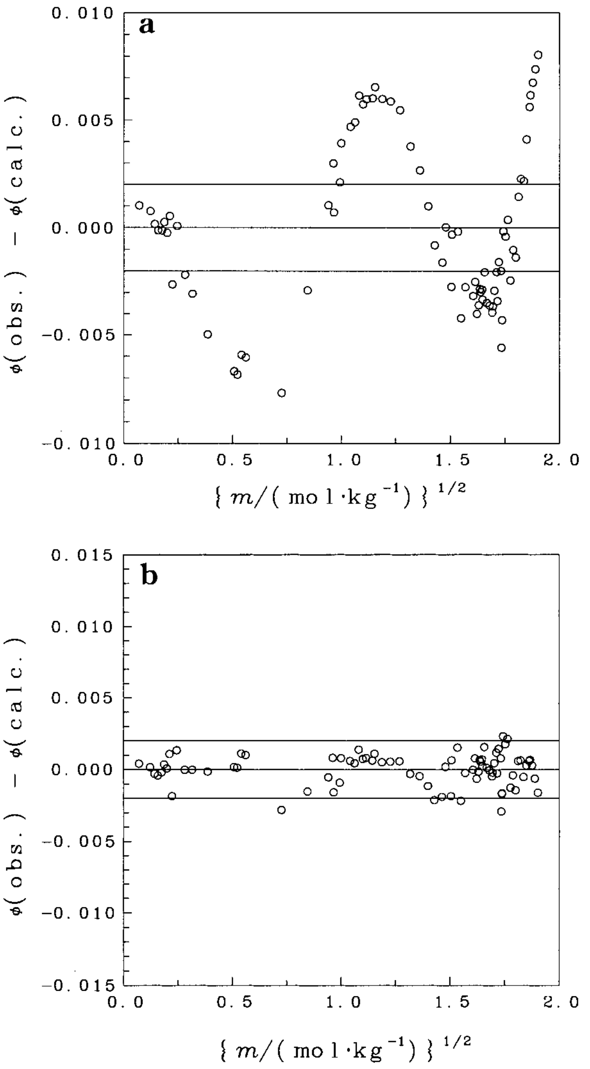

Figure 1. Comparison of effect of ionic strength dependence of the third virial coefficient on the residuals obtained from fitting 298.15 K osmotic coefficients: (a) without the ionic-strength dependence of the third virial coefficient. (b) With the ionic-strength dependence of the third virial coefficient. The symbols correspond to the measurements from Yokoyama and Yamatera (1975), Rard and Miller (1981), and Table 1.

work. The first is the ion-interaction model from Pitzer and co-workers (1973, 1974), and the second is a multiple equilibrium model from Archer and Wood (1985), both with some revision. These are described here briefly.

(1) Ion-Interaction Model. Pitzer and Mayorga (1974) extended Pitzer's (1973) ion-interaction model to incorporate ion-pairing of the solute in cases where this ion-pairing was not too large. The extra linear term added was of the form $\beta^{(2)}_{\mathrm{MX}}\exp(-\alpha_2 I^{1/2})$ for the osmotic coefficient, where α_2 was taken to be 12 kg$^{1/2}$·mol$^{-1/2}$ for 2−2 electrolytes. That value was approximately $32A_\phi$ for 298.15 K, a value obtainable from comparison of expansions of the linear term and the equilibrium constant expression for ion-pairing of a 2−2 electrolyte. Figure 1a shows residuals for fitting the Pitzer and Mayorga equation to 298.15 K osmotic coefficients obtained from isopiestic molalities (Rard and Miller, 1981; present work) and from vapor pressure osmometry measurements (Yokoyama and Yamatera, 1975). A systematic pattern of residuals resulted that was somewhat larger than that expected from the uncertainty of the measurements.

Archer (1991, 1992a) explored previously the use of an ionic strength dependence of the third virial coefficient for other aqueous electrolytes. Figure 1b shows the pattern of residuals for representing the same measurements with the same model as that for Figure 1a, with the exception of incorporation of the ionic-strength dependence of the third virial coefficient. The representation was significantly better.

Accordingly, the ion-interaction model used here was that described by Pitzer and Mayorga with inclusion of Archer's ionic-strength dependence of the third virial coefficient. The resultant equation for the excess Gibbs energy was:

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

where

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + 2\beta^{(1)}_{\mathrm{MX}}[1 - \{1 + \alpha\, I^{1/2}\} \times \exp\{-\alpha\, I^{1/2}\}]/\{\alpha^2\, I\} + 2\beta^{(2)}_{\mathrm{MX}}[1 - \{1 + \alpha_2\, I^{1/2}\} \times \exp\{-\alpha_2\, I^{1/2}\}]/\{\alpha_2{}^2\, I\} \quad (4)$$

and

$$C_{\mathrm{MX}} = C^{(0)}_{\mathrm{MX}} + 4C^{(1)}_{\mathrm{MX}}[6 - \{6 + 6\alpha_3\, I^{1/2} + 3\alpha_3{}^2\, I + \alpha_3{}^3\, I^{3/2}\} \exp\{-\alpha_3\, I^{1/2}\}]/\{\alpha_3{}^4\, I^2\} \quad (5)$$

where $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $\beta^{(2)}_{\mathrm{MX}}$, $C^{(0)}_{\mathrm{MX}}$, 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, α and b were chosen to be constants with the values 1.4 kg$^{1/2}$·mol$^{-1/2}$ and 1.2 kg$^{1/2}$·mol$^{-1/2}$, respectively, ν_{M} and ν_{X} are the stoichiometric numbers of cations and anions formed upon dissociation, 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 (1990) and the dielectric-constant equation from Archer and Wang (1990). The value of α_3 used in the fitted equation was 1.0 kg$^{1/2}$·mol$^{-1/2}$. The value of α_2 used in the fitted equation will be discussed below.

The excess Gibbs energy, G^{ex}, is related to the Gibbs energy of the solution, G, as

$$G^{\mathrm{ex}} = G - n_1 G^{\circ}_{\mathrm{m},\,1} - n_2 \mathrm{G}^{\circ}_{\mathrm{m},\,2} + RT\,\nu n_2\{1 - \ln(m/m°) - (1/\nu)\ln(\nu_{\mathrm{M}}{}^{\nu\mathrm{M}}\nu_X{}^{\nu\mathrm{X}})\} \quad (6)$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively, m is the stoichiometric molality, ν is the number of ions formed upon complete dissociation of the electrolyte and $m°$ is 1.0 mol·kg^{-1}. The standard-state molar Gibbs energy for solvent and solute are $G^{\circ}_{m,1}$ and $G^{\circ}_{m,2}$, respectively. The standard states were chosen to be pure liquid for the solvent and the hypothetical 1 molal ideal solution for the solute at the temperature and pressure of interest, rather than at the temperature of interest and an arbitrary pressure.

Appropriate differentiation of eq 3 leads to the osmotic coefficient, ϕ, and the stoichiometric activity coefficient, $\gamma_\pm$

$$\phi - 1 = -|z_M z_X| A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} + (m/m^\circ)\frac{2\nu_M\nu_X}{\nu}(\beta_{MX}^{(0)} + \beta_{MX}^{(1)}\exp(-\alpha I^{1/2}) + \beta_{MX}^{(2)}\exp(-\alpha_2 I^{1/2})) + (m/m^\circ)^2\frac{4\nu_M{}^2\nu_x z_M}{\nu}(C_{MX}^{(0)} + C_{MX}^{(1)}\exp(-\alpha_3 I^{1/2})) \quad (7)$$

$$\ln\gamma_\pm = -|z_M z_X| A_\phi\left(\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right) + (m/m^\circ)\frac{2\nu_M\nu_X}{\nu}(2\beta_{MX}^{(0)} + 2\beta_{MX}^{(1)}\,h(\alpha I^{1/2}) + 2\beta_{MX}^{(2)}\,h(\alpha_2 I^{1/2})) + (m/m^\circ)^2\frac{2\nu_M{}^2\nu_X z_M}{\nu}(3C_{MX}^{(0)} + 4C_{MX}^{(1)}\,g(\alpha_3 I^{1/2})) \quad (8)$$

where

$$h(\mathrm{x}) = [1 - (1 + x - x^2/2)\exp(-x)]/x^2 \quad (9)$$

and

$$g(x) = [6 - (6 + 6x + 3x^2 + x^3 - x^4/2)\exp(-x)]/x^4 \quad (10)$$

The osmotic coefficient is related to the activity of water as $\phi = -\ln a_w(M_1\nu m)^{-1}$, where M_1 is the molar mass of the solvent, in kg·mol^{-1}.

Appropriate temperature derivatives give equations for enthalpy and heat capacity. For the reasons discussed previously (Archer and Wood, 1985; Phutela and Pitzer; 1986), α_2 should not be expected to be temperature independent. Because of the expected relation of α_2 to A_ϕ, the temperature dependence of α_2 was calculated from the variation of A_ϕ with respect to temperature and so added no additional variable parameters. We follow the example of Phutela and Pitzer (1986a). The relative apparent molar enthalpy, L_ϕ, is

$$L_\phi = \nu|z_M z_X| A_H \ln(1 + bI^{1/2})/2b - 2\nu_M\nu_X RT^2[(m/m^\circ)B_{MX}^L + (m/m^\circ)^2\nu_M z_M C_{MX}^L] \quad (11)$$

where

$$B_{MX}^L = \left(\frac{\partial\beta_{MX}^{(0)}}{\partial T}\right)_p + 2\left(\frac{\partial\beta_{MX}^{(1)}}{\partial T}\right)_p j(\alpha I^{1/2}) + 2\left(\frac{\partial\beta_{MX}^{(2)}}{\partial T}\right)_p j(\alpha_2 I^{1/2}) + \frac{k\,I^{1/2}\,A_H}{2RT^2}\beta_{MX}^{(2)}\,j'(\alpha_2 I^{1/2}) \quad (12)$$

$$C_{MX}^L = \left(\frac{\partial C_{MX}^{(0)}}{\partial T}\right)_p + 4\left(\frac{\partial C_{MX}^{(1)}}{\partial T}\right)_p [6 - (6 + 6\alpha_3 I^{1/2} + 3\alpha_3{}^2 I + \alpha_3{}^3 I^{3/2})\exp(-\alpha_3 I^{1/2})]/(\alpha_3{}^4 I^2) \quad (13)$$

where

$$j(\mathrm{x}) = [1 - (1 + x)\exp(-x)]/x^2 \quad (14)$$

$$\alpha_2 = kA_\phi = 30.65A_\phi \quad (15)$$

$$j'(x) = -(2/x^3)[1 - (1 + x + x^2/2)\exp(-x)] \quad (16)$$

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

$$C_{p,\phi} = C_{p,m,2}^\circ + \nu|z_M z_X| A_C \ln(1 + bI^{1/2})/2b - 2\nu_M\nu_X RT^2[(m/m^\circ)B_{MX}^C + (m/m^\circ)^2\nu_M z_M C_{MX}^C] \quad (17)$$

where

$$B_{MX}^C = \left(\frac{\partial^2\beta_{MX}^{(0)}}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial\beta_{MX}^{(0)}}{\partial T}\right)_p + 2\left\{\left(\frac{\partial^2\beta_{MX}^{(1)}}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial\beta_{MX}^{(1)}}{\partial T}\right)_p\right\} j(\alpha I^{1/2}) + 2\left\{\left(\frac{\partial^2\beta_{MX}^{(2)}}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial\beta_{MX}^{(2)}}{\partial T}\right)_p\right\} j(\alpha_2 I^{1/2}) + k\,I^{1/2}\left(\frac{A_H}{RT^2}\left(\frac{\partial\beta_{MX}^{(2)}}{\partial T}\right)_p + \frac{A_C}{2RT^2}\beta_{MX}^{(2)}\right) j'(\alpha_2 I^{1/2}) + k^2\,I\left(\frac{A_H{}^2}{8R^2\,T^4}\right)\beta_{MX}^{(2)}\,j''(\alpha_2 I^{1/2}) \quad (18)$$

$$C_{MX}^C = \left(\frac{\partial^2 C_{MX}^{(0)}}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial C_{MX}^{(0)}}{\partial T}\right)_p + 4\left\{\left(\frac{\partial^2 C_{MX}^{(1)}}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial C_{MX}^{(1)}}{\partial T}\right)_p\right\}[6 - (6 + 6\alpha_3 I^{1/2} + 3\alpha_3{}^2 I + \alpha_3{}^3 I^{3/2}) \times \exp(-\alpha_3 I^{1/2})]/(\alpha_3{}^4 I^2) \quad (19)$$

where

$$j''(x) = (6/x^4)[1 - (1 + x + x^2/2 + x^3/6)\exp(-x)] \quad (20)$$

and where A_C is the Debye–Hückel coefficient for apparent molar heat capacity and $C_{p,m,2}^\circ$ is the standard-state molar heat capacity of the solute. The latter quantity was calculated as in eq 1 with $C_{p,m,2}^\circ$ for NaCl(aq) from Archer (1992a), $C_{p,m,2}^\circ$ for Na_2SO_4(aq) from Holmes and Mesmer (1986), and $C_{p,m,2}^\circ$ for $MgCl_2$(aq) from White et al. (1988). Each of the three different studies used different formulations of the properties of water for calculation of Debye–Hückel functions. Differences in Debye–Hückel functions will result in slightly different values of $C_{p,m,2}^\circ$ being calculated from the same set of observations. Archer (1990) gave equations by which these effects could be calculated, and adjustments for changes from one basis to another could be generated and applied to linear models. The material in Archer (1990) and the differences of the three different Debye–Hückel functions were used to determine that the effect was significantly smaller than the expected uncertainty in $C_{p,m,2}^\circ$. The values of $C_{p,m,2}^\circ$ were combined and represented for the present purpose as

$$C_{p,\,m,\,2}^\circ/C^\circ = -295.3 - 18.527\,79(T/T^\circ - 298.15) + 0.0728\,295\{(T/T^\circ)^2 - 298.15^2\} - 8.795\ \ 39\times10^{-5}\{(T/T^\circ)^3 - 298.15^3\} \quad (21)$$

where $C^\circ = 1$ J·K^{-1}·mol^{-1} and $T^\circ = 1$ K. Equation 21 is for 0.1 MPa or the saturation pressure of the solution, whichever is larger. The change of $C_{p,m,2}^\circ$ for a change in pressure of 2.0 MPa was calculated from the equation for volumetric properties given by Phutela and Pitzer (1986b) and combined with $C_{p,m,2}^\circ$ calculated from eq 21. This small pressure adjustment arose because Phutela and Pitzer made heat capacity measurements along a 2 MPa isobar. The quantity included in the representations, in the case of the Phutela and Pitzer measurements, was $(C_{p,\phi} - C_{p,m,2}^\circ)$ for 2.0 MPa. The change in $C_{p,\phi}^\circ$ for the 2 MPa pressure difference was on the order of 5–6 J·K^{-1}·mol^{-1}, or less, for temperatures less than 450 K. The uncertainty of $C^{\circ}_{p,\phi}$ calculated from eq 21 is expected to be greater than 5 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. For finite concentrations on the order of 0.1 $\mathrm{mol \cdot kg^{-1}}$ the pressure effect is less. Because all these effects were small, it was assumed that only negligible changes in the least-squares determined parameters would result for the temperatures considered here, and hence the least-squares estimated parameters were assumed independent of pressure for the small pressure range encountered here. Nonetheless, the Debye−Hückel coefficients were calculated for the temperature and pressure of each measurement.

The adjustable parameters $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$, $\beta^{(2)}_{\mathrm{MX}}$, $C^{(0)}_{\mathrm{MX}}$, and $C^{(1)}_{\mathrm{MX}}$ were assumed to be linear combinations of functions of temperature as

$$\beta^{(0)}_{\mathrm{MX}} = f_1(T) \tag{22}$$

$$\beta^{(1)}_{\mathrm{MX}} = f_2(T) \tag{23}$$

$$\beta^{(2)}_{\mathrm{MX}} = f_3(T) \tag{24}$$

$$C^{(0)}_{\mathrm{MX}} = f_4(T) \tag{25}$$

$$C^{(1)}_{\mathrm{MX}} = f_5(T) \tag{26}$$

where

$$f_{\mathrm{i}}(T) = b_{\mathrm{i},1} + b_{\mathrm{i},2}10^{-2}(T - T_{\mathrm{r}})/T^{\circ} + b_{\mathrm{i},3}10^{-5}\{(T - T_{\mathrm{r}})/\mathrm{T}^{\circ}\}^2 + b_{\mathrm{i},4}T^{\circ}10^2/(T - 225\ \mathrm{K}) + b_{\mathrm{i},5}10T^{\circ}/(680\ \mathrm{K} - T) + b_{\mathrm{i},6}10^3T^{\circ}/T + b_{\mathrm{i},7}10^{-7}\{(T - T_{\mathrm{r}})/\mathrm{T}^{\circ}\}^3 \tag{27}$$

and where T_{r} was taken to be 298.15 K. Twelve of the thirty-five possible $b_{i,j}$ were not required to represent the selected measurements within experimental error. Some calculated values of the ion-interaction parameters, against which programs may be tested, are given in Table 4.

(2) Chemical Equilibrium Model. The chemical equilibrium model used here is that described by Archer and Wood (1985). Only a brief description is given here. In this model, the activity of the *i*th ion in solution is given as

$$a_{\mathrm{i}} = (m_{\mathrm{i}}/m^{\circ})\gamma_{\mathrm{i}} = \gamma_{\mathrm{i}}^{\circ}\{m_{\mathrm{i}} - \sum_{n>1} n_i K_{\mathbf{n}} a^{\mathbf{n}}/\gamma_{\mathrm{n}}^{\circ}\}/m^{\circ} \tag{28}$$

$$\ln \gamma_i^{\circ} = \frac{-A_{\gamma}z_i^{\,2}I^{1/2}}{1 + b\ I^{1/2}} + \beta\sum_i(m_i/m^{\circ})\left(1 + \frac{15}{32}\sum_i(m_i/m^{\circ})\right) + \beta'\sum_i(m_i/m^{\circ})^3 \tag{29}$$

$$\ln \gamma_n^{\circ} = \frac{-A_{\gamma}z_n^{\,2}I^{1/2}}{1 + b\ I^{1/2}} + \beta\sum n_i\sum_i(m_i/m^{\circ})\left(1 + \frac{15}{32}\sum_i(m_i/m^{\circ})\right) + \beta'\sum n_i\sum_i(m_i/m^{\circ})^3 \tag{30}$$

where m_i is the stoichiometric molality of ion i. The symbol $\mathbf{n}$ specifies a set $\mathbf{n} = \{n_1, n_2, ..., n_{\sigma}\}$, where each of the n_i are the numbers of component ions of the set $\mathbf{n}$ defining an n-mer species in solution. The product of the activities of the component ions of the set $\mathbf{n}$ is

$$a^{\mathbf{n}} = \prod^{\sigma} a_i^{\,n_i}$$

A_{γ} is the Debye−Hückel coefficient for the activity coefficient; $K_{\mathbf{n}}$ is the equilibrium constant for formation of the n-mer of the set $\mathbf{n}$. $\sum n_i$ is the sum of the numbers of ions ($n_1 + n_2 + ..., + n_{\sigma}$) of the set $\mathbf{n}$. β is an adjustable parameter approximating a volume exclusion term for the solute species. The adjustable parameter β' has been added to the previous model to improve representation of the measurements for molalities that corresponded to supersaturation at 298.15 K. Note that the ionic strength, I, in the chemical equilibrium model is not calculated assuming full dissociation as it was in the ion-interaction formalism. It is not that ionic strength is defined differently in the two models, it is the assumption regarding the numbers of ions present that is different. For the chemical equilibrium model, $b = 2\ \mathrm{kg^{1/2} \cdot mol^{-1/2}}$. The term $15/32\ (\beta)(\sum(m_i/m^{\circ}))^2$ was described by Archer and Wood as arising from the relation of the second and third virial coefficients for a hard-sphere fluid. This was incorrect. In those terms, the third virial coefficient should have been $(15/32)\ \beta^2$; however this quantity is too small to represent adequately the properties of $\mathrm{MgSO_4(aq)}$. The absence of the square of the second virial coefficient in the third virial coefficient was noticed in derivations to obtain the higher virial coefficient for possible inclusion in eqs 29−30 for the present work and has also recently been noticed by Kodytek (1998). In the present work, we retained the same relation of second and third virial coefficients for repulsive interactions used by Archer and Wood and have treated the additional, higher, virial coefficient for this interaction as a variable parameter.

The stoichiometric osmotic coefficient is

$$\sum_i m_{i,\mathrm{st}}\phi_{\mathrm{st}} = \sum_i m_j\phi_j + \sum_n m_n\phi_n \tag{31}$$

where

$$\phi_j = 1 + (1/2)\beta\left(\sum_i(m_i/m^{\circ})\right)\left(1 + \frac{5}{8}\sum_i(m_i/m^{\circ})\right) + \left(\frac{3}{2}\beta'\sum_i(m_i/m^{\circ})^3\right) - [A_{\gamma}z_j^{\,2}/b^3\ I][1 + bI^{1/2} - 2\ln(1 + bI^{1/2}) - (1 + bI^{1/2})^{-1}] \tag{32}$$

and

$$\phi_n = 1 + (1/2)\beta\ (\sum_i n_i)\left(\sum_i(m_i/m^{\circ})\right)\left(1 + \frac{5}{8}\sum_i(m_i/m^{\circ})\right) + (\sum_i n_i)\left(\frac{3}{2}\beta'\sum_i(m_i/m^{\circ})^3\right) - [A_{\gamma}z_j^{\,2}/(b^3\ I)][1 + bI^{1/2} - 2\ln(1 + bI^{1/2}) - (1 + bI^{1/2})^{-1}] \tag{33}$$

The relative apparent molar enthalpy and relative apparent molar heat capacity are obtained as numerical derivatives of the excess Gibbs energy. The temperature dependence of the heat capacity for the association reaction of the n-mer was taken to be

$$\Delta C^{(T)}_{p,\mathbf{n}} = \Delta C^{(T_{\mathrm{r}})}_{p,\mathbf{n}} + a_1(T - T_{\mathrm{r}}) + a_2(T^2 - T_{\mathrm{r}}^{\,2}) \tag{34}$$

The temperature dependence of the equilibrium constant for the $\mathbf{n}$th reaction was obtained from the usual integration of eq 34. For the case where a_1 and a_2 of eq 34 are

Table 2. Literature Sources for the Activity and Thermal Properties of $MgSO_4(aq)$

ref	temp range/K	molality range/mol·kg^{-1}	n	type^a	$\sigma_{est}{}^b$	σ_{fit}	
						ion-interaction	chemical equilibrium
55-bro/pru	T_{fus}	0.006−0.10	24	$\Delta_{fus}T$	5×10^{-4} K	0.0030^c	0.0028^c
71-iso	T_{fus}	0.002−0.18	16	$\Delta_{fus}T$	U	0.006^d	
65-lin	T_{fus}	1.1−1.7	2	$\Delta_{fus}T$	0.05 K	0.058^c	0.060^c
table 1	298.15	0.52−3.48	10	ϕ	0.002	0.0019^c	0.0026^c
81-rar/mil	298.15	0.26−3.62	58	ϕ	0.002	0.0014^c	0.0024^c
75-yok/yam	298.15	0.005−0.15	13	ϕ	0.003−0.005	0.0055^c	0.0078^c
68-wu/rus	298.15	0.6−2.6	10	ϕ	0.005	0.0034^c	0.0035^c
84-fil/che	298.15	1.5−2.5	4	ϕ	0.003	0.0005^c	0.0011^c
80-lib/sad	298.15	0.1−3.7	34	ϕ	U	0.017^c	
85-sei/ros	298.15	1.5−3.0	9	ϕ	U	0.0014^c	
71-chi/pla	288.15	0.1−3.0	14	ϕ	0.005	0.0032^c	0.0026^c
62-kan/gro	293−298	0.5−3.5	14	$p_s - p_w$	U	0.041^c	
73-pla	273.15	1.2−3.1	5	ϕ	0.005^e	0.0036^c	0.0046^c
83-hol/mes	383.14	1.38−5.05	34	ϕ	0.005	0.0030^c	0.0047^c
83-hol/mes	413.22	1.69	2	ϕ	0.005	0.004^c	0.0009^c
60-pat/gil	372.75	1.9−4.7	10	ϕ	U	0.008^c	0.018^c
62-sol/pat	394.25	3.7 − 6.2	9	ϕ	U	0.38^c	
31-lan/str	298.15	$8.2 \times 10^{-5} - 0.05$	26	$\Delta_{dil}L_\phi$	0.05	0.083^f	0.036^f
28-lan	298.15	$3 \times 10^{-4} - 0.002$	2	$\Delta_{dil}L_\phi$	0.1	0.012^f	0.064^f
75-sni/man	298.15	$2 \times 10^{-3} - 1.95$	10	$\Delta_{dil}L_\phi$	0.05	0.091^f	0.067^f
72-poc/orz	298.15	0.046−3.16	17	$\Delta_{dil}L_\phi$	g	0.11^f	0.14^f
32-pla	294.	$2 \times 10^{-4} - 0.25$	10	$\Delta_{dil}L_\phi$	U	0.16^f	
75-leu/mil	303.15	0.34−1.06	6	$\Delta_{dil}L_\phi$	0.01	0.029^f	0.023^f
75-sni/man	313−353	$2 \times 10^{-3} - 1.97$	16	$\Delta_{dil}L_\phi$	0.05	0.34^f	0.27^f
83-may/woo	373.15	0.001−1.99	11	$\Delta_{dil}L_\phi$	h	0.117^f	0.108^f
83-may/woo	423.65	0.001−2.7	19	$\Delta_{dil}L_\phi$	h	0.470^f	0.410^f
66-cap/nap	298.15	0.07−1.11	7	$\Delta_{sol}H_m(\cdot 7H_2O)$	0.50	0.40^f	0.92^f
51-kag/mis	298.15	0.002−2.23	21	$\Delta_{sol}H_m(\cdot 7H_2O)$	U	0.31^f	
30-per	284.15	1.4−2.5	5	$\Delta_{sol}H_m(\cdot 7H_2O)$	0.50	0.08^f	
1882-tho	291.15	0.14	1	$\Delta_{sol}H_m(\cdot 7H_2O)$	0.50	1.0^f	1.2^f
1885-pic	293.35	0.14	1	$\Delta_{sol}H_m(\cdot 7H_2O)$	0.50	0.30^f	0.58^f
1882-tho	291.15	0.14	1	$\Delta_{sol}H_m(\cdot 6H_2O)$	0.1	0.31^f	0.42^f
75-per/des	298.15	0.01−0.25	8	$C_{p,\phi} - C^\circ_{p,\phi}$	0.001	0.002^i	0.002^i
72-poc/orz	298.15	0.38−3.16	15	$C_{p,\phi} - C^\circ_{p,\phi}$	0.02	0.019^i	0.029^i
86-phu/pit	348.15−373.15	0.17−2.2	19	$C_{p,\phi} - C^\circ_{p,\phi}$	0.005	0.006^i	0.012^i
86-phu/pit	398.15	0.17−2.1	8	$C_{p,\phi} - C^\circ_{p,\phi}$	0.01	0.005^i	0.005^i
86-phu/pit	423.15−448.15	0.1−1.5	12	$C_{p,\phi} - C^\circ_{p,\phi}$	0.025	0.042^i	0.069^i
37-dan/tol	294.15−360.15	0.76−4.4	13	$C_{p,\phi} - C^\circ_{p,\phi}$	0.020	0.015^i	0.022^i
73-lik/bro	353−453	0.18−0.9	30	$C_{p,\phi} - C^\circ_{p,\phi}$	U	0.044^i	
table 1	298.15	m_s	1	$m_s(MgSO_4\cdot 7H_2O)$	0.008	0.022^f	0.009^f
34-tin/mcc	303−318	m_s	6	$m_s(MgSO_4\cdot 7H_2O)$	0.015	0.013^f	0.032^f
34-tin/mcc	298.15	m_s	1(comp)^j	$m_s(MgSO_4\cdot 7H_2O)$	0.015	0.008^f	0.001^f
29-sch	298−314	m_s	3	$m_s(MgSO_4\cdot 7H_2O)$	0.015	0.018^f	0.019^f
29-sch	323−336	m_s	3	$m_s(MgSO_4\cdot 6H_2O)$	0.015	0.018^f	0.077^f
23-smi/rin	333−352	m_s	5	$m_s(MgSO_4\cdot 6H_2O)$	k	0.042^f	0.070^f
35-bon/bur	283−298		4	p_{dec}	0.066	0.032^l	
23-sch	298.15		1	p_{dec}	0.066	0.037^l	
23-car/jet	298−318		9	p_{dec}	0.08	0.08^l	

[a] The symbols $\Delta_{sol}H_m(\cdot 7H_2O)$ and $\Delta_{sol}H_m(\cdot 6H_2O)$ refer to the enthalpy of solution of epsomite and hexahydrite, respectively; p_{dec} is the vapor pressure of water in equilibrium with $MgSO_4\cdot 7H_2O$ and $MgSO_4\cdot 6H_2O$; $p_s - p_w$ is the difference in vapor pressure between the solution and water. [b] The letter U indicates that these points were given an insignificant weight in the least-squares procedure. [c] σ_i in terms of osmotic coefficient. [d] Lowest molality point excluded in calculation. [e] One isopiestic ratio against KCl(aq) excluded from representation. [f] Units are kJ·mol^{-1} for enthalpies of dilution and solution and for Gibbs energies of solution. [g] σ_{exp} estimated as ±50 J·mol^{-1} or 5% of $\Delta_{dil}L_\phi$, whichever was largest. Dilutions below 0.46 mol·kg^{-1} excluded from representation. [h] For 373 K, dilutions with initial molalities greater than 0.015 mol·kg^{-1}, $\sigma_{exp} = 0.1$ kJ·mol^{-1}, lesser concentrations σ_{exp} increased to 0.5 kJ·mol^{-1} at the smallest concentration. For 423 K, dilutions with initial molalities greater than 0.01 mol·kg^{-1}; $\sigma_{exp} = 0.1$ kJ·mol^{-1}, lesser concentrations σ_{exp} increased to 0.3 kJ·mol^{-1} at the smallest concentration. [i] Units are kJ·K^{-1}·mol^{-1}. [j] Composite of 298.15 K solubility values, reported by Ting and McCabe (1934). [k] Values of σ_{exp} taken as 0.017 kJ·mol^{-1} for $T < 353$ K; no significant weight given for solubilities above 353 K. [l] Units are kPa.

not significant, this integration results in

$$K_{\mathbf{n}}^{(T)} = K_{\mathbf{n}}^{(T_r)} \exp\left\{\frac{1}{R}\left[\Delta C_{p,\mathbf{n}}^{(T_r)} \ln(T/T_r) + (\Delta H_{\mathbf{n}}^{(T_r)} - T_r \Delta C_{p,\mathbf{n}}^{(T_r)})\left(\frac{1}{T_r} - \frac{1}{T}\right)\right]\right\} \quad (35)$$

The temperature dependence of the volume exclusion terms was represented as

$$\beta^T = \beta^{T_r} + \beta_1(T - T_r)/T^\circ + \beta_2(T^2 - T_r{}^2)/(T^\circ)^2 + \beta_3(T^3 - T_r{}^3)/(T^\circ)^3 \quad (36)$$

and

$$\beta'^T = \beta'^{T_r} + \beta'_1(T - T_r)/T^\circ \quad (37)$$

The model is nonlinear and requires use of appropriate nonlinear methods for evaluation of equilibrium composition and optimization of parameters. The least-squares estimated parameters are given in Table 5.

Phase Equilibria. In the temperature range of interest here, the solid phases that might coexist with the solution consist of ice and a set of crystalline hydrates of definite stoichiometry. The solute-containing hydrate phases that appear in the literature are $MgSO_4\cdot nH_2O$ where n can take any of the values {1, 2, 3, 4, 5, 6, 7, 12}.

Table 3. Least-Squares Estimated Parameters for the Ion-interaction Model of the Thermodynamic Properties of $MgSO_4(aq)$

parameter	value	parameter	value	parameter	value[a]
$b_{1,1}$	−0.526 309 458 086 110	$b_{3,1}$	1347.338 647 226 72	$b_{5,1}$	0.411 919 661 612 742
$b_{1,2}$	0.798 429 374 952 591	$b_{3,2}$	656.287 453 214 204	$b_{5,2}$	−1.241 147 115 300 86
$b_{1,3}$	−8.623 435 830 472 59	$b_{3,3}$	608.536 936 104 363	$b_{5,3}$	11.140 043 326 195 2
$b_{1,4}$		$b_{3,4}$		$b_{5,4}$	−0.055 591 328 596 819 4
$b_{1,5}$	19.167 271 049 776 8	$b_{3,5}$	−73626.453 344 415 6	$b_{5,5}$	
$b_{1,6}$		$b_{3,6}$	161.319 854 373 951	$b_{5,6}$	
$b_{1,7}$	−0.095 677 192 389 777 0	$b_{3,7}$	73.115 539 370 902 7	$b_{5,7}$	
$b_{2,1}$	4.791 380 465 497 94	$b_{4,1}$	0.016 165 666 680 029 8		
$b_{2,2}$	−1.954 157 268 511 80	$b_{4,2}$	−0.044 916 378 309 525 2	$\Delta_{\rm sol}G^\circ_{T_r,p_r(\rm MgSO_4\cdot 7H_2O)}$	$10.616 \pm 0.066\ \rm kJ\cdot mol^{-1}$
$b_{2,3}$	23.181 823 689 080 9	$b_{4,3}$	0.331 353 349 416 800	$\Delta_{\rm sol}S^\circ_{T_r,p_r(\rm MgSO_4\cdot 7H_2O)}$	$5.24 \pm 1.05\ \rm J\cdot K^{-1}\cdot mol^{-1}$
$b_{2,4}$	−0.752 047 721 452 442	$b_{4,4}$		$\Delta_{\rm sol}G^\circ_{T_r,p_r(\rm MgSO_4\cdot 6H_2O)}$	$8.970 \pm 0.073\ \rm kJ\cdot mol^{-1}$
$b_{2,5}$		$b_{4,5}$		$\Delta_{\rm sol}S^\circ_{T_r,p_r(\rm MgSO_4\cdot 6H_2O)}$	$-44.15 \pm 0.88\ \rm J\cdot K^{-1}\cdot mol^{-1}$
$b_{2,6}$		$b_{4,6}$			
$b_{2,7}$		$b_{4,7}$	0.012 959 960 835 412 2		

[a] The ± values are 95% confidence intervals within the global data representation.

Table 4. Values of Ion-interaction Parameters at Selected Temperatures

T/K	$\beta^{(0)}_{\rm MX}$	$\beta^{(1)}_{\rm MX}$	$\beta^{(2)}_{\rm MX}$	$C^{(0)}_{\rm MX}$	$C^{(1)}_{\rm MX}$
273.15	−0.308 55	3.8629	−32.1241	0.029 445 5	0.676 377
298.15	−0.024 35	3.7633	−39.7431	0.016 165 7	0.335 923
323.15	0.156 38	3.6815	−48.6940	0.007 027 8	0.114 619
348.15	0.233 71	3.7832	−63.6938	0.002 153 3	0.024 706
373.15	0.208 05	4.1221	−90.2401	0.001 663 8	0.070 163
398.15	0.080 26	4.7211	−135.292	0.005 680 6	0.252 671
423.15	−0.148 13	5.5913	−208.218	0.014 325 4	0.573 062

The Gibbs energy of solution of the hydrate containing n mol of water is

$$\Delta_{\rm sol}G^\circ_{n-\rm hydrate} = G^\circ_{\rm m,\,2} + {\rm n}G^\circ_{\rm m,\,1} - G^\circ_{{\rm m,cr,}n-\rm hydrate} = -2RT\ln(m_{\rm s}\gamma_{\pm,\,\rm s}/m^\circ) - {\rm n}RT\ln a_{\rm w,sat} \quad (38)$$

where $G^\circ_{\rm m,2}$, $G^\circ_{\rm m,1}$, and $G^\circ_{{\rm m,cr,}i}$ are the standard-state molar Gibbs energies for the solute, the pure liquid water, and the ith crystal phase all at a given T and p, respectively, $\Delta_{\rm sol}G^\circ_i$ is the standard-state molar Gibbs energy for the solution process of the ith crystal phase and $m_{\rm sat}$, $\gamma_{\pm,\rm sat}$ and $a_{\rm w,sat}$ are the saturation molality, the mean stoichiometric activity coefficient for the solute at saturation, and the activity of water for the saturation molality, respectively. Of course, $G^\circ_{\rm m,2}$, $G^\circ_{\rm m,1}$, and $G^\circ_{{\rm m,cr,}i}$ cannot be evaluated and so eq 38 was rewritten as

$$\Delta_{\rm sol}G^\circ_{n-{\rm hydrate},\,T'} = \Delta_{\rm sol}G^\circ_{n-{\rm hydrate},\,T_{\rm r}} - \Delta_{\rm sol}S^\circ_{n-{\rm hydrate},\,T_{\rm r}}(T' - T_{\rm r}) + \int_{T_{\rm r}}^{T'} (C^\circ_{p,\,2} + {\rm n}C^\circ_{p,\,1} - C^\circ_{p,\,n-\rm hydrate}){\rm d}T - T'\int_{T_{\rm r}}^{T'} [(C^\circ_{p,\,2} + {\rm n}C^\circ_{p,\,1} - C^\circ_{p,\,n-\rm hydrate})/T]{\rm d}T = -2RT'\ln(m_{\rm s}\gamma_{\pm,\,\rm s}/m^\circ) - nRT'\ln a_{\rm w,sat} \quad (39)$$

The first term under each integral was obtained from eq 1; the second term under the integral was obtained from the equation of Hill (1990); and the third term, the heat capacity of the crystalline hydrate phase, will be discussed below.

Solubility measurements for epsomite ($n = 7$) and hexahydrite were included in the global data fits. Solubility measurements for other hydrates were not included for reasons discussed below. The two Gibbs energies of solution at the reference temperature, $T_{\rm r}$, and reference pressure, $p_{\rm r} = 0.1$ MPa, were treated as adjustable parameters, as were the two $\Delta_{\rm sol}S^\circ_{{\rm m,cr,}n\text{-hydrate},T_{\rm r},p_{\rm r}}$. In addition, the experimental solubility results make some contribution to the determination of the parameters for the excess Gibbs energy for the solution through eq 39. Because of fundamental differences in the models, linear vs nonlinear, the nature of incorporation of the observed solubilities as fitted data is somewhat different in the two models. This results in different weighting being applied in the models. As a result, the two models can be expected to give slightly different results for the equilibrium phase observations, both solubilities and enthalpies of solution.

For the dehydration (decomposition) reaction

$$\rm MgSO_4\cdot{\it n}H_2O(cr) = MgSO_4\cdot{\it m}H_2O(cr) + ({\it n} - {\it m})H_2O(g) \quad (40)$$

the standard Gibbs energy of reaction for 298.15 K and 0.1 MPa, per mole of H_2O, is

$$\Delta_{\rm dec}G^\circ_{{\rm m},T_{\rm r}} = \{\Delta_{\rm f}G^\circ_{{\rm MgSO_4\cdot}m{\rm H_2O(cr)},T_{\rm r}} + (n - m)\Delta_{\rm f}G^\circ_{{\rm H_2O(g)},T_{\rm r}} - \Delta_{\rm f}G^\circ_{{\rm MgSO_4\cdot}n{\rm H_2O(cr)},T_{\rm r}}\}/(n - m) \quad (41)$$

where $\Delta_{\rm f}G^\circ_{{\rm MgSO_4\cdot}n{\rm H_2O(cr)},T_{\rm r}}$ and $\Delta_{\rm f}G^\circ_{{\rm MgSO_4\cdot}m{\rm H_2O(cr)},T_{\rm r}}$ are the standard-state Gibbs energies of formation of the two hydrated crystal phases at $T_{\rm r}$, and $0 \le m < n$. The standard-state Gibbs energy of formation of $H_2O(g)$ at $T_{\rm r}$, $\Delta_{\rm f}G^\circ_{{\rm H_2O(g)},T_{\rm r},p_{\rm r}}$ was calculated from values given by Cox et al. (1989). At any given temperature T', the standard Gibbs energy of decomposition, $\Delta_{\rm dec}G^\circ_{{\rm m},T',p_{\rm r}}$, is

$$\Delta_{\rm dec}G^\circ_{{\rm m},T',p_{\rm r}} = \Delta_{\rm dec}G^\circ_{{\rm m},T_{\rm r},p_{\rm r}} + \{[(n - m)S^\circ_{{\rm m,\,H_2O(g)},T_{\rm r},p_{\rm r}} + S^\circ_{{\rm m,\,MgSO_4\cdot}m{\rm H_2O},Tr,pr} - S^\circ_{{\rm m,\,MgSO_4\cdot}n{\rm H_2O},\,T_{\rm r},\,p_{\rm r}}](T_{\rm r} - T') + \int_{T_{\rm r}}^{T'}\Delta_{\rm dec}C^\circ_{p,\,{\rm m},\,p_{\rm r}}\,{\rm d}T - T'\int_{T_{\rm r}}^{T'}(\Delta_{\rm dec}C^\circ_{p,\,{\rm m},\,p_{\rm r}}/T)\,{\rm d}T\}/(n - m) \quad (42)$$

where

$$\Delta_{\rm dec}C^\circ_{p,\,{\rm m},\,p_{\rm r}} = (n - m)C^\circ_{p,\,{\rm m,\,H_2O(g)},\,p_{\rm r}} + C^\circ_{p,\,{\rm m,\,MgSO_4\cdot}m{\rm H_2O},\,p_{\rm r}} - C^\circ_{p,\,{\rm m,\,MgSO_4\cdot}n{\rm H_2O},\,p_{\rm r}} \quad (43)$$

again per mole of water. The heat capacities and entropies for the crystal phases of eqs 42 and 43 will be discussed below.

The measurements considered for the present representations are given in Table 2. The weighting factors for the experimental results were calculated from an estimated

Table 5. Least-Squares Estimated Parameters for the Chemical Equilibrium Model of the Thermodynamic Properties of $MgSO_4$(aq)

parameter	value	parameter	value	parameter	value
K_{1-1}	162.46	K_{2-1}	553.61	K_{3-3}	5.0449×10^6
ΔH_{1-1}	5.2205 $kJ\cdot mol^{-1}$	ΔH_{2-1}	8.7418 $kJ\cdot mol^{-1}$	ΔH_{3-3}	11.114 $kJ\cdot mol^{-1}$
$\Delta C_{p\ 1-1}$	164.8 $J\cdot K^{-1}\cdot mol^{-1}$	$\Delta C_{p\ 2-1}$	387.2 $J\cdot K^{-1}\cdot mol^{-1}$	$\Delta C_{p\ 3-3}$	1105.2 $J\cdot K^{-1}\cdot mol^{-1}$
a_1	−9.991 $J\cdot K^{-2}\cdot mol^{-1}$				
a_2	1.644×10^{-2} $J\cdot K^{-3}\cdot mol^{-1}$				
β^{Tr}	0.037136	β'^{Tr}	149.135×10^{-6}		
β_1	6.347×10^{-5}	β'_1	-1919.03×10^{-9}		
β_2	-4.5452×10^{-7}				
β_3	1.11513×10^{-10}				
$\Delta_{sol}G^\circ_{T_r, p_r(MgSO_4\cdot 7H_2O)}$	11.031 $kJ\cdot mol^{-1}$				
$\Delta_{sol}S^\circ_{T_r, p_r(MgSO_4\cdot 7H_2O)}$	5.24 $J\cdot K^{-1}\cdot mol^{-1}$				
$\Delta_{sol}G^\circ_{T_r, p_r(MgSO_4\cdot 6H_2O)}$	9.147 $kJ\cdot mol^{-1}$				
$\Delta_{sol}S^\circ_{T_r, p_r(MgSO_4\cdot 6H_2O)}$	−43.86 $J\cdot K^{-1}\cdot mol^{-1}$				

Table 6. Values of $\gamma_\pm$ Calculated from the Ion-Interaction Model

	$m/(mol\cdot kg^{-1})$							
T/K	0.001	0.01	0.1	0.5	1.0	2.0	3.0	5.0
273.15	0.7400	0.4317	0.1756	0.0788	0.0567	0.0491	0.0613	
298.15	0.7269	0.4123	0.1652	0.0753	0.0544	0.0464	0.0549	
323.15	0.7114	0.3902	0.1505	0.0667	0.0471	0.0385	0.0426	
348.15	0.6906	0.3625	0.1331	0.0563	0.0385	0.0297	0.0305	0.0489
373.15	0.6621	0.3277	0.1138	0.0455	0.0300	0.0216	0.0207	0.0281
398.15	0.6239	0.2864	0.0938	0.0351	0.0222	0.0150	0.0135	0.0172
423.15	0.5745	0.2407	0.0741	0.0258	0.0157	0.0099	0.0085	

Table 7. Values of ϕ Calculated from the Ion-Interaction Model

	$m/(mol\cdot kg^{-1})$							
T/K	0.001	0.01	0.1	0.5	1.0	2.0	3.0	5.0
273.15	0.8992	0.7515	0.6005	0.5168	0.5246	0.6718	0.9759	
298.15	0.8928	0.7397	0.5955	0.5244	0.5299	0.6632	0.9240	
323.15	0.8851	0.7254	0.5784	0.5067	0.5050	0.6176	0.8354	
348.15	0.8744	0.7068	0.5557	0.4779	0.4668	0.5545	0.7317	1.2314
373.15	0.8588	0.6827	0.5298	0.4428	0.4213	0.4822	0.6243	1.0340
398.15	0.8367	0.6531	0.5013	0.4035	0.3717	0.4062	0.5217	0.9236
423.15	0.8061	0.6187	0.4701	0.3607	0.3198	0.3312	0.4329	

Table 8. Values of $\gamma_\pm$ Calculated from the Chemical-Equilibrium Model

	$m/(mol\cdot kg^{-1})$							
T/K	0.001	0.01	0.1	0.5	1.0	2.0	3.0	5.0
273.15	0.7232	0.4154	0.1691	0.0758	0.0551	0.0470	0.0571	
298.15	0.7117	0.4010	0.1605	0.0728	0.0523	0.0438	0.0506	
323.15	0.6926	0.3768	0.1452	0.0639	0.0451	0.0363	0.0396	
348.15	0.6656	0.3452	0.1261	0.0530	0.0364	0.0277	0.0282	0.0511
373.15	0.6292	0.3073	0.1054	0.0417	0.0276	0.0198	0.0187	0.0266
398.15	0.5806	0.2641	0.0844	0.0312	0.0199	0.0133	0.0116	0.0128
423.15	0.5170	0.2172	0.0647	0.0222	0.0136	0.0085	0.0068	

square root of variance for each data set given in Table 2. The agreement of the two models with the measured quantities is also given in Table 2 in the form of root-mean-square deviations (rms). The least-squares estimated parameters for the ion-interaction and the chemical equilibrium model are given in Tables 3 and 4, respectively. Approximately a third more adjustable parameters were used for the ion-interaction model than for the chemical equilibrium model, 23 vs 17, for parameters not directly involving crystalline-hydrate phase behavior. (There are different numbers of “significant digits” given in Tables 3 and 4. This is in large part a consequence of the nature of the temperature-dependence portions of the two models. In the chemical equilibrium model, the temperature dependence of the equilibrium constants is an exponential of the enthalpy and heat capacity. In the ion-interaction model, the temperature dependence of the virial coefficients is given as an arbitrary linear function that is assumed to converge to the true behavior. Without involving term-by-term expansions of the two, one is coarsely attempting to represent an exponential behavior (true thermodynamic relation of association constants and enthalpy) with an arbitrary linear function. In such a representation, one adds and subtracts large quantities to arrive at a final small quantity. This necessarily requires large numbers of digits. The numbers of required digits are increased further because we wish to obtain accurately several higher temperature derivatives. There may be a few too many digits for the parameters given in Table 3, but it is not clear where to truncate these numbers and we feel that it is better to give too many digits than too few, for obvious reasons.)

Calculated values of the stoichiometric activity coefficient and the osmotic coeffecient for the two models, against which calculations may be checked, are given in Tables 6−9.

Agreement with the Experimental Results for $MgSO_4$(aq)

Solution Properties. Osmotic coefficients were calculated from the difference in vapor pressure between the

Table 9. Values of ϕ Calculated from the Chemical-Equilibrium Model

	m/(mol·kg^{-1})							
T/K	0.001	0.01	0.1	0.5	1.0	2.0	3.0	5.0
273.15	0.8907	0.7462	0.6025	0.5240	0.5289	0.6791	0.9780	
298.15	0.8854	0.7380	0.5955	0.5229	0.5292	0.6627	0.9258	
323.15	0.8759	0.7231	0.5789	0.5047	0.5071	0.6198	0.8447	
348.15	0.8621	0.7027	0.5554	0.4757	0.4710	0.5594	0.7430	1.3437
373.15	0.8429	0.6773	0.5269	0.4390	0.4256	0.4878	0.6272	1.0866
398.15	0.8167	0.6476	0.4953	0.3967	0.3749	0.4102	0.5031	0.8134
423.15	0.7817	0.6150	0.4622	0.3525	0.3237	0.3316	0.3754	

solution and the solvent as

$$\phi = \frac{(G^\circ_{\mathrm{m,1,l}} - G^\circ_{\mathrm{m,1,g}})}{RT\nu m M_1} \qquad (44)$$

where the difference in chemical potential for the vapor and the liquid at the temperature and pressure of the solution, $G^\circ_{\mathrm{m,1,g}} - G^\circ_{\mathrm{m,1,l}}$ was calculated from the equation of state for water. Osmotic coefficients were calculated from the difference in freezing temperature of water in the solution from that of pure water by means of the equation given by Craft and VanHook (1975). Osmotic coefficients were determined from isopiestic ratios by means of either the equation for NaCl(aq) (Archer, 1992a) or the equation for KCl(aq) (Archer, 1997).

The osmotic coefficients for 288.15 K from Childs and Platford (1971) were taken from their table of ϕ at round molalities, which they constructed from some manipulation of their measured isopiestic ratios and using H_2SO_4(aq) and urea(aq) as standards. They did not give their measured ratios, and so their osmotic coefficients could not be reevaluated using the newer equations for isopiestic standards.

Osmotic coefficients calculated from the 298.15 K isopiestic ratios reported by Libuš et al. (1980) were systematically biased from the other results and were not included in the fitted data set. The isopiestic ratio determinations from Soldano and co-workers (Patterson et al., 1960; Soldano and Patterson, 1962) showed an rms deviation of about 0.01 to 0.02 from the two models for 373 K and much larger differences (rms = 0.38) for 394 K. As discussed by Rard and Platford (1991), the large errors in their measurements may be partially due to the presence of temperature gradients in their apparatus. Thus, those measurements were given no weight in the representation. Holmes and Mesmer (1983) described Liu and Lindsay's (1971) vapor pressure measurements as inconsistent with other isopiestic and calorimetric measurements; hence, they were given no weight in the least-squares procedures also. The vapor pressure measurements from Kangro and Groenevold (1962) were also biased and not included in the representation. Both models represented all the other osmotic coefficients about equally well. Robinson and Jones (1936) reported osmotic coefficients for 298.15 K for rounded molalities, presumably obtained graphically from their isopiestic measurements, but not their measured isopiestic ratios. Thus their results could not be recalculated for changes in the reference standards. Their tabulated values of ϕ are biased to somewhat greater values than those selected for inclusion in the fitted database and were not included in the data representations. The article from Wu et al. (1969) reported six additional isopiestic measurements for $MgSO_4$(aq). Those values for the higher concentrations (2.5866 and 3.4402) mol·kg^{-1} showed fairly large negative biases (0.007 ≤ absolute value of difference). Because these biases existed with a significant portion of the data set (one-third) and because it is not correct statistically to pick and choose individual data points arbitrarily, the entire data set was not included in the representation. Figure 2 shows differences of some of the osmotic coefficients from the fitted ion-interaction equation.

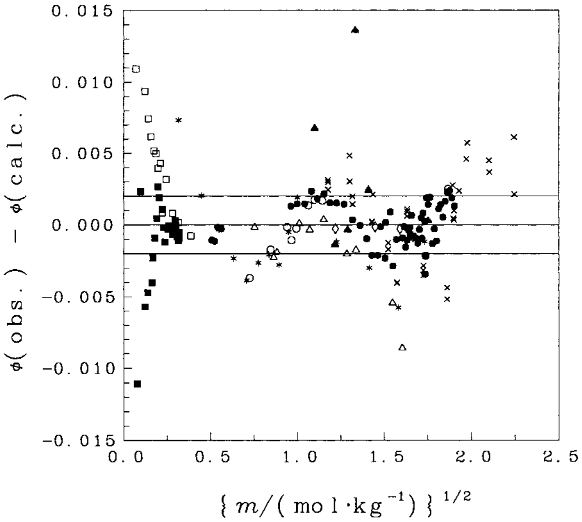

Figure 2. Differences of some osmotic coefficients from the ion-interaction model. The symbols are ○, Table 1; ●, Rard and Miller (1981); □, Yokoyama and Yamatera (1975); ■, Brown and Prue (1955); *, Childs and Platford (1971); ▲, Platford (1973), including the value calculated relative to KCl(aq) that was not given significant weight in the data representation; ×, Holmes and Mesmer (1983); △, Wu et al. (1968); ◇, Filippov and Cheremnkyh (1984).

Poczopko and Orzeszko (1972) described having made enthalpy of dilution measurements for dilutions of a "saturated" solution. They gave the molality of this initial solution as 3.162 mol·kg^{-1}. However, most modern measurements of the 298.15 K saturation molality give values about (4−5) % smaller (~3.02 mol·kg^{-1}). It is not clear to the present authors whether this difference existed because Poczopko and Orzezko indeed prepared and used a supersaturated solution or because there existed an error in composition determination or if the concentration value was taken from some earlier literature value for a saturated solution. In the case of the first possibility, our translation of their article indicated Poczopko and Orzeszko may not have been aware that they were handling a supersaturated solution. Their enthalpies of dilution were included in the representation but were assumed to be fairly uncertain, the estimated standard deviation being the larger of 50 J·mol^{-1} or 5% of $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$.

Plake (1932) measured enthalpies of dilution for low concentrations for temperatures near 294 K. Their measurements did not seem to agree well with those of Lange and co-workers (Lange and Streeck, 1931; Lange,1928) and the excess heat capacity measurements for 298.15 K. Plake (1932) also gave a few other measurements for other temperatures. However, because of biasing of the 294 K values, none of their measurements were included in the representation.

The enthalpies of dilution from Snipes et al. (1975) for 298.15 K were included and assumed to have rms uncertainties of 50 J·mol^{-1}. We reconstructed approximate enthalpies of dilution for their other temperatures (313 K, 333 K, 353 K) from their tabulated relative apparent molar enthalpies for the initial solutions, the dilution ratios extractable from the 298.15 K measurements, and their equations for the apparent molar enthalpy for the final concentrations. Enthalpies of dilution from Mayrath and Wood (1983) were used as reported. We note that the highest concentration solution they reported for 423.65 K may correspond to a supersaturated solution at that temperature if Robson's (1927) saturation molalities are taken to be correct, a matter discussed further below.

Both models gave acceptable representations of the enthalpies of dilution. The chemical equilibrium model gave somewhat better representations in dilute solutions. These differences for dilute soultions can be seen for the representations of Lange and co-worker's (Lange and Streeck, 1931; Lange,1928) measurements where the rms deviations were 80 J·mol^{-1} and 40 J·mol^{-1}, for the ion-interaction and chemical equilibrium models, respectively. Agreement with the higher temperature measurements from Mayrath and Wood (373 K, 423 K) was comparable with both models.

The quantity $(C_{p,\phi} - C^{\circ}_{p,\phi})$ was calculated from several different sets of measurements and included in the set of fitted measurements. The values of $(C_{p,\phi} - C^{\circ}_{p,\phi})$ were assigned weighting factors that were consistent with values $\sigma(C_{p,\phi} - C^{\circ}_{p,\phi})$ smaller than those that would be expected on the basis of $\sigma(C_{p,\phi})$ and $\sigma(C^{\circ}_{p,\phi})$, the latter calculated as eq 1. This was considered necessary because without such an assignment the deviations for isothermal sets of $(C_{p,\phi} - C^{\circ}_{p,\phi})$ did not possess a molality dependence that was consistent with that expected from $\sigma(C_{p,\phi} - C^{\circ}_{p,\phi})$.

The heat capacity determinations from Phutela and Pitzer (1986a) should be significantly more accurate than those from Likke and Bromley (1973); hence, only the former were given significant weight in the data representation for temperatures above 350 K. Values of $(C_{p,\phi} - C^{\circ}_{p,\phi})$ calculated from Likke and Bromley's reported values and from eq 1 agreed with the representations within Likke and Bromley's expected uncertainties.

Both models gave acceptable representations of $(C_{p,\phi} - C^{\circ}_{p,\phi})$ to temperatures of about 423 K. For temperatures of 448 K, both models deviated from these values by increasingly larger amounts, with the deviations being more-or-less independent of molality. It is not clear whether these differences represent a measure of $\sigma(C^{\circ}_{p,\phi})$ for $C^{\circ}_{p,\phi}(MgSO_4)$ calculated as eq 1 or the need for even more parameters in the present models.

Enthalpies of solution of epsomite and hexahydrite were also included in the data representation. Discussion of them is reserved to the next section.

Phase Behavior. Accurate determinations of the aqueous solubility of epsomite exist for temperatures from 298.15 K to the epsomite−hexahydrite 0.1 MPa invariant temperature, ~323 K. For hexahydrite, solubility measurements have been reported from near the epsomite + hexahydrite + solution equilibrium temperature (0.1 MPa) to temperatures corresponding to supersaturation of the solution relative to lower-water-content hydrates, e.g. the mono- or tetrahydrates. These measurements for hexahydrite and epsomite were included in the data representation and are shown in Figure 3. Near 273.15 K, it has been reported that a dodecahydrate phase becomes the dominant solute-containing crystalline phase (Küpper, 1927; Smits et al., 1928; Polo et al., 1971). There are insufficient measurements to establish the thermodynamic properties of this phase. Several different and conflicting reports of the equilibrium precipitating phase for temperatures in excess of 343 K exist. These will be discussed below.

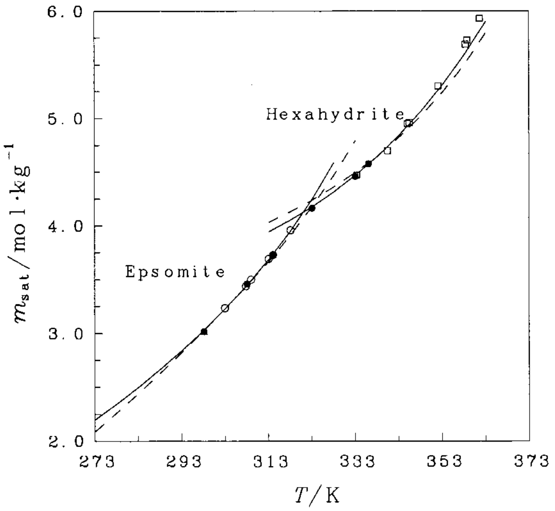

Figure 3. Solubilities of epsomite and hexahydrite against temperature. The symbols are ●, Schröder (1929); ○, Ting and McCabe (1934); ▲, Table 1; □, Smits et al. (1928). The solid lines were calculated from the ion-interaction model. The dashed lines were calculated from the chemical equilibrium model.

Reports of measurement of the enthalpy of solution of crystalline hydrates in water also occur in the literature. The enthalpy of solution is directly related to the Gibbs energy of solution and entropy of solution. The reported enthalpies of solution for epsomite and hexahydrite were included in the data representation. Measurements for the monohydrate phase will be discussed below.

Equations that describe the equilibrium between hydrated solid phases and the aqueous solution were given above. In those equations the entropy of the solution process for T_r appeared. The entropy of solution at T_r for a crystalline hydrate with n waters of hydration is $(S^{\circ}_2 + nS^{\circ}_1 - S^{\circ}_{cr})$, where S°_{cr} is the entropy of the crystalline hydrate phase. This latter quantity is obtainable, in principle, from measurements of the thermal properties, either enthalpy increments or heat capacities, from some temperature near 0 K to T_r and the assumption of the existence of no configurational contribution to the entropy. Such measurements were found for only two of the crystalline hydrates of $MgSO_4$.

For the crystalline monohydrate, Frost et al. (1957) gave a value of S°_{cr} = 126.4 J·K^{-1}·mol^{-1} (298.15 K) obtained from their heat capacity measurements. They gave their heat capacity values only as a graph, which showed measurements from about 150 K to higher temperatures. Therefore, quite a significant extrapolation was required to obtain this value of S°_{cr} for the monohydrate.

For hexahydrite, Cox et al. (1955) reported measurements from 16 K to 326 K. They reported a thermal effect that occurred about 120 K and which they attributed to transformation from a microcrystalline phase to a macrocrystalline phase. They executed and described measurements for different thermal histories in an effort to minimize this effect. We have fitted the series of measurements that they used to generate their tabulated thermal functions (S°_{cr,T_r} = 348 J·K^{-1}·mol^{-1}) with the method

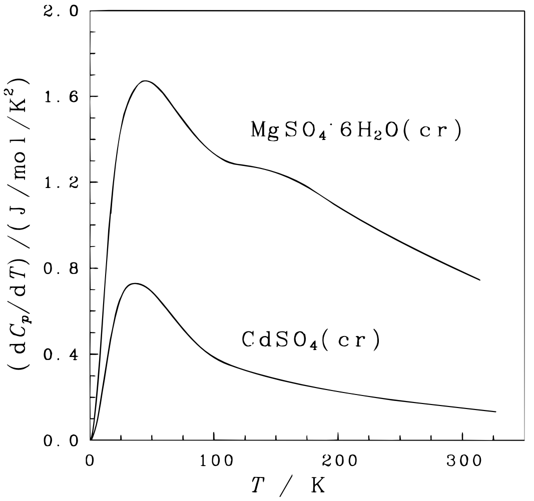

Figure 4. Values of the first derivative of heat capacity with respect to temperature for hexahydrite and cadmium sulfate.

described by Archer (1992b). From that fitted equation we calculated the first derivative of heat capacity with respect to temperature; it is shown in Figure 4. To rule out the possibility that the unusual behavior seen in the derivative could be due to a calorimetric bias, we also fitted heat capacity measurements for $CdSO_4$(cr) and $CdSO_4 \cdot 2.66H_2O$(cr), both reported in the same year, by the same laboratory, and with similar calorimetric procedures, as the hexahydrite measurements (Papadopoulos and Giauque, 1955). Neither showed an effect comparable to that seen in Figure 4 for hexahydrite. The first temperature derivative of the heat capacity for anhydrous cadmium sulfate is shown in Figure 4. Assuming a more typical behavior of $\mathrm{d}C_p/\mathrm{d}T$, there is a possibility that the true 298.15 K heat capacity of hexahydrite could be as much as 10 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ less than that tabulated by Cox et al. (1955).

The difference between the reported 298.15 K entropies for the two hydrates corresponds to 44.4 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, per mole of water. This value is in reasonable agreement with other such examinations. Nonetheless, neither entropy value appears accurate enough to determine unambiguously S_2° from $\Delta_{\mathrm{sol}}S^\circ$.

The heat capacities for the crystal phases required for these calculations were taken as follows: hexahydrite, $C_{p,\mathrm{m}} = \{348.1 + 8.7 \times 10^{-4}(T - 298.15\ \mathrm{K})/T^\circ\}\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ (Cox et al., 1955; Pabalan and Pitzer, 1987); monohydrate, $C_{p,\mathrm{m}} = \{126 + 2.5 \times 10^{-4}(T - 298.15\ \mathrm{K})/T^\circ\}\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ (Frost et al., 1957; Pabalan and Pitzer, 1987); epsomite, $C_{p,\mathrm{m}} = 391.6\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. The value for epsomite was obtained by adding 43.5 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ to the heat capacity value for hexahydrite (this last value is slightly greater than that used by Pabalan and Pitzer (1987)).

The two fitted models represented the measured values for the aqueous solubilities of hexahydrite and epsomite within probable uncertainties. Solubilities calculated from the two models are also shown in Figure 3. The 298.15 K Gibbs energies of solution of epsomite calculated from the two models are somewhat different, 415 $\mathrm{J \cdot mol^{-1}}$. This difference arises from differences in the activity coefficients of the solution components calculated from the two models. The solute activity coefficents for 3 $\mathrm{mol \cdot kg^{-1}}$ and 298.15 K are 0.0549 and 0.0506 for the ion-interaction and the chemical equilibrium models, respectively.

Kieserite (Monohydrate). Figure 5 shows reported values of the solubility of kieserite and the calculated curve for hexahydrite. Robson (1927) reported that the solubility curve for kieserite intersected that for hexahydrite near 341 K and from there showed a retrograde solubility. Benrath (1941) reported a "precipitation curve" (Ausscheidungs-kurve) that occurred at higher concentrations than Robson's measurements but which fell off rapidly near 473 K to intersect Robson's curve there. Bentrath believed that his Ausscheidungs-kurve fell above the true solubility of the high-temperature metal sulfate solution. Polo et al. (1971) claimed their measurements showed the kieserite solubility curve was not retrograde, that the lower-temperature end of the kieserite solubility curve did not intersect the hexahydrite solubility curve but instead intersected the solubility curve of the tetrahydrate, and that the solubility curve for the tetrahydrate was the true equilibrium state for temperatures between the ends of the equilibrium solubility curves of hexahydrite and kieserite. They claimed the high-temperature end of the kieserite solubility curve terminated with precipitation of $Mg(OH)_2$ at 403 K. Their values are shown in the figure as a long-dash line. Also shown are values reported by Smits et al. (1928) and Étard (1894).

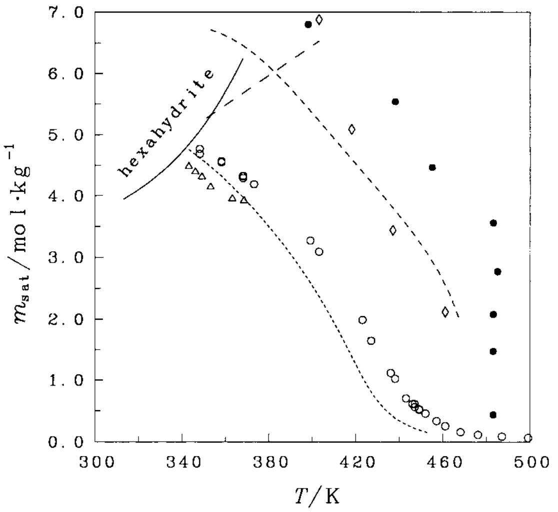

Figure 5. Solubilities of kieserite against temperature. The symbols are ●, Benrath (1941); ◇, Étard (1894); ○, Robson (1927); △, Smits et al. (1928). The lines are − −, Polo et al. (1971); ···, calculated from the enthalpy of formation from Ko and Daut (1980) and the ion-interaction model; - - -, calculated from the enthalpies of solution and the ion-interaction model. The solid line is the hexahydrite solubility line.

Marshall and Slusher (1965) examined the solubility of magnesium sulfate in water with various amounts of sulfuric acid in the system for temperatures from 408 K to 623 K. Most of their measurements were for temperatures of 473 K or higher, although some values for 408 K and 443 K were also obtained and shown in a figure. In their Figure 1, they showed the solubility fields that they found to be stable against both SO_3 molality and the component ratio $m_{\mathrm{MgO}}/m_{\mathrm{SO_3}}$. At 473 K, they found kieserite to be the stable precipitated phase for $m_{\mathrm{MgO}}/m_{\mathrm{SO_3}} < 0.972$, but that an oxysulfate, $MgSO_4 \cdot 5MgO \cdot 8H_2O$, was the equilibrium precipitated phase for $1 > m_{\mathrm{MgO}}/m_{\mathrm{SO_3}} > 0.98$. Similarly for 443 K, Marshall and Slusher's Figure 3 showed the oxysulfate to be the equilibrium precipitated phase for a saturation composition that would roughly correspond to that which Robson indicated kieserite was the precipitating phase. Marshall and Slusher's conclusion for both magnesium sulfate and nickel sulfate was that these metal sulfates were not hydrolytically stable at these temperatures.

In principle, independent determinations of the enthalpy of solution and the entropy of kieserite, combined with properties of the solution phase and water, could establish the, perhaps hypothetical, aqueous solubility of kieserite. Thomsen (1882−1886) measured the enthalpy of solution of crystalline kieserite in water at 291.15 K. By combining his measured value with the concentration dependence of enthalpy and heat capacity of the solution, both calculated from the ion-interaction model and an estimate of the crystal phase heat capacity, we calculated a value of the standard-state enthalpy of solution for 298.15 K, $\Delta_{\mathrm{sol}}H^{\circ}_{\mathrm{m},T_{\mathrm{r}}} = -61.63$ kJ·mol^{-1}. Jamieson and Frost (1956) measured the enthalpies of solution of crystalline epsomite and mixtures of other crystalline hydrates. Although they did not measure directly the enthalpy of solution of kieserite, their measurements for 299.15 K, as a function of water content of the crystalline hydrate, closely paralleled those of Thomsen. From their measurements, we extracted a value of $\Delta_{\mathrm{sol}}H^{\circ}_{\mathrm{m},T_{\mathrm{r}}} = -59.57$ kJ·mol^{-1} for crystalline monohydrate. Phillipson and Finlay (1976) measured the differences in enthalpies of solution of different $MgSO_4$ hydrates in a Bunsen calorimeter. From their difference of the enthalpies of solution of monohydrate and epsomite, they obtained the heat of solvation, −11.84 kJ·$\mathrm{mol}_{\mathrm{H_2O}}{}^{-1}$, per mole of hydrated water. From that value and values calculated from the ion-interaction model, $\Delta_{\mathrm{sol}}H^{\circ}_{\mathrm{m},T_{\mathrm{r}}}$ for epsomite was calculated to be 12.18 kJ·mol^{-1}. Combination of this value and Phillipson and Finlay's value gave $\Delta_{\mathrm{sol}}H^{\circ}_{\mathrm{m},T_{\mathrm{r}}} = -58.86$ kJ·mol^{-1} for kieserite. This last value is in reasonable agreement with the value from Jamieson and Frost's work (difference = 0.7 kJ·mol^{-1}) and with Thomsen's much earlier value (difference = 2.7 kJ·mol^{-1}). Ko and Daut (1980) measured the enthalpies of solution of kieserite, MgO, (H_2SO_4 + 6 H_2O), and H_2O into 4.36 mol·kg^{-1} HCl(aq) so as to obtain the enthalpy of the reaction

$$\mathrm{MgO(cr)} + (\mathrm{H_2SO_4} + 6\ \mathrm{H_2O}) = \mathrm{MgSO_4{\cdot}H_2O(cr)} + 6\mathrm{H_2O(l)} \quad (45)$$

and from there the enthalpy of formation of kieserite. From their value of the enthalpy of formation of kieserite and the enthalpies of formation of $MgSO_4$(aq) and H_2O(l) one can calculate $\Delta_{\mathrm{sol}}H^{\circ}_{\mathrm{m},T_{\mathrm{r}}} = -52.47$ kJ·mol^{-1}, which is approximately (7 to 9) kJ·mol^{-1} different from the independent values from Phillipson and Finlay, from Jamieson and Frost, and from Thomsen. A report of a standard-state enthalpy of solution for kieserite, $\Delta_{\mathrm{sol}}H^{\circ}_{\mathrm{m},T_{\mathrm{r}}} = -45.4$ kJ·mol^{-1}, from Milonjic et al. (1978) is much smaller and can probably be ignored. (Milonjic et al. also reported an enthalpy of solution for epsomite that was too small by 3.4 kJ·mol^{-1}, or approximately 30%. However, the enthalpies of solution of epsomite and kieserite are endothermic and exothermic, respectively. Systematic calorimetric biases for measurements of endothermic and exothermic reactions can be different.)

Combination of the Ko and Daut enthalpy of formation, the estimate of the crystalline entropy, and either of the two models provided calculated solubilities that resembled those given by Robson. Indeed, this is a calculation similar, but not identical, to that performed by Pabalan and Pitzer (1987) and shown in their Figure 7 for kieserite. On the other hand, dismissal of the three independent enthalpies of solution of kieserite into water and also Marshall and Slusher's assertions regarding the hydrolytic instability of $MgSO_4$ should not be undertaken lightly. Combination of the enthalpy of solution values, the estimated entropy of kieserite, and the ion-interaction model gave calculated solubilities that are qualitatively similar to values reported by Étard (1894). Both are shown in Figure 5. We consider the matter to be unresolved.

Comparison of the Two Model Formulations. Phutela and Pitzer (1986a) noted several differences of their ion-interaction model's calculated values from those calculated from Archer and Wood's (1985) chemical equilibrium model, some of which were noted briefly above. The primary remarked differences consisted of (1) a difference in $C_{p,\phi}$ of ∼40 J·K^{-1}·mol^{-1} at 373 K, more-or-less independent of molality to 2 mol·kg^{-1}, (2) differences of the Phutela and Pitzer model from the measured enthalpies of dilution for 423 K for concentrations below 0.01 mol·kg^{-1} and (3) differences of the Archer and Wood model from measured osmotic coefficients at 413 K.

The present work fitted both models to a common database with common estimates of uncertainties. This procedure eliminated the possibility that differences between representations with the equilibrium model and the ion-interaction model were due to differences in the fitted databases. Each of the above items is discussed separately below.

Values of $C_{p,\phi}$ were not extractable solely from the equations given by Archer and Wood (1985). The values that Phutela and Pitzer's (1986a) Figure 1 indicated as being from Archer and Wood were obtained by combining Archer and Wood's values of $(C_{p,\phi} - C^{\circ}_{p,\phi})$ and Phutela and Pitzer's equation for $C^{\circ}_{p,\phi}$($MgSO_4$(aq)). Their equation for $C^{\circ}_{p,\phi}$ was obtained by means of eq 1 and previously published model-calculated values for $C^{\circ}_{p,\phi}$ for NaCl(aq) (Pitzer et al., 1984), Na_2SO_4(aq) (Rogers and Pitzer, 1981), and $MgCl_2$(aq) (Phutela et al., 1987). The values of $C^{\circ}_{p,\phi}$($MgSO_4$(aq)) calculated from the Phutela and Pitzer equation and from the present equation for that quantity are shown in Figure 6. There is a systematic difference between the two representations that is approximately 34 J·K^{-1}·mol^{-1} at 373 K and 20 bar. Combination of the present equation for $C^{\circ}_{p,\phi}$($MgSO_4$(aq)) with the values of $(C_{p,\phi} - C^{\circ}_{p,\phi})$ tabulated by Archer and Wood gave values of $C_{p,\phi}$ that agree with those measured by Phutela and Pitzer for 373 K within expected uncertainties ∼(5 to 6) J·K^{-1}·mol^{-1}. Most of the difference between the two equations for $C^{\circ}_{p,\phi}$($MgSO_4$(aq)) arose from the differences in the two different equations for $C^{\circ}_{p,\phi}$($MgCl_2$(aq)), which arose from the differences of apparent molar heat capacities measured by White et al. (1988) and Likke and Bromley (1973) on one hand and those measured by Saluja and LeBlanc (1987) on the other, the latter disagreeing with the former two. Had the Phutela and Pitzer comparison included an assessment of the uncertainty of their values of $C^{\circ}_{p,\phi}$($MgSO_4$(aq)), perhaps a different picture of the agreement of the two models would have been had.

The differences of $C^{\circ}_{p,\phi}$($MgSO_4$(aq)) seen in Figure 6 for temperatures above 373 K were also partly responsible for the differences of the Phutela and Pitzer (1986a) model from the measured 423.6 K enthalpies of dilution. The average systematic difference of −34 J·K^{-1}·mol^{-1}, integrated over the 50 K temperature interval from where they had agreed with the Mayrath and Wood enthalpies of dilution to 423.6 K, would result in a systematic bias of −1.7 kJ·mol^{-1} for L_{ϕ} between 0.1 mol·kg^{-1} and infinite dilution, most of it occurring in the most dilute solutions ($m < 0.03$ mol·kg^{-1}). The dilute solution residuals for the present ion-interaction model representation of Mayrath and Wood's (1983) enthalpies of dilution are smaller than those described by Phutela and Pitzer and comparable to those obtained with the chemical equilibrium model. This improved agreement should be considered indicative that

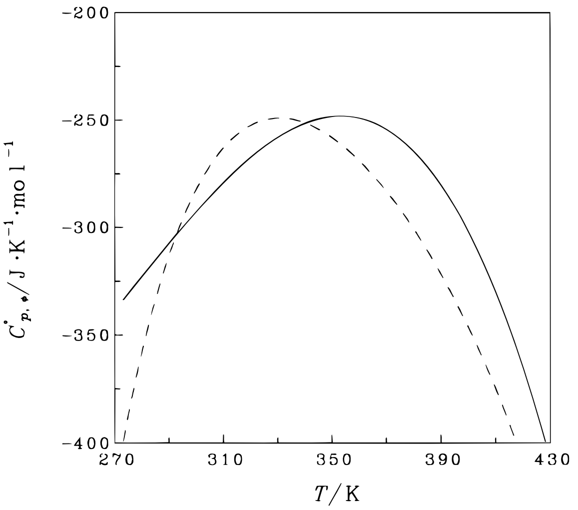

Figure 6. Standard-state molar heat capacity of $MgSO_4$(aq) calculated by means of eq 1. The solid line is calculated as used for the present work. The dashed line was calculated from the equation given by Phutela and Pitzer (1986a).

the present version of eq 1 was more accurate than that cast by Phutela and Pitzer. Of course, the present version of eq 1 was based partially on thermodynamic measurements published after Phutela and Pitzer's article.

The disagreement of the Archer and Wood model from the isopiestic ratio for the one concentration at 413 K, measured by Holmes and Mesmer (1983), in duplicate, can be better considered by recognizing the relation of a change in osmotic coefficient with respect to temperature to the apparent relative molar enthalpy:

$$\phi_{T_2} - \phi_{T_1} = (1/2\nu R)\int_{T_1}^{T_2} m^{1/2}\,(\partial L_{\phi}/\partial m^{1/2})\;\mathrm{d}(1/T) \qquad (46)$$

Hence, the temperature dependence of the osmotic coefficient is related to the slope of the apparent relative molar enthalpy with respect to $m^{1/2}$, as a function of temperature. The Archer−Wood model determined this quantity primarily from the Snipes et al. (1975) and the Mayrath and Wood (1983) enthalpies of dilution. The misrepresentation of the single concentration 413 K osmotic coefficient resulted primarily from the relative numbers of measurements of enthalpies of dilution compared to the small number of isopiestic determinations at 413 K (two) included in the Archer−Wood model. From the text of the Phutela and Pitzer article, it appears that the Snipes et al. enthalpy results, for temperatures other than 298 K, may not have been included in their data treatment. The Phutela and Pitzer heat capacity measurements support the isopiestic determination at 413 K more than they do the Snipes et al. enthalpies. With inclusion of these measurements, the chemical equilibrium model is in good agreement with the 413 K measurement. Therefore, this difference of the previous chemical-equilibrium model from the ion-interaction model appears to be solely a function of the data included in the representations.

Conclusion

Both models gave adequate, but slightly different, representations of the measurements for the $MgSO_4 + H_2O$ system. Each model does a bit better than the other in certain regions of concentration. The ion-interaction model gave more faithful representations of the data in regions of large concentration; the chemical equilibrium model was somewhat better for dilute solutions. Such a difference is illustrated in Figure 7 where differences of some very recent heat capacity measurements (Ballerat-Busserolles and Woolley, 1998) from the fitted model are shown. These values were not included in the data representations. The residuals for the chemical equilibrium model are independent of concentration within experimental uncertainties with the exception of the highest concentration measurement. The residuals for the ion-interaction model are independent of concentration from 0.8 mol·kg^{-1} to about 0.2 mol·kg^{-1}, and below that concentration there is observed a concentration dependent bias. Owing to the adoption of eq 1 for $C^{\circ}_{p,\phi}(MgSO_4)$, one might expect some concentration-independent bias. This is seen in Figure 7 where the measured values show an average bias of about −4 J·K^{-1}·mol^{-1} from eq 1. This difference is within the expected uncertainty of eq 1 for $C^{\circ}_{p,\phi}(MgSO_4)$.

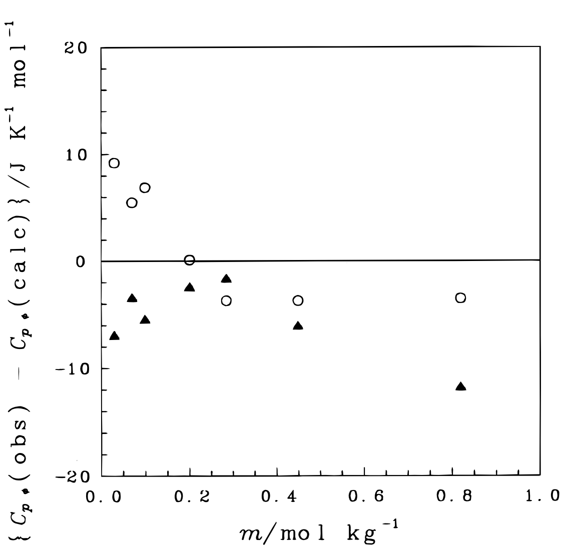

Figure 7. Differences of the 298.15 K heat capacity measurements from Ballerat-Busseroles and Woolley (1998) from the two models against concentration. The symbols are ○, ion-interaction model; ▲, chemical equilibrium model.

Most of the difference in dilute solutions was observed for accurate measurements of enthalpies of dilution. These measurements affect the change of solute activity coefficient with respect to temperature. This temperature dependence of the solute activity coefficient is often determined more accurately than are Gibbs energies for the same concentration range. The small model-dependent differences in activity coefficients at saturation cause significantly larger uncertainties in determining the Gibbs energy of solution for this 2−2 electrolyte, and presumably others, than is the case for nonassociated 1−1 electrolytes, because of the small values of the solute activity coefficient at saturation. For this reason, for the tabulated property to be useful it is essential to present both the calculated Gibbs energy of solution (or other derived property, e.g., Gibbs energy of formation, equilibrium constant, etc.) and the excess Gibbs energy model used for the component activities.

A copy of a program that calculates selected properties from the ion-interaction model is available from one of the authors (D.G.A.).

Acknowledgment

The authors thank Bea Armstrong for the DCAOES analysis.

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Received for review February 16, 1998. Accepted May 25, 1998. The work of J.A.R. was performed under the auspices of the Office of Basic Energy Sciences (Geosciences) of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

JE980047O