

**Thermodynamics of  $\text{Na}_2\text{SO}_4(\text{aq})$  at temperatures  
 $T$  from 273 K to 373 K  
and of  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$   
at  $T = 298.15 \text{ K}^a$**

**Jamey K. Hovey,<sup>b</sup> Kenneth S. Pitzer,**

*Department of Chemistry and Lawrence Berkeley Laboratory,  
University of California, Berkeley, CA 94720, U.S.A.*

**and Joseph A. Rard**

*Lawrence Livermore National Laboratory,  
University of California, Livermore, CA 94550, U.S.A.*

*(Received 26 August 1991; in final form 10 August 1992)*

New isopiestic vapor-pressure measurements on  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  along with earlier experimental investigations that span the range from  $y = 0$  to  $y = 1$  and infinitely dilute to supersaturated molalities have been analyzed in terms of the Pitzer ion-interaction model. Refined ion-interaction parameters for  $\text{Na}_2\text{SO}_4(\text{aq})$  valid over the temperature range 273 K to 373 K have been calculated and used for analyzing results for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  at 298.15 K. Analysis of experimental results for these aqueous mixtures required explicit consideration of the dissociation reaction of  $\text{HSO}_4^-$ . Previous treatments of  $\text{H}_2\text{SO}_4(\text{aq})$  and subsequently the equilibrium for the dissociation of  $\text{HSO}_4^-$  valid in the range 273 K to 343 K were employed as a first approximation in representing the mixed solutions. Two sets of Pitzer ion-interaction parameters are presented for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$ . The validity of the first set is limited in ionic strength and molality to supersaturated solutions of  $y = 1$  ( $I = 12 \text{ mol} \cdot \text{kg}^{-1}$ ). The second set corresponds to a slightly less precise representation but is valid over the entire range of experimental results considered. Both sets of parameters provide a more complete description of solutions with  $y = 0$  because of the removal of various redundancies in ion-interaction parameters. The specific ion-interaction terms used and the overall fitting procedure are described as well as selected examples of relevant thermodynamic calculations for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$ .

## 1. Introduction

The aqueous binary solutions composed of sulfuric acid or sodium sulfate or the ternary solution formed from both are immensely important for a variety of chemical, geochemical, and industrial processes. The equilibrium properties of the binaries have been extensively investigated especially at low molalities and near room temperature.<sup>(1)</sup> The importance of thermodynamic values leading to activities for these binaries and in complex solutions formed by combinations of all of these

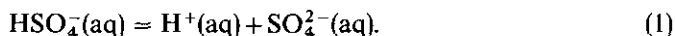
<sup>a</sup>This paper is dedicated to Professor Loren Hepler in honor of his retirement.

<sup>b</sup>Present address: Institut für Mineralogie und Petrographie, Sonneggstrasse 5, ETH-Zentrum, CH-8092 Zürich, Switzerland.

electrolytic species is paramount to understanding many equilibria of practical importance especially those involving dissolved species and (vapor + liquid) equilibria.<sup>(2)</sup>

Appropriate thermodynamic values leading to the variation of the Gibbs free energies with  $y$  for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  are limited. The current status on the amount and type of information available has been discussed by one of the authors.<sup>(3)</sup> Rard<sup>(3,4)</sup> has provided the most complete set of osmotic coefficients to date for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$ . His results cover the range  $y = 0.12$  to  $y = 0.85$  and extend to supersaturated molalities. Rard<sup>(3)</sup> has considered the mixture to consist in one case of two completely ionized electrolytes. In the second case, the system is treated as a mixture of a 1-1 (sulfuric acid) and a 2-1 (sodium sulfate) electrolyte.

The present analysis is intended to go further in that the speciation of the solutions determined by the dissociation of  $\text{HSO}_4^-$  is explicitly considered. The equilibrium that accounts for deviations in treatments considering either total dissociation of  $\text{H}_2\text{SO}_4$  or treating  $\text{H}_2\text{SO}_4$  as a 1-1 electrolyte, is the dissociation of  $\text{HSO}_4^-$ :



There is good agreement among several investigators for the equilibrium constant for this reaction at 298.15 K,<sup>(5,6)</sup> and the temperature dependence is well defined in the range 283.15 K to 328.15 K.<sup>(5,7)</sup> The stoichiometric activity coefficients and the ratio of appropriate ionic activity coefficients required for calculation of amounts of species present at finite ionic strengths are well known to  $6 \text{ mol} \cdot \text{kg}^{-1}$  for  $\text{H}_2\text{SO}_4$  (stoichiometric). Here we explicitly consider this equilibrium reaction in the representation of the experimental osmotic coefficients and subsequently the various activity coefficients required for use in such a treatment.

We have used the Pitzer ion-interaction model to treat the available osmotic coefficients for this mixture at 298.15 K. The range of ionic strengths and molalities considered in the following treatment push the molality-based ion-interaction model to near its limit. Previous precise formulations represent the thermodynamic properties of  $\text{H}_2\text{SO}_4(\text{aq})$ <sup>(5,8,9)</sup> up to approximately  $6 \text{ mol} \cdot \text{kg}^{-1}$ . Revised parameters for pure  $\text{Na}_2\text{SO}_4(\text{aq})$  presented later, extend to the limit of the available values (supersaturated). Many calculations involving the species of present interest are focussed on truly low ionic-strength regimes. We thus present results representative of the thermodynamic properties of the mixture useful in this dilute range of ionic strengths. There are of course other important uses of thermodynamic values for the mixed system at higher molalities for a variety of water-activity calculations, vapor pressures, and solubility experiments. To this end, we present a complete set of parameters valid to  $15 \text{ mol} \cdot \text{kg}^{-1}$  of  $\text{H}_2\text{SO}_4$  and correspondingly high ionic-strength values for the mixtures.

## 2. Speciation

The dissociation reaction of  $\text{HSO}_4^-$  controls the distribution of species and thus the molalities of all species (except  $\text{Na}^+$ ) for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$ . Initial

molalities of  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  in combination with the equilibrium-constant expression and a suitable expression for the activity coefficients of the participating species can be solved for the molalities of ionic species present at equilibrium.

The equilibrium constant corresponding to equation (1) is given by

$$K_a^\circ = a_{\text{H}}a_2/a_1 = \{m_{\text{H}}m_2/(m^\circ m_1)\}(\gamma_{\text{H}}\gamma_2/\gamma_1), \quad (2)$$

where  $a$ ,  $m$ , and  $\gamma$  represent activity, molality, and activity coefficient, respectively, and various abbreviations are defined as follows:  $m^\circ$  is a standard molality, and  $m_{\text{H}}$ ,  $m_1$ ,  $m_2$ , and  $m_{\text{Na}}$  denote molalities of  $\text{H}^+(\text{aq})$ ,  $\text{HSO}_4^-(\text{aq})$ ,  $\text{SO}_4^{2-}(\text{aq})$ , and  $\text{Na}^+(\text{aq})$ , respectively.

The initial molalities of species are unambiguously defined for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}$  according to the total molality  $m_{\text{T}}$  and the mole fraction  $y$ . The various molalities of species written in terms of the equilibrium molality of  $\text{H}^+(\text{aq})$  and the initial molalities of  $\text{Na}_2\text{SO}_4$  ( $m_{2,\text{i}}$ ) and  $\text{H}_2\text{SO}_4$  ( $m_{1,\text{i}}$ ) are

$$m_1 = 2m_{1,\text{i}} - m_{\text{H}}, \quad (3)$$

$$m_2 = m_{2,\text{i}} - m_{1,\text{i}} + m_{\text{H}}, \quad (4)$$

where

$$m_{1,\text{i}} = (1-y)m_{\text{T}}, \quad (5)$$

$$m_{2,\text{i}} = ym_{\text{T}}. \quad (6)$$

Here  $m_{\text{T}}$  represents the *total* molality and is equal to the sum of stoichiometric molalities of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ .

The exact iterative procedure used to refine the speciation is discussed in detail in section 5. It suffices here to show the relation of initial and equilibrium molalities.

### 3. Ion-interaction equations: sodium sulfate and sulfuric acid

Isopiestic results for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  were obtained over such a wide range of ionic strengths and molalities that a new higher precision fit was required for  $\text{Na}_2\text{SO}_4(\text{aq})$ . Pabalan and Pitzer<sup>(10)</sup> have provided a detailed description of  $\text{Na}_2\text{SO}_4(\text{aq})$  in terms of the ion-interaction model. This treatment was intended for and covers a broad and higher temperature and pressure range and, thus, is not as precise at 298.15 K as a less broad representation could be. We have chosen representative values at 298.15 K and below from literature sources and the results of the Pabalan and Pitzer treatment from 303.15 K to 372.75 K to generate new parameters for  $\text{Na}_2\text{SO}_4(\text{aq})$  valid from 273.15 K to 372.75 K. The results of these calculations are presented following the presentation of appropriate equations.

Ion-interaction treatments of thermodynamic values for  $\text{H}_2\text{SO}_4(\text{aq})$  from 278.15 K to 328.15 K have been presented by Pitzer *et al.*<sup>(5)</sup> and from 273.15 K to 343.15 K by Reardon and Beckie.<sup>(8)</sup> These treatments are valid only up to an ionic strength set by  $6 \text{ mol} \cdot \text{kg}^{-1} \text{H}_2\text{SO}_4(\text{aq})$ . Reardon and Beckie<sup>(8)</sup> also included the higher-order terms for unsymmetrical mixing that Pitzer *et al.*<sup>(5)</sup> had omitted. These terms are included in the present work. Results of fits employing both of these treatments are presented along with refined parameters derived from results for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}$ .

Because several different applications of the ion-interaction equation are used, including refinement of parameters for the binary solutions, we summarize all of the appropriate ion-interaction equations below.

The fundamental ion-interaction equation can be written for the excess specific Gibbs energy  $G^E$  of a pure electrolyte:

$$G^E/w_w RT = f + 2\nu_M \nu_X m^2 (B_{MX} + \nu_M z_M m C_{MX}), \quad (7)$$

where appropriate quantities are defined by

$$f = -(4I/b)A_\phi \cdot \ln(1 + bI^{1/2}), \quad (8)$$

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \cdot g(\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} \cdot g(\alpha_2 I^{1/2}), \quad (9)$$

$$g(\alpha I^{1/2}) = 2\{1 - (1 + \alpha I^{1/2}) \cdot \exp(-\alpha I^{1/2})\}/(\alpha^2 I). \quad (10)$$

Also,  $A_\phi$  is the Debye-Hückel slope for the osmotic coefficient,  $w_w$  is the mass of water present, and  $\beta$  and  $C$  are interaction parameters that are functions of the solute, temperature, and pressure, and describe binary and ternary ion-interactions. All Debye-Hückel slopes were derived from Archer and Wang.<sup>(11)</sup> The maximum difference in  $A_\phi$  from the earlier values of Bradley and Pitzer<sup>(12)</sup> is  $0.0003 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  in the range 273 K to 373 K. The  $\alpha$  terms represent the ionic-strength dependence of the various  $B$  terms as given by equation (9). The optimum values of  $\alpha_1$  have been found to range from 1.4 to  $2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for various electrolytes depending on the ions present. Usually, 1-1 and 2-1 electrolytes are best treated when  $\alpha_1$  has the value  $2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ . There is theoretical evidence that  $\alpha_2$  is proportional to  $A_\phi$ .<sup>(13)</sup> The significance of the  $\alpha_2$  and thus the  $\beta^{(2)}$  term has been thoroughly discussed by Pitzer.<sup>(13)</sup> The term in  $\beta^{(2)}$  was omitted except for one final calculation discussed in section 5.

The osmotic coefficient of  $\text{Na}_2\text{SO}_4(\text{aq})$  is given in terms of the ion-interaction model by

$$\phi - 1 = -(\partial G^E / \partial w_w)_{n_i} / (RT \sum_i m_i) \quad (11)$$

$$= 2f^\phi + (4/3)mB_{\text{Na}2}^\phi + (4/3) \cdot 2^{1/2} m^2 C_{\text{Na}2}^\phi. \quad (12)$$

The stoichiometric activity coefficient is represented by

$$\ln \gamma_\pm = (\nu_M \cdot \ln \gamma_M + \nu_X \cdot \ln \gamma_X) / \nu \quad (13)$$

$$= [\nu_M \{ \partial(G^E/w_w RT) / \partial m_M \}_{n_w} + \nu_X \{ \partial(G^E/w_w RT) / \partial m_X \}_{n_w}] / \nu. \quad (14)$$

For  $\text{Na}_2\text{SO}_4$ ,  $\nu_M = 1$ ,  $\nu_X = 2$ , and  $\nu = 3$  whereupon

$$\ln \gamma_\pm = 2f^\gamma + (4/3)mB_{\text{Na}2}^\gamma + (4/3) \cdot 2^{1/2} m^2 C_{\text{Na}2}^\gamma, \quad (15)$$

and the various terms are defined by

$$f^\phi = -A_\phi I^{1/2} / (1 + bI^{1/2}), \quad (16)$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \cdot \exp(-\alpha_1 I^{1/2}) + \beta_{MX}^{(2)} \cdot \exp(-\alpha_2 I^{1/2}), \quad (17)$$

$$f^\gamma = -A_\phi \{I^{1/2}/(1 + bI^{1/2}) + (2/b) \cdot \ln(1 + bI^{1/2})\}, \quad (18)$$

$$B^\gamma = B_{\text{MX}} + B_{\text{MX}}^\phi, \quad (19)$$

$$C^\phi = 2|z_{\text{M}}z_{\text{X}}|^{1/2}C_{\text{MX}} = (2/3)C_{\text{MX}}^\gamma. \quad (20)$$

Here and elsewhere  $b$  is a universal parameter equal to  $1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ .

Aqueous solutions containing  $\text{H}_2\text{SO}_4$  are not completely ionized at any range of molalities of practical interest. As such, this electrolyte must be treated as a mixture of species, amounts of which are defined according to the dissociation equilibrium for  $\text{HSO}_4$  represented by equation (1).

The excess Gibbs energy for a solution containing any number of cations and anions (excluding neutral solutes) is given by<sup>(13)</sup>

$$\begin{aligned} G^E/w_w RT = & f + 2 \sum_c \sum_a m_c m_a \{B_{ca} + (\sum_c m_c z_c) C_{ca}\} + \\ & \sum_c \sum_{c'} m_c m_{c'} (2\Phi_{cc'} + \sum_a m_a \psi_{cc'a}) + \\ & \sum_a \sum_{a'} m_a m_{a'} (2\Phi_{aa'} + \sum_c m_c \psi_{aa'c}) + \dots \end{aligned} \quad (21)$$

The  $\Phi$  and  $\psi$  terms represent the contributions from mixing dissimilar electrolytes and are present only for systems containing different cations and/or anions. The exact form of these terms is discussed later in reference to  $\text{H}_2\text{SO}_4(\text{aq})$ . Equation (21) is appropriate for systems containing any number of ionic species and is easily modified to handle mixtures of ionic species with neutral molecules. Equation (21) reduces to equation (7) for the special case of a single electrolyte.

The acidity constant of  $\text{HSO}_4^-$  is well defined at 298.15 K by results of fits to osmotic coefficients and electromotive-force measurements by Pitzer *et al.*<sup>(5)</sup> This result combined with the corresponding enthalpy and heat-capacity change for dissociation of  $\text{HSO}_4$  leads to the equation for the equilibrium constant presented by Hovey and Hepler<sup>(7)</sup> that is valid over a wider temperature range. Potentiometric measurements leading to values for the acidity constant at still higher temperatures<sup>(14)</sup> are consistent with these more precise low-temperature results.

Previous applications of the ion-interaction model to sulfuric acid solutions have not utilized all possible ion-interaction terms because of various near-redundancies among parameters. The dissociation of  $\text{HSO}_4$  restricts the molality ratios of the species present to slowly varying values that hinder reliable regression of some parameters, especially the mixing terms. A detailed treatment of  $\text{H}_2\text{SO}_4(\text{aq})$  in terms of the ion-interaction model and the various parameter redundancies is given by Pitzer *et al.*<sup>(5)</sup> The new isopiestic measurements for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  cover such a wide range of ionic strengths and molalities that all available interaction parameters become significant, some in the sense that they are of a small enough magnitude to have a zero value.

The ion-interaction equations for the osmotic coefficients of  $\text{H}_2\text{SO}_4(\text{aq})$  on a mixed basis are given by:

$$\begin{aligned} \phi_{\text{mix}} - 1 = & \{2/(m_{\text{H}} + m_1 + m_2)\} [f^\phi I + m_{\text{H}} m_1 (B_{\text{H}1}^\phi + ZC_{\text{H}1}) + \\ & m_{\text{H}} m_2 (B_{\text{H}2}^\phi + ZC_{\text{H}2}) + m_1 m_2 \{\Phi_{12}^\phi + m_{\text{H}} \psi_{12\text{H}}\}], \end{aligned} \quad (22)$$

where

$$Z = \sum_i m_i |z_i|, \quad (23)$$

and  $m_1$  and  $m_2$  are equilibrium molalities of  $\text{HSO}_4^-(\text{aq})$  and  $\text{SO}_4^{2-}(\text{aq})$ , respectively.

This expression is easily derived from equation (21) and its appropriate derivative represented by equation (11). The activity-coefficient factor for reaction (1) in pure  $\text{H}_2\text{SO}_4(\text{aq})$  is given by

$$\begin{aligned} \ln(\gamma_{\text{H}}\gamma_2/\gamma_1) = & 4F + (m_1 - m_{\text{H}})(2B_{\text{H}1} + ZC_{\text{H}1}) + (m_2 + m_{\text{H}})(2B_{\text{H}2} + ZC_{\text{H}2}) + \\ & 2m_{\text{H}}m_1C_{\text{H}1} + 2m_{\text{H}}m_2C_{\text{H}2} + 2(m_1 - m_2)\Phi_{12} + \\ & (m_1m_2 + m_1m_{\text{H}} - m_2m_{\text{H}})\psi_{12\text{H}}, \end{aligned} \quad (24)$$

where  $F$  for  $\text{H}_2\text{SO}_4(\text{aq})$  is given by

$$F = f^\gamma + m_{\text{H}}m_1B'_{\text{H}1} + m_{\text{H}}m_2B'_{\text{H}2} + m_1m_2\Phi'_{12}, \quad (25)$$

and  $f^\gamma$  was defined by equation (18), and the  $B'$  terms that represent the ionic-strength derivatives of the various  $B$  terms are given by

$$B'_{\text{MX}} = \{\beta_{\text{MX}}^{(1)}g'(\alpha_1 I^{1/2}) + \beta_{\text{MX}}^{(2)}g'(\alpha_2 I^{1/2})\}/I, \quad (26)$$

where

$$g'(\alpha I^{1/2}) = -2\{1 - (1 + \alpha I^{1/2} + \alpha^2 I/2) \cdot \exp(-\alpha I^{1/2})\}/(\alpha^2 I). \quad (27)$$

The binary mixing parameter  $\Phi_{12}$  in equation (24) is related to the parameter  $\Phi_{12}^\phi$  appearing in equation (22) and others by:

$$\Phi_{12}^\phi = \Phi_{12} + I\Phi'_{12}, \quad (28)$$

where  $\Phi'_{12}$  is the derivative with respect to  $I$  of  $\Phi_{12}$ . Theoretical investigations by Pitzer<sup>(15)</sup> and Friedman<sup>(16)</sup> have led to rigorous expressions for  $\Phi'_{12}$  for the case of unsymmetrical mixing. Here unsymmetrical mixing refers to the mixing of ions of the same sign but with different valency. Appropriate expressions for this binary term are thus

$$\Phi'_{12} = {}^E\theta'_{12}(I), \quad (29)$$

where  $\Phi_{12}$  is defined to have the ionic-strength dependence:

$$\Phi_{12} = \theta_{12} + {}^E\theta_{12}(I). \quad (30)$$

Combining these expressions with equation (28) leads to

$$\Phi_{12}^\phi = \theta_{12} + I \cdot {}^E\theta'_{12}(I) + {}^E\theta_{12}(I). \quad (31)$$

The quantities  ${}^E\theta'_{12}(I)$  and  ${}^E\theta_{12}(I)$  can be determined from theory. Convenient polynomial expressions for calculation of these terms were derived by Harvie<sup>(17)</sup> and are summarized by Pitzer.<sup>(13)</sup> These expressions were used here to calculate all theoretical unsymmetrical mixing terms. The term  $\theta_{12}$  is determined by regression of experimental results.

The stoichiometric osmotic coefficient  $\phi$  for  $\text{H}_2\text{SO}_4(\text{aq})$  refers to the completely ionized standard state and is related to the osmotic coefficient on a mixed basis by

$$\phi = \{(m_1 + m_2 + m_{\text{H}})/(3m)\}\phi_{\text{mix}}, \quad (32)$$

where  $m$  is the stoichiometric molality of  $\text{H}_2\text{SO}_4$  and the various  $m_i$  values are equilibrium molalities of the various species present.

#### 4. Ion-interaction equations: mixtures of sodium sulfate and sulfuric acid

The main purpose of the present work is to represent satisfactorily the thermodynamic properties and, hence, the osmotic coefficients for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  over the range from  $y = 0$  to  $y = 1$ . Because of the molality range of the experimental investigations, the ion-interaction model must be applied to extremely concentrated solutions and hence to very severely non-ideal conditions. The extensive array of osmotic coefficients for this system is extremely valuable in that it may be used to generate expressions useful for thermodynamic properties *anywhere in the three-component system up to the molality limit investigated*.

Rard<sup>(3,4)</sup> has precisely fitted his isopiestic values for the mixtures for the mole fractions investigated. These fits, however, do not permit calculations of thermodynamic properties outside of these exact fractions. We attempt maximum utility and a complete representation by the present calculations.

The appropriate equation required for fits of osmotic coefficients pertaining to  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  is given by

$$\begin{aligned} \phi_{\text{mix}} - 1 = & 2\{f^\phi I + m_{\text{H}}m_1(B_{\text{H}1}^\phi + ZC_{\text{H}1}) + m_{\text{H}}m_2(B_{\text{H}2}^\phi + ZC_{\text{H}2}) + \\ & m_{\text{Na}}m_1(B_{\text{Na}1}^\phi + ZC_{\text{Na}1}) + m_{\text{Na}}m_2(B_{\text{Na}2}^\phi + ZC_{\text{Na}2}) + \\ & m_{\text{H}}m_{\text{Na}}(\Phi_{\text{HNa}}^\phi + m_1\psi_{\text{HNa}1} + m_2\psi_{\text{HNa}2}) + \\ & m_1m_2(\Phi_{12}^\phi + m_{\text{H}}\psi_{12\text{H}} + m_{\text{Na}}\psi_{12\text{Na}})\}/(m_{\text{H}} + m_{\text{Na}} + m_1 + m_2). \end{aligned} \quad (33)$$

All amounts of species, except  $\text{Na}^+(\text{aq})$ , are controlled by the dissociation equilibrium involving  $\text{HSO}_4^-$ , for which the activity-coefficient product is given by

$$\begin{aligned} \ln(\gamma_{\text{H}}\gamma_2/\gamma_1) = & 4F + (m_1 - m_{\text{H}})(2B_{\text{H}1} + ZC_{\text{H}1}) + (m_2 + m_{\text{H}})(2B_{\text{H}2} + ZC_{\text{H}2}) - \\ & m_{\text{Na}}(2B_{\text{Na}1} + ZC_{\text{Na}1}) + m_{\text{Na}}(2B_{\text{Na}2} + ZC_{\text{Na}2}) + \\ & 2m_{\text{H}}m_1C_{\text{H}1} + 2m_{\text{H}}m_2C_{\text{H}2} + 2m_{\text{Na}}m_1C_{\text{Na}1} + \\ & 2m_{\text{Na}}m_2C_{\text{Na}2} + 2(m_1 - m_2)\Phi_{12} + 2m_{\text{Na}}\Phi_{\text{HNa}} + \\ & (m_1m_2 + m_1m_{\text{H}} - m_2m_{\text{H}})\psi_{12\text{H}} + m_{\text{Na}}(m_1 - m_2)\psi_{12\text{Na}} + \\ & m_{\text{Na}}(m_1 - m_{\text{H}})\psi_{\text{HNa}1} + m_{\text{Na}}(m_{\text{H}} + m_2)\psi_{\text{HNa}2}, \end{aligned} \quad (34)$$

where  $F$  is defined for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$

$$\begin{aligned} F = & f^\gamma + m_{\text{H}}m_1B'_{\text{H}1} + m_{\text{H}}m_2B'_{\text{H}2} + m_{\text{Na}}m_1B'_{\text{Na}1} + \\ & m_{\text{Na}}m_2B'_{\text{Na}2} + m_1m_2\Phi'_{12} + m_{\text{H}}m_{\text{Na}}\Phi'_{\text{NaH}}, \end{aligned} \quad (35)$$

and  $f^\gamma$  and the form of the  $B'$  terms were defined previously.

Now that the ion-interaction equations have been outlined, the actual fitting procedure and relevant discussion can be approached. The power of the ion-interaction model is the logical framework on which it is based. This can be most easily seen by examination of equation (21) for the excess Gibbs energy of a mixture of species. Although the final equations may look cumbersome, their simplicity can be realized by the manner in which they are extended to more complex mixtures.

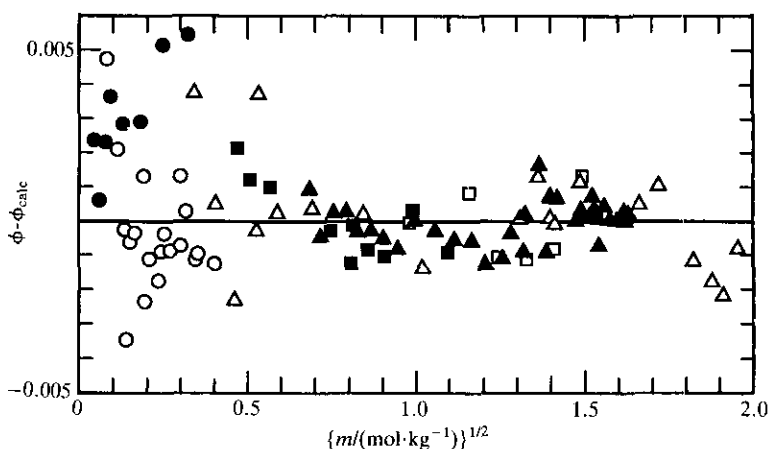


FIGURE 1. Difference in experimental and fitted, equation (12), osmotic coefficients from a variety of sources for  $\text{Na}_2\text{SO}_4(\text{aq})$  at 298.15 K plotted against the square root of molality: ▲, Rard and Miller;<sup>(19)</sup> △, Platford;<sup>(28)</sup> ■, Downes and Pitzer;<sup>(27)</sup> □, Gibson and Adams (from vapor pressures);<sup>(20)</sup> ●, Randall and Scott (from freezing temperatures);<sup>(25)</sup> ○, Indelli (from freezing temperatures).<sup>(26)</sup>

## 5. Results of calculations

The thermodynamic properties of  $\text{Na}_2\text{SO}_4(\text{aq})$  have been extensively investigated over wide ranges of temperature and pressure.<sup>(10, 18)</sup> However, there are no precise representations that cover the range from the freezing temperature to the normal boiling temperature of pure water. We are specifically interested in this temperature range for future analyses of properties for pure and mixed electrolytes. Because of these requirements, we have re-evaluated the ion-interaction parameters for  $\text{Na}_2\text{SO}_4(\text{aq})$  from 273 K to 373 K.

Experimental results that lead to the osmotic coefficient of  $\text{Na}_2\text{SO}_4(\text{aq})$  from isopiestic, direct vapor-pressure, and freezing-temperature depression measurements were selected for the regression. Rard and Miller<sup>(19)</sup> have reviewed most appropriate results for  $\text{Na}_2\text{SO}_4(\text{aq})$  and have indicated which are of sufficient precision to include in meaningful fits. At 298.15 K, the vapor-pressure measurements from Gibson and Adams<sup>(20)</sup> were used after conversion from 300.65 K to 298.15 K using enthalpies of dilution at 298.15 K from Thompson *et al.*<sup>(21)</sup> and appropriate heat capacities from Desnoyers *et al.*<sup>(22)</sup> Methods for converting osmotic coefficients at various temperatures to another reference temperature are outlined in standard texts.<sup>(23, 24)</sup> Freezing temperatures of  $\text{Na}_2\text{SO}_4(\text{aq})$  determined by Randall and Scott<sup>(25)</sup> and Indelli<sup>(26)</sup> were converted to 273.15 K and to 298.15 K (the latter for comparison with fitted results by Rard and Miller<sup>(19)</sup>) using the same procedure and auxiliary values. Isopiestic measurements leading to osmotic coefficients at 298.15 K were taken from Rard and Miller,<sup>(19)</sup> Downes and Pitzer,<sup>(27)</sup> and Platford.<sup>(28)</sup> Other isopiestic measurements valid at 273.15 K were taken from Platford,<sup>(29)</sup> and at 288.15 K from Childs and Platford.<sup>(30)</sup> For temperatures between 298.15 K and 372.75 K, osmotic coefficients were calculated from the equations presented by Pabalan and Pitzer.<sup>(10)</sup> These equations are based on a wide array of thermodynamic



TABLE 1. Coefficients for equations of type (36) for the temperature dependence of the Pitzer parameters for sodium sulfate:  $\beta_{\text{Na}_2}^{(0)}$ ,  $\beta_{\text{Na}_2}^{(1)}$ , and  $C_{\text{Na}_2}^\phi$  ( $\alpha_1 = 1.7 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ ) ( $m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$ )

Parameter $p$	$p(298.15 \text{ K})$	$b$	$c$
$\beta_{\text{Na}_2}^{(0)} m^\circ$	$0.006536438 \pm 0.00024$	$-30.197349 \pm 1.1$	$-0.20084955 \pm 0.022$
$\beta_{\text{Na}_2}^{(1)} m^\circ$	$0.87426420 \pm 0.0037$	$-70.014123 \pm 8.9$	$0.2962095 \pm 0.18$
$C_{\text{Na}_2}^\phi (m^\circ)^2$	$0.007693706 \pm 0.000054$	$4.5879201 \pm 0.30$	$0.019471746 \pm 0.0057$

results leading to osmotic coefficients as well as the various temperature derivatives of the Gibbs energies. Since the Pabalan and Pitzer treatment is intended for representation to high temperatures, the fitting procedure defined above generates thermodynamic values for  $\text{Na}_2\text{SO}_4(\text{aq})$  consistent with this treatment at the higher temperatures.

The parameters represented by equation (12) were initially fitted to the experimental results at 298.15 K using  $\alpha_1 = 2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  to obtain values for the parameters  $\beta_{\text{Na}_2}^{(0)}$ ,  $\beta_{\text{Na}_2}^{(1)}$ , and  $C_{\text{Na}_2}^\phi$ . Systematic deviations from the experimental results were found both for this and for a value of  $\alpha_1 = 1.4 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  used by Pabalan and Pitzer.<sup>(10)</sup> The value  $\alpha_1 = 1.7 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  resulted in removing essentially all systematic deviations between fitted and experimental results and led to the lowest overall standard deviation of fit. The  $\beta^{(2)}$  term did not significantly improve the fits and was thus omitted. The quality of fit at 298.15 K can be seen in figure 1 where differences between fitted and experimental osmotic coefficients are plotted against  $m^{1/2}$ .

Results from experimental measurements at temperatures other than 298.15 K were fitted using the value of  $1.7 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for  $\alpha_1$  whilst constraining the temperature dependence of the interaction parameters to be of the form:

$$p(T) = p(T_{\text{ref}}) + b\{(1/T) - (1/T_{\text{ref}})\} + c \cdot \ln(T/T_{\text{ref}}), \quad (36)$$

where  $T_{\text{ref}}$  is chosen as 298.15 K. Slightly higher overall standard deviations were found using quadratic or other three-parameter equations. The temperature dependences of  $\beta_{\text{Na}_2}^{(0)}$ ,  $\beta_{\text{Na}_2}^{(1)}$ , and  $C_{\text{Na}_2}^\phi$  are described by parameters for use in equation (36), and are given in table 1 along with values for the parameters at 298.15 K.

The results of fits with the same weighting for the various sets as used by Rard and Miller,<sup>(19)</sup> led to an overall standard deviation of 0.0014 compared with the standard deviation of 0.0013 for their 6-parameter fit. With a weighting involving a lowered contribution of the freezing temperature and vapor pressures, the final weighted standard deviation for the set at 298.15 K was found to be 0.0010 for osmotic coefficients. The overall standard deviation for the global regression to results in the range 273.15 K to 372.75 K was found to be 0.0019 using temperature-dependent equations for the interaction parameters represented by equation (36). Deviations between calculated and experimental values from 273.15 K to 372.75 K are shown in figure 2. Smoothed values of the osmotic coefficient and activity coefficient at various temperatures are shown in figure 3 and are listed in table 2.

As can be seen in figure 1 and by the relative standard deviations cited above, the results for  $\text{Na}_2\text{SO}_4(\text{aq})$  are represented within experimental uncertainty at 298.15 K

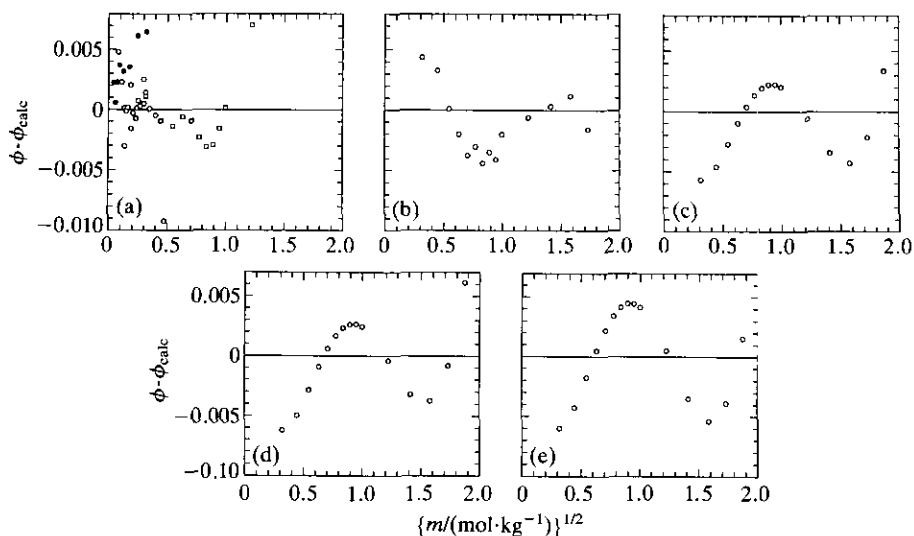


FIGURE 2. Difference in experimental and fitted, equation (12), osmotic coefficients  $\phi$  for  $\text{Na}_2\text{SO}_4(\text{aq})$  at various temperatures plotted against the square root of molality. (a), ( $T = 273.15 \text{ K}$ ):  $\square$ , Platform;<sup>(29)</sup>  $\bullet$ , Randall and Scott (freezing temperatures);<sup>(25)</sup>  $\circ$ , Indelli (freezing temperatures);<sup>(26)</sup> (b), ( $T = 288.15 \text{ K}$ ):  $\circ$ , Childs and Platform;<sup>(30)</sup> (c), ( $T = 323.15 \text{ K}$ ):  $\circ$ , Pabalan and Pitzer;<sup>(10)</sup> (d), ( $T = 348.15 \text{ K}$ ):  $\circ$ , Pabalan and Pitzer;<sup>(10)</sup> (e), ( $T = 372.75 \text{ K}$ ):  $\circ$ , Pabalan and Pitzer.<sup>(10)</sup>

and just outside experimental uncertainty at other temperatures as illustrated by figure 2. The activity coefficients and osmotic coefficients of  $\text{Na}_2\text{SO}_4(\text{aq})$  resulting from this treatment are very similar to the results from Pabalan and Pitzer.<sup>(10)</sup> Smoothed values for these quantities are presented in figure 3. The effect of

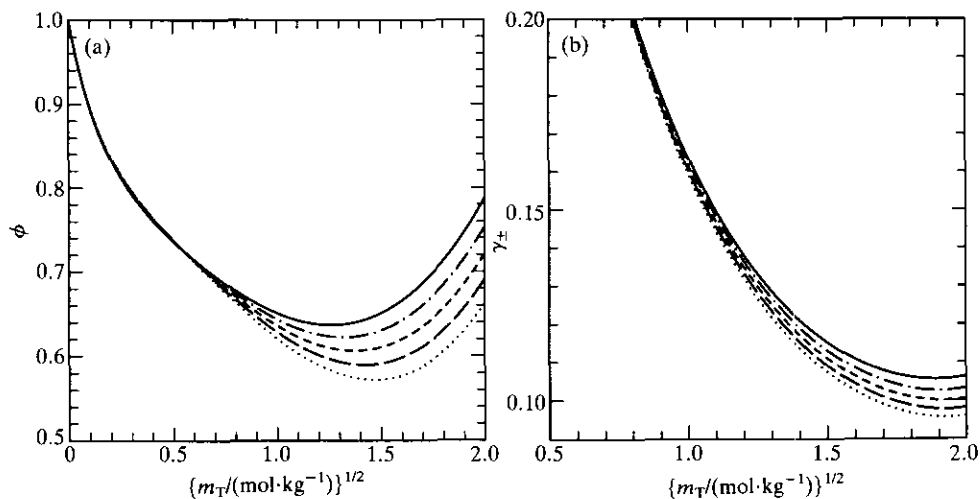


FIGURE 3. Smoothed values of properties for  $\text{Na}_2\text{SO}_4(\text{aq})$  at various temperatures plotted against the square root of molality  $m$ : (a) osmotic coefficients  $\phi$ ; (b) activity coefficients  $\gamma_{\pm}$ . Temperatures are as follows: —, 273.15 K; ---, 298.15 K; ···, 323.15 K; — · —, 348.15 K; — — —, 373.15 K.

TABLE 2. Smoothed osmotic coefficients  $\phi$  and activity coefficients  $\gamma_{\pm}$  of  $\text{Na}_2\text{SO}_4(\text{aq})$  at (273.15, 298.15, 323.15, 348.15 and 373.15) K

$m$ $\text{mol} \cdot \text{kg}^{-1}$	273.15 K		298.15 K		323.15 K		348.15 K		373.15 K	
	$\phi$	$\gamma_{\pm}$	$\phi$	$\gamma_{\pm}$	$\phi$	$\gamma_{\pm}$	$\phi$	$\gamma_{\pm}$	$\phi$	$\gamma_{\pm}$
0.0001	0.9868	0.9607	0.9868	0.9608	0.9869	0.9608	0.9869	0.9608	0.9869	0.9608
0.0010	0.9605	0.8846	0.9608	0.8849	0.9611	0.8851	0.9612	0.8853	0.9613	0.8854
0.0050	0.9195	0.7715	0.9212	0.7728	0.9222	0.7736	0.9229	0.7741	0.9234	0.7745
0.0100	0.8934	0.7026	0.8965	0.7047	0.8984	0.7061	0.8997	0.7070	0.9007	0.7077
0.0150	0.8755	0.6568	0.8799	0.6597	0.8827	0.6615	0.8846	0.6627	0.8859	0.6637
0.0200	0.8617	0.6222	0.8673	0.6257	0.8709	0.6279	0.8733	0.6294	0.8750	0.6305
0.0500	0.8116	0.5034	0.8236	0.5094	0.8310	0.5132	0.8360	0.5158	0.8396	0.5176
0.1000	0.7680	0.4102	0.7882	0.4186	0.8005	0.4237	0.8088	0.4272	0.8146	0.4297
0.2000	0.7179	0.3201	0.7505	0.3306	0.7701	0.3370	0.7828	0.3413	0.7917	0.3443
0.3000	0.6840	0.2708	0.7263	0.2823	0.7513	0.2893	0.7674	0.2938	0.7782	0.2970
0.4000	0.6573	0.2381	0.7077	0.2500	0.7371	0.2572	0.7558	0.2619	0.7682	0.2651
0.5000	0.6350	0.2143	0.6924	0.2264	0.7256	0.2337	0.7464	0.2383	0.7600	0.2415
0.6000	0.6158	0.1960	0.6795	0.2081	0.7160	0.2154	0.7386	0.2200	0.7532	0.2230
0.7000	0.5992	0.1814	0.6684	0.1934	0.7079	0.2006	0.7321	0.2052	0.7474	0.2081
0.8000	0.5846	0.1695	0.6590	0.1814	0.7011	0.1884	0.7266	0.1928	0.7426	0.1956
0.9000	0.5719	0.1596	0.6509	0.1713	0.6953	0.1782	0.7220	0.1824	0.7385	0.1851
1.0000	0.5609	0.1513	0.6441	0.1627	0.6905	0.1694	0.7182	0.1735	0.7352	0.1760
1.2000	0.5434	0.1381	0.6336	0.1489	0.6835	0.1551	0.7127	0.1589	0.7302	0.1611
1.4000	0.5312	0.1283	0.6269	0.1383	0.6792	0.1440	0.7095	0.1473	0.7271	0.1492
1.6000	0.5238	0.1209	0.6234	0.1300	0.6773	0.1351	0.7080	0.1380	0.7255	0.1395
1.8000	0.5209	0.1153	0.6228	0.1235	0.6775	0.1279	0.7080	0.1302	0.7250	0.1314
2.0000	0.5221	0.1112	0.6249	0.1182	0.6793	0.1219	0.7092	0.1237	0.7253	0.1244
2.2000	0.5272	0.1083	0.6293	0.1140	0.6826	0.1168	0.7113	0.1180	0.7261	0.1184
2.4000	0.5361	0.1064	0.6359	0.1107	0.6872	0.1125	0.7142	0.1131	0.7274	0.1130
2.6000	0.5486	0.1053	0.6445	0.1080	0.6930	0.1089	0.7176	0.1088	0.7289	0.1082
2.8000	0.5647	0.1051	0.6550	0.1060	0.6997	0.1057	0.7215	0.1049	0.7304	0.1038
3.0000	0.5841	0.1056	0.6674	0.1045	0.7074	0.1030	0.7257	0.1014	0.7319	0.0998
3.2000	0.6069	0.1068	0.6815	0.1034	0.7159	0.1007	0.7301	0.0982	0.7333	0.0961
3.4000	0.6329	0.1088	0.6973	0.1028	0.7251	0.0986	0.7347	0.0953	0.7345	0.0926
3.6000	0.6622	0.1114	0.7146	0.1026	0.7349	0.0968	0.7394	0.0926	0.7353	0.0894
3.8000	0.6946	0.1149	0.7335	0.1028	0.7454	0.0953	0.7441	0.0902	0.7359	0.0863
4.0000	0.7301	0.1191	0.7540	0.1033	0.7564	0.0940	0.7488	0.0878	0.7360	0.0834

temperature, as can be seen in the figure, is not large on the scale presented but of course does account for the temperature-derivative properties ( $H_m - H_m^\circ$ ) and ( $C_{p,m} - C_{p,m}^\circ$ ).

The treatments of  $\text{H}_2\text{SO}_4(\text{aq})$  have been discussed in a preceding section. The most useful treatments are from Pitzer *et al.*<sup>(5)</sup> and Reardon and Beckie.<sup>(8)</sup> The latter investigation covers a wider temperature range and includes the higher-order mixing terms although some details of the analysis are unclear.

Though Pitzer *et al.*<sup>(5)</sup> did not include the theoretical unsymmetrical mixing terms, their regression does represent the thermodynamic values within experimental uncertainty and thus is entirely satisfactory for replication of stoichiometric osmotic coefficients. We have tested both treatments in our calculations for the mixed system. Both sets of parameters are based on fits that omitted certain empirical mixing parameters because of redundancy. It is possible that these redundancies will be

removed for the mixed system and thus a more complete set of parameters may be obtained.

Rard<sup>(3,4)</sup> has summarized experimental results for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  at 298.15 K and associated uncertainties for each set. The only other set of osmotic coefficients used for the regression were the results of Stokes<sup>(32)</sup> for  $y = 0.5$  (i.e. pure sodium bisulfate). The iterative procedure for regression of the mixed system is outlined below.

We have used an iterative procedure using  $m_{\text{H}}$  as the variable to solve the dissociation equilibrium and hence amounts of all species. Various molalities of species are related to the equilibrium molality of  $\text{H}^+(\text{aq})$  and initial molalities as described by equations (3) through (6). The molality of hydrogen ion is conveniently defined by the quadratic solution to the equilibrium-constant expression written solely in terms of initial molalities and hydrogen-ion molality.

$$a = \gamma_{\text{H}}\gamma_2/\gamma_1 \quad (37)$$

$$b = (\gamma_{\text{H}}\gamma_2/\gamma_1)(m_{2,i} - m_{1,i}) + m^\circ K_a^\circ \quad (38)$$

$$c = -2m_{1,i}m^\circ K_a^\circ \quad (39)$$

$$m_{\text{H}} = \{-b \pm (b^2 - 4ac)^{1/2}\}/2a. \quad (40)$$

The iterative solution is attained by initially setting  $m_1$  and  $m_{\text{H}}$  equal to  $m_{1,i}$  (stoichiometric  $\text{H}_2\text{SO}_4$ ),  $m_2$  equal to  $m_{2,i}$  (stoichiometric  $\text{Na}_2\text{SO}_4$ ) and  $(\gamma_{\text{H}}\gamma_2/\gamma_1)$  calculated as described by equation (24), and  $K_a^\circ$  was taken from Pitzer *et al.*,<sup>(5)</sup>  $(\gamma_{\text{H}}\gamma_2/\gamma_1)$  is then used to modify all molalities of species, and the calculation is repeated until convergence of  $m_{\text{H}}$  is observed.

The non-linear regression optimizes the ion-interaction parameters based iteratively on converged speciation solutions for each composition studied. The sequentially optimized interaction parameters then lead to new values of  $(\gamma_{\text{H}}\gamma_2/\gamma_1)$  and a whole new set of equilibrium molalities of species. Eventually, convergence is obtained for the ion-interaction parameters when speciation calculations from successive iterations produce the same result. This calculation was sensitive to the initial guesses of the ion-interaction parameters, although well defined minima were found for each type of regression.

The only variable ion-interaction parameters generated when fitting the results for mixtures using previous formulations for the ion-interaction parameters of  $\text{Na}_2\text{SO}_4(\text{aq})$  and of  $\text{H}_2\text{SO}_4(\text{aq})$ , are the binary and ternary interactions not present in either of the two binary systems. As can be seen by examination of equations (33) through (35), the only variable parameters are the binary terms:  $\beta_{\text{Na}1}^{(0)}$ ,  $\beta_{\text{Na}1}^{(1)}$ ,  $C_{\text{Na}1}^\phi$ ,  $\theta_{\text{NaH}}$ , and the ternary parameters  $\psi_{12\text{Na}}$ ,  $\psi_{\text{HNa}1}$ , and  $\psi_{\text{HNa}2}$ . Rard<sup>(3,4)</sup> has used a total of 46 empirical parameters for representation of osmotic coefficients for the mixture along the seven values of  $y$  studied. The results of these regressions by Rard are extremely precise, and in most cases within estimates of experimental uncertainty.

The experimental osmotic coefficients reported by Rard<sup>(3,4)</sup> and by Stokes<sup>(32)</sup> must be modified slightly for conversion to mixed-basis quantities since both sets refer to completely ionized standard states. Rard<sup>(3,4)</sup> has reported osmotic

coefficients at specified values of  $y$  as a function of the total molality  $m_T$ . The total molality is merely the sum of stoichiometric molalities of  $\text{Na}_2\text{SO}_4$  and of  $\text{H}_2\text{SO}_4$ . The reported osmotic coefficients  $\phi$  are related to the mixed-basis osmotic coefficients  $\phi_{\text{mix}}$  defined in equation (33) by

$$\phi_{\text{mix}} = 3m_T\phi/(2m_1 + 3m_2), \quad (41)$$

where  $m_1$  and  $m_2$  are equilibrium molalities of  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  ions, respectively. The actual function fitted was thus not the osmotic coefficients on a mixed-solution basis, since these values are not known until the exact amounts of all species present are known. The regression minimized deviations of the stoichiometric osmotic coefficients after multiplication of the ion-interaction equation for the mixed osmotic coefficients, equation (33), by the factor  $(2m_1 + 3m_2)/3m_T$ . This same fitting procedure was used for all other sets, including those from Stokes,<sup>(32)</sup> and for pure  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$ .

All fits were done using a non-linear least-squares regression routine. The convergence of the various fits was slow because of the multi-level iterative-solution calculation employed for speciation as well as ion-interaction parameter convergence. The ion-interaction parameters define the activity-coefficient product that in turn modifies amounts of species present at equilibrium and then the ion-interaction parameters, and so on.

Initial fits using the entire array of osmotic coefficients were quite poor in high-molality regions, especially for low values of  $y$ . Shortcomings here can be traced to the Reardon and Beckie<sup>(8)</sup> and Pitzer *et al.*<sup>(5)</sup> treatments of  $\text{H}_2\text{SO}_4$  in that they extend to only  $6 \text{ mol} \cdot \text{kg}^{-1}$  of  $\text{H}_2\text{SO}_4(\text{aq})$ . The present osmotic coefficients for the mixtures extend to nearly  $15 \text{ mol} \cdot \text{kg}^{-1}$  total ionic strength at low values of  $y$ . Giving zero weight to osmotic coefficients for the mixtures with molalities exceeding the range of applicability of treatments for  $\text{H}_2\text{SO}_4$  and for  $\text{Na}_2\text{SO}_4$  led to the following results. Initial fits using the Reardon and Beckie evaluation for  $\text{H}_2\text{SO}_4$  and the revised  $\text{Na}_2\text{SO}_4$  parameters cited in table 1, led to an overall standard deviation of 0.0062. Substitution of the Pitzer *et al.* formulation provided essentially identical results with a standard deviation of 0.0063. Neither of these fits represents the experimental  $\phi$  values to within the precision of the measurements or within an amount acceptable for a "good fit". As such, we found that treatments using constrained  $\text{H}_2\text{SO}_4$  ion-interaction parameters were not satisfactory.

Allowing optimization of the  $\text{H}_2\text{SO}_4$  parameters while keeping the parameters for  $\text{Na}_2\text{SO}_4$  constrained to the results cited in table 1 and giving zero weight to molalities and ionic strengths outside of the range of the treatment of  $\text{Na}_2\text{SO}_4(\text{aq})$ , led to an overall standard deviation of 0.0012. The additional ion-interaction parameters that were optimized were:  $\beta_{\text{H}_1}^{(0)}$ ,  $\beta_{\text{H}_1}^{(1)}$ ,  $C_{\text{H}_1}^\phi$ ,  $\beta_{\text{H}_2}^{(0)}$ ,  $\beta_{\text{H}_2}^{(1)}$ ,  $C_{\text{H}_2}^\phi$ ,  $\theta_{12}$ , and the ternary parameter  $\psi_{12\text{H}}$ . The coefficients generated using this procedure are recommended as the *low-ionic-strength* set and are listed in table 3. The  $\alpha_1$  value used to represent the ionic-strength dependence of the binary interactions of  $\text{H}^+$  with  $\text{HSO}_4^-$  and with  $\text{SO}_4^{2-}$ , here and in the following section, was  $2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  as recommended by Pitzer.<sup>(13)</sup> Plots of the deviation between calculated and experimental results for mixtures considered in this treatment are shown in figure 4.

TABLE 3. Low-ionic-strength set of Pitzer ion-interaction parameters for  $\text{NaHSO}_4(\text{aq})$ ,  $\text{H}_2\text{SO}_4(\text{aq})$ , and the various non-ideal mixing parameters  $\theta$  and  $\psi$  at 298.15 K. These parameters are valid only to  $4 \text{ mol} \cdot \text{kg}^{-1}$  of  $\text{Na}_2\text{SO}_4$  and  $6 \text{ mol} \cdot \text{kg}^{-1}$  of  $\text{H}_2\text{SO}_4$ . They were derived using the  $\text{Na}_2\text{SO}_4$  parameters listed in table 1. The  $\alpha_1$  value was set equal to  $2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for H1, H2, and Na1  $B$  terms and  $1.7 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for Na2  $B$  terms.  $\sigma$  values represent standard deviations.  $C^\phi$  values are related to  $C$  values as described by equation (20). ( $m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$ )

Parameter	Value	$\sigma$	Parameter	Value	$\sigma$	Parameter	Value	$\sigma$
$\beta_{\text{Na1}}^{(0)} m^\circ$	0.0670967	0.00112	$C_{\text{H1}}^\phi (m^\circ)^2$	-0.0026601	0.00032	$\theta_{12} m^\circ$	-0.1353418	0.00221
$\beta_{\text{Na1}}^{(1)} m^\circ$	0.3826401	0.01355	$\beta_{\text{H2}}^{(0)} m^\circ$	0.0642129	0.01077	$\psi_{12\text{H}} (m^\circ)^2$	0.0278059	0.00380
$C_{\text{Na1}}^\phi (m^\circ)^2$	-0.0039056	0.00011	$\beta_{\text{H2}}^{(1)} m^\circ$	0.2259017	0.09475	$\psi_{12\text{Na}} (m^\circ)^2$	0.0186163	0.00050
$\beta_{\text{H1}}^{(0)} m^\circ$	0.2229662	0.00220	$C_{\text{H2}}^\phi (m^\circ)^2$	0.0311257	0.00614	$\psi_{\text{HNa1}} (m^\circ)^2$	-0.0017565	0.00034
$\beta_{\text{H1}}^{(1)} m^\circ$	0.4600160	0.01954	$\theta_{\text{NaH}} m^\circ$	-0.0072672	0.00181	$\psi_{\text{HNa2}} (m^\circ)^2$	0.0378356	0.00209

The complete set of osmotic coefficients for the mixtures was analyzed by allowing all interaction parameters to vary. To help retain a high quality of fit for  $\text{H}_2\text{SO}_4(\text{aq})$ , representative values (osmotic coefficients) were calculated from Pitzer *et al.*<sup>(5)</sup> and Rard<sup>(31)</sup> up to  $15 \text{ mol} \cdot \text{kg}^{-1}$  of  $\text{H}_2\text{SO}_4(\text{aq})$ . Also included in the regression were the  $\phi$  values for  $\text{Na}_2\text{SO}_4(\text{aq})$  as outlined in the preceding section.

While other values of  $\alpha_1$  were tested for interaction of  $\text{Na}^+$  with  $\text{SO}_4^{2-}$ , including the common value  $2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ , it was found that the best value was

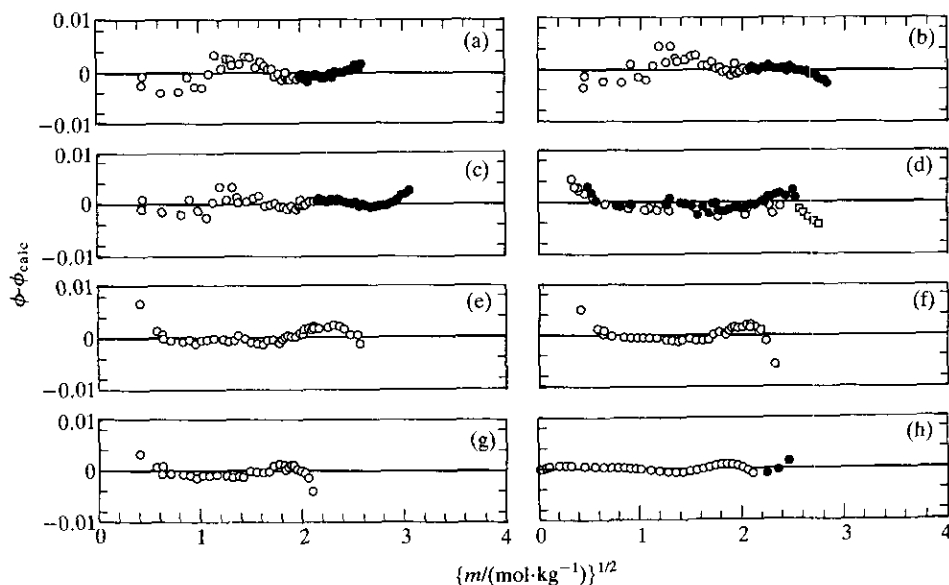


FIGURE 4. Low-ionic-strength differences between experimental and fitted, equations (33) and (38), osmotic coefficients for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  at  $T = 298.15 \text{ K}$  plotted against the square root of total molality: (a),  $y = 0.12471$ : ●, Rard (referenced to  $\text{CaCl}_2$ );<sup>(31)</sup> ○, Rard (referenced to  $\text{NaCl}$ ).<sup>(31)</sup> (b),  $y = 0.24962$ : ●, Rard (referenced to  $\text{CaCl}_2$ );<sup>(31)</sup> ○, Rard (referenced to  $\text{NaCl}$ ).<sup>(31)</sup> (c),  $y = 0.37439$ : ●, Rard (referenced to  $\text{CaCl}_2$ );<sup>(31)</sup> ○, Rard (referenced to  $\text{NaCl}$ ).<sup>(31)</sup> (d),  $y = 0.500$ : □, Rard (referenced to  $\text{CaCl}_2$ );<sup>(4)</sup> ●, Rard (referenced to  $\text{NaCl}$ ).<sup>(4)</sup> ○, Stokes (referenced to  $\text{NaCl}$ ).<sup>(32)</sup> (e),  $y = 0.55595$ : ○, Rard (referenced to  $\text{NaCl}$ ).<sup>(4)</sup> (f),  $y = 0.70189$ : ○, Rard (referenced to  $\text{NaCl}$ ).<sup>(4)</sup> (g),  $y = 0.84920$ : ○, Rard (referenced to  $\text{NaCl}$ ).<sup>(4)</sup> (h),  $y = 0$ : ●, Rard;<sup>(31)</sup> ○, Pitzer *et al.*<sup>(5)</sup>

TABLE 4. Complete set of Pitzer ion-interaction parameters for  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHSO}_4$ , and  $\text{H}_2\text{SO}_4$ , and the various non-ideal mixing parameters  $\theta$  and  $\psi$  at  $T = 298.15$  K. These parameters are valid over the entire range of mole ratios at infinitely dilute to supersaturated molalities. The  $\alpha_1$  value was set equal to  $2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for H1, H2, and Na1  $B$  terms and  $1.4 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for Na2  $B$  terms.  $\sigma$  values represent standard deviations.  $C^\phi$  values are related to  $C$  values as described by equation (20). ( $m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$ )

Parameter	Value	$\sigma$	Parameter	Value	$\sigma$	Parameter	Value	$\sigma$
$\beta_{\text{Na}1}^{(0)} m^\circ$	0.0665218	0.00159	$\beta_{\text{H}2}^{(1)} m^\circ$	-0.7672550	0.06223	$\theta_{12} m^\circ$	-0.0857672	0.00238
$\beta_{\text{Na}1}^{(1)} m^\circ$	0.4638041	0.02964	$C_{\text{H}2}^\phi (m^\circ)^2$	0.0076309	0.00177	$\psi_{12\text{H}} (m^\circ)^2$	0.0189687	0.00100
$C_{\text{Na}1}^\phi (m^\circ)^2$	-0.0036978	0.00012	$\beta_{\text{Na}2}^{(0)} m^\circ$	-0.0005221	0.00106	$\psi_{12\text{Na}} (m^\circ)^2$	0.0057457	0.00042
$\beta_{\text{H}1}^{(0)} m^\circ$	0.2246349	0.00191	$\beta_{\text{Na}2}^{(1)} m^\circ$	0.5040399	0.01574	$\psi_{\text{HNa}1} (m^\circ)^2$	0.0008142	0.00017
$\beta_{\text{H}1}^{(1)} m^\circ$	0.7102037	0.03290	$\beta_{\text{Na}2}^{(2)} m^\circ$	0.5530419	0.04374	$\psi_{\text{HNa}2} (m^\circ)^2$	0.0479435	0.00150
$C_{\text{H}1}^\phi (m^\circ)^2$	-0.0040052	0.00012	$C_{\text{Na}2}^\phi (m^\circ)^2$	0.0087956	0.00020			
$\beta_{\text{H}2}^{(0)} m^\circ$	0.1131042	0.00539	$\theta_{\text{NaH}} m^\circ$	-0.0423702	0.00159			

$1.4 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for the combined-system results. As discussed earlier, the best value of  $\alpha_1$  was found to be  $1.7 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$  for pure  $\text{Na}_2\text{SO}_4$ . The  $\beta_{\text{Na}2}^{(2)}$  term was included for these fits using  $\alpha_2 = 2.623 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ . Fits performed without the binary or ternary mixing parameters had such large uncertainties that they are not reported here. The complete set of ion-interaction parameters for the final chosen fit is presented in table 4, along with the corresponding standard deviation of each parameter. The overall standard deviation of the fit, employing all of the osmotic coefficients for  $\text{Na}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}$ , was found to be 0.0033. Representative figures showing deviations between calculated and experimental results are given in figure 5. Useful summaries of ion-interaction parameters for a wide variety of aqueous electrolytes have been published by Pitzer.<sup>(33)</sup> The derived ion-interaction parameters are within the general pattern of ionic interactions for species of similar structure and charge.

## 6. Discussion

The overall standard deviation of the *low-ionic-strength* fit of 0.0012 is substantially lower than the standard deviation from the regression to the complete set of  $\phi$  values (over 650 points) found to be 0.0033. The precision of the experimental osmotic coefficients is marginally lower than 0.001, although the accuracy of these results is about twice this value. The ion-interaction model thus represents these *low-ionic-strength* values to within estimated total uncertainties. The ion-interaction parameters do not represent the experimental values completely within known experimental uncertainties when applied to results extending to a total ionic strength of  $15 \text{ mol} \cdot \text{kg}^{-1}$ . However, the theoretical framework guides the form of the ion-interaction equations, and the range of applicability from infinitely dilute to well over saturation, and from  $y = 0$  to  $y = 1$ , makes this treatment extremely useful. Although the standard deviation for the entire set is outside experimental uncertainties, the value is low enough for this to be a "good" fit to the available results. Because calculations of other thermodynamic properties, including solubilities, require values well removed from investigated compositions, the

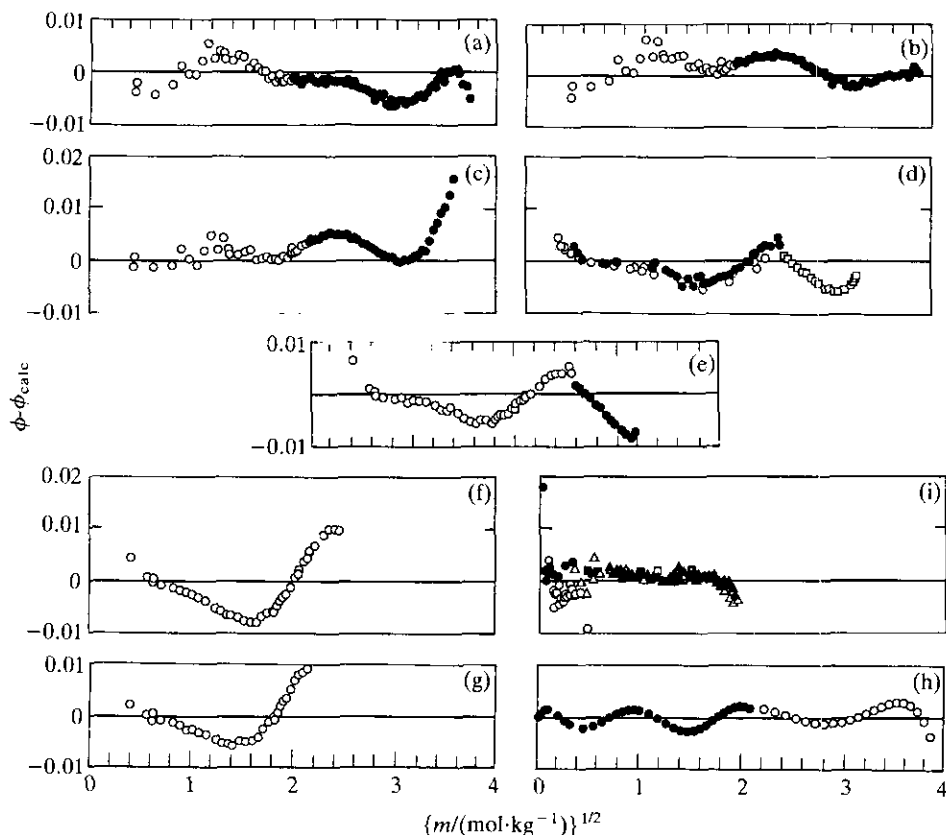


FIGURE 5. High-ionic-strength (complete set) differences between experimental and fitted, equations (33) and (38), osmotic coefficients for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  at  $T = 298.15\text{ K}$  plotted against the square root of total molality: (a),  $y = 0.12471$ :  $\bullet$ , Rard (referenced to  $\text{CaCl}_2$ );<sup>(3)</sup>  $\circ$ , Rard (referenced to  $\text{NaCl}$ ).<sup>(3)</sup> (b),  $y = 0.24962$ :  $\bullet$ , Rard (referenced to  $\text{CaCl}_2$ );<sup>(3)</sup>  $\circ$ , Rard (referenced to  $\text{NaCl}$ ).<sup>(3)</sup> (c),  $y = 0.37439$ :  $\bullet$ , Rard (referenced to  $\text{CaCl}_2$ );<sup>(3)</sup>  $\circ$ , Rard (referenced to  $\text{NaCl}$ ).<sup>(3)</sup> (d),  $y = 0.500$ :  $\square$ , Rard (referenced to  $\text{CaCl}_2$ );<sup>(4)</sup>  $\bullet$ , Rard (referenced to  $\text{NaCl}$ );<sup>(4)</sup>  $\circ$ , Stokes (referenced to  $\text{NaCl}$ ).<sup>(32)</sup> (e),  $y = 0.55595$ :  $\bullet$ , Rard (referenced to  $\text{CaCl}_2$ );<sup>(4)</sup>  $\circ$ , Rard (referenced to  $\text{NaCl}$ ).<sup>(4)</sup> (f),  $y = 0.70189$ :  $\circ$ , Rard (referenced to  $\text{NaCl}$ ).<sup>(4)</sup> (g),  $y = 0.84920$ :  $\circ$ , Rard (referenced to  $\text{NaCl}$ ).<sup>(4)</sup> (h),  $y = 0$ :  $\circ$ , Rard;<sup>(13)</sup>  $\bullet$ , Pitzer *et al.*<sup>(5)</sup> (i),  $y = 1$ :  $\blacktriangle$ , Rard and Miller;<sup>(19)</sup>  $\triangle$ , Platford;<sup>(28)</sup>  $\blacksquare$ , Downes and Pitzer;<sup>(27)</sup>  $\square$ , Gibson and Adams (from vapor pressures);<sup>(20)</sup>  $\bullet$ , Randall and Scott (from freezing temperatures);<sup>(25)</sup>  $\circ$ , Indelli (from freezing temperatures).<sup>(26)</sup>

importance of this global representation is immediately clear. The present treatment can be readily extended to more complex mixtures.

Increased precision of fit for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  could certainly be obtained by adding fourth-order interaction parameters for the extended ionic-strength region (see Appendix H of reference 13), but their physical meaning would be questionable. Also, the introduction of  $\text{NaSO}_4^-(\text{aq})$  as an additional species with its equilibrium constant of formation might be considered. Values of  $\ln K^\circ$  have been reported in the range 1.9 to 2.5.<sup>(6)</sup> Many additional ion-interaction terms would be generated because of the increased interactions of all species with  $\text{NaSO}_4^-(\text{aq})$ . While



TABLE 5. Representative speciation and smoothed osmotic coefficients at round mole ratios for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  ( $m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$ ;  $m_2 = m_1 - m_1$ )

$\frac{m_1}{m^\circ}$	$\frac{m_{\text{H}}}{m^\circ}$	$\frac{m_1}{m^\circ}$	$\frac{\gamma_{\text{H}}\gamma_2}{\gamma_1}$	$\phi$	$\frac{m_{\text{H}}}{m^\circ}$	$\frac{m_1}{m^\circ}$	$\frac{\gamma_{\text{H}}\gamma_2}{\gamma_1}$	$\phi$
$y = 0$				$y = 0.2$				
0.1	0.130	0.070	0.188	0.677	0.096	0.064	0.197	0.683
0.2	0.255	0.145	0.107	0.667	0.185	0.135	0.120	0.666
0.3	0.383	0.217	0.072	0.668	0.274	0.206	0.084	0.662
0.4	0.513	0.287	0.052	0.672	0.365	0.275	0.064	0.661
0.5	0.645	0.355	0.040	0.678	0.456	0.344	0.051	0.663
0.6	0.778	0.422	0.032	0.685	0.549	0.411	0.042	0.666
0.7	0.913	0.487	0.026	0.693	0.643	0.477	0.035	0.670
0.8	1.049	0.551	0.022	0.702	0.737	0.543	0.030	0.674
0.9	1.185	0.615	0.019	0.711	0.831	0.609	0.026	0.680
1.0	1.322	0.678	0.017	0.721	0.925	0.675	0.024	0.686
1.5	2.010	0.990	0.010	0.779	1.394	1.006	0.015	0.724
2.0	2.694	1.306	0.007	0.845	1.848	1.352	0.012	0.771
2.5	3.365	1.635	0.006	0.917	2.279	1.721	0.010	0.822
3.0	4.020	1.980	0.005	0.992	2.683	2.117	0.009	0.875
3.5	4.655	2.345	0.005	1.069	3.058	2.542	0.009	0.929
4.0	5.268	2.732	0.004	1.147	3.406	2.994	0.009	0.980
4.5	5.858	3.142	0.004	1.224	3.729	3.471	0.009	1.029
5.0	6.424	3.576	0.004	1.299	4.030	3.970	0.010	1.075
5.5	6.967	4.033	0.004	1.373	4.312	4.488	0.011	1.117
6.0	7.488	4.512	0.004	1.443	4.578	5.022	0.012	1.156
7.0	8.470	5.530	0.005	1.575	5.076	6.124	0.014	1.222
8.0	9.387	6.613	0.005	1.693	5.545	7.255	0.018	1.275
9.0	10.256	7.744	0.006	1.797	6.002	8.398	0.024	1.317
10.0	11.094	8.906	0.008	1.887	6.460	9.540	0.034	1.351
11.0	11.915	10.085	0.010	1.965	6.929	10.671	0.049	1.378
12.0	12.732	11.268	0.013	2.032	7.419	11.781	0.076	1.400
13.0	13.557	12.443	0.017	2.090	7.934	12.866	0.127	1.421
14.0	14.399	13.601	0.025	2.143	8.475	13.925	0.231	1.441
15.0	15.267	14.733	0.038	2.191	9.038	14.962	0.455	1.460
$y = 0.4$				$y = 0.5$				
0.1	0.065	0.055	0.200	0.696	0.051	0.049	0.198	0.706
0.2	0.121	0.119	0.126	0.672	0.094	0.106	0.127	0.679
0.3	0.177	0.183	0.092	0.662	0.136	0.164	0.093	0.666
0.4	0.234	0.246	0.072	0.657	0.178	0.222	0.074	0.658
0.5	0.290	0.310	0.059	0.654	0.220	0.280	0.061	0.653
0.6	0.347	0.373	0.050	0.653	0.262	0.338	0.051	0.650
0.7	0.404	0.436	0.043	0.653	0.305	0.395	0.045	0.648
0.8	0.461	0.499	0.038	0.654	0.347	0.453	0.040	0.647
0.9	0.519	0.561	0.034	0.655	0.388	0.512	0.036	0.647
1.0	0.575	0.625	0.030	0.657	0.430	0.570	0.032	0.647
1.5	0.852	0.948	0.021	0.676	0.628	0.872	0.023	0.657
2.0	1.108	1.292	0.017	0.703	0.805	1.195	0.019	0.676
2.5	1.337	1.663	0.016	0.734	0.954	1.546	0.018	0.698
3.0	1.535	2.065	0.015	0.766	1.073	1.927	0.018	0.722
3.5	1.705	2.495	0.015	0.797	1.165	2.335	0.018	0.744
4.0	1.849	2.951	0.016	0.826	1.231	2.769	0.019	0.765
4.5	1.971	3.429	0.017	0.852	1.277	3.223	0.021	0.783
5.0	2.074	3.926	0.019	0.875	1.306	3.694	0.023	0.799
5.5	2.162	4.438	0.020	0.895	1.320	4.180	0.025	0.812
6.0	2.238	4.962	0.022	0.912	1.324	4.676	0.028	0.822

TABLE 5—continued

$\frac{m_T}{m^\circ}$	$\frac{m_H}{m^\circ}$	$\frac{m_1}{m^\circ}$	$\frac{\gamma_H \gamma_2}{\gamma_1}$	$\phi$	$\frac{m_H}{m^\circ}$	$\frac{m_1}{m^\circ}$	$\frac{\gamma_H \gamma_2}{\gamma_1}$	$\phi$	$\phi$
7.0	2.364	6.036	0.028	0.938	1.308	5.692	0.035	0.836	
8.0	2.469	7.131	0.035	0.955	1.270	6.730	0.044	0.841	
9.0	2.562	8.238	0.044	0.964	1.220	7.780	0.055	0.840	
10.0	2.650	9.350	0.057	0.966	1.163	8.837	0.069	0.833	
11.0	2.740	10.460	0.074	0.961	1.101	9.899	0.086	0.819	
12.0	2.834	11.566	0.099	0.951					
13.0	2.936	12.664	0.135	0.936					
$y = 0.6$					$y = 0.8$			$y = 1$	
0.1	0.038	0.042	0.195	0.718	0.017	0.023	0.183	0.750	0.790
0.2	0.070	0.090	0.124	0.689	0.030	0.050	0.114	0.716	0.751
0.3	0.100	0.140	0.092	0.673	0.043	0.077	0.083	0.696	0.726
0.4	0.130	0.190	0.073	0.663	0.056	0.104	0.066	0.681	0.706
0.5	0.161	0.239	0.060	0.656	0.069	0.131	0.054	0.670	0.691
0.6	0.191	0.289	0.051	0.651	0.082	0.158	0.046	0.660	0.678
0.7	0.221	0.339	0.045	0.647	0.094	0.186	0.040	0.653	0.667
0.8	0.251	0.389	0.040	0.644	0.106	0.214	0.036	0.646	0.657
0.9	0.280	0.440	0.036	0.642	0.118	0.242	0.033	0.641	0.649
1.0	0.309	0.491	0.033	0.640	0.130	0.270	0.030	0.637	0.643
1.5	0.445	0.755	0.024	0.643	0.182	0.418	0.022	0.627	0.624
2.0	0.559	1.041	0.020	0.654	0.218	0.582	0.020	0.629	0.624
2.5	0.647	1.353	0.019	0.670	0.236	0.764	0.020	0.639	0.639
3.0	0.708	1.692	0.019	0.688	0.237	0.963	0.021	0.652	0.668
3.5	0.743	2.057	0.020	0.705	0.223	1.177	0.024	0.668	0.707
4.0	0.756	2.444	0.022	0.720	0.199	1.401	0.029	0.686	0.758
4.5	0.750	2.850	0.024	0.733	0.167	1.633	0.036	0.704	
5.0	0.730	3.270	0.027	0.744	0.134	1.866	0.047	0.724	
5.5	0.699	3.701	0.031	0.753					
6.0	0.659	4.141	0.035	0.760					
7.0	0.564	5.036	0.048	0.768					
8.0	0.460	5.940	0.066	0.771					
9.0	0.356	6.844	0.094	0.769					
10.0	0.259	7.741	0.139	0.766					

this array of additional parameters would presumably allow a better fit to the full array of  $\phi$  values, its meaning would be very questionable because these terms were not required for pure  $\text{Na}_2\text{SO}_4(\text{aq})$ . For the present purposes, however, application of the ion-interaction model in its present form has provided a very good representation of these  $\phi$ s, especially when it is considered that only 18 parameters were used to fit over 700 points.

Representative calculations of the speciation of solutions at smoothed values of  $y$  and  $m_T$  are presented in table 5. Plots of osmotic coefficients and activity-coefficient factors for dissociation of  $\text{HSO}_4^-$  are plotted in figure 6.

For the osmotic coefficients of certain mixtures, one finds shapes that are very different from those of pure electrolytes or of ideally ionized solutions. The contributions to the measured osmotic coefficients from changing speciation is obvious in this plot. If  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  were both completely ionized at all

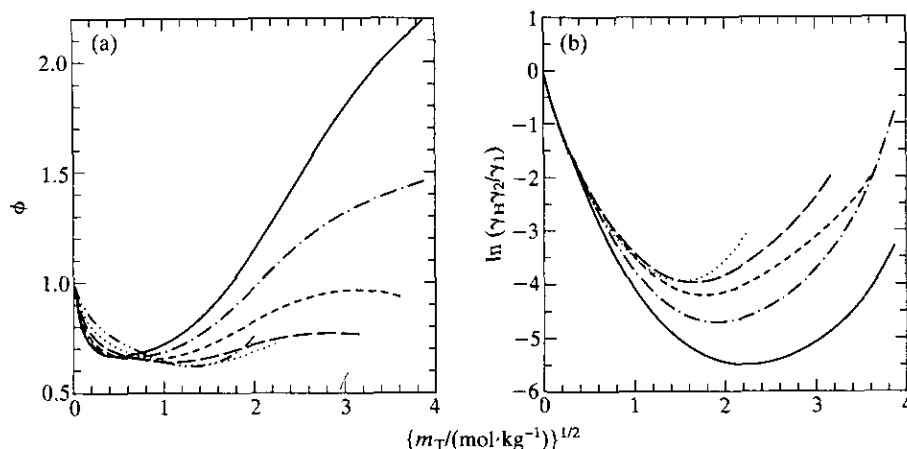


FIGURE 6. Smoothed values of properties for  $\{(1-y)\text{H}_2\text{SO}_4 + y\text{Na}_2\text{SO}_4\}(\text{aq})$  at round values of  $y$  plotted against the square root of the total molality  $m_T$ : (a), osmotic coefficients; (b),  $\ln(\gamma_H \gamma_2 / \gamma_1)$  for reaction (1). —,  $y = 0$ ; - - -,  $y = 0.2$ ; ---,  $y = 0.4$ ; - · - ·,  $y = 0.6$ ; ····,  $y = 0.8$ ; - - - - -,  $y = 1$ .

molalities and ionic strengths encountered, all curves in figure 6a would have the general shape defined by  $y = 0$  and  $y = 1$ .

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. JKH is grateful to the Natural Sciences and Engineering Research Council of Canada for postdoctoral fellowship support for a substantial portion of this project. JAR thanks the Office of Basic Energy Sciences, Division of Geosciences, for support. We are grateful to Professor Eric Reardon and Dr Howard Holmes for noticing a problem late in the development of this work. We are further grateful to Professor Reardon for helping with resolution of this problem. Finally, JKH wishes to express sincere thanks to Professor Loren Hepler to whom this paper is dedicated, for longstanding scientific advice, collaboration, direction, and friendship that started when JKH was his graduate student.

## REFERENCES

1. Goldberg, R. N.; Staples, B. R.; Nuttall, R. L.; Arbuckle, R. *A bibliography of sources of experimental data leading to activity or osmotic coefficients for polyvalent electrolytes in aqueous solution*. NBS special publication 485. 1977.
2. Bolsaitis, P.; Elliott, J. F. *J. Chem. Eng. Data* **1990**, 35, 69.
3. Rard, J. A. *J. Chem. Thermodynamics* **1992**, 24, 45.
4. Rard, J. A. *J. Chem. Thermodynamics* **1989**, 21, 539.
5. Pitzer, K. S.; Roy, R. N.; Silvester, L. F. *J. Am. Chem. Soc.* **1977**, 99, 4930.
6. Millero, F. J.; Schreiber, D. R. *Am. J. Sci.* **1982**, 282, 1508.
7. Hovey, J. K.; Hepler, L. G. *J. Chem. Soc. Faraday Trans.* **1990**, 86, 2831.
8. Reardon, E. J.; Beckie, R. D. *Geochim. Cosmochim. Acta* **1987**, 51, 2355.
9. Harvie, C. E.; Møller, N.; Weare, J. H. *Geochim. Cosmochim. Acta* **1984**, 48, 723.

10. Pabalan, R. T.; Pitzer, K. S. *Geochim. Cosmochim. Acta* **1988**, 52, 2393.
11. Archer, D. G.; Wang, P. J. *Phys. Chem. Ref. Data* **1990**, 19, 371.
12. Bradley, D. J.; Pitzer, K. S. *J. Phys. Chem.* **1979**, 83, 1599.
13. Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*. Pitzer, K. S.: editor. CRC Press: Boca Raton. **1991**, Chapter 3.
14. Dickson, A. G.; Wesolowski, D. J.; Palmer, D. A.; Mesmer, R. E. *J. Phys. Chem.* **1990**, 94, 7978.
15. Pitzer, K. S. *J. Solution Chem.* **1975**, 4, 249.
16. Friedman, H. L. *Ionic Solution Theory*. Wiley-Interscience: New York. **1962**.
17. Harvie, C. E. *Theoretical Investigations in Geochemistry and Atom Surface Scattering*. PhD thesis, University of California, San Diego. **1981**.
18. Rogers, P. S. Z.; Pitzer, K. S. *J. Phys. Chem.* **1981**, 85, 2886.
19. Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1981**, 26, 33.
20. Gibson, R. E.; Adams, L. H. *J. Am. Chem. Soc.* **1933**, 55, 2679.
21. Thompson, P. T.; Smith, D. E.; Wood, R. H. *J. Chem. Eng. Data* **1974**, 19, 386.
22. Desnoyers, J. E.; de Visser, C.; Perron, G.; Picker, P. *J. Solution Chem.* **1976**, 5, 605.
23. Lewis, G. N.; Randall, M. *Thermodynamics*. Pitzer, K. S.; Brewer, L.: Revisers. McGraw-Hill: New York. **1961**.
24. Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed., Butterworths: London. **1959**.
25. Randall, M.; Scott, G. N. *J. Am. Chem. Soc.* **1927**, 49, 647.
26. Indelli, A. *Ric. Sci.* **1953**, 23, 2258.
27. Downes, C. J.; Pitzer, K. S. *J. Solution Chem.* **1976**, 5, 389.
28. Platford, R. F. *J. Chem. Eng. Data* **1968**, 13, 46.
29. Platford, R. F. *J. Chem. Eng. Data* **1973**, 18, 215.
30. Childs, C. W.; Platford, R. F. *Aust. J. Chem.* **1971**, 24, 2487.
31. Rard, J. A. *J. Chem. Eng. Data* **1983**, 28, 384.
32. Stokes, R. H. *J. Am. Chem. Soc.* **1948**, 70, 874.
33. Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*. Pytkowicz, R. M.: editor. CRC Press: Boca Raton. **1979**. Vol I, Chapter 7.