

# An Equilibrium Model for the Calculation of Activity and Osmotic Coefficients in Aqueous Solutions

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A procedure is described for the calculation of activity and osmotic coefficients which is based upon a knowledge of the equilibria in solution and assumed single-ion activity coefficients. The procedure permits one to introduce chemical equilibria of various types (ion-pairing, complexation, hydration, and hydrolysis) into a model which can be used to calculate values of the excess Gibbs energy and the activity and osmotic coefficients. Both the Debye-Hückel theory and Pitzer's expression are used to calculate the electrostatic contribution to the single-ion activity coefficients. Calculations have been performed on aqueous sulfuric acid, acetic acid, hydrofluoric acid, cadmium chloride, copper sulfate, and sodium carbonate. Properties which have been calculated are the excess Gibbs energy, the osmotic coefficient, the mean ionic activity coefficient, and Frank's single-ion activity coefficient function. Agreement between calculated and measured properties has been obtained up to molalities of  $\approx 1.0 \text{ mol kg}^{-1}$

Key words: acetic acid; activity coefficient; cadmium chloride; copper sulfate; equilibrium; excess Gibbs energy; hydrofluoric acid; models of solutions; osmotic coefficient; sodium carbonate; sulfuric acid.

## 1. Introduction

Equilibrium models have been used [1–15]<sup>1</sup> both for the prediction and for the correlation of activity and osmotic coefficient data in aqueous electrolyte solutions. These equilibrium models are particularly appropriate when one is dealing with solutions which exhibit association, complexation, hydration, or hydrolysis. When applied to such solutions, they are superior to the use of a model that assumes the electrolyte in solution to be a fully dissociated strong electrolyte. A variety of

approaches has been used in these equilibrium models for treating these various types of equilibria in solution and for the calculation of the activity and osmotic coefficients. Several different types of functions for the calculation of the electrostatic contribution to the activity coefficient of the ions in solution have also been used.

The purposes of this paper are to 1) describe a procedure for (a) the calculation of activity and osmotic coefficients in aqueous solutions that uses a generalized approach for treating the equilibria in solution, and (b) the calculation of the Gibbs energy properties, 2) clarify the distinction between the stoichiometric and species quantities, frequently a source of confusion in the literature, and 3) explore the effects of parameter variations in the model on calculated values of the thermodynamic properties as applied to several representative types of electrolyte solutions. Using the equilibrium model, one can also calculate the values of the activity coefficients of individual ions. This permits one to then calculate values for Frank's [16] single-ion activity coefficient function.

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<sup>1</sup> Figures in brackets indicate literature references at the end of this paper.

## 2. The Model

A fundamental idea used here is the distinction between the stoichiometric components of which a system is composed and the particle constituents, or species, which are introduced to account for the properties of a solution. Stoichiometric quantities will be designated by "st" when not otherwise clearly indicated. Species or particle quantities will always be designated by a " ^ " placed over the quantity. For example, for the solution formed from 0.1 moles of pure  $\text{H}_2\text{SO}_4(\ell)$  and 1 kg/ $M_1$  moles of  $\text{H}_2\text{O}(\ell)$ , the stoichiometric molality of  $\text{H}_2\text{SO}_4$  is  $m(\text{H}_2\text{SO}_4)=0.1 \text{ mol kg}^{-1}$ ,  $m(\text{SO}_4^{2-})=0.1 \text{ mol kg}^{-1}$ ,

and  $m(\text{H}^+)=0.2 \text{ mol kg}^{-1}$  if one views the electrolyte as being completely dissociated. However, if one considers the equilibrium:  $\text{SO}_4^{2-}(\text{aq}) + \text{H}^+(\text{aq}) = \text{HSO}_4^-(\text{aq})$ , adopts a  $K$  of 99 for it [17], and uses a Debye-Hückel type expression (see eq (5)) for the activity coefficients of the ions with a  $B$  parameter equal to zero, one calculates  $\hat{m}(\text{H}^+)=0.134 \text{ mol kg}^{-1}$ ,  $\hat{m}(\text{SO}_4^{2-})=0.0342 \text{ mol kg}^{-1}$ ,  $\hat{m}(\text{HSO}_4^-)=0.0658 \text{ mol kg}^{-1}$ , and  $\hat{m}(\text{H}_2\text{SO}_4)=0.0$

<sup>2</sup> Throughout this paper the activity will always have units of mol  $\text{kg}^{-1}$ . The equilibrium constants, formed as products and quotients of activities, will have units of mol  $\text{kg}^{-1}$ , or  $\text{kg mol}^{-1}$ , or, for symmetrical reactions, will be dimensionless. For sake of brevity, the units for equilibrium constants will be omitted.

# GLOSSARY

### Roman

<i>a</i>	activity
<i>b</i>	constant equal to 1.2 in Pitzer's equation
<i>h</i>	hydration number
<i>m</i>	molality/mol $\text{kg}^{-1}$
<i>n</i>	amount or moles of substance
<i>p</i>	pressure
<i>l<sub>jk</sub></i>	number of moles of species $S_{jk}$ participating in a given reaction
<i>z</i>	charge
<i>A</i>	an anion
<i>A<sub>m</sub>, A<sub>φ</sub></i>	Debye-Hückel constants; $A_m=3A_\phi=1.17642 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ at 298.15 K
<i>B</i>	parameter in the Debye-Hückel equation
<i>C</i>	a cation
<i>I</i>	ionic strength
<i>G</i>	Gibbs energy
<i>K</i>	equilibrium constant
<i>M</i>	molar mass/kg $\text{mol}^{-1}$
<i>N<sub>s</sub>, N<sub>c</sub>, N<sub>e</sub>, N<sub>k</sub></i>	number of species in solution, equilibria, components, and, respectively, species in the <i>k</i> <sup>th</sup> equilibrium
<i>R</i>	gas constant
<i>S<sub>j</sub></i>	the <i>j</i> <sup>th</sup> species in the <i>k</i> <sup>th</sup> equilibrium
<i>T</i>	temperature
<i>X</i>	mole fraction

### Greek

$\gamma$	activity coefficient
$\delta_{ij}$	Kronecker delta; $\delta_{ij}=1$ if $i=j$ , $\delta_{ij}=0$ if $i \neq j$
$\delta_{\pm}$	Frank's single-ion activity coefficient function
$\lambda_{ij}$	pair-wise interaction parameter
$\mu_{ijk}$	triplet interaction parameter
$\nu$	ion number
$\xi$	extent of reaction variable
$\phi$	osmotic coefficient
$\phi_x$	rational osmotic coefficient

### Superscripts

ex	excess
id	ideal
st	stoichiometric
o	standard value quantity
*	the property of the pure substance
^	a species quantity

### Subscripts

<i>a</i>	an anion
<i>c</i>	a cation except when used with capital Roman <i>N</i> as $N_c$
<i>e</i>	see Roman $N_e$
<i>i, j, k</i>	a species or used as indices; also see $N_k$ under Roman
<i>ℓ</i>	a component
<i>m</i>	see $A_m$ under Roman
<i>r</i>	a reference cation or anion
<i>s</i>	see $N_s$ under Roman
<i>l</i>	water
$\pm$	mean ionic
$\phi$	see $A_\phi$ under Roman

mol kg<sup>-1</sup>. Physical quantities other than amounts of substance can also be viewed as particle quantities. In particular it is the distinction between  $G^{\text{ex}}$  and  $\hat{G}^{\text{ex}}$  which forms the basis of the model presented herein.

The general system to be considered is formed from 1 kg/M<sub>1</sub> moles of water and  $n_{\ell}$  ( $\ell=2$  to  $N_c$ ) moles of other components. In terms of a particle model, the system can be viewed as being formed from  $\hat{n}_i$  moles of water and  $\hat{n}_i$  ( $i=2$  to  $N_s$ ) moles of particles or species. The amount of water ( $n_1$ ) will always be designated by a subscript "1." The components and the species other than water will be designated by subscripts " $\ell$ " and " $i$ ," respectively, with  $i$  and  $\ell \geq 2$ .

Each component  $\ell$  in the solution is represented as  $C_{\nu_{\ell c}}^{z_{\ell c}} A_{\nu_{\ell a}}^{z_{\ell a}}$  where C and A are the reference cations and anions, respectively. The charges of the cations and anions are  $z_{\ell c}$  and  $z_{\ell a}$ , respectively; the ion-numbers are  $\nu_{\ell c}$  and  $\nu_{\ell a}$ , respectively. It is important to note that the choice of reference species is arbitrary; e.g., for a solution of aqueous sulfuric acid, the reference species could be selected as either two H<sup>+</sup> ions and one SO<sub>4</sub><sup>2-</sup> ion or as one H<sup>+</sup> ion and one HSO<sub>4</sub><sup>-</sup> ion. In the former case, sulfuric acid would be represented as (H<sup>+</sup>)<sub>2</sub>(SO<sub>4</sub><sup>2-</sup>)<sub>1</sub> and in the latter case as (H<sup>+</sup>)<sub>1</sub>(HSO<sub>4</sub><sup>-</sup>)<sub>1</sub>. While the choice of reference species is arbitrary, it will not affect the amounts of the various species one calculates given the same set of equilibrium constants and allowed species. However, as will be seen later, the choice does affect the values of several of the stoichiometric thermodynamic properties.

The Gibbs energy of the solution in the stoichiometric representation is given by

$$G = (m^* \text{kg})G_1 + \sum_{\ell=2}^{N_c} (\nu_{\ell c} G_{\ell c} + \nu_{\ell a} G_{\ell a}) m_{\ell} \quad (1)$$

where  $m^*$  is the molality of water in pure water and  $G_{\ell c}$  and  $G_{\ell a}$  are, respectively, the chemical potentials of the reference cation and anion of the  $\ell^{\text{th}}$  component in the solution. In terms of an equilibrium or species model of the solution, the Gibbs energy is given by

$$G = \sum_{i=1}^{N_s} \hat{n}_i \hat{G}_i \quad (2)$$

If the equilibrium model is accurate, the Gibbs energy of the solution calculated using eqs (1) and (2) will be identical and the chemical potentials and the activities of the  $i^{\text{th}}$  species will be the same in both the stoichiometric and species representations. The development to follow will start with a description of the solution in terms of the equilibria assumed to be present in solution, an assumed expression(s) for the activity coefficients of the solute species in solution, and the calculation of the

activity of the water using the Gibbs-Duhem equation. It is important to note that there may be several equilibrium models of a solution which yield agreement with calculated properties. Thus agreement between calculated and measured properties does not, in the absence of direct molecular information, prove the correctness of the model used.

The equilibria in solution are described by a series of chemical equations:

$$\sum_{j=1}^{N_k} t_{jk} S_{jk} = 0, \quad k = 1 \text{ to } N_e \quad (3)$$

where  $S_{jk}$  is the  $j^{\text{th}}$  species in the  $k^{\text{th}}$  equilibrium,  $N_k$  is the number of species in the  $k^{\text{th}}$  equilibrium,  $N_e$  is the total number of equilibria, and  $t_{jk}$  is the number of moles of species  $S_{jk}$  participating in a given equilibrium;  $t_{jk}$  is positive if  $S_{jk}$  is a product and is negative if  $S_{jk}$  is a reactant. The equilibrium constants are:

$$K_k = \pi \prod_{j=1}^{N_k} \hat{a}_{jk}^{t_{jk}} \quad k = 1 \text{ to } N_e \quad (4)$$

where  $\hat{a}_{jk}$  is the activity of species  $S_{jk}$ . Since  $\hat{a}_i$  is equal to the product of the molality of the  $i^{\text{th}}$  species ( $\hat{m}_i$ ) and its activity coefficient ( $\hat{\gamma}_i$ ), the complete formulation of the equations which describe the equilibria in solution requires that some assumptions(s) be made concerning the form of the  $\hat{\gamma}_i$ 's ( $i \geq 2$ ) in solution. In this paper two different expressions for the  $\hat{\gamma}_i$ 's will be used:

$$\ell n \hat{\gamma}_i = -A_m \hat{z}_i^2 \hat{I}^{1/2} / (1 + B \hat{I}^{1/2}) \quad (5)$$

and

$$\ell n \hat{\gamma}_i = -\hat{z}_i^2 A_{\phi} \hat{I}^{1/2} / (1 + b \hat{I}^{1/2}) + (2/b) \ell n (1 + b \hat{I}^{1/2}) \quad (6)$$

Equation (5) is the Debye-Hückel equation with an excluded volume or "ion-size" parameter  $B$  in the denominator. Equation (6) is the leading term of Pitzer's expression for  $\hat{\gamma}_i$  [18]; he has set  $b$  equal to 1.2.  $A_m$  and  $A_{\phi}$  are Debye-Hückel constants, where  $A_m = 3A_{\phi} = 1.17642 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  at 298.15 K. Equations (5) and (6) can be extended by the addition of the expression:

$$\sum_{i=j}^{N_s} \sum_{j=1}^{N_s} \lambda_{ij} \hat{m}_j + \sum_{i=1}^{N_s} \sum_{j=1}^{N_s} \sum_{k=1}^{N_s} \mu_{ijk} \hat{m}_j \hat{m}_k \quad (7)$$

where  $\lambda_{ij}$  and  $\mu_{ijk}$  are, respectively, the interaction parameters for pairs and triplets of particles. We shall later return to the subject of the extensions of eqs (5) and (6) and to several other aspects of the choice of an expression for  $\hat{\gamma}_i$ . It should be noted that  $I$  is calculated as

$$I = (1/2) \sum_{i=2}^{N_s} \hat{m}_i \hat{z}_i^2 \quad (8)$$

We have formulated the equilibrium equations using an extent of reaction variable  $\xi$ . Thus, the amount of the  $i^{\text{th}}$  species in solution is given by

$$\begin{aligned} \hat{n}_i = & (m^* \text{kg}) \delta_{ij} + \sum_{r=1}^{N_c} (\nu_{r,c} n_r \delta_{ir} + \nu_{r,a} n_r \delta_{ir}) \\ & + \sum_{k=1}^{N_c} \sum_{j=1}^{N_k} t_{jk} \xi_k \delta_{ij}, \quad i \geq 1 \end{aligned} \quad (9)$$

where  $\xi_k$  is the extent of reaction variable for the  $k^{\text{th}}$  equilibrium and  $\delta_{ij}$  is the Kronecker delta;  $r$  is an integer which serves to identify the reference cation and anion of each of the components in the solution. The first summation term on the right side of eq (9) specifies the amount of species  $i$  which is formed in the absence of any equilibria in solution; the second summation term specifies the contributions, which may be positive or negative, to the amount of species  $i$  in solution from the equilibria in solution. If the water is a participant in the equilibria in solution,  $\hat{n}_1$  must also be calculated using the above equation. Hydration numbers can be introduced directly using

$$\hat{n}_1 = \hat{n}_1 (\text{eq (9)}) - \sum_{i=2}^{N_s} \hat{h}_i \hat{n}_i \quad (10)$$

where  $\hat{n}_1$  (eq(9)) is the amount of water calculated using eq (9) and  $\hat{h}_i$  is the number of waters of hydration attached to the  $i^{\text{th}}$  species. If the water participates in the equilibria in solution or if hydration numbers are introduced,  $\hat{n}_1 \text{ kg}^{-1}$  will not be equal to  $m^*$ . The  $\hat{m}_i$  are given by

$$\hat{m}_i = \hat{n}_i (m^* / \hat{n}_1), \quad i \geq 2 \quad (11)$$

The activities of the species are given by

$$\hat{a}_i = \hat{m}_i \hat{\gamma}_i, \quad i \geq 2 \quad (12)$$

Thus in a model where hydration is introduced, both  $\hat{m}_i$  and  $\hat{a}_i$  will be affected by changes in both  $\hat{n}_1$  and  $\hat{n}_i$  ( $i \geq 2$ ).

To obtain a numerical solution of eq (4), it is necessary to make some initial guess for the activity of water if it is a participant in the equilibria in solution; we have generally used a value of unity. Thus, having formulated the simultaneous nonlinear eq (4), which necessarily include eqs (8) to (12) and eq (5) or (6), one is left with a numerical problem to obtain a self-consistent solution of these equations. It is assumed that, while such a solution may be difficult to obtain for large systems, a unique solution does exist and that one now has

values for  $I$ ,  $\hat{m}_i$  and  $\hat{n}_i$  for  $i \geq 1$  and for  $\hat{\gamma}_i$  and  $\hat{a}_i$  for  $i \geq 2$ .

The activity of the water can now be calculated by application of the Gibbs-Duhem equation stated in terms of excess properties of the species

$$\hat{n}_1 d\hat{G}_1^{\text{ex}} = - \sum_{i=2}^{N_s} \hat{n}_i d\hat{G}_i^{\text{ex}} \quad (13)$$

Use of eqs (11) and (13) leads to

$$m^* d\hat{G}_1^{\text{ex}} = - \sum_{i=2}^{N_s} \hat{m}_i d\hat{G}_i^{\text{ex}} \quad (14)$$

It is also necessary to adopt some conventions concerning the limits of  $\hat{a}_i$  and  $\hat{\gamma}_i$ . The conventions used herein are  $\hat{a}_i \rightarrow 1$  and, for  $i \geq 2$ ,  $\hat{\gamma}_i \rightarrow 1$  as  $\sum_{i=2}^{N_s} \hat{m}_i \rightarrow 0$ ; also,  $\hat{\gamma}_i^{\text{id}}$  ( $i \geq 2$ ) is defined to be equal to unity<sup>3</sup>. These conventions, together with the definitions of the activity  $\hat{a}_i$ , the activity coefficient  $\hat{\gamma}_i$ , and the definition of the excess Gibbs energy of the  $i^{\text{th}}$  species given in the following equations

$$\hat{a}_i = \exp[(G_i - G_i^0)/RT], \quad i \geq 1 \quad (15)$$

$$\hat{\gamma}_i = \hat{a}_i / \hat{m}_i, \quad i \geq 2 \quad (16)$$

and

$$G_i^{\text{ex}} = G_i - G_i^{\text{id}}, \quad i \geq 1 \quad (17)$$

lead to

$$G_i^{\text{ex}} = RT \ell \hat{n} \hat{\gamma}_i \quad (18)$$

The introduction of eqs (5) and (18) into eq (14) yields

$$\begin{aligned} \hat{G}_1^{\text{ex}} = & (2A_m RT / m^* B^3) [(1 + B\hat{I}^{1/2}) \\ & - 2 \ell n(1 + B\hat{I}^{1/2}) - (1 + B\hat{I}^{1/2})^{-1}] \end{aligned} \quad (19)$$

Similarly, one obtains, using eq (6) instead of eq (5), the relationship

$$\hat{G}_1^{\text{ex}} = (2A_\phi RT / m^*) [\hat{I}^{3/2} / (1 + b\hat{I}^{1/2})] \quad (20)$$

We now consider an ideal reacting solution in which  $\hat{\gamma}_i$  ( $i \geq 2$ ) is equal to unity at all temperatures, pressures,

<sup>3</sup> This is the convention most frequently used in the description of aqueous electrolyte solutions. It is based upon the molality scale. A different convention based upon the mole fraction scale is commonly used for the description of non-electrolyte solutions.

and compositions and which also allows for the presence of both equilibria and hydration in solution. Application of the Gibbs-Duhem equation to such a solution leads to

$$\ell n \hat{a}_1^{\text{id}} = - \sum_{i=2}^{N_s} \hat{m}_i / m_1^* \quad (21)$$

and this in turn with eq (15) leads to

$$\hat{G}_1^{\text{id}} = \hat{G}_1^{\circ} - (RT/m_1^*) \sum_{i=2}^{N_s} \hat{m}_i \quad (22)$$

Since an excess property is defined as the difference between the real and the ideal, it follows from eqs (15) and (22) that

$$\ell n \hat{a}_1 = \hat{G}_1^{\text{ex}} / RT - \left( \sum_{i=2}^{N_s} \hat{m}_i / m_1^* \right) \quad (23)$$

If the equilibrium model is an accurate representation of the solution,  $a_1$  is equal to  $\hat{a}_1$ . We thus have a procedure for the computation of the activity of the water which starts with an equilibrium model of the solution and an assumed expression for the activity coefficients in the solution. Since it is necessary to make an initial guess as to the value of the activity of the water, the calculation should be repeated using the value of  $\hat{a}_1$  from the previous iteration until convergence to within a given tolerance in its value is obtained. The (stoichiometric) osmotic coefficient is calculated as

$$\phi = - (m_1^* / \sum_{\ell=2}^{N_c} \nu_{\ell} m_{\ell}) \ell n a_1 \quad (24)$$

where  $m_{\ell}$  is the stoichiometric molality of component  $\ell$  and  $\nu_{\ell}$  is equal to  $(\nu_{\ell c} + \nu_{\ell a})$ . Note that  $\nu_{\ell}$  is unity for a non-electrolytic component and that, as stated earlier, the value of the osmotic coefficient is dependent upon the choice of the reference species selected for each component in the solution.

The stoichiometric activity coefficients can be calculated using the principle that the chemical potential is independent of any representation of it. Equating  $\hat{a}_i$  to  $a_i$ , the stoichiometric single-ion activity coefficient is given by

$$\gamma_i^{\text{st}} = \hat{m}_i \hat{\gamma}_i / m_i^{\text{st}} \quad (25)$$

where  $m_i^{\text{st}}$  is the total stoichiometric molality of the  $i^{\text{th}}$  species in solution. The mean ionic activity coefficient

of component  $\ell$  is given by

$$\gamma_{\ell \pm} = (\gamma_{\ell c}^{\nu_{\ell c}} \cdot \gamma_{\ell a}^{\nu_{\ell a}})^{1/\nu_{\ell}} \quad (26)$$

As was the case for the osmotic coefficient, the value of the mean ionic activity coefficient is dependent upon the reference species selected for a given component.

Other stoichiometric Gibbs energy properties can be calculated in addition to the activity of the water, the osmotic coefficient, and the mean ionic activity coefficient of the  $\ell^{\text{th}}$  component. Additional properties of the water are calculated as follows:

$$G_1^{\text{ex}} = RT \ell n a_1 + (RT/m_1^*) \sum_{\ell=2}^{N_c} \nu_{\ell} m_{\ell} \quad (27)$$

$$G_1 = G_1^{\circ} + RT \ell n a_1 \quad (28)$$

$$\gamma_1 = a_1 / X_1 \quad (29)$$

and

$$\phi_x = (\ell n a_1) / (\ell n X_1) \quad (30)$$

Note that eqs (29) and (30) are definitions of the activity coefficient of the water ( $\gamma_1$ ), and of the rational osmotic coefficient ( $\phi_x$ ), respectively. These two quantities have not been frequently used in the literature. The properties of the solutes are:

$$G_{\ell}^{\text{ex}} = \nu_{\ell} RT \ell n \gamma_{\ell \pm} \quad (31)$$

$$\gamma_{\ell} = \exp(G_{\ell}^{\text{ex}} / RT) \quad (32)$$

$$a_{\ell} = m_{\ell} \gamma_{\ell} \quad (33)$$

$$G_{\ell} - G_{\ell}^{\circ} = RT \ell n a_{\ell} \quad (34)$$

and

$$a_{\ell \pm} = m_{\ell \pm} \gamma_{\ell \pm} \quad (35)$$

where the mean ionic molality of component  $\ell$  is defined as

$$m_{\ell \pm} = \{ (\nu_{\ell c} m_{\ell})^{\nu_{\ell c}} (\nu_{\ell a} m_{\ell})^{\nu_{\ell a}} \}^{1/\nu_{\ell}} \quad (36)$$

Finally, the total properties of the solution are

$$G^{\text{ex}} = \sum_{\ell=1}^{N_c} n_{\ell} G_{\ell}^{\text{ex}} \quad (37)$$

and

$$G - G^{\circ} = \sum_{\ell=1}^{N_c} n_{\ell} (G_{\ell} - G_{\ell}^{\circ}) \quad (38)$$

Equation (27) is the stoichiometric analogue of eq (23). Equations (29) and (30) are, respectively, the definitions of the activity coefficient of the water and of the rational osmotic coefficient. The steps used in the overall computational procedure are summarized in figure 1.

It is interesting to consider the consequences of the ideal behavior of all of the solute particles in the species representation, i.e.,  $\hat{\gamma}_i = 1$  for  $i \geq 2$ . Application of eqs (21), (23), and (24) to such a solution leads to

$$\phi = \frac{\sum_{i=2}^{N_s} \hat{m}_i / \sum_{\ell=2}^{N_c} \nu_{\ell} m_{\ell}}{\sum_{i=2}^{N_s} \hat{m}_i / \sum_{\ell=2}^{N_c} \nu_{\ell} m_{\ell}} \quad (39)$$

Application of eqs (25) and (26) leads to

$$\gamma_{\ell \pm} = (\hat{m}_c / m_c)^{\nu_{\ell c}} (\hat{m}_a / m_a)^{\nu_{\ell a}} \quad (40)$$

If the stoichiometric and species representations are identical, then  $\phi$  and  $\gamma_{\ell \pm}$  will be equal to unity. This is

the case when there are no chemical interactions (i.e., association, hydration, or hydrolysis) present in solution and the stoichiometric reference species chosen are the only ones present in solution.

An additional interesting feature of this model is that properties of individual ions and species are calculated (eq (25)). Unlike the stoichiometric properties given in eq (24) and eqs (26) to (35), there are presently no experimental data available with which one can compare these calculated values. Frank [16] has defined a quantity  $\delta_{\pm}$  characteristic of single-ion properties for a binary electrolyte:

$$\delta_{\pm} = (\gamma_c^{\nu_c} / \gamma_a^{\nu_a})^{1/\nu} \quad (41)$$

The definition is easily extended to multicomponent systems as was done for the case of the mean ionic activity coefficient (see eq (26)) and values of  $\delta_{\ell \pm}$  can also be calculated if the equilibria in solution are known.

An alternative way of viewing this model uses the definition of the excess Gibbs energy

$$G^{\text{ex}} = G - G^{\text{id}} \quad (42)$$

and its analogue for the species representation

**Figure 1**—Steps for the calculation of the amounts of species in solution and of the stoichiometric Gibbs energy properties of the solution.

1. Set up the equilibrium eqs (1).
2. Specify the stoichiometric amounts of each component in the solution.
3. Specify the values of  $K_x$ , eq (4).
4. Choose an expression for  $\hat{\gamma}_i$ , eq (5) or (6).
5. Make an initial guess for  $\hat{a}_i$ .
6. Solve eqs (4) in a manner self-consistent with eqs (8) to (12) and with eq (5) or (6).
7. Calculate  $\hat{G}_i^{\text{ex}}$ , using eq (19) or (20).
8. Calculate  $a_i = \hat{a}_i$ , eq (23).
9. If  $a_i$  is equal to the initial guess of  $\hat{a}_i$ , go to step 10; if not, return to step 6.
10. Make a choice of stoichiometric reference species.
11. Calculate  $\phi$  using eq (24) and  $\gamma_{\pm}$  using eqs (25) and (26).
12. Calculate the other stoichiometric properties, eqs (27) to (35).

$$\hat{G}^{\text{ex}} = G - \hat{G}^{\text{id}} \quad (43)$$

Since the Gibbs energy is independent of representation,

$$G^{\text{ex}} = \hat{G}^{\text{ex}} + \hat{G}^{\text{id}} - G^{\text{id}} \quad (44)$$

Similar equations hold for  $G^{\ell}$ ,  $\ell \geq 1$ . From the definition of ideality,

$$\hat{G}_i^{\text{id}} = \hat{G}_i^{\circ} + RT \ell n \hat{m}_i \quad (45)$$

Equations analogous to the foregoing expression and to eq (39) exist for the stoichiometric components of a solution. Thus, introduction of eqs (22) and (45) and their stoichiometric analogues into eq (44) yields

$$\begin{aligned} G^{\text{ex}} = & \left\{ \sum_{i=1}^{N_s} \hat{n}_i \hat{G}_i^{\text{ex}} \right\} \\ & + \left\{ n_i [\hat{G}_i^{\circ} - RT (\sum_{i=2}^{N_s} \hat{m}_i / m^{\dagger})] \right. \\ & \left. + \sum_{i=2}^{N_s} \hat{n}_i (\hat{G}_i^{\circ} + RT \ell n \hat{m}_i) \right\} \\ & - \left\{ n_i [\hat{G}_i^{\circ} - RT (\sum_{\ell=2}^{N_c} \nu_{\ell} m_{\ell} / m^{\dagger})] \right. \\ & \left. + \sum_{\ell=2}^{N_c} \{ \nu_{\ell} m_{\ell} (G_{\ell}^{\circ} + RT \ell n \nu_{\ell} m_{\ell}) \right. \\ & \left. + \nu_{\ell} m_{\ell} (G_{\ell}^{\circ} + RT \ell n_{\ell} m_{\ell}) \right\} \quad (46) \end{aligned}$$

Note that  $G_i^{\circ} = \hat{G}_i^{\circ}$  in the above equation.

The three terms in { } on the right side of eq (46) correspond, respectively, to  $\hat{G}^{\text{ex}}$ ,  $\hat{G}^{\text{id}}$ , and  $G^{\text{id}}$ . Inspection of the terms for  $\hat{G}^{\text{id}}$  shows that the differences between these quantities involve two factors: 1) a difference in Gibbs energies, i.e.,  $G_i^{\circ}$  terms multiplied by  $n_i$  and  $\hat{n}_i$ , and 2) entropic terms, i.e., the  $(RT \sum n_i \ell n m_i)$  terms for the solute particles and the  $(RT \sum m_i)$  terms for the solvent. If one views  $\hat{G}^{\text{ex}}$  as the electrostatic or ionic contribution to  $G^{\text{ex}}$ , the stoichiometric excess Gibbs energy is seen to also consist of energetic and entropic contributions which are formally accounted for with this model. While eq (46) could be used to compute  $G^{\text{ex}}$  directly, it is numerically preferable to use the computational scheme outlined earlier (see fig. 1).

In this paper, two different expressions have been used for  $\hat{\gamma}_i$  (see eqs (5) and (6)). While classical thermodynamics has little to say about the correctness of either

of these or any other choices for  $\hat{\gamma}_i$ , it does impose one important constraint on such a choice, namely that

$$(\partial \hat{G}_i^{\text{ex}} / \partial \hat{n}_i)_{T,p,n_{j \neq i}} = (\partial \hat{G}_j^{\text{ex}} / \partial \hat{n}_i)_{T,p,n_{j \neq i}} \quad (47)$$

or equivalently,

$$(\partial \ell n \hat{\gamma}_i / \partial \hat{n}_i)_{T,p,n_{j \neq i}} = (\partial \ell n \hat{\gamma}_j / \partial \hat{n}_i)_{T,p,n_{j \neq i}} \quad (48)$$

Thus, while it is tempting to try to assign a different value of  $B$  or  $b$  to each species in a solution in eqs (5) and (6), respectively, to do so would violate eqs (47) and (48). However, the extension of eqs (5) and (6) using eq (7) does not violate this thermodynamic constraint. Note that the use of eqs (5) or (6) for  $\hat{\gamma}_i$  does not allow for the introduction of specific-ion effects attributable to long-range electrostatic interactions. These effects can be introduced by the use of eq (7). Specific-ion effects attributable to chemical equilibria are accounted for in the equilibrium part of the model. Expressions other than those in eqs (5) and (6) could be used to represent the electrostatic part of  $\hat{\gamma}_i$ .

The long range electrostatic contributions to the Gibbs energy properties are introduced via eq (5) or (6) and the use of an equilibrium model. Other interactions accounted for in this model include: 1) chemical interactions, 2) hydration, and 3) volume exclusion effects. The attractive chemical interactions are accounted for by the use of the equilibrium constants for the processes which describe the equilibria in solution. These processes can involve ion-pairing, complexation, and hydrolysis. The effects of hydration are accounted for either by the introduction of equilibrium constants for specific reactions involving hydration or by the use of hydration numbers for each species in solution. The use of hydration numbers reduces the value of  $\hat{n}_i$  in eq (10) which in turn has consequent effects on the  $\hat{m}_i$ ,  $\hat{I}$ ,  $\hat{\gamma}_i$ ,  $a_w$ , and other properties. Volume exclusion effects are represented by the  $B$  or  $b$  parameter in eqs (5) or (6). Short range repulsive forces between particles can also be accounted for using the  $\lambda_{ij}$  and/or  $\mu_{ijk}$  parameters. It is worth noting that there are similarities in the effects that changes in certain parameters have on thermodynamic properties. Specifically, an increased value of  $B$  (or  $b$ ) is similar to the introduction of a positive  $\lambda_{ij}$  or  $\mu_{ijk}$  and also to the introduction of hydration effects. Physically this should be the case since the excluded volume for a hydrated ion is larger than for one that is not hydrated. Also, a negative  $\lambda_{ij}$  is similar to an association between particles  $i$  and  $j$ . The remainder of this paper will discuss the application of this model to several aqueous salt

solutions containing representative types of chemical interactions.

### 3. Results and Discussion

We now compare the results of calculations using this model with experimental data and examine the results of perturbing the various input parameters in the model, i.e., the single-ion activity coefficient expressions, the assumed equilibrium constants, and the assumed state of

hydration of the species in solution. To do this, calculations have been made on the following aqueous electrolyte solutions: sulfuric acid, acetic acid, hydrofluoric acid, cadmium chloride, copper sulfate, and sodium carbonate.

The results of calculations on aqueous sulfuric acid are shown in figures 2 through 4, where the chemical equilibrium considered is

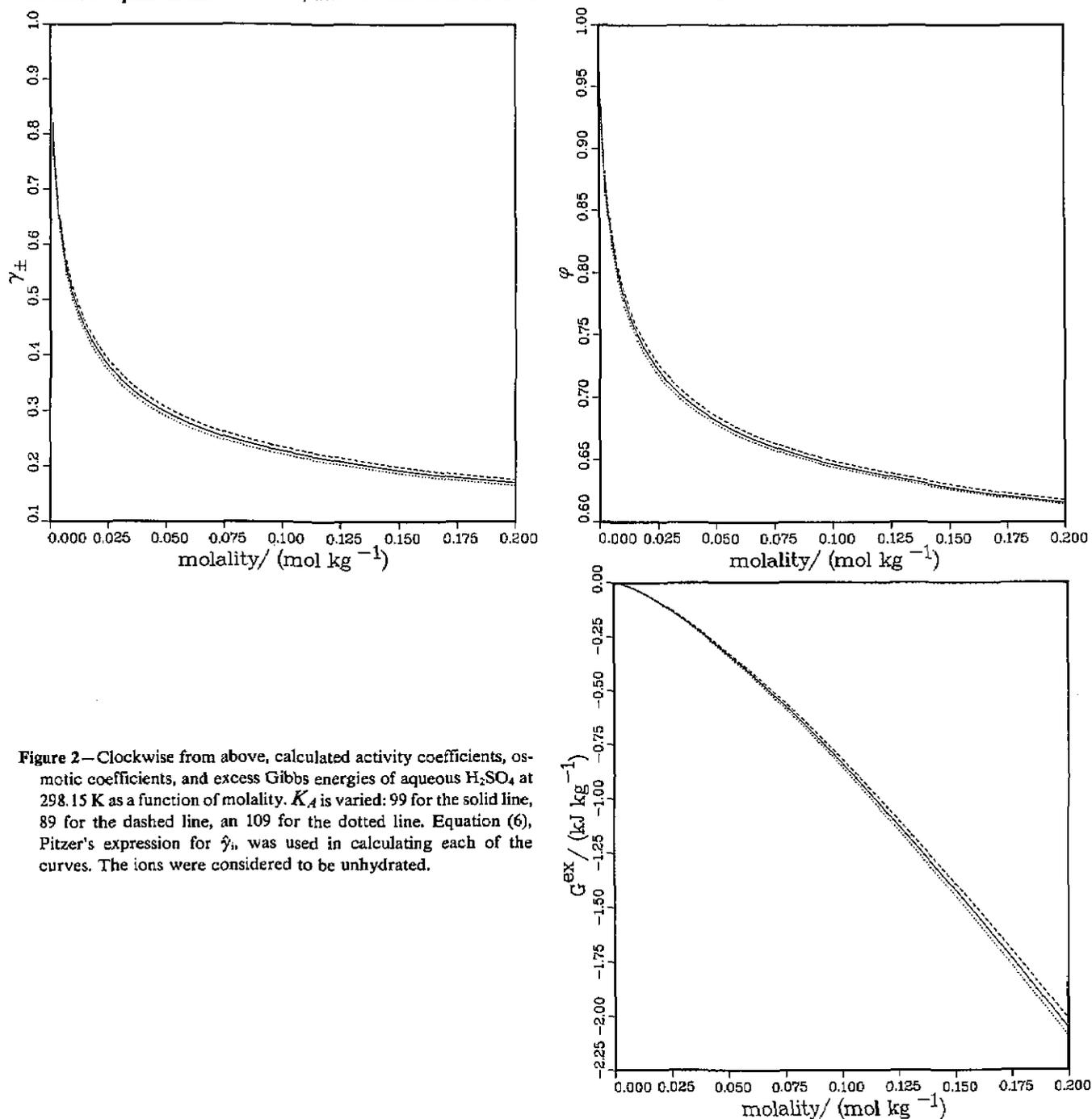
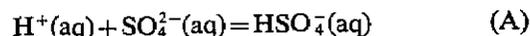
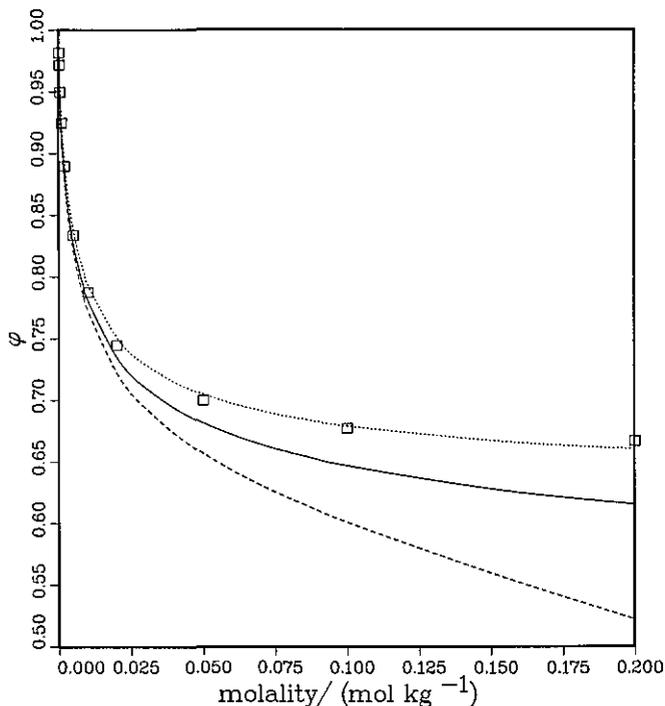


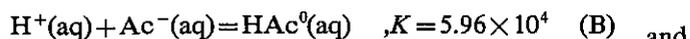
Figure 2—Clockwise from above, calculated activity coefficients, osmotic coefficients, and excess Gibbs energies of aqueous  $\text{H}_2\text{SO}_4$  at 298.15 K as a function of molality.  $K_A$  is varied: 99 for the solid line, 89 for the dashed line, an 109 for the dotted line. Equation (6), Pitzer's expression for  $\hat{\gamma}_i$ , was used in calculating each of the curves. The ions were considered to be unhydrated.



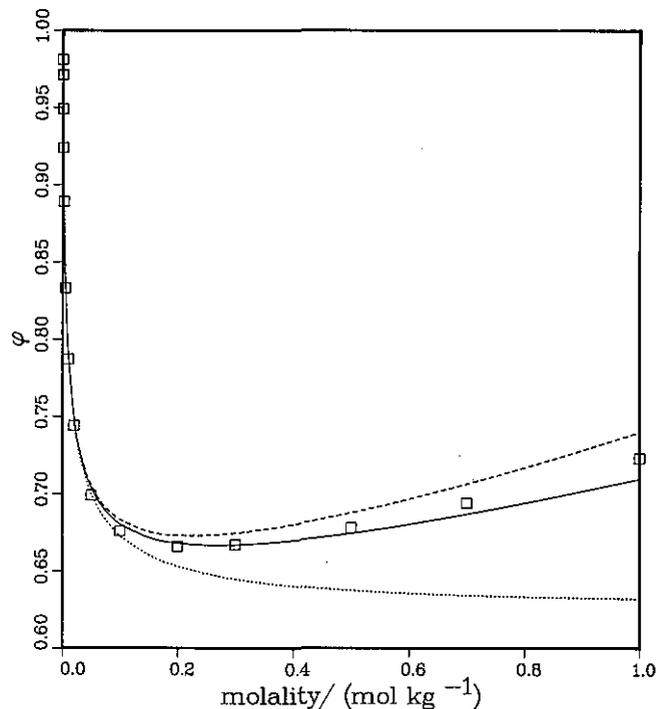
**Figure 3**—Comparison of calculated osmotic coefficients for aqueous  $\text{H}_2\text{SO}_4$  at 298.15 K. The squares are the correlated values of Pitzer, Roy, and Silvester [10]. The solid line was calculated using a value of  $K_A = 99$  and Pitzer's expression for  $\hat{\gamma}_i$ . The dashed and dotted lines were calculated using the same value of  $K_A$  and values of  $B$  equal to zero and 2.5 respectively, in a Debye-Hückel expression for  $\hat{\gamma}_i$  (eq (5)). The ions were considered to be unhydrated.

The value of  $K_A$  is 99 at 298.15 K [17]. It is seen that the calculated values of  $\gamma_{\pm}$ ,  $\phi$ , and  $G^{\text{ex}}$  are relatively insensitive to moderate variations in  $K_A$  up to molalities of 0.2 mol  $\text{kg}^{-1}$ . However, as seen in figure 3, significant changes in the osmotic coefficient are produced by perturbing the value of the  $B$  parameter. Use of a value of  $B$  equal to 2.5 in a Debye-Hückel expression for  $\hat{\gamma}_i$  (see eq (5)) produces good agreement with the experimental osmotic coefficients (the squares in fig. 2d) up to a molality of  $\approx 0.2$  mol  $\text{kg}^{-1}$ . The effects of variations in hydration numbers is shown in figure 4. The minimum in the osmotic coefficient curve cannot be produced by variation in the  $B$  parameter, but, as seen in figure 4, a minimum is observed when hydration is introduced.

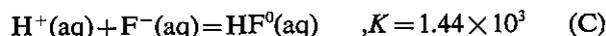
The equilibrium considered in the description of aqueous acetic acid (HAc) is



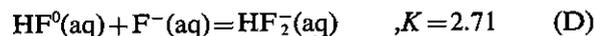
For aqueous hydrofluoric acid, the equilibria are



**Figure 4**—Calculated osmotic coefficients of aqueous  $\text{H}_2\text{SO}_4$  at 298.15 K in which the extent of hydration of the ions is varied. All three curves were calculated using a value of 99 for  $K_A$  and a Debye-Hückel expression for  $\hat{\gamma}_i$  with  $B$  equal to 2.0. The dotted line was calculated assuming that all of the ions were not hydrated. The solid and dashed line were calculated, respectively, by assuming all three ions ( $\text{H}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{HSO}_4^-$ ) to be hydrated with three and four waters each. The squares are from the correlation of Pitzer, Roy, and Silvester [10].



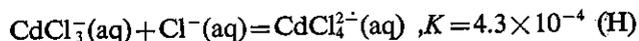
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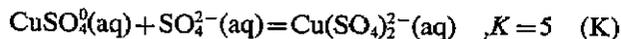
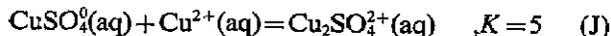
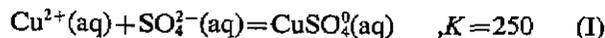
For aqueous cadmium chloride the stepwise equilibria considered are:



and



The equilibria considered for aqueous copper sulfate and



For aqueous sodium carbonate the equilibria considered are:

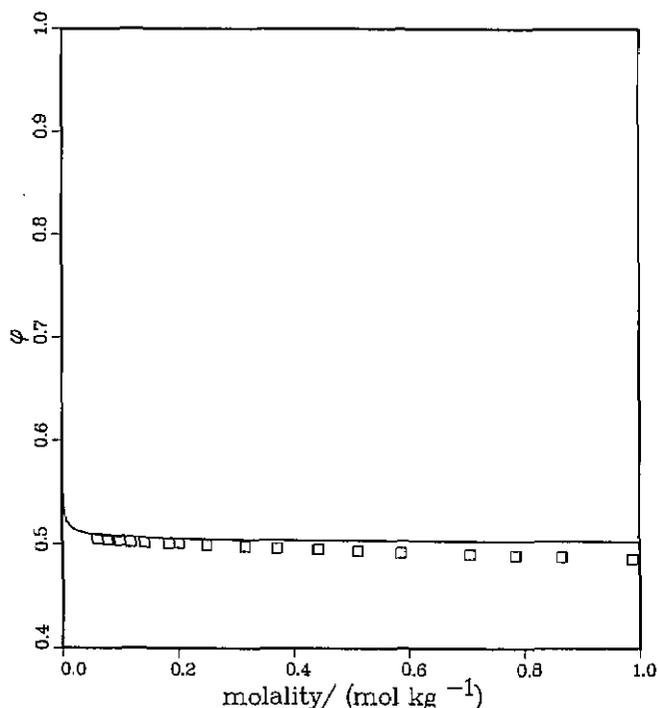
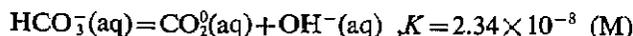
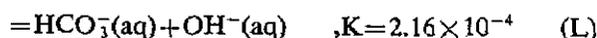
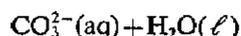
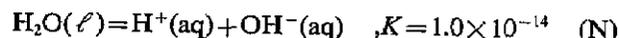


Figure 5—The osmotic coefficients of aqueous acetic acid at 273.15 K. The squares are the experimental osmotic coefficients reported by Harris, Thompson, and Wood [21]. The solid curve was calculated using a value of  $K_B = 5.96 \times 10^4$  which was obtained from the values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta C_p^\circ$  for process (B) given by Larson and Hepler [19]. The solid curve was also calculated using either Pitzer's  $\hat{\gamma}_i$  or a Debye-Hückel  $\hat{\gamma}_i$  where B varied from zero to 2.0. In this figure and in all subsequent ones, the ions were considered to be unhydrated.



All of the above equilibrium constants refer to a temperature of 298.15 K with the exception of the value for process (B) which refers to 273.15 K. The Gibbs energies of formation given in the NBS Tables of Chemical Thermodynamic Properties [17] were used to calculate the above values for equilibria (C), (D), (K), (L), and (M). The value for process (B) was calculated from the data for acetic acid tabulated by Larson and Hepler [19]; the values for processes (E), (F), (G), and (H) are those given by Reilly and Stokes [12]; and the values for processes (I), (J), and (K) are those given by Pitzer [9]. The Debye-Hückel constants recommended by Clarke and Glew [20] were used in all calculations.

The results of the calculations are shown in figures 5 through 9. For acetic acid, since the species ionic strength ( $\hat{I}$ ) is very low (it has a value of  $0.044 \text{ mol kg}^{-1}$  at  $I^s = 1.0 \text{ mol kg}^{-1}$ ), the choice of the expression for  $\hat{\gamma}_i$  makes very little difference. Near agreement with the experimental osmotic coefficients is obtained to a molality of  $\approx 0.2 \text{ mol kg}^{-1}$ . The difference between the measured osmotic coefficients and the calculated ones

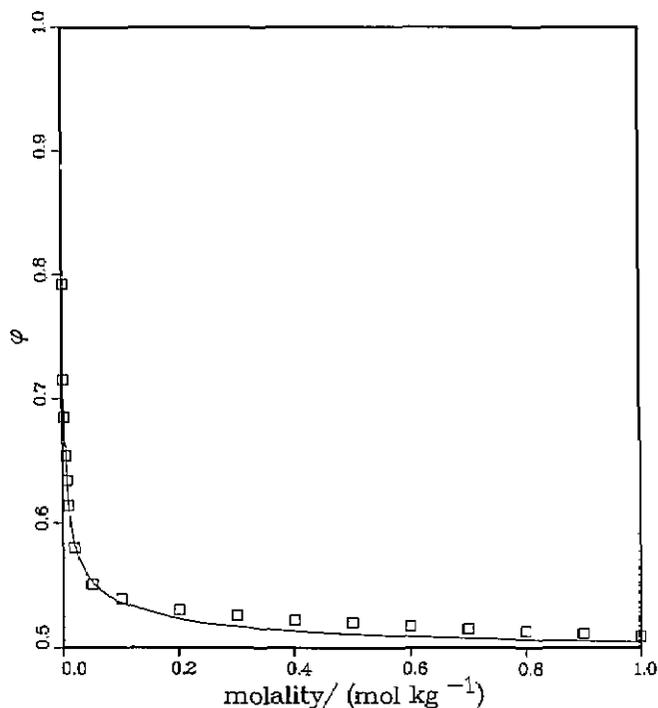


Figure 6—The osmotic coefficients of aqueous HF at 298.15 K. Values of  $K_c = 1442$  and  $K_D = 2.63$  were used to calculate the solid curve together with Pitzer's expression for  $\hat{\gamma}_i$ . The squares are from the correlation of Hamer and Wu [22].

can be attributed to the formation of dimers and trimers of acetic acid [21] and cannot be explained either by the introduction of hydration or by the use of different  $B$  parameters in eq (5) or by the choice of a different expression for  $\hat{\gamma}_i$ .

For aqueous HF, CdCl<sub>2</sub>, CuSO<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub>, agreement of calculated with measured properties can be obtained to molalities between 0.6 and 1.0 mol kg<sup>-1</sup> by the variation of the  $B$  parameter in eq (5) and, for the case of CdCl<sub>2</sub>, using only eq (6) for  $\hat{\gamma}_i$ . Neither the use of eq (5) nor eq (6) is able to produce the minima in the calculated values of  $\phi$  or  $\gamma_{\pm}$  which is observed for many electrolyte solutions. These minima can be produced, however, either by the introduction of hydration or by the use of eq (7) to extend the equations for  $\hat{\gamma}_i$ . It should be noted that for Na<sub>2</sub>CO<sub>3</sub> solutions the osmotic coefficient does not approach the usual limit of unity as  $m^{\text{st}}$  approaches zero mol kg<sup>-1</sup>; instead it approaches a value of 1.395 [14]. This is a consequence of eq (39) and the presence of equilibria (L), (M), and (N).

Calculated values of  $\delta_{\pm}$  are shown in figure 10. The fact that values of  $\delta_{\pm}$  for acetic acid and for copper sulfate are essentially unity is attributable to a very near cancellation of terms in eqs (25) and (36). It should be noted that the value of  $\delta_{\pm}$  for Na<sub>2</sub>CO<sub>3</sub>, unlike the other

systems shown in figure 10, does not approach a value of unity as the molality approaches zero mol kg<sup>-1</sup>; the minimum value of  $\delta_{\pm}$  for Na<sub>2</sub>CO<sub>3</sub> occurs at a molality of 0.0040 mol kg<sup>-1</sup>. While there are presently no experimental values of  $\delta_{\pm}$  available with which to compare our calculated values, this property is potentially measurable [24].

In summary, an equilibrium model for aqueous solutions has several important applications: 1) the Gibbs energy properties can be reliably estimated at low molalities if the appropriate equilibrium constants are known, 2) an equation of state can be generated which is appropriate for a particular type of solution, 3) amounts of species in a given solution can be calculated, 4) single-ion activities can be calculated, and 5) as was done here, effects of variations in the equilibria, state of hydration, and electrostatic contributions to the Gibbs energy properties can be investigated. A natural extension of this model is the calculation of enthalpies, heat capacities, and volumes of aqueous solutions.

The author thanks Drs. Graham Morrison, Ralph L. Nuttall, and, in particular, Robert H. Wood, for useful and stimulating discussions on the topics of this paper.

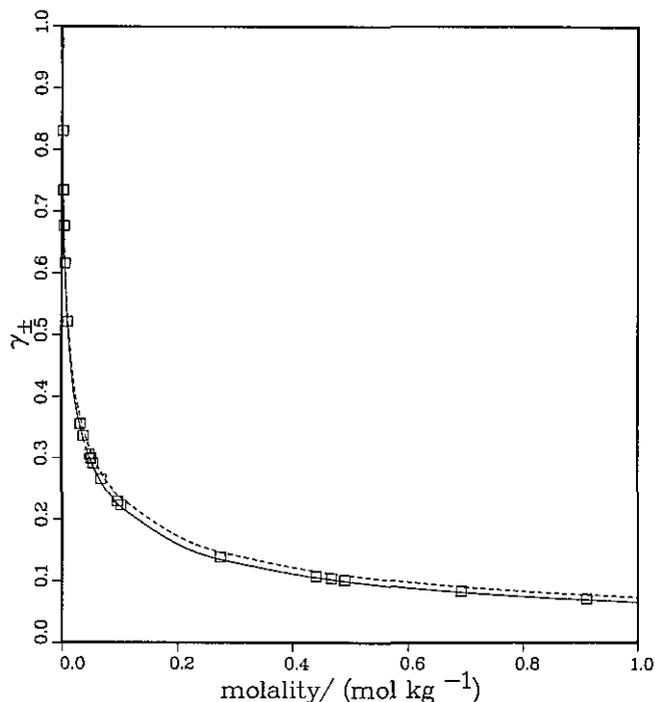


Figure 7—The activity coefficients of aqueous CdCl<sub>2</sub> at 298.15 K. The successive formation constants given by Reilly and Stokes [12] were used in doing the calculations. The solid line was calculated using Pitzer's expression for  $\hat{\gamma}_i$  and the dashed line was calculated using the Debye-Hückel  $\hat{\gamma}_i$  with  $B$  set equal to 2.0. The squares are based on the measurements of Reilly and Stoke [12].

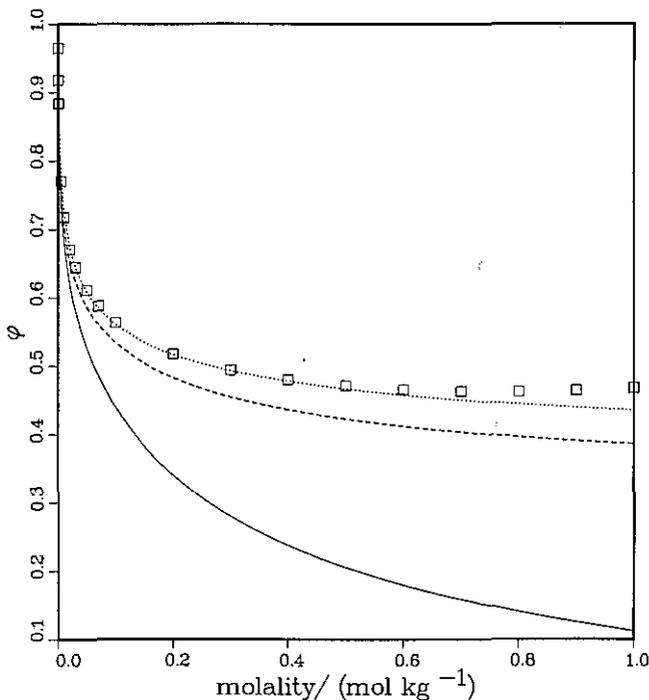
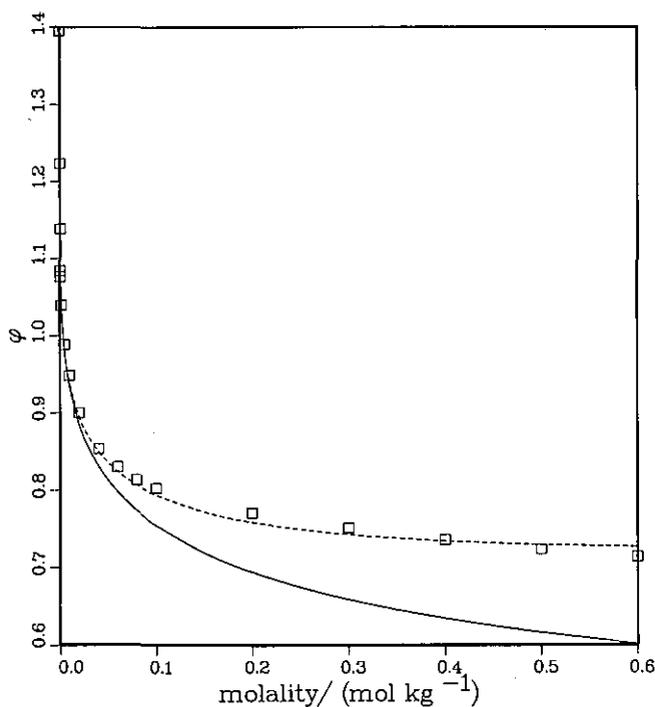
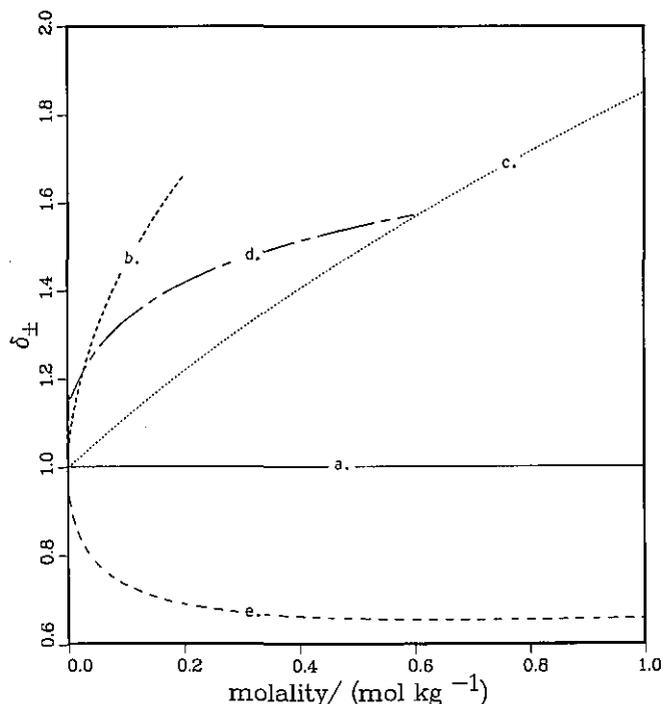


Figure 8—The osmotic coefficients of aqueous CuSO<sub>4</sub> at 298.15 K. The squares are the experimental data of Miller et al [23]. The three curves were obtained using values of  $K_E=250$  and  $K_F=K_G=5$ . The solid line was calculated using Pitzer's expression for  $\hat{\gamma}_i$ , the dashed and dotted lines were obtained using the Debye-Hückel  $\hat{\gamma}_i$  with  $B$  set equal to 2.0 and 5.0, respectively.



**Figure 9**—The osmotic coefficients of aqueous  $\text{Na}_2\text{CO}_3$  at 289.15 K. The squares are from the correlation of Vanderzee [14]. The solid line was calculated using Pitzer's expression for  $\hat{\gamma}_i$  and values of  $K_L$ ,  $K_M$ , and  $K_N$  from reference [17]. The dashed line was calculated using these same values of  $K$  and a Debye-Hückel  $\hat{\gamma}_i$  with  $B$  equal to 1.0.



**Figure 10**—Calculated values of  $\delta_{\pm}$  for several electrolyte solutions: (a) corresponds to acetic acid and to  $\text{CuSO}_4$ , (b) corresponds to  $\text{H}_2\text{SO}_4$ , (c) corresponds to HF; (d) corresponds to  $\text{Na}_2\text{CO}_3$ ; and (e) corresponds to  $\text{CdCl}_2$ . These curves were calculated using the values of the equilibrium constants cited above (a value of  $K_A$  equal to 99 was used). Pitzer's expression for  $\hat{\gamma}_i$  (eq (6)) was used for acetic acid, hydrofluoric acid, and cadmium chloride. The Debye-Hückel expression for  $\hat{\gamma}_i$  (eq (5)) was used for sulfuric acid, copper sulfate and sodium carbonate with respective values of  $B$  equal to 2.5, 5.9, and 1.0.

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