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DISCLAIMER

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NOTATION

a	activity; also a negative ion; also parameter in eq. (46)
A	Helmholtz energy
A_ϕ	Debye-Hückel parameter
B_{ij}	second virial coefficient or binary ion interaction parameter for interaction i-j (also B^ϕ_{ij})
b	parameter in extended Debye-Hückel expression; also parameter in eq. (46)
c	positive ion; also parameter in eq. (46)
C_{ij}	(also C^ϕ_{ij}) third virial coefficient
d_w	density of water
e	electronic charge
$f(I)$	extended Debye-Hückel function
F	collection of terms for the activity coefficient (eq. 32,33)
$g(x)$	defined function (eq. 19)
$g'(x)$	defined function (eq. 20)
G^{ex}	excess Gibbs energy
H	enthalpy
I	ionic strength
J_{ij}	defined function (eq. A11)
k	Boltzmann constant
K	equilibrium constant
ℓ	electrostatic length (eq. A9)
m_i	molality of i
M	positive ion
n_w	number of moles of water
N_o	Avogadro's number
P	pressure

q_{ij}	defined function (eq. A12)
r	interparticle distance
R	gas constant
S	entropy
t	temperature in °C
T	absolute temperature
X	negative ion
z_i	charge on ion i
Z	total charge molality (eq. 35)
u_{ij}	short range potential
v_{ij}	interionic potential of mean force

Greek letters

α	parameter in second virial coefficient expression (also α_1, α_2)
$\beta^{(0)}_{ij}$	(also $\beta^{(1)}_{ij}$, $\beta^{(2)}_{ij}$) second virial coefficient for interaction i-j
γ_i	activity coefficient of ion i
γ_{MX}	mean activity coefficient for electrolyte MX
θ_{ij}	second virial coefficient contribution from short-range forces
${}^E\theta_{ij}$	same but for long-range force
κ	Debye length (eq. A3)
λ_{ij}	second virial coefficient for interaction i-j
μ_i	standard chemical potential of species i
μ_{ijk}	third virial coefficient for interaction i-j-k
ν_i	number of ions of type i in the complete salt
ν_{MX}	total number of ions in salt MX
ϕ	osmotic coefficient
ϕ_{ij}	total second virial coefficient for ions i-j of the same sign
ψ_{ijk}	third virial coefficient for mixing effects

INTRODUCTION

There are many geologically important natural systems involving multicomponent aqueous solutions; other similar systems are important in steam power generation, chemical processing, and other industrial operations. Thus it is important to have an accurate and convenient model for the prediction of the thermodynamic properties of such aqueous solutions since it would be very burdensome to make experimental measurements for each composition at all of the temperatures and pressures of interest. Aqueous solutions are also of theoretical interest, and existing theory provides a general structure for the desired model as well as the precise form of certain terms, but other terms are best evaluated empirically from appropriate experiments. The model and its applications are described and discussed in the present chapter and the following one by Weare.

This model was initially developed (Pitzer, 1973, 1975; Pitzer and Kim, 1974) for solutions near room temperature, but it has been found to be applicable to aqueous systems up to 300°C or a little higher temperature. A liquid-like density and relatively small compressibility are assumed. Thus the present model is not applicable close to the critical point of water at 374°C. The requirements for a theory applicable to ionic solutions in the critical region were discussed by Levelt Sengers et al. (1986). Progress has been made toward models valid for aqueous systems at above critical temperatures and pressures (Sverjensky, a chapter in this volume; Pitzer and Li, 1983, 1984; Bischoff and Pitzer, 1985), but much more research is needed for these more extreme conditions.

A typical application is the prediction of the equilibrium between an aqueous phase (brine) and one or more solid phases (minerals). There are many published examples of solubility calculations; especially pertinent are those of Harvie and Weare (1980), Krumgalz and Millero (1983), and Harvie et al.(1984) for 25°C, and for high temperatures that of Pabalan and Pitzer (1987b). The following chapter by Weare emphasizes solubility calculations. The vapor phase may also be present and important. A complete calculation of either type involves several steps which can be considered separately as follows:

1. <u>The standard state chemical potential or molar Gibbs energy of formation of each substance involved</u>. For aqueous species the standard state is a hypothetical state with ideal properties at one molal which is actually evaluated in a limiting process at infinite dilution. General tables of standard state chemical potentials for solids, gases, and solution species at the reference temperature, 25°C = 298.15 K, and the reference pressure of 1 bar are available from several sources (Robie et al., 1978; Wagman et al., 1982). Our interest is in accurate values for particular differences, and the tables of Harvie and Weare (1980), Harvie et al.(1984), and in the following chapter of this volume have been prepared to best meet this need.

2. <u>The excess Gibbs energy for the solution, which yields the activity coefficients of all solute species and the osmotic coefficient</u>. The model for these quantities is described below. Additional information concerning the theoretical basis for the model is given in Appendix A. This model was first tested at 25°C and the most extensive array of parameters pertain to that temperature. Also there have been a very extensive array of successful applications at 25°C, some of which are described below and others by Weare in the next chapter. Recently, this model has been extended to 200°C or above for a number of the geologically important solutes and these results are also described below. Appendix B gives numerical values for several solutes at elevated temperatures.

3. For high temperature applications, the changes of standard-state chemical potential values from 25° to the temperature of interest. This calculation is normally based on values for the standard-state entropy (or enthalpy) at 25°C and for the standard-state heat capacity over a range of temperature from 25°C upward. Sample calculations of this type are discussed and a summary of entropy values and heat capacity equations are given below.

Since the model is based on a general equation for the Gibbs energy of the aqueous fluid, any thermodynamic property can be obtained from the appropriate derivative. Phase equilibria with several solid minerals are especially interesting applications which are discussed by Weare in the following chapter. Thermal properties of the brine are sometimes required, and these are discussed below, as are equilibria of the aqueous fluid with a vapor phase.

There are, of course, other models which with similar accuracy treat some of the properties and systems here considered. But none of the other models has shown a comparably wide range of applicability and accuracy. Hence, we shall not burden this paper with extensive discussions of other models and comparisons of results. Such comparisons are available elsewhere; many publications here cited contain such comparisons.

EXCESS GIBBS ENERGY; ACTIVITY AND OSMOTIC COEFFICIENTS

Basic Equation

In constructing a model for aqueous ionic solutions all valid and useful theory should be included. The statistics of ideal solution behavior are first included in the definitions of the excess Gibbs energy and the activity and osmotic coefficients. Next in importance and now fully confirmed is the limiting law of Debye and Hückel; this is the leading term for departure from ideality for any ionic solution. It depends only on the concentrations of the electrically charged species, the temperature, and the macroscopic properties of the solvent, the density and dielectric constant. This type of term arises purely from long-range electrostatic forces. There are higher order terms of the same type, depending only on electrical forces, but in many cases these are indistinguishable from terms arising from short-range forces between solute species. These short-range forces are complex and not practically predictable at present; hence, their effects are treated empirically.

There is one higher-order electrostatic term that yields effects quite different from those from short-range forces. It arises only when ions of different charge of the same sign are mixed, i.e., Ca^{2+} and Na^{+} or SO_4^{2-} and Cl^{-}. It can be calculated from theory and the properties of the solvent.

Neutral solute species interact only through short-range forces. These effects are easily included in any general equation for the excess Gibbs energy. The remaining questions relate to the choice of variables for the basic equation. The basic theory is developed in terms of the total volume and the concentrations of solute species as well as the temperature. But for most practical systems pressure is a more appropriate variable than total volume. Also composition variables such as molality or mole fraction, which are independent of pressure and temperature, are much more convenient than concentration. For electrolytes, molality is so widely used that it seems desirable to adopt it. It is possible to make rigorous transformations from volume to pressure and from concentration to molality, but these are very cumbersome in general. Thus, it is convenient and satisfactory for most purposes to set up the basic equation with the variables T, P, m_i and with guidance from theory for the details of certain terms and the general structure of the equation. The empirical terms can be accepted as such or can be related to the corresponding theoretical terms in the T, V, c_i equation, if desired. But, it must be remembered that the volume to pressure transformation breaks down with the infinite compressibility at the solvent critical point. Hence, the present treatment has this limitation and should not be used above 350°C, except at pressures far above critical. Most of the applications of the present model have been at 300°C or lower temperatures, and in that range the pressure basis is fully satisfactory.

There are alternate presentations of the basic statistical mechanics of multicomponent ionic fluids which suggest the basic equation adopted for the present model. Appendix A describes the most rigorous analysis which, however, is abstract. In the original presentation and an early summary of this model (Pitzer, 1973, 1979), a basic but approximate treatment was presented which suggests the same form of equation and gives an easier understanding of the general physical picture. The approximations of the latter treatment do not carry over to the basic equation of the model, however. The model is postulated for empirical use and is to be justified by its empirical success. This equation (A7 in Appendix A) expresses the excess Gibbs energy as follows:

$$G^{ex}/n_w RT = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} + \cdot \cdot \cdot \qquad (1)$$

Here n_w is the number of kg of water and m_i, m_j,... are the molalities of all solute species. The ionic strength is given by

$$I = 1/2 \sum_i m_i z_i^2$$

where z_i is the number of charges on the i^{th} solute. The first term on the right in equation (1) includes the Debye-Hückel limiting law, but is an extended form chosen for empirical effectiveness. Note that f(I) depends only on the ionic strength and not on individual ionic molalities or other solute properties.

The quantity $\lambda_{ij}(I)$ represents the short range interaction in the presence of the solvent between solute particles i and j. This binary interaction parameter or second virial coefficient does not itself have any composition dependence for neutral species, but for ions it is dependent on the ionic strength; it does depend, of course, on the particular solute species i and j and the temperature and pressure. The similar quantity for triple interaction is μ_{ijk}; in principle it might be ionic strength dependent, but with a single possible exception (Phutela and Pitzer, 1986a), there is no indication of such dependence. Hence, we shall write our equations without considering any I-dependence for μ. Fourth or higher order interactions could be included, but we will not do so in this presentation. They are needed only for extremely concentrated solutions (Ananthaswany and Atkinson, 1985), and then alternate methods may be preferable (Pitzer and Simonson, 1986).

The standard definitions and thermodynamic transformations yield the equations for the activity and osmotic coefficients

$$\begin{aligned} ln\gamma_i &= [\partial(G^{ex}/n_w RT)/\partial m_i]_{n_w} \\ &= (z_i^2/2)f' + 2\sum_j \lambda_{ij} m_j + (z_i^2/2)\sum_j \sum_k \lambda'_{jk} m_j m_k \\ &\qquad + 3\sum_j \sum_k \mu_{ijk} m_j m_k + \cdots \end{aligned} \tag{2}$$

$$\begin{aligned}\phi-1 &= -(\partial G^{ex}/\partial n_w)_{n_i}/kT\sum_i m_i \\ &= (\sum_i m_i)^{-1}[(If'-f)+\sum_i\sum_j(\lambda_{ij}+I\lambda'_{ij})m_im_j \\ &\quad + 2\sum_i\sum_j\sum_k \mu_{ijk}m_im_jm_k + \cdot\ \cdot] \end{aligned} \tag{3}$$

Here f' and λ' are the ionic strength derivatives of f and λ. Also $m_i = n_i/n_w$ with n_i the number of moles of species i. The multiple sums in equations (1, 2, 3) are unrestricted, i.e., each sum covers all solute species. Also, we note the definition of the excess Gibbs energy in the molality system and another useful relationship.

$$G^{ex} = G - n_1\bar{G}_1^\circ - \Sigma\, n_i[\bar{G}_i^\circ - RT(1-\ln m_i)] \tag{4}$$

$$G^{ex}/n_wRT = \Sigma\, m_i(\ln\gamma_i + 1 - \phi) \tag{5}$$

Here $\bar{G}_1^\circ$ is the molar Gibbs energy of water and $\bar{G}_i^\circ$ the partial molar Gibbs energy for species i, each in its standard state.

For solutions containing ions, the requirement of electrical neutrality makes it impossible to evaluate certain individual ionic quantities. This becomes more explicit as one derives the working equation for an electrolyte with a single solute.

Pure Electrolytes

If the electrolyte MX has ν_M positive ions of charge z_M in its formula and ν_X negative ions of charge z_X; neutrality requires $z_M\nu_M = |z_X|\nu_X$; also we take $\nu = \nu_M + \nu_X$. For a salt molality m, the ion molalities are $m_M = \nu_Mm$ and $m_X = \nu_Xm$. The osmotic coefficient becomes

$$\phi-1 = (\nu m)^{-1}\{(If' - f) + m^2[2\nu_M\nu_X(\lambda_{MX} + I\lambda'_{MX}) + \nu_M^2(\lambda_{MM} + I\lambda'_{MM}) + \nu_X^2(\lambda_{XX} + I\lambda'_{XX})] + m^2(6\nu_M^2\nu_X\mu_{MMX} + 6\nu_M\nu_X^2\mu_{MXX} + 2\nu_M^3\mu_{MMM} + 2\nu_X^3\mu_{XXX}) + \cdot\cdot\cdot\} \; . \tag{6}$$

From the experimentally measured properties of the pure electrolyte, together with the Debye-Hückel term (IF'-f), one can evaluate only the bracketed term in λ's, a function of ionic strength, and the final term in parentheses involving μ's. Thus we define f^ϕ, $B^\phi(I)$ and C^ϕ as follows

$$f^\phi = (f' - f/I)/2 \tag{7}$$

$$B^\phi_{MX} = \lambda_{MX} + I\lambda'_{MX} + (\nu_M/2\nu_X)(\lambda_{MM} + I\lambda'_{MM}) + (\nu_X/2\nu_M)(\lambda_{XX} + I\lambda'_{XX}) \tag{8}$$

$$C^\phi_{MX} = [3/(\nu_M\nu_X)^{\frac{1}{2}}](\nu_M\mu_{MMX} + \nu_X\mu_{MXX}) \tag{9}$$

At this point we could have included the terms in μ_{MMM} and μ_{XXX} in the definition of C^ϕ, but we shall neglect them later so omit them now. These terms relate to short-range interactions of three ions all of the same sign. Since electrical repulsions make it unlikely that three ions of the same sign are often close together, these terms are expected to be very small, and no indication has arisen that they need to be included. Equation (6) now reduces to the simple form

$$\phi-1 = |z_M z_X| f^\phi + m(2\nu_M\nu_X/\nu)B^\phi_{MX} + m^2[2(\nu_M\nu_X)^{3/2}/\nu]C^\phi_{MX} \tag{10}$$

For a 1-1 electrolyte all of the coefficients became unity.

In originally developing this model (Pitzer, 1973), two choices were made at this point: the extended form of the Debye-Hückel term f^ϕ and the form for the ionic strength dependence of B^ϕ_{MX}. All combinations of the most likely forms were tested with an array of accurately measured experimental osmotic coefficients for several 1-1, 2-1, and 1-2 type salts at 25°C, and the best results were obtained for the forms:

$$f^{\phi} = -A_{\phi}I^{\frac{1}{2}}/(1+bI^{\frac{1}{2}}) \tag{11}$$

$$B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp(-\alpha I^{\frac{1}{2}}) \tag{12}$$

The general pattern of ionic strength dependence was indicated theoretically for each function, but alternate forms were equally plausible, and the choice was made for empirical effectiveness. Here b is a universal parameter with the value 1.2 $\mathrm{kg}^{\frac{1}{2}}\cdot\mathrm{mol}^{-\frac{1}{2}}$ and α has the value 2.0 $\mathrm{kg}^{\frac{1}{2}}\cdot\mathrm{mol}^{-\frac{1}{2}}$ for all of the salts in the test set. It will be possible to use a different value of α for other salts or salts of other charge types; this will be discussed below. The parameters $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$ are specific to the salt MX. It was expected that these parameters representing short-range interactions would be specific to the interacting ions.

As salts of other valence types were studied, it was found that equation (12) with $\alpha = 2.0$ served well for 3-1 and even 4-1 salts but not for 2-2 salts such as $MgSO_4$ (Pitzer and Mayorga, 1973, 1974). The 2-2 type salts show an electrostatic ion pairing effect which has usually been represented by considering the ion pair as a separate solute species. Introduction of such a species in equilibrium with other species complicates the calculations considerably, however. We found that good agreement with observed properties was obtained for the 2-2 salts if one simply added another term to B^{ϕ}_{MX} as follows:

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} \exp(-\alpha_1 I^{\frac{1}{2}}) + \beta^{(2)}_{MX} \exp(-\alpha_2 I^{\frac{1}{2}}) \tag{13}$$

The values $\alpha_1 = 1.4$ $\mathrm{kg}^{\frac{1}{2}}\cdot\mathrm{mol}^{-\frac{1}{2}}$ and $\alpha_2 = 12$ $\mathrm{kg}^{\frac{1}{2}}\cdot\mathrm{mol}^{-\frac{1}{2}}$ were satisfactory for all 2-2 electrolytes at 25°C. The parameter $\beta^{(2)}_{MX}$ is negative and is related to the association equilibrium constant.

In a very extensive investigation of aqueous HCl Holmes et al.(1987) found that the $\beta^{(2)}$ term was unnecessary below 250°C. From 250 to 375°C they obtained a good fit with a $\beta^{(2)}$ term and with $\alpha_1 = 1.4$ and $\alpha_2 = 6.7\ A_\phi$. There is theoretical support for the proportionality of α_2 to the Debye-Hückel parameter A_ϕ.

Finally, we note the theoretical expression for the Debye-Hückel parameter

$$A_\phi = (1/3)(2\pi N_o d_w/1000)^{1/2}(e^2/\varepsilon kT)^{3/2} \tag{14}$$

with N_o Avogadro's number, d_w the density of water, e the electronic charge, k Boltzmann's constant, and ε the dielectric constant or the relative permittivity of water. For SI units ε is multiplied by $4\pi\varepsilon_o$ with ε_o the permittivity of free space. In many papers the symbol D is used instead of ε for the dielectric constant.

Next we transform B^ϕ_{MX} and C^ϕ_{MX} as defined by equations (8) and (9) to the corresponding forms for the excess Gibbs energy as follows:

$$B_{MX} = \lambda_{MX} + (\nu_M/2\nu_X)\lambda_{MM} + (\nu_X/2\nu_M)\lambda_{XX} \tag{15}$$

$$C_{MX} = (3/2)(\mu_{MMX}/z_M + \mu_{CXX}/|z_X|) \tag{16}$$

These quantities are used for the equations for mixed electrolytes. Introduction of the selected forms from equations (11) and (13) yields

$$f = -(4IA_\phi/b)\,ln(1+bI^{\frac{1}{2}}) \tag{17}$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\ g(\alpha_1 I^{\frac{1}{2}}) + \beta^{(2)}_{MX}\ g(\alpha_2 I^{\frac{1}{2}}) \tag{18}$$

$$g(x) = 2[1-(1+x)\ \exp(-x)]/x^2 \tag{19}$$

Further manipulations yield the useful relationships

$$B'_{MX} = [\beta^{(1)}_{MX} g'(\alpha_1 I^{\frac{1}{2}}) + \beta^{(2)}_{MX} g'(\alpha_2 I^{\frac{1}{2}}]/I \tag{20}$$

$$g'(x) = -2[1-(1+x+x^2/2)\ \exp(-x)]/x^2 \tag{21}$$

$$C_{MX} = C^{\phi}/2|z_M z_X|^{\frac{1}{2}} \tag{22}$$

For the activity coefficient equation, it is useful to define the following:

$$f^{\gamma} = -A_{\phi}[I^{\frac{1}{2}}/(1+bI^{\frac{1}{2}}) + (2/b)\ln(1+bI^{\frac{1}{2}})] \tag{23}$$

$$B^{\gamma}_{MX} = B_{MX} + B^{\phi}_{MX} \tag{24}$$

$$C^{\gamma}_{MX} = 3C^{\phi}_{MX}/2 \tag{25}$$

The mean activity coefficient for a salt is defined as

$$\ln\gamma_{\pm} = (\nu_M \ln\gamma_M + \nu_X \ln\gamma_X)/\nu \tag{26}$$

and for the present model with a single salt this becomes

$$\ln\gamma_{\pm} = |z_M z_X| f^{\gamma} + m(2\nu_M \nu_X/\nu) B^{\gamma}_{MX} + m^2[2(\nu_M \nu_X)^{3/2}/\nu] C^{\gamma}_{MX} \tag{27}$$

Equations (10) and (27) were applied to the very extensive array of data for 25°C with excellent agreement to about 6 $\text{mol}\cdot\text{kg}^{-1}$ for various types of electrolytes (Pitzer and Mayorga, 1973, 1974). The resulting parameters are discussed in a subsequent section.

Mixed Electrolytes

In order to treat mixed electrolytes it is desirable to rewrite equation (1) in terms of the experimentally determinable quantities B and C instead of the individual ion quantities λ and μ. Appropriate transformations yield for the excess Gibbs energy

$$G^{ex}/(n_w RT) = f(I) + 2\sum_c\sum_a m_c m_a[B_{ca} + (\sum_c m_c z_c)C_{ca}]$$

$$+ \sum_{c<c'}\sum m_c m_{c'}[2\Phi_{cc'} + \sum_a m_a \psi_{cc'a}] + \sum_{a<a'}\sum m_a m_{a'}[2\Phi_{aa'} + \sum_c m_c \psi_{caa'}]$$

$$+ 2\sum_n\sum_c m_n m_c \lambda_{nc} + 2\sum_n\sum_a m_n m_a \lambda_{na} + 2\sum_{n<n'}\sum m_n m_{n'} \lambda_{nn'} + \cdot\cdot \quad (28)$$

where the sums are over the various cations c,c' and over the anions a,a'. If neutral solute species n, n' are present, the terms from equation (1) in λ_{ij} and μ_{ijk} are retained; only those in λ_{ij} are shown in the last three sums. Difference combinations of λ's and μ's arise which are defined as follows:

$$\Phi_{cc'} = \lambda_{cc'} - (z_{c'}/2z_c)\lambda_{cc} - (z_c/2z_{c'})\lambda_{c'c'} \quad (29)$$

$$\psi_{cc'a} = 6\mu_{cc'a} - (3z_{c'}/z_c)\mu_{cca} - (3z_c/z_{c'})\mu_{c'c'a} \quad (30)$$

Analogous expressions for $\Phi_{aa'}$ and $\psi_{caa'}$ arise from permutation of the indices. These quantities account for interactions between ions of like sign, which arise only for mixed solutions, and can best be determined from simple common-ion mixtures.

In terms of various quantities defined above, the following equations give the osmotic coefficient of the mixed electrolyte and the activity coefficients of cation M and anion X, respectively.

$$(\phi-1) = (2/\sum_i m_i)[-A_\phi I^{3/2}/(1+bI^{1/2}) + \sum_c\sum_a m_c m_a(B^\phi_{ca} + Z\,C_{ca})$$

$$+ \sum_{c<c'}\sum m_c m_{c'}(\Phi^\phi_{cc'} + \sum_a m_a \psi_{cc'a}) + \sum_{a<a'}\sum m_a m_{a'}(\Phi^\phi_{aa'} + \sum_c m_c \psi_{caa'})$$

$$+ \sum_n\sum_c m_n m_c \lambda_{nc} + \sum_n\sum_a m_n m_a \lambda_{na} + \sum_{n<n'}\sum m_n m_{n'} \lambda_{nn'} + \ldots] \quad (31)$$

$$\ln\gamma_M = z_M^2 F + \sum_a m_a(2B_{Ma} + Z\,C_{Ma}) + \sum_c m_c(2\Phi_{Mc} + \sum_a m_a\psi_{Mca})$$

$$+ \sum_{a<a'}\sum m_a m_{a'}\psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca} + 2\sum_n m_n\lambda_{nM} + \cdot\cdot\cdot \qquad (32)$$

$$\ln\gamma_X = z_X^2 F + \sum_c m_c(2B_{cX} + Z\,C_{cX}) + \sum_a m_a(2\Phi_{Xa} + \sum_c m_c\psi_{cXa})$$

$$+ \sum_{c<c'}\sum m_c m_{c'}\psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca} + 2\sum_n m_n\lambda_{nX} + \cdot\cdot\cdot \qquad (33)$$

The third virial terms for neutrals are omitted in equations (31)-(33).

The quantity F includes the Debye-Hückel term and other terms as follows:

$$F = -A_\phi[I^{1/2}/(1+bI^{1/2}) + (2/b)\ \ln(1+bI^{1/2})] + \sum_c \sum_a m_c m_a B'_{ca}$$

$$+ \sum_{c<c'}\sum m_c m_{c'}\Phi'_{cc'} + \sum_{a<a'}\sum m_a m_{a'}\Phi'_{aa'} \qquad (34)$$

Also, Φ' is the ionic strength derivative of Φ, and

$$Z = \sum_i m_i|z_i| \qquad (35)$$

$$\Phi^\phi_{cc'} = \Phi_{cc'} + I\Phi'_{cc'} \qquad (36)$$

It should be remembered that single ion activity coefficients are not measurable by ordinary thermodynamic methods because of space charge limitations. Also in the transformation from equation (2) to (32) and (33) certain terms in λ's and μ's remain which cancel for any neutral combination of ions; see Pitzer (1979) for more details. Thus there is no pretense that equations (32) and (33) yield absolute values of single-ion activity coefficients; rather these are practical values for use in all practical thermodynamic calculations. For complex mixed electrolytes, the use of the single ion activity coefficients is much more convenient than the use of mean activity coefficients and electrically neutral differences of activity coefficients, although the final results are identical.

Since like charged ions repel one another, we expect their short-range interactions to be small and that $\lambda_{cc'}$, $\lambda_{cc'}$, etc. are all small. We further note that $\Phi_{cc'}$ and $\psi_{cc'a}$ are differences between these small quantities; hence, they should certainly be small. Indeed both Bronsted (1922) and Guggenheim (1935) neglected these terms completely. We do not neglect these quantities, but we do find them to be small in most cases. There is an exception, noted above, where the long-range electrical forces yield a term that appears in $\Phi_{cc'}$ in this formulation. It appears only for unsymmetrical mixing, i.e., where the charges on c and c' (or a and a') differ. This term is given by theory (Pitzer, 1975, 1983). The complete expressions for Φ_{ij} are:

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \tag{37}$$

$$\Phi'_{ij} = {}^{E}\theta'_{ij}(I) \tag{38}$$

$$\Phi^{\phi}_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I\,{}^{E}\theta'_{ij}(I) \tag{39}$$

where ${}^{E}\theta(I)$ and ${}^{E}\theta'(I)$ account for these electrostatic unsymmetrical mixing effects and depend only on the charges of the ions i and j, the total ionic strength, and on the solvent properties ε and d_w (hence, on the temperature and pressure). The theory and equations for calculating these terms are given in Appendix A, which also describes a method of numerical calculation by Chebyshev approximations devised by Harvie (1981). The remaining term θ_{ij} arising from short-range forces is taken as a constant for any particular c,c' or a,a' at a given T and P. Its ionic strength dependence is very small and is usually neglected as we have done here, but this effect may be significant in some cases as shown by recent calculations of heats of mixing by Phutela and Pitzer (1986a).

Thus starting from theoretical considerations, the ion-interaction model gives an expression for the activity and osmotic coefficients of electrolyte mixtures in terms of the empirical parameters, $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, C_{MX}^{ϕ}, θ_{ij}, and ψ_{ijk}. Provided that their temperature and pressure dependencies are known, these coefficients permit the calculation of solubilities in binary, ternary and more complex mixtures at different temperatures and pressures.

It is important to recognize that the same equation for total excess Gibbs energy yields other thermodynamic functions such as excess volumes, enthalpies, entropies, and heat capacities by appropriate differentiation. These other functions are directly obtainable from experiment and their evaluation yields accurate data on the pressure or temperature-dependencies of the ion-interaction coefficients. Also the entropy or enthalpy of the fluid is required for analysis of some important processes,and it can be calculated from the temperature derivative of the Gibbs energy. Since these relationships are standard thermodynamics, we will not burden this paper with the detailed equations for mixtures. The equations for pure electrolytes were given by Pitzer et al.(1984).

There is, therefore, a wide array of experimental data from which the ion-interaction parameters and their temperature functions can be determined. This includes measurements of

1) freezing point depression

2) boiling point elevation

*3) vapor pressure

*4) isopiestic concentrations

5) E.M.F.

*6) enthalpy of dilution

7) enthalpy of mixing

8) enthalpy of solution

*9) heat capacity

*10) solubility

Those marked with an asterisk are those that so far have been most useful at temperatures greater than 100°C. Enthalpies of dilution measured at 25°C are also important for their relation to the temperature dependency of the Gibbs energy.

Neutral Solutes

The situation is much simpler for uncharged solute species, and there is no need to rearrange the terms in λ_{ij} and μ_{ijk} in the basic equations (1), (2), and (3). The terms for neutral species were included in equations (32) and (33) for the activity coefficients of ions. The corresponding equation for the activity coefficient of a neutral species is

$$\ln\gamma_N = 2(\sum_c m_c\lambda_{Nc} + \sum_a m_a\lambda_{Na} + \sum_n m_n\lambda_{N,n}) \tag{40}$$

Third virial terms from equation (2) can be added to equation (40), if needed. Even for neutral molecules interacting with ions, the forces are short ranged, and there is no need to modify the λ's and μ's. Electrical neutrality limits the evaluation of λ's and μ's to electrically neutral sums and differences, but it does not seem worthwhile to define new quantities. Since Setchenow in 1892, the departure of neutral-species activity coefficients from unity has traditionally been described in terms equivalent to the λ's of these equations. An extensive review of neutral solutes in aqueous salt solutions was presented by Long and McDevit (1952).

Empirically there is no evidence for an ionic-strength dependence for the λ's for neutral species. Thus all λ'_{ij} terms in equations (2) and (3) can be omitted for both neutral-neutral and neutral-ion interactions. There is some theoretical basis for a small ionic strength effect for interactions of ions with neutrals having large dipole moments (or higher-order electric moments); this is described in Appendix A. But this effect is so small that there is no reason to complicate the equations at present.

Also the question may be asked whether the dielectric constant should be that of a mixed solvent, including neutral solute species, instead of the value for water. It is possible to set up equations for mixed solvents, and this is necessary if the solvent composition varies over a wide range, e.g., from pure water to pure methanol. But the present equations assume a pure solvent, and its dielectric constant must be used. The effect of neutral-molecule solutes on interionic effects via changes in dielectric constant are included along with other effects in the second and third virial coefficients including a possible ionic-strength dependence of the ion-neutral second virial coefficient. Such an ionic-strength dependence has not been detected up to the present, but the possibility should be kept in mind.

Silica dissolves in water to form a neutral species, presumably $Si(OH)_4$; this is an interesting example to discuss briefly. Silica solubility, both in pure water and in salt solutions, has been measured by various investigators including Chen and Marshall (1981).

For the three-component system SiO_2 - salt - H_2O with salt molality m, they summarized their results with the equation

$$\log \gamma = Dm + E\,m^2 \tag{41a}$$

where γ is the activity coefficient of the silica. If S represents silica and the salt MX has ν_M and ν_X ions, respectively, our equation (2) reduces in this case to

$$\ln\gamma_S = 2m(\nu_M\lambda_{SM} + \nu_X\lambda_{SX}) + 3m^2(\nu_M^2\mu_{SMM} + \nu_X^2\mu_{SXX}) \qquad (41b)$$

Evidently $2.303D = 2(\nu_M\lambda_{SM} + \nu_X\lambda_{SX})$ and $2.303E = 3(\nu_M^2\mu_{SMM} + \nu_X^2\mu_{SXX})$. Chen and Marshall fit their equation to their data both with and without the term in E and then give equations for the parameters over the range of temperature 25-300°C. Even for solutions extending to as high molality as 7, the effect of the E term was rather small for the salts NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$.

In an accompanying paper Marshall and Chen (1981) restated their results (with E = 0) in terms of ion molalities. Since all of the individual ion parameters cannot be evaluated, they set the parameter for Na^+ to zero. Their parameter D_i now becomes just $(2/2.303)\ \lambda_{Si}$ in our equation (2). Marshall and Chen also made solubility measurements for silica in mixed salt solutions and verified that the ionic effects were additive as implied by equation (2).

Association Equilibria

Up to this point we have assumed that the selection of solute species was unambiguous and that electrical neutrality was the only supplementary relationship between solute molalities. But there may be association equilibria such as $H^+ + HCO_3^- = CO_2(aq) + H_2O$ which relate one solute molality to other molalities. The chemical thermodynamics of each such equilibrium is straightforward with an equilibrium constant relationship involving molalities and activity coefficients. For the carbonic acid case this is

$$K_{assoc.} = a_{H_2O} m_{CO_2} \gamma_{CO_2} / m_{H^+} m_{HCO_3^-} \gamma_{H^+} \gamma_{HCO_3^-} \tag{42}$$

Each such equilibrium adds one or more relationships between the molalities and an equilibrium-constant equation all of which must be satisfied simultaneously in the complete solution of the problem.

For carbonates and many other cases the association constants are large (i.e., the dissociation constants are very small) and there is no question about the need to recognize the associated species. Examples treated using the present model include $Na^+ - HCO_3^- - CO_3^{2-} - Cl^- - CO_2 - H_2O$ (Peiper and Pitzer, 1982), $H^+ - HSO_4^- - SO_4^{2-} - H_2O$ (Pitzer et al., 1977), and $H^+ - K^+ - H_2PO_4^- - H_3PO_4 - H_2O$ (Pitzer and Silvester, 1976). The last example is interesting in that it models the phosphoric acid to such high molality that a third virial coefficient for triple interaction of the neutral species is required.

In some cases the association, although significant, is not strong, and the fraction in the associated form is never large. In the dilute range the degree of association increases with concentration. But at higher concentration, the activity coefficients of the ions decrease, and the degree of association levels off and may even decrease. This last effect is particularly strong for multiply charged ions such as the divalent metal sulfates. In the case of the $M^{2+} - SO_4^{2-}$ solutions it was found (Pitzer and Mayorga, 1974) that the associated species could be omitted provided an additional ionic-strength dependent term with a large exponent α_2 was added to the second virial coefficient, see equation (13). The coefficient in this term $\beta_{MX}^{(2)}$ is negative and, in the limit of low molality, is related to the association constant K by $\beta^{(2)} = -K/2$. Also the exponent α_2 is related to the Debye-Hückel parameter A_ϕ. Indeed, the equation without the MSO_4 neutral species and with the $\beta^{(2)}$ term represented the properties to high molality without difficulty. In contrast, association treatments with the simple inclusion of the ion-pair association equilibrium constant are not successful at high molality; further terms are required - either virial coefficients involving the MSO_4 species or association equilibria to triple or quadruple ions. Thus the treatment with the $\beta^{(2)}$ term and without the association equilibrium has many advantages.

With increase in temperature the dielectric constant of water decreases rather rapidly and one expects ion pairing to become stronger. Archer and Wood (1985) found this to be the case in a general treatment of $MgSO_4$(aq). They included not only the neutral ion pair but also the triplets M_2X^+, MX_2^- and a sextuplet M_3X_3 with association constants at 25°C of 126.4, 557.3, and 3.813 x 10^6, respectively, and enthalpies of association of approximately 6, 6, and 27 $kJ \cdot mol^{-1}$. They also adjusted heat capacities of association for each reaction as well as a simple pattern of temperature-dependent second and third virial coefficients to account for repulsive interactions and obtained good agreement with the available data up to 3 $mol \cdot kg^{-1}$ and 150°C. Soon thereafter Phutela and Pitzer (1986b) presented high-temperature heat capacity measurements for $MgSO_4$(aq) and a comprehensive treatment of that system without association equilibria but with temperature-dependent $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ and C^{ϕ}. They found that $-\beta^{(2)}$ increased with temperature, as expected. They also investigated the effect of change of the exponent α_2 with temperature proportionally to A_ϕ. The temperature-dependent α_2 gave better agreement below 0.1 $mol \cdot kg^{-1}$, but there was no difference above 0.1 $mol \cdot kg^{-1}$. Thus for mixed electrolytes at ionic strength above 0.4 $mol \cdot kg^{-1}$ the simple treatment with constant α_2 is fully satisfactory. The general agreement for various properties for the two treatments was comparable; the treatment without association equilibria gave agreement for the osmotic coefficient at 110°C to higher molality (5 $\mathrm{mol \cdot kg^{-1}}$) and better agreement at 140°C. The association treatment gives a better fit to the heats of dilution at high temperatures in the dilute range below 0.03 $\mathrm{mol \cdot kg^{-1}}$. The more recent heat capacity measurements were not available at the time of Archer and Wood's treatment; as expected, the Phutela and Pitzer treatment fits these data much more accurately.

In estimating the need to introduce associated species, these results for $MgSO_4$ give the best guide for 2-2 electrolytes. For less highly charged ions, the ion pairs must be recognized for somewhat smaller values of the association constant because the activity coefficient for the ions decreases less rapidly with increase of molality. The case of aqueous HCl was investigated very thoroughly by Holmes et al. (1987). They found no need to include a $\beta^{(2)}$ term below 250°C. For higher temperatures up to 375°C, they obtained good agreement with an equation including a $\beta^{(2)}$ term. In the range of their data $-\beta^{(2)}$ is as large as 32 corresponding to an association constant of 64.

At room temperature most 1-1 electrolytes are either unambiguously associated, such as acetic acid or ammonia, or are clearly strong electrolytes where the present equations are adequate without the $\beta^{(2)}$ term. The situation for 2-1 or 1-2 electrolytes at 25°C was studied carefully by Harvie et al. (1984); they concluded that association should be recognized for cases with association constants greater than 20 (or dissociation constants less than 0.05). This general topic is also discussed by Weare in the following chapter.

TEMPERATURE AND PRESSURE EFFECTS ON STANDARD-STATE PROPERTIES

For the calculation of equilibria one requires the chemical potentials of all substances at the temperature and pressure of interest.

We first consider the change of the chemical potential from the reference temperature, normally 25°C, to another temperature. The entropy and heat capacity determine this difference as follows:

$$(\partial \mu_i^\circ/\partial T)_P = -S_i^\circ \qquad (43)$$

or

$$\mu_{i,T}^\circ - \mu_{i,T_r}^\circ = -(T-T_r)S_{i,T_r}^\circ + \int_{T_r}^{T} C_{p,i}^\circ dT' - T \int_{T_r}^{T} (C_{p,i}^\circ/T')dT' \qquad (44)$$

Here S_i° represents the standard absolute entropy of component i, and $C_{p,i}^\circ$ is the standard state heat capacity (at constant pressure) which itself is expressed as a function of temperature. T_r and T represent the reference temperature and temperature of interest, respectively. An analogous but somewhat more complex expression for the temperature dependence of the chemical potential can be written in terms of the enthalpy and heat capacity.

For aqueous species the heat capacities become large as the critical temperature of water is approached; for ions the heat capacity becomes negative but for neutral species it can be positive. At the critical pressure this trend becomes a divergence to plus or minus infinity at the critical point.

For solids the heat capacities remain moderate in magnitude except at certain solid phase transitions. In the case of transitions, the integration is divided into ranges and the entropy change for the transition is included explicitly.

The effect of pressure on the chemical potential is given by the molar or partial molar volume and can be determined from density data. At saturation pressure these effects are usually small, particularly for the solids, but can be significant at higher pressures (Rogers and Pitzer, 1982; Pitzer, 1986).

The basic equation for pressure dependency is

$$\mu^\circ_{i,P} - \mu^\circ_{i,P_r} = \int_{P_r}^{P} \bar{V}^\circ_i dP \qquad (45)$$

where $\bar{V}^\circ_i$ is the partial molar volume of solute species i in its standard state at the temperature of interest. The data base for volumes is discussed below.

DATA BASE

Standard State Values for 25°C

There are many sources of standard-state chemical potentials (molar Gibbs energies) of formation, entropies, heat capacities, and volumes at 25°C (298.15 K) and 1 bar for substances of geological interest. Wagman et al (1982) give very extensive tables while Robie et al.(1978) consider geological interest in their selection. For solubility calculations, the accuracy of particular differences is especially important and the tables of Harvie and Weare (1980), of Harvie et al.(1984), and of Weare in the following chapter have been prepared to meet this need. Table 1 contains, for convenience, an abbreviated list of chemical potentials and enthalpies of formation, and of entropies and parameters for heat capacity equations. The sources of the entropies and heat capacities will be discussed below; the chemical potentials are from Harvie et al. (1984).

Standard-State Enthalpies, Entropies, Heat Capacities, and Volumes

The conversion of standard-state chemical potentials to other temperatures requires entropy values for the reference temperature and heat capacities as a function of temperature. The entropy values are generally available from the tables of Wagman et al.(1982) or Robie et al.

(1978). In some cases the entropy was obtained indirectly from the enthalpy and the Gibbs energy (chemical potential), and in such cases one should revise the entropy to be consistent with any change in the Gibbs energy. The properties of solids do not ordinarily depend appreciably on crystal size, but there are cases where extremely small crystals are obtained with significantly larger molar entropies and chemical potentials. Kieserite ($MgSO_4 \cdot H_2O$) is an example where the data of Ko and Daut (1979) for the enthalpy and Frost et al.(1957) for the heat capacity and entropy show significant differences with crystal size.

In Table 1 parameters are given for the following equation for the heat capacity of a solid:

$$C_p/R = a + bT + cT^{-2} \tag{46}$$

The range of validity is also indicated. These heat capacity parameters were taken mostly from Kelley (1960). The coefficients given by Kelley (1960) for KCl(s) are incorrect, and the values listed are from Holmes and Mesmer (1983). The values for $Na_2SO_4 \cdot 10\ H_2O(s)$ and $Na_2SO_4(s)$ were fitted by Pabalan and Pitzer (1987b) to data from Brodale and Giauque (1958, 1972), while those for $MgSO_4(s)$ were derived from JANAF data (Stull and Prophet, 1971). The C_p coefficients for $MgSO_4 \cdot H_2O(s)$ and $MgSO_4 \cdot 6H_2O(s)$ were derived from linear fits to the low temperature data of Frost et al.(1957) and Cox et al.(1955), respectively.

Heat capacity data for $MgSO_4 \cdot 4H_2O(s)$, $MgSO_4 \cdot 5H_2O(s)$, and $MgSO_4 \cdot 7H_2O(s)$ are not available. However, the contribution of each water molecule to the entropy or heat capacity of a hydrated solid is expected to be about the same. Pabalan and Pitzer (1987b) present isothermal plots of the measured entropies and heat capacities of $MgCl_2 \cdot nH_2O(s)$ and $MgSO_4 \cdot nH_2O(s)$ versus the number of hydration waters

Table 1: The Chemical Potentials, Enthalpies of Formation, and Entropies at 298.15 K of the Species and Minerals of the Na-K-Mg-Cl-SO_4-OH-H_2O System and the Temperature Functions of the Heat Capacity of the Solids

					$C_p/R = a + bT + cT^{-2}$			
Substance	Formula	$-\mu_f^\circ/RT$	$-\Delta_f H^\circ/RT$	S°/R	a	$10^3 b$	$10^{-5} c$	T(K)range
Water	$H_2O(\ell)$	95.6635	115.304	8.409				
Hydroxide ion	OH^-(aq)	63.452	92.780	-1.293				
Chloride ion	Cl^-(aq)	52.955	67.432	6.778				
Sulfate ion	SO^{2-}(aq)	300.386	366.800	2.42				
Magnesium ion	Mg^{2+}(aq)	183.468	188.329	-16.64				
Calcium ion	Ca^{2+}(aq)	223.30	218.98	-6.39				
Sodium ion	Na^+(aq)	105.651	96.865	7.096				
Potassium ion	K^+(aq)	113.957	101.81	12.33				
Arcanite	K_2SO_4(c)	532.39	580.01	21.12	14.48	11.98	-2.14_4	298 - 856
Bischofite	$MgCl_2 \cdot 6H_2O$(c)	853.1	1008.11	44.03	29.08	29.56	-	298 - 385
Epsomite	$MgSO_4 \cdot 7H_2O$(c)	1157.74	(1366.27)	44.79	11.8	118	-	~273 -~473
Halite	NaCl(c)	154.99	165.88	8.676	5.525	1.96_3	-	298 -1073
Hexahydrite	$MgSO_4 \cdot 6H_2O$(c)	1061.37	(1244.79)	41.87	10.9	104	-	~273 -~473
Kieserite	$MgSO_4 \cdot H_2O$(c)	579.18_4	649.34	(14.99)	6.89	31.05	-	~273 -~473
Leonhardtite	$MgSO_4 \cdot 4H_2O$(c)	868.55	1007.13	(30.64)	9.39	74.8	-	~273 -~473
Magnesium chloride	$MgCl_2$(c)	238.74	258.71	10.78	9.511	0.714_6	-1.03_7	298 - 987
Magnesium chloride hydrate	$MgCl_2 \cdot H_2O$(c)	347.66	389.94	16.505	10.95	9.788	-	298-650
Magnesium chloride dihydrate	$MgCl_2 \cdot 2H_2O$(c)	451.06	516.24	21.64	15.05	13.74	-	298 - 500
Magnesium chloride tetrahydrate	$MgCl_2 \cdot 4H_2O$(c)	654.93	766.06	31.75	22.56	21.65	-	298 - 450
Magnesium sulfate	$MgSO_4$(c)	472.26	518.33	11.02	6.71	16.30	-	298 - 700
Mirabilite	$Na_2SO_4 \cdot 10H_2O$(c)	1471.15	1475.75	71.21	10.65	196.0	-	~200 -~450
Pentahydrite	$MgSO_4 \cdot 5H_2O$(c)	965.13	-	(35.7)	10.2	89.3	-	~273 -~473
Sylvite	KCl(c)	164.84	176.034	9.934	5.575	2.011	-	~298 -~700
Thenardite	Na_2SO_4(c)	512.39	559.55	17.99	13.16	13.70	-1.666	270 - 700

which show a linear trend. Thus the unknown C_p temperature functions for $MgSO_4 \cdot 4H_2O(s)$, $MgSO_4 \cdot 5H_2O(s)$, and $MgSO_4 \cdot 7H_2O(s)$ were estimated on this basis.

The $S°/R$ values in Table 1 are mostly from Wagman et al.(1982). Values in parentheses were calculated from $\mu_f°/RT$ and $\Delta H_f°/RT$. For pentahydrite, whose entropy is not known independently, its value was estimated from the entropy values of the other $MgSO_4$ hydrous salts. With the exception of $MgSO_4 \cdot H_2O(s)$, values of $\Delta H_f°/RT$ values given in the table were calculated from $\mu_f°/RT$ and $S°/R$ or were taken from Wagman et al.(1982) when the value of $S°/R$ is in parenthesis. For $MgSO_4 \cdot H_2O(s)$, the enthalpy of formation at 25°C was taken from Ko and Daut (1979).

Numerical equations for the aqueous standard state heat capacities as a function of temperature are given along with the solution properties for several solutes in Appendix B. Table 2 includes several other solutes for which this information is available (sometimes over a more limited range) together with appropriate references.

The volumetric properties of many aqueous electrolytes have been measured to high pressure at 25°C or over the 0 - 50°C range. This information is of oceanographic interest. Above 50°C the volumetric information is much more limited. NaCl(aq) has been investigated over a wide range of temperature and pressure and general correlations are available (Rogers and Pitzer, 1982). Gates (1985) has made further measurements by an additional method. Information on aqueous HCl is now extensive (Holmes et al, 1987). The densities of a number of other aqueous systems have been measured at moderate pressure to 200°C and in additional cases to 100°C. Equations have been fitted to these data yielding standard state volumes; the particular solutes are listed in Table 2 which includes the pertinent references.

Table 2: Binary Electrolyte Solutions with Available High Temperature Data

	Range of T and P		Ref.
	T/°C	P/kbar	
	1:1 Electrolytes		
HCl	0 - 375	0-0.4	a,b
LiCl	0 - 250	-	c
NaCl	0 - 300	0-1.0	d
NaI	25 - 100	0-0.1	a
NaOH	0 - 350	0-0.4	e
KCl	0 - 250	-	c
CsF	25 - 100	0-0.1	a
CsCl	0 - 250	0-0.1	a,c
CsI	25 - 100	0-0.1	a
	1:2 or 2:1 Electrolytes		
Li_2SO_4	0 - 225	-	f
Na_2SO_4	0 - 225	0-0.1	f,j
K_2SO_4	0 - 225	-	f
Cs_2SO_4	0 - 225	-	f
$MgCl_2$	25 - 200	0-0.1	g,h
$CaCl_2$	25 - 250	0-0.1	k,ℓ
$SrCl_2$	25 - 200	0-0.1	g
	2:2 Electrolytes		
$MgSO_4$	25-200	0-0.1	i,j

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[a] Saluja et al. (1986).

[b] Holmes et al. (1987).

[c] Holmes and Mesmer (1983)

[d] Pitzer et al. (1984).

[e] Pabalan and Pitzer (1987a).

[f] Holmes and Mesmer (1986).

[g] Phutela et al. (1987).

[h] Holmes et al. (1978)

[i] Phutela and Putzer (1986b).

[j] Phutela and Pitzer (1986c).

[k] Ananthaswamy and Atkinson (1985).

[ℓ] Møller (submitted).

Since compressibilities of aqueous solutions decrease with increase in pressure, the assumption of a constant molar volume in equation (45) usually overestimates the effect of pressure on the chemical potential. In any case, there is no divergence of the partial molar volume at high pressure as there is with temperature for the heat capacity as the critical point is approached. Thus one can make reasonable estimates of pressure effects to higher pressures than those listed in Table 2.

There have been several general correlations of high-temperature volumetric data with use of approximate theory. A very recent study is by Tanger and Helgeson (1987), while an earlier paper was presented by Zarembo and L'vov (1982); these papers give references to additional experimental measurements. Thus it is possible to estimate the change of chemical potential with pressure even in cases where there are no experimental measurements for a particular solute.

Pure Electrolyte Parameters for 25°C

The activity and osmotic coefficients at 25°C of many electrolytes as well as neutral solutes in water were measured quite accurately many years ago. Robinson and Stokes with their collaborators made many of these measurements, and their book (Robinson and Stokes, 1965) includes excellent tables of selected values over wide ranges of molality. The parameters for the present equations were derived by least squares regression for a very wide range of electrolytes by Pitzer and Mayorga (1973, 1974) using more recent measurements as well as the selected values of Robinson and Stokes. Subsequently, Pitzer et al.(1978) obtained values for the parameters for the rare earth chlorides, nitrates, and perchlorates from the extensive measurements of Spedding and associates. Other research has contributed new or improved values for particular solutes. Table 3 contains values selected for possible geological interest.

Table 3: Single Electrolyte Solution Parameter Values for 25°C[a]

Cation	Anion	$\beta^{(0)}_{ca}$	$\beta^{(1)}_{ca}$	$\beta^{(2)}_{ca}$	C^{ϕ}_{ca}
H	Cl	0.1775	0.2945	-	0.0008
H	SO_4	0.0298	-	-	0.0438
H	HSO_4	0.2065	0.5556	-	-
Li	Cl	0.1494	0.3074	-	0.00359
Na	Cl	0.0765	0.2644	-	0.00127
Na	Br	0.0973	0.2791	-	0.00116
Na	SO_4	0.01958	1.113	-	0.00497
Na	HSO_4	0.0454	0.398	-	-
Na	OH	0.0864	0.253	-	0.0044
Na	HCO_3	0.0277	0.0411	-	-
Na	CO_3	0.0399	1.389	-	0.0044
Na	SiO_4H_3[a]	0.043	0.024	-	-
K	Cl	0.04835	0.2122	-	-0.0084
K	Br	0.0569	0.2212	-	-0.00180
K	SO_4	0.04995	0.7793	-	-
K	HSO_4	-0.0003	0.1735	-	-
K	OH	0.1298	0.320	-	0.0041
K	HCO_3	0.0296	-0.013	-	-0.008
K	CO_3	0.1488	1.043	-	-0.0015
Cs	Cl	0.0300	0.0558	-	0.00038
NH_4	Cl	0.0522	0.1918	-	-0.00301
Mg	Cl	0.35235	1.6815	-	0.00519
Mg	Br	0.43268	1.75275	-	0.00312
Mg	SO_4	0.2210	3.343[b]	-37.23[c]	0.0025
Mg	HSO_4	0.4746	1.729	-	-
Mg	OH	-	-	-	-
Mg	HCO_3	0.329	0.6072	-	-
MgOH	Cl	-0.010	1.658	-	-
Ca	Cl	0.3159	1.614	-	-0.00034
Ca	Br	0.3816	1.61325	-	-0.00257
Ca	SO_4	0.20	3.1973[b]	-54.24[c]	-
Ca	HSO_4	0.2145	2.53	-	-
Ca	OH	-0.1747	-0.2303	-5.72[c]	-
Ca	HCO_3	0.004	2.977	-	-
UO_2	Cl	0.4274	1.644	-	-0.03686
UO_2	SO_4[b]	0.322	1.827[b]	(-40)[c]	-0.0176
Al	Cl	0.6993	5.845	-	0.00273
La	Cl	0.5889	5.600	-	-0.0238
Th	Cl	1.0138	13.331	-	-0.1034

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[a] From Pitzer (1979) or Harvie et al. (1984) except $Na(SiO_4H_3)$ from Hershey and Millero (1986); note that $C_{ca} = C^{\phi}_{ca}/2|z_c z_a|$.

[b] $\alpha_1 = 1.4\ kg \cdot mol^{-1}$ (otherwise $\alpha_1 = 2.0\ kg \cdot mol^{-1}$).

[c] $\alpha_2 = 12\ kg \cdot mol^{-1}$.

Very recently, Kodytek and Dolejs (1986) refitted the rare-earth-salt data including a $\beta^{(2)}$ term. Their values of $\beta^{(2)}$ are positive; thus there is no indication of ion-pairing. But the extra flexibility does give a better fit for the low molalities. Their treatment emphasisized the dilute range, and the older values may be preferable at high molalities.

Pure Electrolyte Parameters for High Temperature

In an earlier section the various measurements were listed from which the pure electrolyte parameters can be derived. The isopiestic method, which is so useful at 25°C, has provided valuable data up to about 250°C. The reference solution is usually NaCl which has been thoroughly studied by other methods including the vapor pressure relative to that of pure water. Provided the heat of dilution as well as the excess Gibbs energy are known at 25°C, measurements of the heat capacity at higher temperatures provide the required information for both the solution parameters and the standard state entropy and chemical potential. In practice two or more methods are usually used, and the parameters determined from a least-squares optimization of the parameters to fit all of the accurate measurements.

There is now an extensive array of data for the most important aqueous solutes extending upward in temperature as indicated in Table 2. But in many cases further work would be welcome to extend the temperature range further, to better account for the effect of pressure, and to increase accuracy. Appendix B gives a brief listing of the numerical parameters in the temperature dependency expressions for both standard-state heat capacities and nonideality properties for several pure electrolytes and includes remarks concerning the Debye-Hückel parameter.

For NaCl(aq), there is an extensive array of thermodynamic data as reported by Pitzer, Peiper, and Busey (1984). Their evaluation of these data yield a complete set of parameters valid in the region 0-300°C and saturation pressure to 1 kbar. Solubility data were not used in the general regression; hence a comparison of calculated solubilities with experimentally measured values is a check on a prediction. As shown in figures 1, there is excellent agreement between calculated and experimentally determined values with a maximum deviation of 1.5% at 275°C. This general equation is also consistent with the very recent heat capacity measurements of Gates et al.(1987); most values agree within the uncertainty stated for the equation. For KCl(aq), Holmes and Mesmer (1983a) combined their isopiestic vapor pressure measurements to 250°C with other literature data to yield a thermodynamically consistent set of parameters for KCl solutions.

In the case of $MgCl_2$ there is no fully satisfactory general treatment. The ion-interaction parameters of de Lima and Pitzer (1983) were based on isopiestic measurements of Holmes et al.(1978) at high temperature and Rard and Miller (1981) at 25°C. Pabalan and Pitzer (1987b) adjusted the trend of C^{ϕ} at the higher temperatures to better fit the solubility of the various hydrates of $MgCl_2$ which rises to 14 $mol \cdot kg^{-1}$ at 200°C. This adjustment affects the agreement with the osmotic coefficients of Holmes et al, which extend only to 3.5 $mol \cdot kg^{-1}$, but the agreement is still good with standard deviations less than 0.003. The standard state heat capacity is taken from Phutela et al.(1987). This investigation also reported ion-interaction parameters, but their validity is limited to about 2 $mol \cdot kg^{-1}$; hence, they are not useful for solubility calculations. The final comparison of calculated and observed solubilities is shown on figure 2.

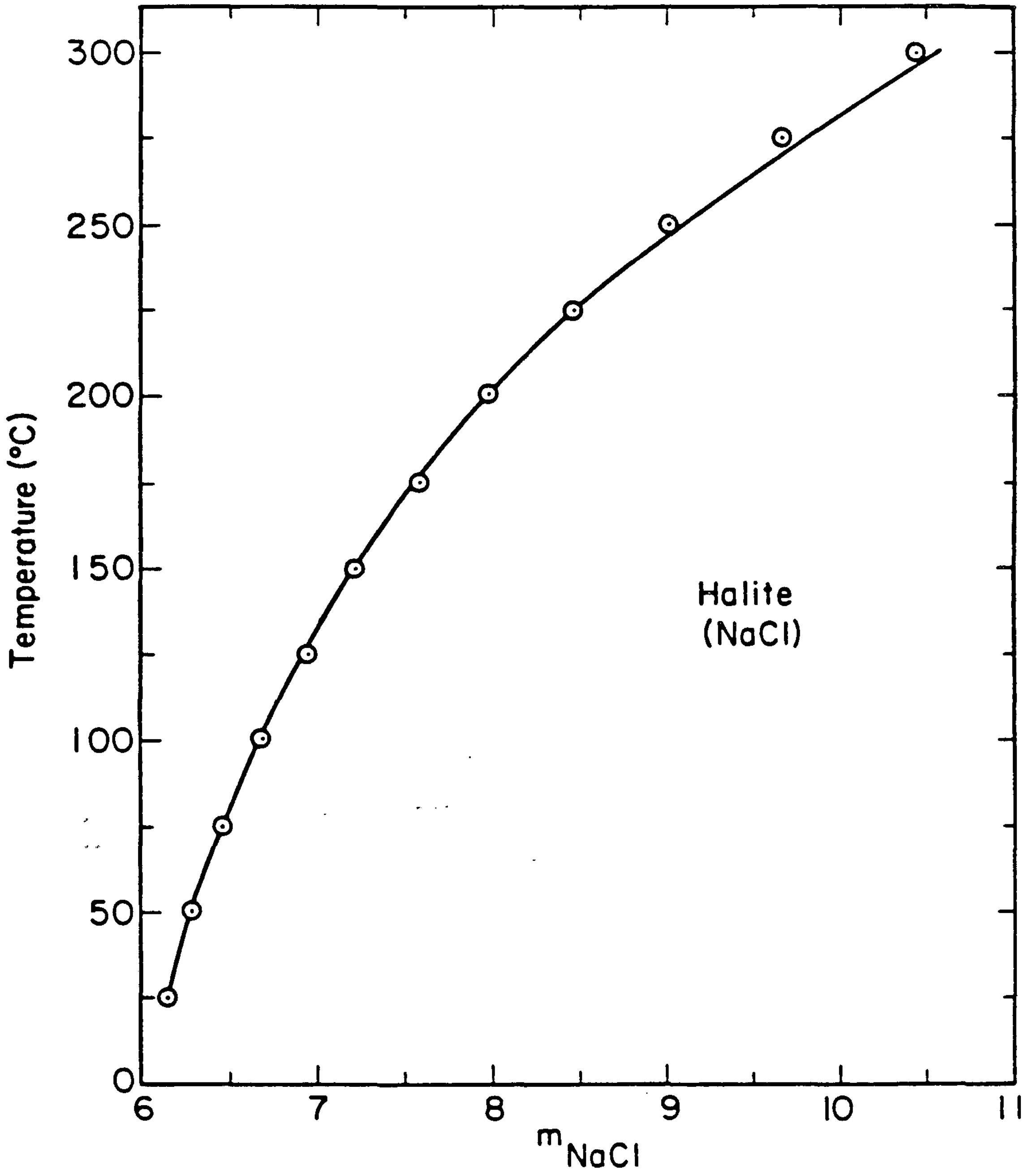

Figure 1. Calculated halite (NaCl) solubilities in the binary $NaCl-H_2O$ system compared to experiment. The solubility data from 75-300°C are from Liu and Lindasy (1972), and those below 75°C are from Linke and Seidell (1965).

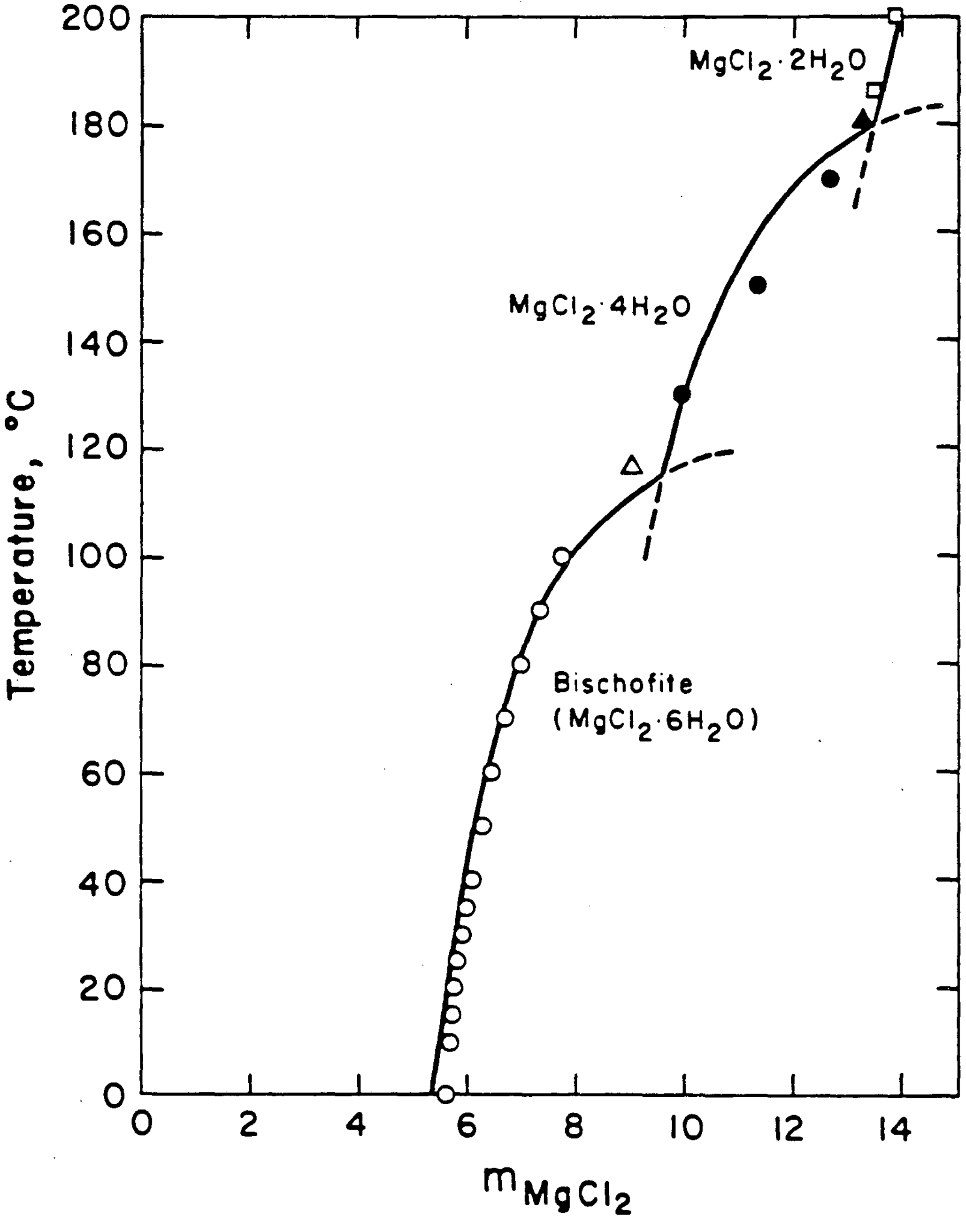

Figure 2. Calculated solubilities in the $MgCl_2$-H_2O binary system compared to experimental data from Linke and Seidell (1965). The triangles represent experimental data at the triple points. The C_{MX} function above 100°C was adjusted to fit the solubilities.

For $CaCl_2$ Phutela and Pitzer (1983) gave equations valid to 200°C and 4.3 $mol \cdot kg^{-1}$ based on osmotic-coefficient and heat-of-dilution data. Above 5 $mol \cdot kg^{-1}$ the usual form of equation terminating with the third virial coefficient is inadequate, and Ananthaswamy and Atkinson (1985) used a form extended through the sixth virial coefficient. Their treatment is valid to 100°C. Very recently Møller (submitted) has considered vapor pressure data for $CaCl_2(aq)$ above 200°C and derived equations for the ion-interaction parameters valid to 250°C. Møller (submitted) also considered $CaSO_4$ and reported appropriate parameters. Although it is not necessary to recognize the neutral $CaSO_4$ species at 25°C, Møller found that the equilibrium forming this species should be included at higher temperature.

For $Na_2SO_4(aq)$ and $K_2SO_4(aq)$, one has the equations of Holmes and Mesmer (1986) which were fit to data up to 225°C including heat capacities of Na_2SO_4 to 200°C from Rogers and Pitzer (1981). Pabalan and Pitzer (1987b) made solubility comparisons based on these equations and found excellent agreement to 175°C for Na_2SO_4 but some deviation at higher temperature. For K_2SO_4 the comparison showed some differences in the 100-215°C interval, but the agreement was reasonably good over the entire range.

In the case of $MgSO_4(aq)$ solutions, a comprehensive regression of heat capacity, enthalpy, and osmotic coefficient data by Phutela and Pitzer (1986b) yielded parameters that are valid from 25-200°C. Figure 3 shows that calculated solubilities are in very good agreement with experimental data to 200°C.

Holmes et al. (1987) presented a comprehensive treatment for $HCl(aq)$. They gave three sets of parameters for the present model. The first, valid to 523 K and 7 $mol \cdot kg^{-1}$, involves only the usual terms for a 1-1 electrolyte and is summarized in Appendix B. A second treatment adds a

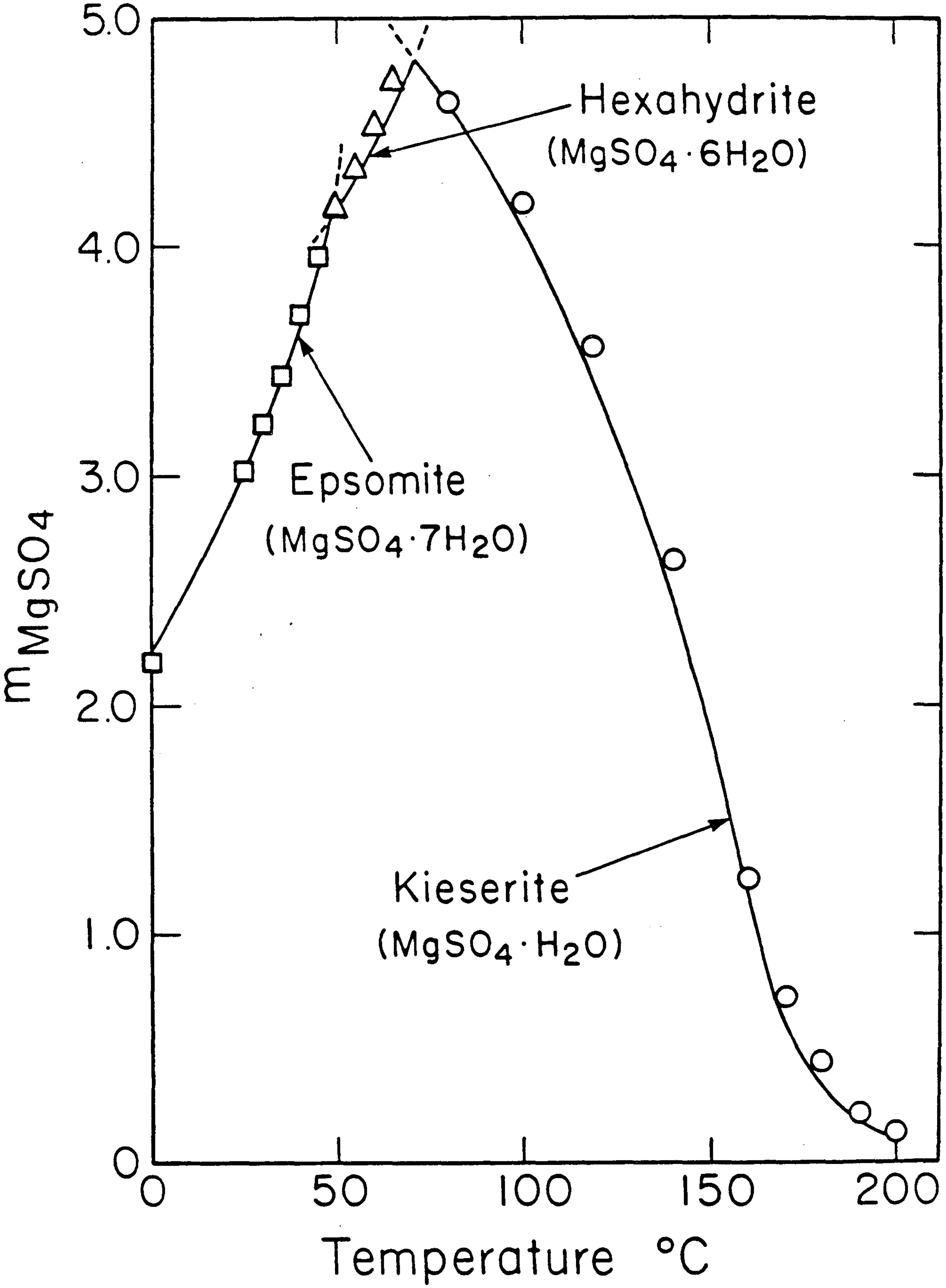

Figure 3. Calculated solubilities in the system $MgSO_4$-H_2O compared to experimental data from Linke and Seidell (1965).

fourth virial coefficient and is valid to 16 $mol \cdot kg^{-1}$. For temperatures from 523 to 648 K and from 0 to 7 $mol \cdot kg^{-1}$, they include a $\beta^{(2)}$ term.

For NaOH(aq) the available volumetric and vapor pressure data to 10 $mol \cdot kg^{-1}$ were evaluated by Pabalan and Pitzer (1987a) who give equations for the virial coefficients extending to 350°C. Standard state heat capacities could not be obtained from these data, but this is not a deficiency for solubility calculations since the solubility of NaOH exceeds the range of validity of the solution model. These parameters are useful, however, for the calculation of the effect of NaOH on mixed solution properties including the solubility of other salts.

Various forms have been used to describe the temperature dependency of the ion-interaction coefficients. No attempt has been made to find a singular form to describe this dependency; the parameters obtained in the cited studies are listed in Appendix B for the solutes discussed above. There are equations covering less extensive temperature ranges for a few other solutes as noted in Table 2 where references are listed. The initial change with temperature above 25°C for an even wider range of solutes is given by Silvester and Pitzer (1978).

Mixing Parameters

The mixing parameters θ_{ij} and ψ_{ijk} for many simple ions at 25°C were derived from the available measurements of activity and osmotic coefficients by Pitzer and Kim (1974). These parameters are best evaluated from data for common-ion mixtures. For example, the values of $\theta_{Na,K}$ and $\psi_{Na,K,Cl}$ may be determined from osmotic coefficient data for NaCl-KCl solutions. The θ_{ij} parameters are independent of the oppositely charged ions. Thus, all the data for $Na^+ - K^+$ mixing are considered simultaneously (NaCl-KCl, Na_2SO_4-K_2SO_4, $NaNO_3$-KNO_3, etc.) to determine a single value of $\theta_{Na,K}$ and values of $\psi_{Na,K,Cl}$, ψ_{Na,K,SO_4}, etc. Solubility measurements also contribute valuable information concerning these parameters, and they were not considered by Pitzer and Kim. Harvie and Weare (1980) and Harvie et al. (1984) obtained additional values and recommended some changes, primarily of the third virial ψ_{ijk}, on the basis of solubility data. Since the effect of the term in ψ_{ijk} increases with the square of the molality, this quantity is best determined from measurements at the highest molalities, i.e., in saturated solutions where the solubility of a solid is measured.

Table 4 lists values of θ_{ij} and ψ_{ijk} for 25°C for various interionic interactions while Table 5 lists values of λ_{ij} for ion-neutral interactions on the basis of zero for the interaction with H^+. The values in Tables 4 and 5 are the same as those of Harvie et al. (1984), except for the parameters involving Cl-SO_4 interactions, where slightly different values from Downes and Pitzer (1976) and Pabalan and Pitzer (1987b) are listed.

In their 1974 work Pitzer and Kim obtained reasonable results without the higher-order electrostatic terms for cases of unsymmetrical 2-1 mixing of ions of one sign and a common ion of the opposite sign. But they concluded that the more extreme 3-1 mixing showed clear deviation, and this was explained by the higher-order terms (Pitzer, 1975). Subsequently, the case of $CaSO_4$ solubility in NaCl, with 2-1 mixing of both cations and anions, clearly required the higher-order terms (Harvie and Weare, 1980). The result is that two sets of values are often given for θ_{ij}: one to be used with the higher-order electrostatic functions ${}^E\theta_{ij}$ and ${}^E\theta'_{ij}$, and the other to be used without these terms. It now seems best always to include the ${}^E\theta$ and ${}^E\theta'$ terms for all cases of unsymmetrical mixing, and all values in Table 4 are for that basis. Once a modern computer has a subroutine for the calculation of these terms,

Table 4: Mixing Parameters for 25°C

c°	c'	$\theta_{cc'}$	$\psi_{cc'Cl}$	$\psi_{cc'SO_4}$	$\psi_{cc'HSO_4}$	$\psi_{cc'OH}$	$\psi_{cc'HCO_3}$	$\psi_{cc'CO_3}$
Na	K	-0.012	-0.0018	-0.010	-	-	-0.003	0.003
Na	Ca	0.07	-0.007	-0.055	-	-	-	-
Na	Mg	0.07	-0.012	-0.015	-	-	-	-
Na	MgOH	-	-	-	-	-	-	-
Na	H	0.036	-0.004	-	-0.0129	-	-	-
K	Ca	0.032	-0.025	-	-	-	-	-
K	Mg	0.	-0.022	-0.048	-	-	-	-
K	MgOH	-	-	-	-	-	-	-
K	H	0.005	-0.011	0.0197	-0.0265	-	-	-
Ca	Mg	0.007	-0.012	0.024	-	-	-	-
Ca	MgOH	-	-	-	-	-	-	-
Ca	H	0.092	-0.015	-	-	-	-	-
Mg	MgOH	-	0.028	-	-	-	-	-
Mg	H	0.010	-0.011	-	-0.0178	-	-	-

a	a'	$\theta_{aa'}$	$\psi_{aa'Na}$	$\psi_{aa'K}$	$\psi_{aa'Ca}$	$\psi_{aa'Mg}$	$\psi_{aa'MgOH}$	$\psi_{aa'H}$
Cl	SO_4	0.030	0.000	-0.005	-0.002	-0.008	-	-
Cl	HSO_4	-0.006	-0.006	-	-	-	-	0.013
Cl	OH	-0.050	-0.006	-0.006	-0.025	-	-	-
Cl	HCO_3	0.003	-0.015	-	-	-0.096	-	-
Cl	CO_3	-0.002	0.0085	0.004	-	-	-	-
SO_4	HSO_4	-	-0.0094	-0.0677	-	-0.425	-	-
SO_4	OH	-0.013	-0.009	-0.050	-	-	-	-
SO_4	HCO_3	0.001	-0.005	-	-	-0.161	-	-
SO_4	CO_3	0.002	-0.005	-0.009	-	-	-	-
OH	CO_3	0.010	-0.017	-0.001	-	-	-	-
HCO_3	CO_3	-0.004	0.002	0.012	-	-	-	-

Table 5: Neutral-ion Parameter Values for 25°C

i	$\lambda_{CO_2,i}$	$\lambda_{CaCO_3,i}$	$\lambda_{MgCO_3,i}$
H	0.0	-	-
Na	.100	-	-
K	.051	-	-
Ca	.183	-	-
Mg	.183	-	-
MgOH	-	-	-
Cl	-.005	-	-
SO_4	.097	-	-
HSO_4	-.003	-	-
HCO_3	-	-	-
CO_3	-	-	-

the further complications are minimal. Thus, it is easier and less likely to lead to error if these terms are always included than if choices are made in each case to include or exclude them.

Both θ_{ij} and ψ_{ijk} undoubtedly vary with temperature, and there are heat of mixing data which give their temperature derivatives at 25°C (Phutela and Pitzer, 1986a). Until heat of mixing measurements become generally available at higher temperature, however, we must depend primarily on solubility data for the values of θ_{ij} and ψ_{ijk} at high temperatures. Pabalan and Pitzer (1987b) found that the mineral solubilities in many systems could be fitted with constant θ's at their 25°C values together with ψ's either constant or varying with temperature in a simple manner. Figures 4 and 5 show the results for the systems $NaCl-KCl-H_2O$ and $NaCl-MgCl_2-H_2O$, respectively. In each case the parameter giving the temperature dependence of $\psi_{Na,K,Cl}$ or $\psi_{Na,Mg,Cl}$ was determined to best fit the array of solubility measurements above 25°C. Møller (submitted) obtained excellent agreement for the solubility of NaCl in the $NaCl-CaCl_2-H_2O$ system with a temperature-independent $\psi_{Na,Ca,Cl}$. Table 6 includes the θ's and ψ's valid at elevated temperatures for several systems of interest.

APPLICATIONS

Solubilities of Solids

Since solubility calculations are discussed in detail by Weare in his chapter, only brief comments are included here. A multicomponent example at high temperature is shown in Figure 6. Here the solubilities of both NaCl and of KCl at fixed $MgCl_2$ molality are indicated for the four-component system $NaCl-KCl-MgCl_2-H_2O$. Since all parameters were evaluated in simpler systems, the curves on Figure 6 are independently

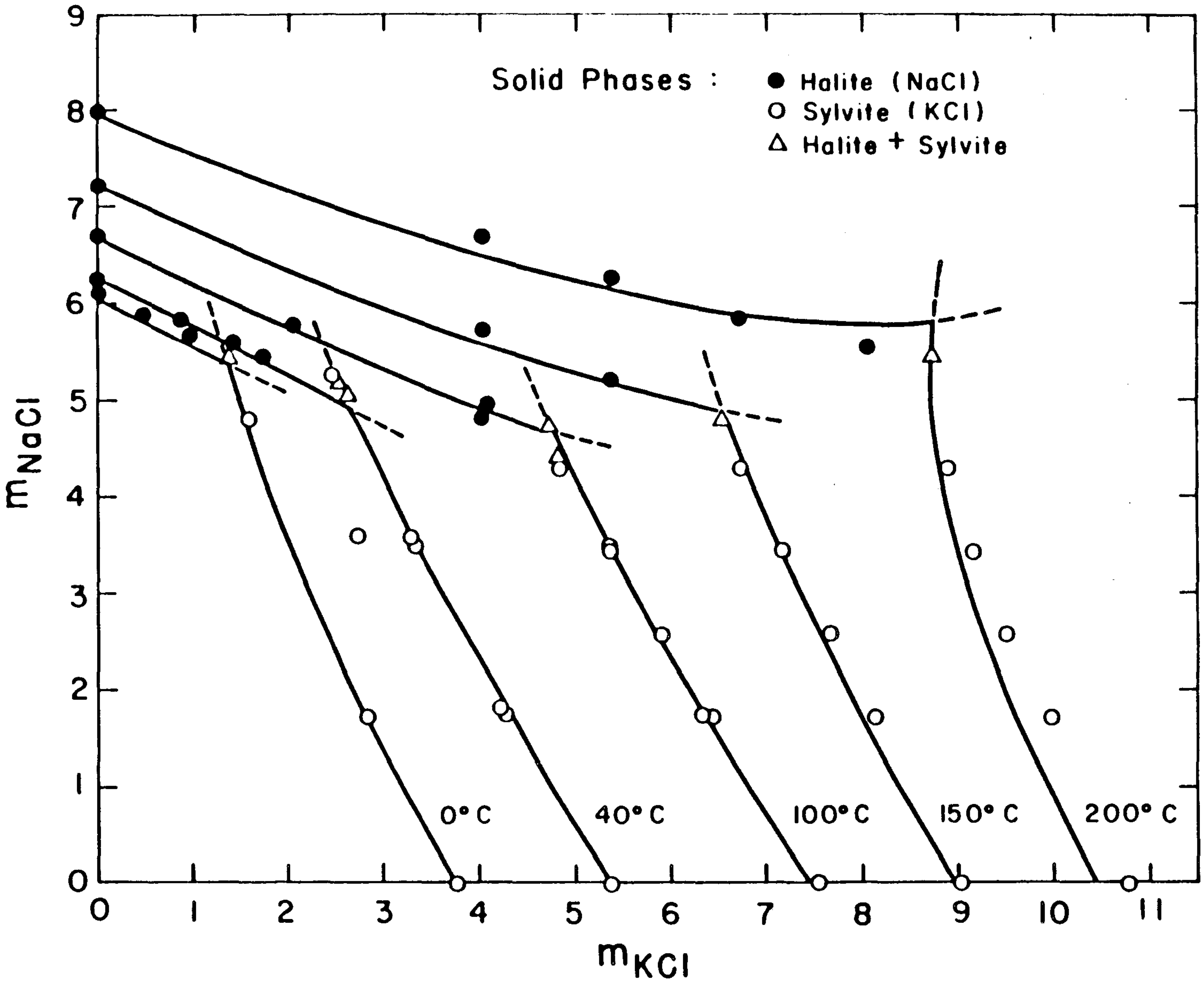

Figure 4. Calculated solubilities in the ternary mixture NaCl-KCl-H_2O compared with experimental data taken from Linke and Seidell (1965). The intersections of isothermal curves represent calculated triple points. One parameter in the $\psi_{Na,K,Cl}$ function was adjusted to fit the solubilities above 25°C.

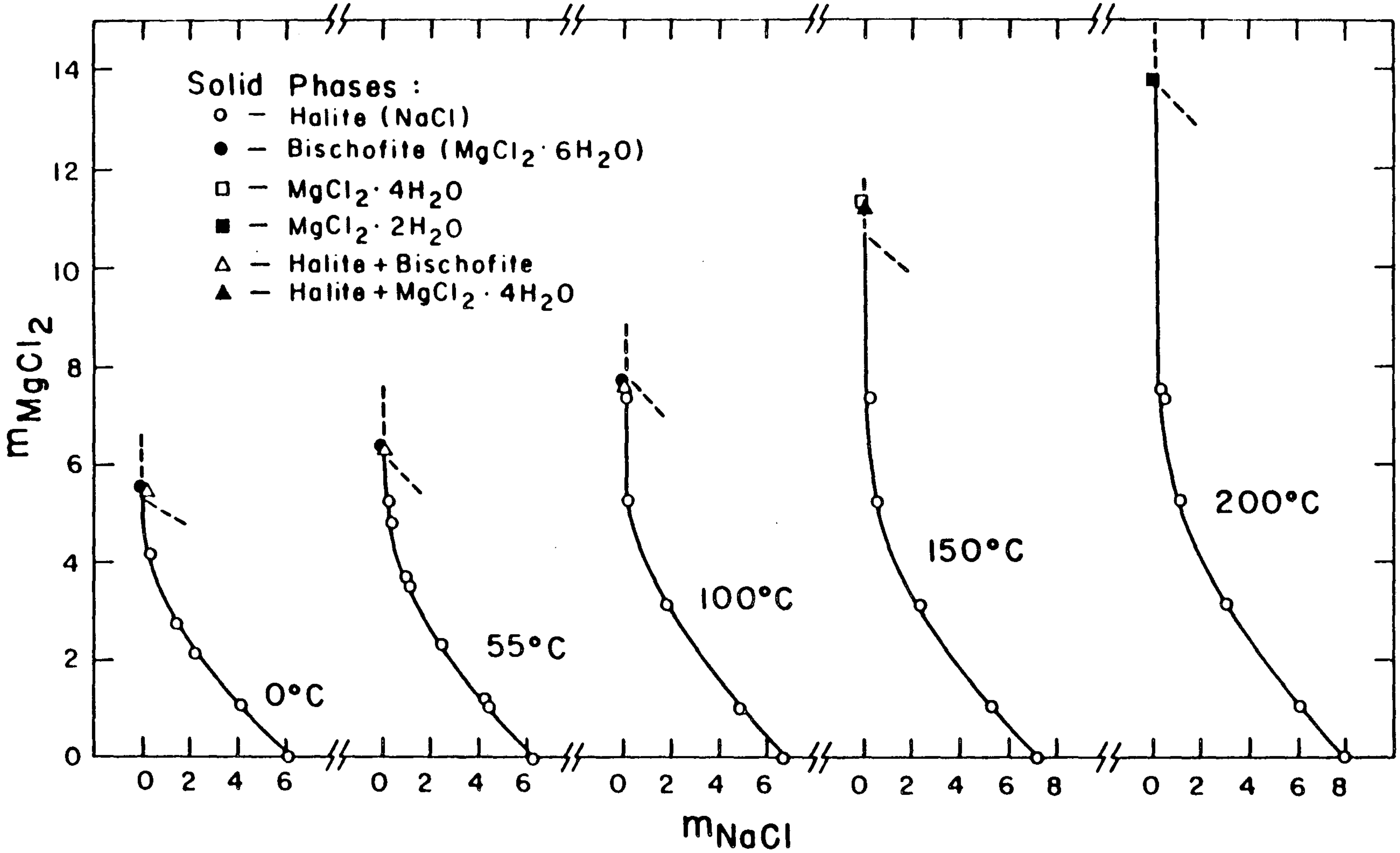

Figure 5. Calculated and experimental solubilities in the $NaCl-MgCl_2-H_2O$ system. Experimental data below 100°C are from Linke and Seidell (1965), while those above 100°C are from Akhumov and Vasil'ev (1932). The dashed curves are extrapolations of the solubilities of either $MgCl_2 \cdot nH_2O$ or NaCl into the supersaturated solution concentration of the other solid. The intersection of the curves denotes the calculated triple point. One parameter in the $\psi_{Na,Mg,Cl}$ function was adjusted to fit the solubilities above 25°C.

Table 6: Mixed Electrolyte Parameters for High Temperatures

i	j	k	θ_{ij}	ψ_{ijk}
Na	K	Cl	-0.012	-0.0068 + 1.68E-5T
Na	Mg	Cl	0.07	0.0199 - 9.51/T
Na	Ca	Cl	0.05	-0.003
K	Mg	Cl	0	0.0259 - 14.27/T
Cl	SO_4	Na	0.030	0.00
		K		-0.005
		Mg		-0.1175 + 32.63/T
Cl	OH	Na	-0.050	0.0273 - 9.93/T
SO_4	OH	Na	-0.013	0.0302 - 11.69/T

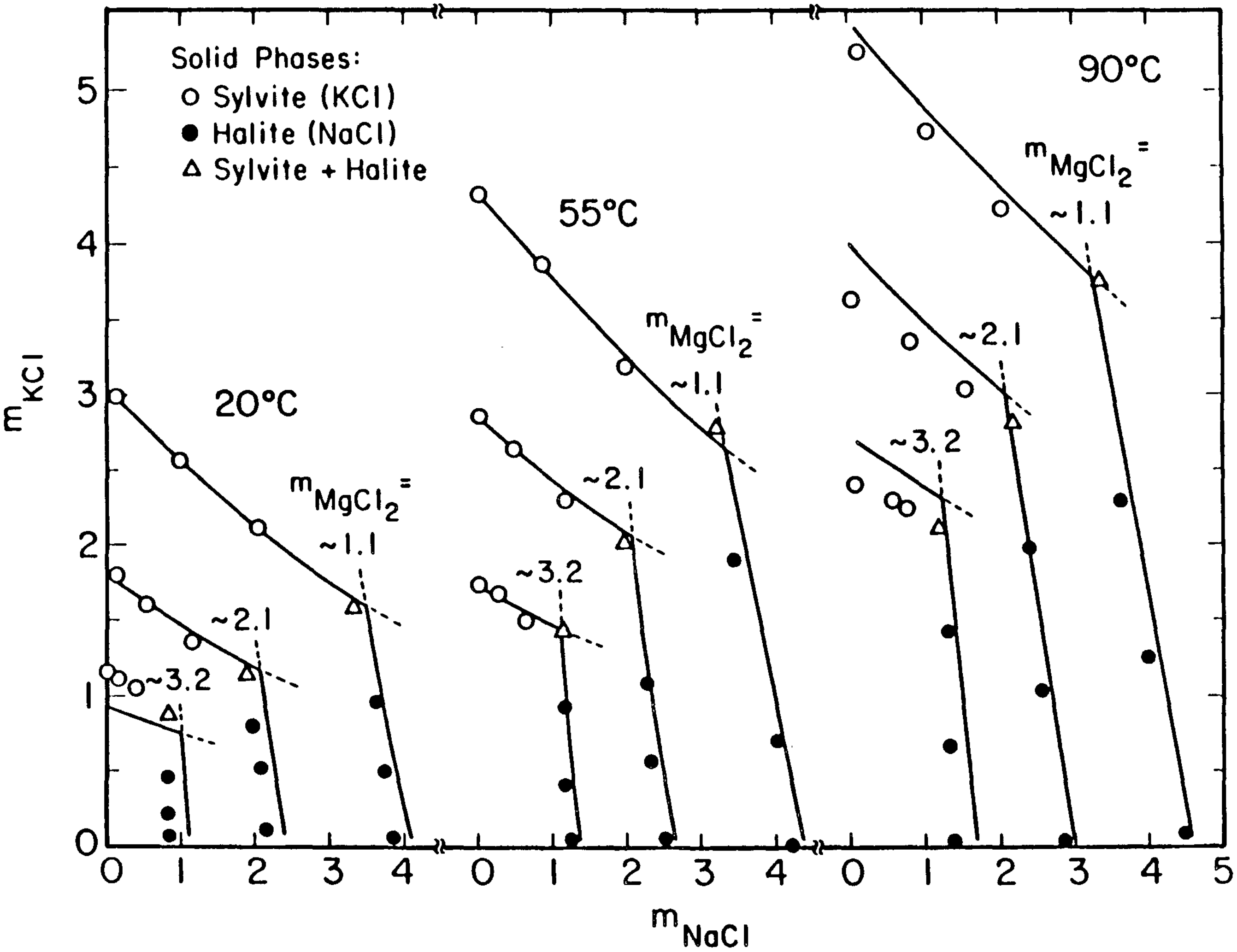

Figure 6. Predicted and experimental solubilities of halite and/or sylvite in the quaternary system NaCl-KCl-$MgCl_2$-H_2O at 20, 55, and 90°C and at $MgCl_2$ molalities of approximately 1.1, 2.1, and 3.2. Experimental data are from Kayser (1923).

determined predictions of the solubilities shown. While the agreement is not perfect, it approaches the accuracy of the solubility measurements. This calculation was first presented by Pabalan and Pitzer (1987b).

There are many calculations for 25°C of mineral solubilities in complex, concentrated brines. In addition to those of Harvie and Weare (1980) and Harvie et al. (1982, 1984), other notable examples include Krumgalz and Millero (1982, 1983), Gueddari et al. (1983), Monnin and Schott (1984), and Langmuir and Melchior (1985).

Complex-Ion Equilibria

Many heavy metals form a series of complex ions with chloride and other anions. Multiply charged cations also form various complex ions with hydroxide. Various other ions, if present in the solution, have specific effects on these complex-ion equilibria. A good example of the use of the present model is the treatment of lead chloride complexes by Millero and Byrne (1984). They consider the effects of H^+, Na^+, Mg^{2+}, and Ca^{2+} on the effective complexation constants.

Vapor-Phase Equilibria

Within the criterion of the present model, water of liquid-like density as solvent, one can calculate the fugacities of vapor species in equilibrium. The activity of water is obtained from the osmotic coefficient.

$$\ln a_1 = -\phi M_1 \sum m_i/1000 \tag{47}$$

where M_1 is the molecular mass of water and the sum is over all solute species. The activity of a volatile solute species is given by

$$a_i = m_i\gamma_i \tag{48}$$

provided that species is recognized as a solute in the liquid phase. In some cases a solute is so fully dissociated in the liquid that one considers a direct relationship between the ν_M cations and ν_X anions of the ionized solute and the associated vapor, whereupon

$$ln\ a_i = \nu_M\ ln(m_M\gamma_M) + \nu_X\ ln(m_X\gamma_X). \qquad (49)$$

Given the activities of the volatile species, one can calculate the vapor fugacities from the Henry's constants and the vapor fugacity of water. Then the pressure and composition of the vapor phase is easily calculated on an ideal-gas basis. For moderately imperfect gases, the fugacity coefficients are readily obtained if the pertinent gas-phase second virial coefficients are known or can be estimated by a method such as that of Tsonopoulos (1974). More substantial departure from the ideal gas requires the use of a more comprehensive equation of state to determine the fugacities (see Holloway, 1977). These methods are steadily improving and are often reported in the chemical engineering journals.

An interesting application of the present solution model concerns the vapor in equilibrium with atmospheric aerosols where droplets contain mixed electrolytes. When the relative humidity decreases below 75%, these solutions become very concentrated with ionic strength above 10 $\text{mol}\cdot\text{kg}^{-1}$. Clegg and Brimblecomb (submitted) show that strong acids such as HNO_3 and HCl develop appreciable vapor pressure under these conditions. They have extended these studies to include the vapor pressures of various acids with marine seasalt aerosols (Brimblecomb and Clegg, submitted).

Another set of interesting applications involving neutral as well as ionized solutes and vapor equilibria were presented by Chen et al. (1979). One example involves vapor-liquid equilibrium for the system $K^+ - CO_3^{2-} - HCO_3^- - CO_2 - H_2O$ at temperatures to 140°C and concentrations to 40 wt. % carbonate.

Thermal Properties

The enthalpy, entropy, and heat capacity of the liquid are all given by appropriate temperature derivatives of the Gibbs energy. These are standard thermodynamic relationships. Since temperature dependent expressions are given in Appendix B for various parameters of the present model, these derivatives are readily taken. Indeed, it is the standard-state heat capacity that is given, and it must be integrated to obtain the enthalpy or entropy. The total entropy of the liquid as a function of temperature and pressure is required for reversible flow processes where entropy is conserved. Similarly the enthalpy is required for irreversible, throttled processes. In other cases where heat transfer is recognized, the enthalpy of the fluid is also needed.

The total fluid entropy and enthalpy for $NaCl-H_2O$ are tabulated by Pitzer et al. (1984) for the range to 6 $mol \cdot kg^{-1}$, 300 C, and 1 kbar. For calculations concerning seawater and related fluids, it is often sufficient to take the thermal properties of an appropriate molality of NaCl in H_2O. The parameters of the present model, however, allow the explicit inclusion of other substantial components if desired.

SUPPLEMENTARY COMMENTS

With increasing accuracy and precision of experimental measurements, empirical functions that first seemed adequate will need to be improved or replaced. Some comments concerning the desirable procedure for improvement may be appropriate. Since there is now a very extensive base of parameters for various interactions, their continued validity should be retained as far as possible. Since the extended Debye-Hückel term f(I) or its derivative enters the equations for all properties, it should remain unchanged. It is shown in Appendix A that modifications of the ionic-strength dependence of this term will only make corresponding changes in the ionic-strength dependence of the second virial coefficients. Thus one can accomplish an improvement of this type by a change in the second virial coefficients instead of f(I).

Implicit in f(I) is the Debye-Hückel parameter A and in turn the dielectric constant or relative permittivity. At 25°C the uncertainty is so small, that no problem seems likely, but the temperature dependence of the dielectric constant is not as accurately known as would be desired. Most of the high-temperature correlations within the present model have used the equation of Bradley and Pitzer (1979) for the dielectric constant. This equation is valid to 350°C and 1 kbar. Until an alternate equation is clearly established as superior, it seems desirable to retain the Bradley and Pitzer equation.

At present, the other equation in significant use is that of Uematsu and Franck (1980). It is somewhat more complex but has the advantage of validity to higher temperature, 550°C. In the range below 350°C it is not clear which equation better represents the true property of water, since measurements disagree by more than the difference between the equations. The values from 0 to 100°C recommended by the International Union of Pure and Applied Chemistry (Kienitz and Marsh, 1981), fall closer to those given by the Bradley and Pitzer equation. Thus, for work below 350°C there is no need to change at this time. When a change to a definitely superior equation is made, it will be necessary to present alternate sets of values of those other parameters that are very accurately known for use with each dielectric constant equation until the entire array is available on the new basis.

Fortunately, activity and osmotic coefficients and as a result, solubilities and vapor pressures, depend only on the dielectric constant itself, and the uncertainties are quite small. The problem is more serious where the temperature derivative is required for enthalpies and entropies, and it is much more serious for heat capacities which involve the second temperature derivative.

In contrast to changes in f(I) which have a general effect, changes can be made in the ionic-strength dependence of the second virial coefficient for a particular ion interaction or even for a subcategory of ions without any affect on the rest of the model. Thus Holmes and Mesmer (1986) recommend the use of $\alpha_1 = 1.4$ instead of 2.0 for the alkali metal sulfates. Kodytek and Dolejs (1986) found that inclusion of a $\beta^{(2)}$ term (with $\alpha_2 = 6$) for 3-1 electrolytes gave an appreciably better fit. Since their $\beta^{(2)}$ values are positive, this is not an indication of ion pairing in the lanthanide salts; rather it represents just a more flexible empirical expression for the ionic-strength dependence in this case. Improvements of this type can be made without disturbing the previously determined expressions for other parameters.

ACKNOWLEDGEMENTS

I thank all of my collaborators in research on this electrolyte model and especially Dr. Roberto Pabalan whose advice and assistance was particularly related to parts of this chapter. It has been a pleasure to cooperate with Dr. John Weare in this area of research. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering, and Geosciences of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

APPENDIX A: THEORETICAL BACKGROUND

There are alternate formulations of rigorous statistical mechanics for multicomponent fluid systems. The McMillan-Mayer (1945) system is appropriate where a solvent, in our case water, is always the most abundant component. In this system the interactions between solute species are given by potentials of mean force in the solvent and the detailed interaction of individual solvent molecules can largely be ignored. The excess Helmholtz energy can be expressed in a power series in concentrations $c_i, c_j, \cdots$ of solute species

$$A^{ex}/VkT = \sum_i \sum_j c_i c_j \overset{\circ}{B}_{ij} + \sum_i \sum_j \sum_k c_i c_j c_k \overset{\circ}{C}_{ijk} + \cdots \qquad (A1)$$

The quantities $\overset{\circ}{B}_{ij}$, $\overset{\circ}{C}_{ijk}$, etc. arise from the binary, tertiary, etc. solute-solute interactions in the presence of the solvent and in the limit of low solute concentration; they depend on the solvent and the temperature but not on the solute concentrations. They can be calculated from the potentials of mean force and can be called the second, third, etc. virial coefficients.

When ions are present, with long-range (R^{-1}) interparticle potentials, the integrals for $\overset{\circ}{B}_{ij}$, $\overset{\circ}{C}_{ijk}$, etc. for interionic interactions diverge. Mayer (1950) showed how the calculation could be rearranged to avoid this divergence and Friedman (1962) developed further this method. Friedman's equations (6.10) and (13.44), with minor changes in symbols, give for the excess Helmholtz energy

$$A^{ex}/VkT = -\kappa^3/12\pi + \sum_i \sum_j c_i c_j B_{ij}(\kappa) + \sum_i \sum_j \sum_k c_i c_j c_k C_{ij}(\kappa) + \cdots (A2)$$

The first term on the right is just the Debye-Hückel limiting law with the reciprocal length κ defined by

$$\kappa^2 = (4\pi e^2/\varepsilon kT) \sum_i c_i z_i^2 \qquad \text{(A3)}$$

Here ε is the dielectric constant or relative permittivity of the solvent, e the electronic charge, and z_i the number of charges on particle i. The sum in equation (A3) is clearly related to the ionic strength.

In equation (A2) the virial coefficients B_{ij}, C_{ijk}, etc. differ from the corresponding B°_{ij}, C°_{ijk}, etc. in equation (A1) by the omission of the terms which, when rearranged, became the Debye-Hückel term. This transformation gives B_{ij}, C_{ijk}, etc. a dependence on κ in addition to their dependence on solvent properties, etc.

In proceeding to the general equation of the model, one shifts to the Gibbs energy and to molalities instead of concentrations. The Debye-Hückel term can be transformed exactly. It is assumed that other effects of this transformation can be absorbed in the virial coefficients which will be determined empirically. One then has

$$G^{ex}/n_w RT = -\alpha I^{3/2} + \sum_i \sum_j m_i m_j \, \beta_{ij}(I) + \cdot \cdot \cdot \qquad \text{(A4)}$$

where n_w is number of kg of water and α is the Debye-Hückel parameter. If one sums only over interactions of ions of opposite sign and ignores the ionic strength dependency of β_{ij}, this is equivalent to the equation proposed by Bronsted (1922). One now finds that the ionic strength dependency of β_{ij} is very great, but that it can be reduced by replacing the Debye-Hückel limiting law by an extended term. This was first suggested on an empirical basis by Guggenheim (1935). A test of several extended forms for the Debye-Hückel term (Pitzer, 1973) led to the choice $(\alpha/b)I\,ln(1+bI^{\frac{1}{2}})$ with b an empirical constant. This can be rearranged

$$\begin{aligned}\alpha I \ln(1 + bI^{1/2})/b &= \alpha(I^{3/2} - bI^2/2 + b^2I^{5/2}/3 \cdot \cdot \cdot \cdot) \\ &= \alpha I^{3/2} - I^2\alpha q(I) \\ &= \alpha I^{3/2} - (\sum_i \sum_j m_i m_j z_i{}^2 z_j{}^2) q(I)(\alpha/4) \qquad \text{(A5)}\end{aligned}$$

where q(I) is a function of ionic strength but not of individual molalities. Thus, in addition to the limiting law term $\alpha I^{3/2}$, the remaining contribution of the extended D-H term has exactly the same molality dependence as the second virial coefficient term of equation (A4) and these can be combined. The particular form for the extended D-H term was chosen to minimize the ionic strength dependence of the resulting second virial coefficient term

$$\lambda_{ij}(I) = \beta_{ij}(I) + z_i{}^2 z_j{}^2 \; q(I)(\alpha/4) \qquad \text{(A6)}$$

at high ionic strength.

The higher-order electrostatic term for unsymmetrical mixing of ions of the same sign, which was identified by Friedman (1962), appears as a special term within the ionic strength dependent second virial coefficient. Hence it does not need to be recognized separately at this point. Its evaluation on the molality basis was given by Pitzer (1975, 1983) and is discussed below. Our final form of equation can then be written as

$$\begin{aligned}G^{ex}/n_w RT = f(I) &+ \sum_i \sum_j m_i m_j \lambda_{ij}(I) \\ &+ \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk}(I) + \cdot \cdot \cdot \cdot \cdot \qquad \text{(A7)}\end{aligned}$$

The Debye-Hückel term f(I) includes the limiting law and depends only on the ionic strength. The second virial coefficients $\lambda_{ij}(I)$ are functions of ionic strength and include terms for mixing of ions of the same sign but different charge as appropriate. With increasing molalities of solutes, additional terms will be required in this power series to attain a given accuracy. In the semi-empirical application, the required number of terms will become apparent.

An alternate presentation of basic theory (Pitzer, 1973, 1979) is less abstract and gives more of a physical picture and an estimate of the pattern of ionic strength dependency of the second virial coefficient. These aspects may be useful to readers. But this alternate presentation includes approximations which the Mayer-Friedman treatment avoids and which are not intrinsic to the form of equation (A7).

We return now to the higher-order electrostatic term for unsymmetrical mixing (Pitzer, 1975, 1983). The second virial coefficient $B_{ij}(\kappa)$ of equation (A2) is shown by Friedman (1962) to be given by

$$B_{ij}(\kappa) = (2\pi z_i z_j \ell/\kappa^2)\ J_{ij}(\kappa, z_i, z_j \cdot \cdot \cdot) \tag{A8}$$

with the electrostatic length

$$\ell = e^2/\varepsilon kT \tag{A9}$$

We note that the interionic potential of mean force can be written as

$$v_{ij} = u_{ij} + kTz_i z_j \ell/r \tag{A10}$$

where the second term is the electrostatic interaction and u_{ij}, a function of the interionic distance r, is the short-range potential. Then the function J_{ij} of (A8) is

$$J_{ij} = -(\kappa^2/z_i z_j \ell) \int_0^\infty [\exp(q_{ij} - u_{ij}/kT)-1-q_{ij}-q_{ij}{}^2/2]r^2 dr \tag{A11}$$

with

$$q_{ij} = -(z_i z_j \ell/r)\ \exp(-\kappa r) \tag{A12}$$

The integral in equation (A11) cannot be evaluated, in general, without knowledge of the short-range potential u_{ij}. Since that quantity is not known accurately, the entire second virial coefficient is treated as an empirical quantity. But for the particular case of ions of the same sign, an approximation yields useful results.

Ions of the same sign repel one another strongly enough that they seldom approach one another closely; hence the short-range potential should have little or no effect. This can be seen mathematically in equation (A11). If q_{ij} is large and negative for the range of r for which u_{ij} differs from zero, then the value of $\exp(q_{ij})$ is extremely small throughout this range. Thus, provided u_{ij} is positive (or if negative, is small), the effect of u_{ij} will be negligible.

In view of this situation, one can evaluate the effect of electrostatic forces on the difference terms Φ_{ij} without making any detailed assumption about short-range forces. We write

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \tag{A13}$$

where the first term on the right arises from the combined effects of short-range forces acting directly or through the solvent, of the use of molalities instead of concentration, and of the difference in the Debye-Hückel term in equation (A2) from that in (A7) or (28). The second term ${}^{E}\theta_{MN}$ will be calculated from the corresponding terms of the cluster-integral theory with the omission of short-range forces. From the definition of Φ_{MN} we have

$${}^{E}\theta_{MN} = {}^{E}\lambda_{MN} - (z_N/2z_M)\,{}^{E}\lambda_{MM} - (z_M/2z_N)\,{}^{E}\lambda_{NN} \tag{A14}$$

$${}^{E}\lambda_{ij} = (z_i z_j/4I)J_{ij} \text{ with } u_{ij} = 0 \tag{A15}$$

$$J_{ij} = \frac{\kappa^2}{z_i z_j \ell}\int_0^\infty \left(1 + q_{ij} + \frac{1}{2}q_{ij}^2 - e^{q_{ij}}\right)r^2\,dr \tag{A16}$$

With the substitutions

$$y = \kappa r \tag{A17}$$

$$x = z_i z_j \ell \kappa \tag{A18}$$

$$q = -(x/y)e^{-y} \tag{A19}$$

$$J(x) = x^{-1} \int_0^\infty (1 + q + \frac{1}{2} q^2 - e^q)y^2 \, dy \tag{A20}$$

In our working units

$$x_{ij} = 6 z_i z_j A_\phi I^{1/2} \tag{A21}$$

where for ions of the same sign x_{ij} is always positive. Also

$${}^{E}\theta_{MN} = (z_M z_N/4I)[J(x_{MN}) - \frac{1}{2} J(x_{MM}) - \frac{1}{2} J(x_{NN})] \tag{A22}$$

We also need the temperature derivative of ${}^{E}\theta$ and therefore of J. If $J' = \partial J/\partial x$, we find for ${}^{E}\theta'$ the expression

$${}^{E}\theta'_{MN} = -{}^{E}\theta_{MN}/I + (z_M z_N/8I^2)[x_{MN}J'(x_{MN}) - \frac{1}{2} x_{MM}J'(x_{MM}) - \frac{1}{2} x_{NN}J'(x_{NN})] \tag{A23}$$

For J the integrals of the second and third terms in the parentheses in equation (A20) are straightforward with the results

$$J = \frac{1}{4} x - 1 + J_2 \tag{A24}$$

$$J' = \frac{1}{4} - (J_2/x) + J_3 \tag{A25}$$

$$J_2 = x^{-1} \int_0^\infty (1 - e^q)y^2 dy \tag{A26}$$

$$J_3 = x^{-1} \int_0^\infty \exp(q - y) y dy \tag{A27}$$

There are no simple integrals for J_2 and J_3 but they are readily evaluated numerically with modern computers. The resulting functions ${}^E\theta$ and ${}^E\theta'$ for 2-1, 3-1, and 4-1 mixing are shown in figure A1.

For more efficient compution of these functions than numerical integration, several methods have been proposed (Pitzer, 1975), (Roy et al., 1983), (Harvie, 1981). Harvie's method uses two Chebyshev polynomial approximations, one for $x \leq 1$ and the other for $x \geq 1$. The appropriate equations for these regions follow:

Region I. $x \leq 1$

$$z = 4\,x^{1/5} - 2 \tag{A28}$$

$$\frac{dz}{dx} = \frac{4}{5}\,x^{-4/5} \tag{A29}$$

$$\left.\begin{aligned} b_k &= z\,b_{k+1} - b_{k+2} + a_k^{I} &\quad \text{(A30)}\\ d_k &= b_{k+1} + z\,d_{k+1} - d_{k+2} &\quad \text{(A31)}\end{aligned}\right\}\ k = 0,\ 20$$

Region II. $x \geq 1$

$$z = \frac{40}{9}\,x^{-1/10} - \frac{22}{9} \tag{A32}$$

$$\frac{dz}{dx} = -\frac{40}{90}\,x^{-11/10} \tag{A33}$$

$$\left.\begin{aligned} b_k &= z\,b_{k+1} - b_{k+2} + a_k^{II} &\quad \text{(A34)}\\ d_k &= b_{k+1} + z\,d_{k+1} - d_{k+2} &\quad \text{(A35)}\end{aligned}\right\}\ k = 0,\ 20$$

Using the calculated values for the b_k and the d_k, $J(x)$ and $J'(x)$ can be calculated from the following formulas:

$$J(x) = \frac{1}{4}\,x - 1 + \frac{1}{2}(b_0 - b_2) \tag{A36}$$

$$J'(x) = \frac{1}{4} + \frac{1}{2}\frac{dz}{dx}\,(d_0 - d_2) \tag{A37}$$

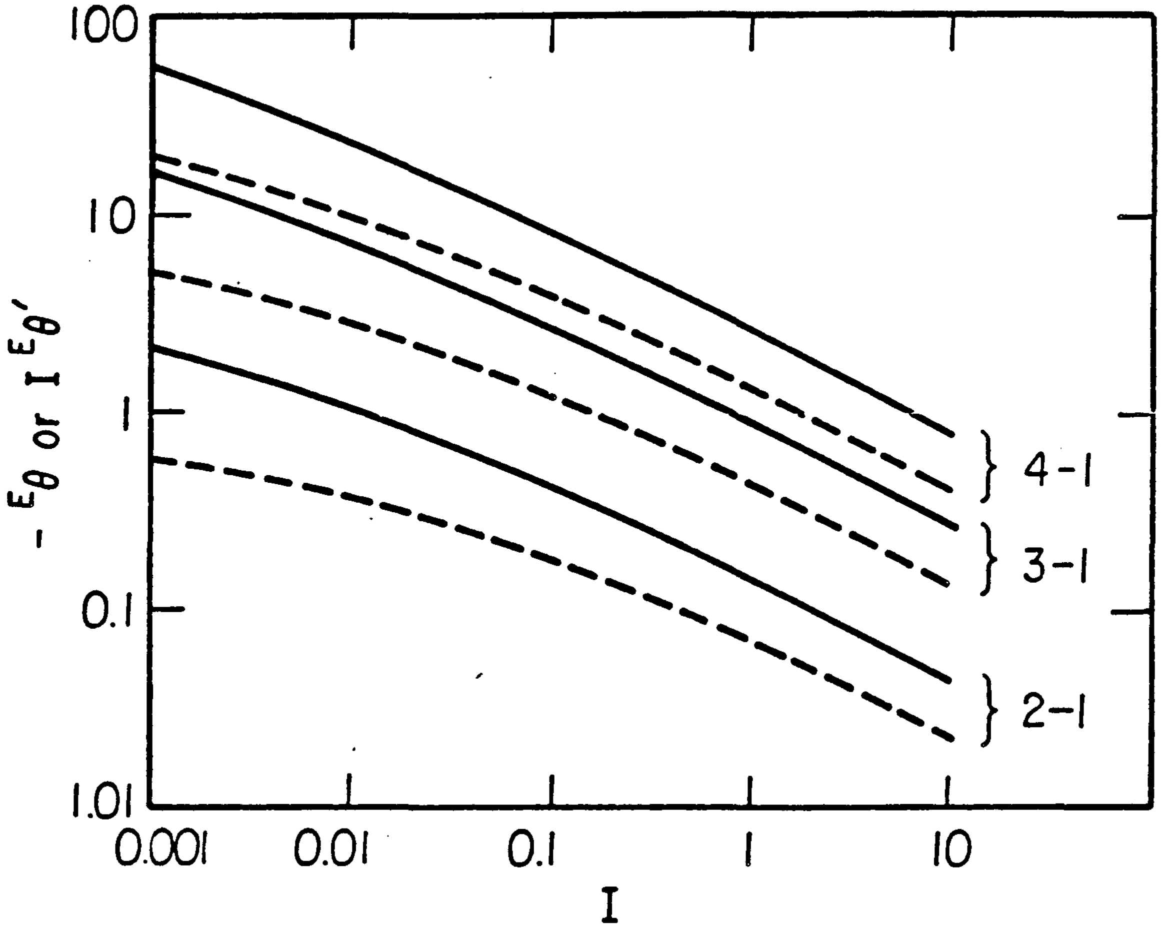

Figure A1. The functions - $^E\theta$ (solid curves) and I $^E\theta'$ (dashed curves) for mixing ions of charge types 2-1, 3-1, and 4-1.

Some discussion with regard to the calculation of the arrays b_k and d_k is appropriate. The coefficients a_k^I and a_k^{II} are given in Table A1. By definition $b_{21} = b_{22} = d_{21} = d_{22} = 0$. Therefore, by using Eq. (A30) or (A34) the numbers b can be generated in decreasing sequence. Similar arguments apply to the array d. The values $J(1) = 0.116437$ and $J'(1) = 0.160527$ can be used to check a program for this calculation.

Another theoretical topic concerns the possible ionic-strength dependence of second virial coefficients for interactions of ions with neutral molecules containing dipole or higher electrical moments. The work of Kirkwood (1934) pertains to this question, but it considers only electrical effects subject to a distance of closest approach and ignores all other effects of short range forces which are normally the dominant terms. For charge-dipole effects on the activity coefficient of the dipolar molecule i, Kirkwood's equation (21) yields

$$\delta \ln \gamma_i = - \frac{3\pi e^2 \mu_i^2 \sum c_j z_j^2}{2a\varepsilon^2 k^2 T^2 (1 + \kappa a + \kappa^2 a^2/3)} \qquad \text{(A38)}$$

with μ_i the dipole moment of i and c_j and z_j the concentration and charge on ion j. Also a is the distance of closest approach of an ion to the molecule and κ is the Debye reciprocal length which is related to the ionic strength. For each term in the sum, equation (A38) yields the electrical contribution to a second virial coefficient λ_{ij}. The appearance of κ in the denominator indicates an ionic strength dependence. But for typical values of the dipole moment and other quantities, this term is very small compared to that for short-range forces. For quadrupole or higher moments the corresponding term is even smaller. Hence there is no present indication that an ionic-strength dependence need be considered for the second virial coefficients for neutral-ion interactions.

Table A1. Numerical arrays for calculating J(x) and J'(x)

k	a_k^I	a_k^{II}
0	1.925154014814667	.628023320520852
1	-.060076477753119	.462762985338493
2	-.029779077456514	.150044637187895
3	-.007299499690937	-.028796057604906
4	.000388260636404	-.036552745910311
5	.000636874599598	-.001668087945272
6	.000036583601823	.006519840398744
7	-.000045036975204	.001130378079086
8	-.000004537895710	-.000887171310131
9	.000002937706971	-.000242107641309
10	.000000396566462	.000087294451594
11	-.000000202099617	.000034682122751
12	-.000000025267769	-.000004583768938
13	.000000013522610	-.000003548684306
14	.000000001229405	-.000000250453880
15	-.000000000821969	.000000216991779
16	-.000000000050847	.000000080779570
17	.000000000046333	.000000004558555
18	.000000000001943	-.000000006944757
19	-.000000000002563	-.000000002849257
20	-.000000000010991	.000000000237816

APPENDIX B: NUMERICAL PARAMETERS FOR TEMPERATURE DEPENDENCY EXPRESSIONS

The following are the temperature functions for the parameters of the present solution model and for the standard state heat capacities of aqueous electrolytes reported by various investigators. The pressure dependencies of the ion-interaction coefficients are currently neglected except for NaCl(aq), HCl(aq), and NaOH(aq), which have the requisite PVT data available in sufficient quantity to allow their evaluation. In the case of standard state heat capacities, only NaCl(aq) and HCl(aq) have both P- and T-dependent functions. The standard state heat capacities of NaOH(aq) are not included since present information is inadequate. This lack is not important for the solubility of NaOH, however, since it is beyond the valid concentration range of the present model. In all the equations, T_R and T refer to the reference temperature of 298.15 K and the temperature of interest, respectively. Pressures are designated by P and are in bars; standard state heat capacities are in units of J K^{-1} mol^{-1}.

NaCl(aq)

Ion-interaction parameters - Pitzer et al. (1984), 273-573 K and saturation pressure to 1 kbar. P refers to pressure in bars.

$$f(T) = Q1/T + Q2 + Q3\,P + Q4\,P^2 + Q5\,P^3 + Q6\,ln(T) + (Q7 + Q8\,P + Q9\,P^2 + Q10\,P^3)T + (Q11 + Q12\,P + Q13\,P^2)T^2 + (Q14 + Q15\,P + Q16\,P^2 + Q17\,P^3)/(T-227) + (Q18 + Q19\,P + Q20\,P^2 + Q21\,P^3)/(680-T)$$

	$\beta^{(0)}$	$\beta^{(1)}$	$C^{\phi} = 2C$
Q1	-656.81518	119.31966	-6.1084589
Q2	24.86912950	-0.48309327	4.0217793E-1
Q3	5.381275267E-5	0	2.2902837E-5
Q4	-5.588746990E-8	0	0
Q5	6.589326333E-12	0	0
Q6	-4.4640952	0	-0.075354649
Q7	0.01110991383	1.4068095E-3	1.531767295E-4
Q8	-2.657339906E-7	0	-9.0550901E-8
Q9	1.746006963E-10	0	0
Q10	1.046261900E-14	0	0
Q11	-5.307012889E-6	0	-1.538600820E-8
Q12	8.634023325E-10	0	8.6926600E-11
Q13	-4.178596200E-13	0	0
Q14	-1.579365943	-4.2345814	0.3531041360
Q15	2.202282079E-3	0	-4.3314252E-4
Q16	-1.310550324E-7	0	0
Q17	-6.381368333E-11	0	0
Q18	9.706578079	0	-0.09187145529
Q19	-0.02686039622	0	5.1904777E-4
Q20	1.534474401E-5	0	0
Q21	-3.215398267E-9	0	0

Standard state heat capacity - the following equation was fit to values from 273-573 K and at 1 bar or saturation pressure tabulated by Pitzer et al. (1984), Table A-4). For values at other pressures, the reader is referred to the tables and equations given by Pitzer et al. (1984) which are valid in the range 273-573 K and to 1 kbar pressure.

$$C_p^\circ = -1.848175E6 + 4.411878E7/T + 3.390654E5\,ln(T)$$
$$- 8.893249E2T + 4.005770E\text{-}1T^2 - 7.244279E4/(T-227)$$
$$- 4.098218E5/(647-T)$$

KCl(aq)

Ion-interaction parameters - Holmes and Mesmer (1983a), 273-523 K.

$$f(T) = Q1 + Q2(1/T-1/T_R) + Q3\,ln(T/T_R) + Q4(T-T_R) + Q5(T^2-T_R^2) + Q6\,ln(T-260)$$

	$\beta^{(0)}$	$\beta^{(1)}$	$C^{\phi} = 2C$
Q1	0.04808	0.0476	-7.88E-4
Q2	-758.48	303.9	91.270
Q3	-4.7062	1.066	0.58643
Q4	0.010072	0	-0.0012980
Q5	-3.7599E-6	0	4.9567E-7
Q6	0	0.0470	0

Standard state heat capacity - Holmes and Mesmer (1983a), 273-523 K.

$$C_p^\circ = -991.51 + 5.56452T - 0.00852996T^2 - 686/(T-270)$$

$\underline{MgCl_2(aq)}$

Ion-interaction parameters - de Lima and Pitzer (1983b), with equation for C_{MX}^{ϕ} modified to fit the solubility data, 298-473 K.

$f(T) = Q1\ T^2 + Q2\ T + Q3$

	$\beta^{(0)}$	$\beta^{(1)}$	$C^{\phi} = 2^{3/2}\ C$
Q1	5.93915E-7	2.60169E-5	2.41831E-7
Q2	-9.31654E-4	-1.09438E-2	-2.49949E-4
Q3	0.576066	2.60135	5.95320E-2

Standard state heat capacity - Phutela et al. (1987), 298-453 K

$$C_p^\circ = -7.39872E6/T + 7.96487E4 - 3.25868E2T + 5.98722E\text{-}1T^2 - 4.21187E\text{-}4T^3$$

$\underline{CaCl_2(aq)}$

Ion-interaction parameters - Møller (submitted), 298-523 K, 0-4 $mol \cdot kg^{-1}$.

$f(T) = Q1 + Q2\ T + Q3/T + Q4\ \ln T + Q5/(T-263) + Q6\ T^2 + Q7/(680-T)$

	$\beta^{(0)}$	$\beta^{(1)}$	$C^{\phi} = 2^{3/2}\ C$
Q1	-9.41895832E1	3.4787	-3.03578731E1
Q2	-4.0475002E-2	-1.5417E-2	-1.36264728E-2
Q3	2.34550368E3	0	7.64582238E2
Q4	1.70912300E1	0	5.50458061
Q5	-9.22885841E-1	0	-3.27377782E-1
Q6	1.51488122E-5	3.1791E-5	5.69405869E-6
Q7	-1.39082000	0	-5.36231106E-1

A simpler equation valid to 473 K and 4.3 $mol \cdot kg^{-1}$ is given by Phutela and Pitzer (1983).

Standard state heat capacity - Phutela et al. (1987), 298-373 K.

$$C_p^\circ = -1.26721E6/T + 7.41013E3 - 11.5222\ T$$

NA_2SO_4(aq)

Ion-interaction parameters - Holmes and Mesmer (1986), 273-498 K.

Note: these parameters are consistent with using a value of $\alpha_1 = 1.4$, instead of the usual value of 2.0.

$$f(T) = Q1 + Q2(T_R - T_R^2/T) + Q3(T^2 + 2T_R^3/T - 3T_R^2) + Q4(T + T_R^2/T - 2T_R) + Q5[ln(T/T_R) + T_R/T - 1] + Q6\{1/(T-263) + (263T - T_R^2)/[T(T_R - 263)^2]\} + Q7\{1/(680-T) + (T_R^2 - 680T)/[T(680 - T_R)^2]\}$$

	$\beta^{(0)}$	$\beta^{(1)}$	$C^{\phi} = 2^{3/2}\ C$
Q1	-1.727E-2	0.7534	1.1745E-2
Q2	1.7828E-3	5.61E-3	-3.3038E-4
Q3	9.133E-6	-5.7513E-4	1.85794E-5
Q4	0	1.11068	-3.9200E-2
Q5	-6.552	-378.82	14.2130
Q6	0	0	0
Q7	-96.90	1861.3	-24.950

Standard state heat capacity - Holmes and Mesmer (1986), 273-498 K.

$$C_p^\circ = -1206.2 + 7.6405T - 1.23672E{-}2T^2 - 6045/(T-263)$$

K_2SO_4(aq)

Ion-interaction parameters - Holmes and Mesmer (1986), 273-498 K.

Note: these parameters are consistent with using a value of $\alpha_1 = 1.4$, instead of the usual value of 2.0.

$$f(T) = Q1 + Q2(T_R - T_R^2/T) + Q3(T^2 + 2T_R^3/T - 3T_R^2) + Q4(T + T_R^2/T - 2T_R) + Q5[ln(T/T_R) + T_R.T - 1] + Q6\{1/(T-263) + (263T - T_R^2)/[T(T_R - 263)^2]\} + Q7\{1/(680-T) + (T_R^2 - 680T)/[T(680 - T_R)^2]\}$$

	$\beta^{(0)}$	$\beta^{(1)}$	$C^{\phi} = 2^{3/2}\ C$
Q1	0	0.6179	9.1547E-3
Q2	7.476E-4	6.85E-3	0
Q3	0	5.576E-5	0
Q4	4.265E-3	-5.841E-2	-1.81E-4
Q5	-3.088	0	0
Q6	0	-0.90	0
Q7	0	0	0

Standard state heat capacity;

$$C_p^\circ(K_2SO_4) = 2C_p^\circ(KCl) + C_p^\circ(Na_2SO_4) - 2C_p^\circ(NaCl)$$

$MgSO_4$(aq)

Ion-interaction parameters - Phutela and Pitzer (1986), 298-473 K. Note that the final column gives the temperature coefficients for C. For $MgSO_4$, this is related to C^{ϕ} by: $C^{\phi} = 4C$ (see equation 22).

$$f(T) = Q1(T/2 + 298^2/2T - 298) + Q2(T^2/6 + 298^3/3T - 298^2/2)$$
$$+ Q3(T^3/12 + 298^4/4T - 298^3/3) + Q4(T^4/20 + 298^5/5T - 298^4/4)$$
$$+ (298 - 298^2/T)Q5 + Q6$$

	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C = C^{\phi}/4$
Q1	-1.0282	-2.9596E-1	-1.3764E-1	1.0541E-1
Q2	8.4790E-3	9.4564E-4	1.2121E-1	-8.9316E-4
Q3	-2.33667E-5	0	-2.7642E-4	2.51E-6
Q4	2.1575E-8	0	0	-2.3436E-9
Q5	6.8402E-4	1.1028E-2	-2.1515E-1	-8.7899E-5
Q6	0.21499	3.3646	-32.743	0.006993

Standard state heat capacity - Phutela and Pitzer (1986), 298-473 K.

$$C_p^\circ = -6.2543E6/T + 6.5277E4 - 2.6044E2T + 4.6930E{-}1T^2 - 3.2656E{-}4T^3$$

HCl(aq)

Ion-interaction parameters - Holmes et al. (1987), 273-523 K. The equation and parameters listed are valid to 7 $mol\cdot kg^{-1}$, but this paper also includes more complex equations valid to 648 K and to 16 $mol\cdot kg^{-1}$; also note that the equations use ρ, the density in $kg\cdot m^{-3}$ of pure water at the particular P and T and that they include pressure dependence to 400 bars.

$$f(T) = Q1 + Q2\ \ln(\rho/997) + Q3(\rho-997) + Q4(T-T_R) + Q5(P-1)$$

	$\beta^{(0)}$	$\beta^{(1)}$	$C = C^{\phi}/2$
Q1	0.17690	0.2973	0.362E-3
Q2	-9.140E-2	16.147	0
Q3	0	-1.7631E-2	0
Q4	-4.034E-4	0	-3.036E-5
Q5	6.20E-6	7.20E-5	0

Standard State heat capacity - Holmes et al. (1987), 273-648 K.

$$C^{\circ}_p = 17.93 - 16.79T/(T-240) + 6.4579E5\ TX_p$$

where

$$X_p = [(\partial^2 \ln\varepsilon/\partial T^2)_P - (\partial \ln\varepsilon/\partial T)^2_P]/\varepsilon$$

with ε the dielectric constant (relative permittivity)

NaOH(aq)

Ion-interaction parameters - Pabalan and Pitzer (1987a), 0-350°C and saturation pressure to 400 bars. P refers to pressure in bars.

$$f(T) = Q1 + Q2\ P + (Q3 + Q4\ P)/T + Q5\ \ln(T) + (Q6 + Q7\ P)T$$
$$+ (Q8 + Q9\ P)T^2 + Q10/(T-227.) + (Q11 + Q12\ P)/(647.-T)$$

	$\beta^{(0)}$	$\beta^{(1)}$	$C^{\phi} = 2\ C$
Q1	2.7682478E+2	4.6286977E+2	-1.6686897E+1
Q2	-2.8131778E-3	0	4.0534778E-4
Q3	-7.3755443E+3	-1.0294181E+4	4.5364961E+2
Q4	3.7012540E-1	0	-5.1714017E-2
Q5	-4.9359970E+1	-8.5960581E+1	2.9680772
Q6	1.0945106E-1	2.3905969E-1	-6.5161667E-3
Q7	7.1788733E-6	0	-1.05530373E-6
Q8	-4.0218506E-5	-1.0795894E-4	2.3765786E-6
Q9	-5.88474E-9	0	8.9893405E-10
Q10	1.1931144E-1	0	-6.8923899E-1
Q11	2.4824963	0	-8.1156286E-2
Q12	-4.8217410E-3	0	0

Debye-Hückel Parameter

Most calculations for the present model have used the equation of Bradley and Pitzer (1979) for the dielectric constant and the density of water from the equation of Haar et al. (1984). Tables of values of A_{ϕ} and of the corresponding parameters for enthalpy, heat capacity, and volume were given by Bradley and Pitzer (1979) and are also available in other papers including Pitzer et al.(1984) and Ananthaswamy and Atkinson (1984). Møller (submitted) gives a seven-constant equation for A_ϕ at saturation pressure to 300°C.

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