

3. Activity Coefficients of Aqueous Species

3.1. Introduction

The thermodynamic activities (a_i) of aqueous solute species are usually defined on the basis of molalities. Thus, they can be described by the product of their molal concentrations (m_i) and their molal activity coefficients (γ_i):

$$a_i = m_i \gamma_i \quad (77)$$

The thermodynamic activity of the water (a_w) is always defined on a mole fraction basis. Thus, it can be described analogously by product of the mole fraction of water (x_w) and its mole fraction activity coefficient (λ_w):

$$a_w = x_w \lambda_w \quad (78)$$

It is also possible to describe the thermodynamic activities of aqueous solutes on a mole fraction basis. However, such mole fraction-based activities ($a_i^{(x)}$) are not the same as the more familiar molality-based activities ($a_i^{(m)}$), as they are defined with respect to different choices of standard states. Mole fraction based activities and activity coefficients (λ_i), are occasionally applied to aqueous nonelectrolyte species, such as ethanol in water. In geochemistry, the aqueous solutions of interest almost always contain electrolytes, so mole-fraction based activities and activity coefficients of solute species are little more than theoretical curiosities. In EQ3/6, only molality-based activities and activity coefficients are used for such species, so a_i always implies $a_i^{(m)}$. Because of the nature of molality, it is not possible to define the activity and activity coefficient of water on a molal basis; thus, a_w always means $a_w^{(x)}$.

Solution thermodynamics is a construct designed to approximate reality in terms of deviations from some defined ideal behavior. The complex dependency of the activities on solution composition is thus dealt with by shifting the problem to one of describing the activity coefficients. The usual treatment of aqueous solutions is one which simultaneously employs quantities derived from, and therefore belonging to, two distinct models of ideality (Wolery, 1990). All solute activity coefficients are based on molality and have unit value in the corresponding model of ideality, called molality-based ideality. The activity and activity coefficient of water are not constant in an ideal solution of this type, though they do approach unit value at infinite dilution. These solvent properties are derived from mole fraction-based ideality, in which the mole fraction activity coefficients of all species components in solution have unit value. In an ideal solution of this type, the molal activity coefficients of the solutes are not unity, though they approach it at infinite dilution (see Wolery, 1990).

Any geochemical modeling code which treats aqueous solutions must provide one or more models by which to compute the activity coefficients of the solute species and the solvent. In many codes, what is computed is the set of γ_i plus a_w . As many of the older such codes were constructed to deal only with dilute solutions in which the activity of water is no less than about 0.98, some of these just take the activity of water to be unity. With the advent of activity coefficient models

of practical usage in concentrated solutions (mostly based on Pitzer's 1973, 1975 equations), there has been a movement away from this particular and severe approximation. Nevertheless, it is generally the activity of water, rather than the activity coefficient of water, which is evaluated from the model equations. This is what was previously done in EQ3/6. However, EQ3/6 now evaluates the set of γ_i plus λ_w . This is done to avoid possible computational singularities that may arise, for example if heterogeneous equilibria happen to fix the activity of water (e.g., when a solution is saturated with both gypsum and anhydrite).

Good models for activity coefficients must be accurate. A prerequisite for general accuracy is thermodynamic consistency. The activity coefficient of each aqueous species is not independent of that of any of the others. Each is related to a corresponding partial derivative of the excess Gibbs energy of the solution (G^{EX}). The excess Gibbs energy is the difference between the complete Gibbs energy and the ideal Gibbs energy. Because there are two models of ideality, hence two models for the ideal Gibbs energy, there are two forms of the excess Gibbs energy, G^{EXm} (molality-based) and G^{EXx} (mole fraction-based). The consequences of this are discussed by Wolery (1990). In version 7.0 of EQ3/6, all activity coefficient models are based on ideality defined in terms of molality. Thus, the excess Gibbs energy of concern is G^{EXm} . The activity of water, which is based on mole-fraction ideality, is imported into this structure as discussed by Wolery (1990). The relevant differential equations are:

$$\ln \gamma_i = \frac{1}{RT} \frac{\partial G^{EXm}}{\partial n_i} \quad (79)$$

$$\ln a_w = -\frac{\Sigma m}{\Omega} + \frac{1}{RT} \frac{\partial G^{EXm}}{\partial n_w} \quad (80)$$

where R is the gas constant, T the absolute temperature, Ω the number of moles of solvent water comprising a mass of 1 kg ($\Omega \approx 55.51$), and:

$$\Sigma m = \sum_i m_i \quad (81)$$

the sum of molalities of all solute species. Given an expression for the excess Gibbs energy, such equations give a guaranteed route to thermodynamically consistent results (Pitzer, 1984; Wolery, 1990). Equations that are derived by other routes may be tested for consistency using other relations, such as the following forms of the cross-differentiation rule (Wolery, 1990):

$$\frac{\partial \ln \gamma_j}{\partial m_i} = \frac{\partial \ln \gamma_i}{\partial m_j} \quad (82)$$

$$\frac{\partial \ln a_w}{\partial n_i} = \frac{\partial \ln \gamma_i}{\partial n_w} - \frac{1}{n_w} \quad (83)$$

In general, such equations are most easily used to prove that a set of model equations is not thermodynamically consistent. The issue of sufficiency in proving consistency using these and related equations (Gibbs-Duhem equations and sum rules) is addressed by Wolery (1990).

The activity coefficients in reality are complex functions of the composition of the aqueous solution. In electrolyte solutions, the activity coefficients are influenced mainly by electrical interactions. Much of their behavior can be correlated in terms of the ionic strength, defined by:

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (84)$$

where the summation is over all aqueous solute species and z_i is the electrical charge. However, the use of the ionic strength as a means of correlating and predicting activity coefficients has been taken to unrealistic extremes (e.g., in the mean salt method of Garrels and Christ, 1965, p. 58-60). In general, model equations which express the dependence of activity coefficients on solution composition only in terms of the ionic strength are restricted in applicability to dilute solutions.

The three basic options for computing the activity coefficients of aqueous species in EQ3/6 are models based respectively on the Davies (1962) equation, the “B-dot” equation of Helgeson (1969), and Pitzer’s (1973, 1975, 1979, 1987) equations. The first two models, owing to limitations on accuracy, are only useful in dilute solutions (up to ionic strengths of 1 molal at most). The third basic model is useful in highly concentrated as well as dilute solutions, but is limited in terms of the components that can be treated.

With regard to temperature and pressure dependence, all of the following models are parameterized along the 1 atm/steam saturation curve. This corresponds to the way in which the temperature and pressure dependence of standard state thermodynamic data are also presently treated in the software. The pressure is thus a function of the temperature rather than an independent variable, being fixed at 1.013 bar from 0-100°C and the pressure for steam/liquid water equilibrium from 100-300°C. However, some of the data files have more limited temperature ranges.

3.2. The Davies Equation

The first activity coefficient model in EQ3/6 is based on the Davies (1962) equation:

$$\log \gamma_i = -A_{\gamma, 10} z_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} + 0.2I \right) \quad (85)$$

(the constant 0.2 is sometimes also taken as 0.3). This is a simple extended Debye-Hückel model (it reduces to a simple Debye-Hückel model if the “0.2I” part is removed). The Davies equation is frequently used in geochemical modeling (e.g., Parkhurst, Plummer, and Thorstenson, 1980; Stumm and Morgan, 1981). Note that it expresses all dependence on the solution composition through the ionic strength. Also, the activity coefficient is given in terms of the base ten logarithm, instead of the natural logarithm. The Debye-Hückel A_{γ} parameter bears the additional label “10” to ensure consistency with this. The Davies equation is normally only used for temperatures close to 25°C. It is only accurate up to ionic strengths of a few tenths molal in most solutions. In

some solutions, inaccuracy, defined as the condition of model results differing from experimental measurements by more than the experimental error, is apparent at even lower concentrations.

In EQ3/6, the Davies equation option is selected by setting the option flag **iopg1** = -1. A supporting data file consistent with the use of a simple extended Debye-Hückel model must also be supplied (e.g., **data1** = **data1.com**, **data1.sup**, or **data1.nea**). If **iopg1** = -1 and the supporting data file is not of the appropriate type, the software terminates with an error message.

The Davies equation has one great strength: the only species-specific parameter required is the electrical charge. This equation may therefore readily be applied to a wide spectrum of species, both those whose existence is well-established and those whose existence is only hypothetical.

The Davies equation predicts a unit activity coefficient for all neutral solute species. This is known to be inaccurate. In general, the activity coefficients of neutral species that are non-polar (such as $O_{2(aq)}$, $H_{2(aq)}$, and $N_{2(aq)}$) increase with increasing ionic strength (the “salting out effect,” so named in reference to the corresponding decreasing solubilities of such species as the salt concentration is increased; cf. Garrels and Christ, 1965, p. 67-70). In addition, Reardon and Langmuir (1976) have shown that the activity coefficients of two polar neutral species (the ion pairs $CaSO_{4(aq)}$ and $MgSO_{4(aq)}$) decrease with increasing ionic strength, presumably as a consequence of dipole-ion interactions.

The Davies equation is thermodynamically consistent. It is easy to show, for example, that it satisfies the solute-solute form of the cross-differentiation equation.

Most computer codes using the Davies equation set the activity of water to one of the following: unity, the mole fraction of water, or a limiting expression for the mole fraction of water. Usage of any of these violates thermodynamic consistency, but this is probably not of great significance as the inconsistency is numerically not significant at the relatively low concentrations at which the Davies equation itself is accurate. For usage in EQ3/6, we have used standard thermodynamic relations to derive the following expression:

$$\log a_w = \frac{1}{\Omega} \left(-\frac{\sum m}{2.303} + \frac{2}{3} A_{\gamma, 10} I^{\frac{3}{2}} \sigma(\sqrt{I}) - 2(0.2) A_{\gamma, 10} I^2 \right) \quad (86)$$

where “2.303” is a symbol for and approximation of $\ln 10$ (warning: this is not in general a sufficiently accurate approximation) and:

$$\sigma(x) = \frac{3}{x^3} \left(1 + x - \frac{1}{1+x} - 2 \ln(1+x) \right) \quad (87)$$

This result is thermodynamically consistent with the Davies equation.

3.3. The B-dot Equation

The second model for activity coefficients available in EQ3/6 is based on the B-dot equation of Helgeson (1969) for electrically charged species:

$$\log\gamma_i = -\frac{A_\gamma 10z_i^2 \sqrt{I}}{1 + \hat{a}_i B_\gamma \sqrt{I}} + \dot{B}I \quad (88)$$

Here \hat{a}_i is the hard core diameter of the species, B_γ is the Debye-Hückel B parameter, and \dot{B} is the characteristic B-dot parameter. Like the Davies equation, this is a simple extended Debye-Hückel model, the extension being the “ $\dot{B}I$ ” term. The Debye-Hückel part of this equation is equivalent to that of the Davies equation if the product “ $\hat{a}_i B_\gamma$ ” has a value of unity. In the extended part, these equations differ in that the Davies equation has a coefficient in place of \dot{B} which depends on the electrical charge of the species in question.

In EQ3/6, the B-dot equation option is selected by setting the option flag **io_{pg}1** = 0. A supporting data file consistent with the use of a simple extended Debye-Hückel model must also be supplied (e.g., **data1** = **data1.com**, **data1.sup**, or **data1.nea**). Note that these data files support the use of the Davies equation as well (the \hat{a}_i data on these files is simply ignored in that case). If **io_{pg}1** = 0 and the supporting data file is not of the appropriate type, the software terminates with an error message.

The B-dot equation has about the same level of accuracy as the Davies equation, and almost as much universality (one needs to know \hat{a}_i in addition to z_i). However, it fails to satisfy the solute-solute form of the cross-differentiation rule. The first term is consistent with this rule only if all hard core diameters have the same value. The second is consistent only if all ions share the same value of the square of the electrical charge. However, the numerical significance of the inconsistency is small in the range of low concentrations in which this equation can be applied with useful accuracy. On the positive side, the B-dot equation has been developed (Helgeson, 1969) to span a wide range of temperature (up to 300°C).

For electrically neutral solute species, the B-dot equation reduces to:

$$\log\gamma_i = \dot{B}I \quad (89)$$

As \dot{B} has positive values at all temperatures in the range of application, the equation predicts a salting out effect. However, by tradition (Helgeson et al., 1970), the B-dot equation itself is not used in the case of neutral solute species. The practice, as suggested by Garrels and Thompson (1962) and reiterated by Helgeson (1969), is to assign the value of the activity coefficient of aqueous CO_2 in otherwise pure sodium chloride solutions of the same ionic strength. This function was represented in previous versions of EQ3/6 by a power series in the ionic strength:

$$\log\gamma_i = k_1 I + k_2 I^2 + k_3 I^3 + k_4 I^4 \quad (90)$$

The first term on the right hand side dominates the others. The first coefficient is positive, so the activity coefficient of CO_2 increases with increasing ionic strength (consistent with the “salting out” effect). As it was applied in EQ3/6, the coefficients for the power series themselves were represented as similar power series in temperature, and this model was fit to data taken from Ta-

ble 2 of Helgeson (1969). These data (including extrapolations made by Helgeson) covered the range 25-300°C and 0-3 molal *NaCl*.

The high order power series in eq (90) was unfortunately very unstable when extrapolated outside the range of the data to which it was fit. EQ3NR and EQ6 would occasionally run into an unrecoverable problem attempting to evaluate this model for high ionic strength values generated in the process of attempting to find a numerical solution (not necessarily because the solutions in question really had high ionic strength). To eliminate this problem, the high order power series has been replaced by a new expression after Drummond (1981, p. 19):

$$\ln\gamma_i = \left(C + FT + \frac{G}{T} \right) I - (E + HT) \left(\frac{I}{I+1} \right) \quad (91)$$

where T is the absolute temperature and C = -1.0312, F = 0.0012806, G = 255.9, E = 0.4445, and H = -0.001606. Note that this is presented in terms of the natural logarithm. Conversion is accomplished by using the relation:

$$\log x = \frac{\ln x}{2.303} \quad (92)$$

This expression is both much simpler (considering the dependencies on both temperature and ionic strength) and is more stable. However, in deriving it, the ionic strength was taken to be equivalent to the sodium chloride molality. In the original model (based on Helgeson, 1969), the ionic strength was based on correcting the sodium chloride molality for ion pairing. This correction is numerically insignificant at low temperature. It does become significant at high temperature. However, neither this expression nor the power series formulation it replaced is thermodynamically consistent with the B-dot equation itself, as can be shown by applying the solute-solute cross-differentiation rule.

The more recent previous versions of EQ3/6 only applied the “*CO*₂” approximation to species that are essentially nonpolar (e.g., *O*_{2(aq)}, *H*_{2(aq)}, *N*_{2(aq)}), for which salting-out would be expected. In the case of polar neutral aqueous species, the activity coefficients were set to unity (following the recommendation of Garrels and Christ, 1965, p. 70); i.e., one has:

$$\log\gamma_i = 0 \quad (93)$$

This practice is still followed in the present version of the code.

EQ3/6 formerly complemented the B-dot equation with an approximation for the activity of water that was based on assigning values in pure sodium chloride solutions of the same “stoichiometric” ionic strength (Helgeson et al., 1970). This approximation was fairly complex and was, of course, not thermodynamically consistent with the B-dot equation itself. In order to simplify the data requirements, as well as avoid the need to employ a second ionic strength function, this formulation has been replaced by a new one which depends on the *B* parameter and is quasi-consistent with the B-dot equation:

$$\log a_w = \frac{1}{\Omega} \left(-\frac{\Sigma m}{2.303} + \frac{2}{3} A_{\gamma} 10^{\frac{3}{2}} I^{\frac{3}{2}} \sigma(\hat{a} B_{\gamma} \sqrt{I}) - \dot{B} I^2 \right) \quad (94)$$

The solute hard core diameter (\hat{a}) is assigned a fixed value of 4.0Å (a reasonable value). This equation is consistent with the B-dot equation if all solute species are ions, have the same fixed value of the hard core diameter, and have the same value of the square of the electrical charge.

3.4. Scaling of Individual Ionic Activity Coefficients: pH Scales

Before proceeding to a discussion of Pitzer's (1973, 1975) equations, we will address the problem of scaling associated with the activity coefficients of individual ions. It is not possible to observe (measure) any of the thermodynamic functions of such species, because any real solution must be electrically balanced. Thus, the activity coefficients of aqueous ions can only be measured in electrically neutral combinations. These are usually expressed as the mean activity coefficients of neutral electrolytes. The mean activity coefficient of neutral electrolyte MX (M denoting the cation, X the anion) is given by:

$$\log \gamma_{\pm, MX} = \frac{\nu_M \log \gamma_M + \nu_X \log \gamma_X}{\nu_{MX}} \quad (95)$$

where ν_M is the number of moles of cation produced by dissociation of one mole of the electrolyte, ν_X is the number of moles of anion produced, and:

$$\nu_{MX} = \nu_M + \nu_X \quad (96)$$

Electrical neutrality requires that:

$$z_M \nu_M = -z_X \nu_X \quad (97)$$

Although the activity coefficients of ions can not be individually observed, the corresponding molal concentrations can be. The corresponding products, the thermodynamic activities of the ions, are not individually observable, precisely because of the problem with the activity coefficients. Thus, the problem of obtaining individual activity coefficients of the ions and the problem of obtaining individual activities of the same species is really the same problem.

Individual ionic activity coefficients can be defined on a conventional basis by introducing some arbitrary choice. This can be made by adopting some expression for the activity coefficient of a single ion. The activity coefficients of all other ions then follow via electroneutrality relations. The activities for all the ions are then also determined (cf. Bates and Alfenaar, 1969). Because this applies to the hydrogen ion, such an arbitrary choice then determines the pH . Such conventions are usually made precisely for this purpose, and they are generally known as pH scales. The NBS pH scale, which is the basis of nearly all modern conventional pH measurement, is based on the Bates-Guggenheim equation (Bates, 1964):

$$\log \gamma_{Cl^-} = \frac{-A_{\gamma} 10 \sqrt{I}}{1 + 1.5 \sqrt{I}} \quad (98)$$

This scale is significant not only to the measurement of *pH*, but of corresponding quantities (e.g., *pCl*, *pBr*, *pNa*) obtained using other specific-ion electrodes (cf. Bates and Alfenaar, 1969; Bates, 1973; Bates and Robinson, 1974).

The Bates-Guggenheim equation, like the Davies equation and the B-dot equation, is an extended Debye-Hückel formula. However, if one applies the Davies equation or the B-dot equation to the chloride ion, the result is not precisely identical. The difference approaches zero as the ionic strength approaches zero, and is not very significant quantitatively in the low range of ionic strength in which either the Davies equation or the B-dot equation has useful accuracy. Nevertheless, the use of either of these equations in uncorrected form introduces an inconsistency with measured *pH* values, as use of the Davies equation for example would interpret the *pH* as being on an implied “Davies” scale.

Activity coefficients (and activities) of ions can be moved from one scale to another. The general relation for converting from scale (1) to scale (2) is (Knauss, Wolery, and Jackson, 1991):

$$\log \gamma_i^{(2)} = \log \gamma_i^{(1)} = \frac{z_i}{z_j} (\log \gamma_j^{(2)} - \log \gamma_j^{(1)}) \quad (99)$$

For example, if we evaluate the Davies equation for all ions, we may take the results as being on scale (1). To convert these to the NBS scale (here scale (2)), we take the *j*-th ion to be the chloride ion and evaluate the Bates-Guggenheim equation. We then apply the scale conversion equation to every other ion *i*.

In EQ3/6, activity coefficients are first calculated from the “raw” single-ion equations. They are then immediately rescaled, unless no rescaling is to be done. Thus, rescaling occurs during the iteration process; it is not deferred until convergence has been achieved. The user has control over rescaling via the option switch **iopg2**. If **iopg2** = 0, all single-ion activity coefficients and activities are put on the NBS scale. If **iopg2** = -1, no rescaling is performed. If **iopg2** = 1, all single-ion activity coefficients and activities are put on a scale which is defined by the relation:

$$\log \gamma_{H^+} = 0 \quad (100)$$

This has the effect of making the activity and the molality of the hydrogen ion numerically equal. This may have some advantages in comparing with experimental measurements of the hydrogen ion molality. Such measurement techniques have recently been discussed by Mesmer (1991).

The problem of scaling the activity coefficients of ions is more acute in concentrated solutions, and the need to discriminate among different scales in geochemical modeling codes has only been addressed as such codes have been written or modified to treat such solutions (e.g., Harvie, Møller, and Weare, 1984; Plummer et al., 1988).

3.5. Pitzer's Equations

3.5.1. Introduction

Pitzer (1973, 1975) proposed a set of semi-empirical equations to describe activity coefficients in aqueous electrolytes. These equations have proven to be highly successful as a means of dealing with the thermodynamics of concentrated solutions (e.g., Pitzer and Kim, 1974). Models based on these equations have been developed to describe not only solution properties, but also equilibrium between such solutions and salt minerals (e.g., Harvie and Weare, 1980; Harvie, Møller, and Weare, 1984). The utility of these models in geochemical studies has been well established. For example, such models have been shown to account for the mineral sequences produced by evaporation of seawater (Harvie et al., 1980), the process of trona deposition in Lake Magadi, Kenya (Monnin and Schott, 1984), and the formation of the borate-rich evaporite deposits at Searles Lake, California (Felmy and Weare, 1986).

Pitzer's equations are based on a semi-theoretical (see Pitzer, 1973) interpretation of ionic interactions, and are written in terms of interaction coefficients (and parameters from which such coefficients are calculated). There are two main categories of such coefficients, "primitive" ones which appear in the original theoretical equations, but most of which are only observable in certain combinations, and others which are "observable" by virtue of corresponding to observable combinations of the primitive coefficients or by virtue of certain arbitrary conventions. Only the observable coefficients are reported in the literature.

There is a very extensive literature dealing with Pitzer's equations and their application in both interpretation of experimental data and calculational modeling. A complete review is beyond the scope of the present manual. Discussion here will be limited to the equations themselves, how to use them in EQ3/6, and certain salient points that are necessary in order to use them in an informed manner. Readers who wish to pursue the subject further are referred to reviews given by Pitzer (1979, 1987, 1992). Jackson (1988) has addressed the verification of the addition of Pitzer's equations to EQ3/6.

In EQ3/6, the Pitzer's equations option is selected by setting the option flag **iopg1** = 1. A supporting data file consistent with this option must also be supplied (e.g., **data1** = **data1.hmw** or **data1.pit**). If **iopg1** = 1 and the supporting data file is not of the appropriate type, the software terminates with an error message.

Pitzer's equations are based on the following virial expansion for the excess Gibbs energy:

$$G^{EXm} = RT \left(w_w f(I) + \left(\frac{1}{w_w} \right) \sum_{ij} \lambda_{ij}(I) n_i n_j + \left(\frac{1}{w_w^2} \right) \sum_{ijk} \mu_{ijk} n_i n_j n_k \right) \quad (101)$$

where w_w is the number of kilograms of solvent water, $f(I)$ is a Debye-Hückel function describing the long-range electrical interactions to first order, the subscripts i , j , and k denote aqueous solute species, and n_i is the number of moles of the i -th solute species. The equation also contains two kinds of interaction or virial coefficients: the λ_{ij} are second order interaction coefficients, and the μ_{ijk} are third order interaction coefficients. A key element in the success of Pitzer's equations is the treatment of the second order interaction coefficients as functions of ionic strength. As will

be discussed later in more detail, the λ_{ij} consist of both theoretically defined and empirical parts, while the μ_{ijk} are completely empirical. As the term is used here, “empirical” means that at least some of the parameter values required to evaluate a quantity must be obtained by fitting experimental data.

The sums in the interaction coefficient terms are actually double and triple sums. As the number of components in a system increases, the number of interaction coefficients of the type shown above becomes very large. It turns out there are many more of the λ_{ij} and μ_{ijk} than can actually be observed, other than in combination. For example, in the equation for the excess Gibbs energy, it is quickly obvious that λ_{12} and λ_{21} can only be seen in the combination $(\lambda_{12} + \lambda_{21})$, and a similar situation holds in the case of the μ_{ijk} . This leads to the first simplification in dealing with these coefficients, which is that those with the same subscripts (regardless of order or permutation) are required to be equal (Pitzer, 1973). This is not the end of the story, as other constraints (mostly related to electrical neutrality) force even more simplifications (which will be addressed later).

A set of thermodynamically consistent equations for the activity coefficients follows by application of the partial differential equations given previously. In the case of solute species, this leads to:

$$\ln \gamma_i = \left(\frac{z_i^2}{2}\right) f(I) + 2 \sum_i \lambda_{ij}(I) m_j + \sum_{ik} \left(\left(\frac{z_i^2}{2}\right) \lambda'_{jk}(I) + 3\mu_{ijk} \right) m_j m_k \quad (102)$$

where $f(I)$ is the derivative df/dI and $\lambda'_{ij}(I)$ is similarly $d\lambda_{ij}/dI$. For water, the corresponding result is:

$$\begin{aligned} \ln a_w = & -\frac{\sum m}{\Omega} - \frac{1}{\Omega} (If'(I) - f(I)) \\ & + \frac{1}{\Omega} \left(\sum_{ii} (\lambda_{ij}(I) + \lambda'_{ij}(I)) m_i m_j + 2 \sum_{ijk} \mu_{ijk} m_i m_j m_k \right) \end{aligned} \quad (103)$$

The activity of water is closely related to the osmotic coefficient (ϕ):

$$\ln a_w = -\left(\frac{\sum m}{\Omega}\right) \phi \quad (104)$$

The thermodynamic properties of water are often discussed in the physical chemistry literature in terms of the osmotic coefficient instead of the activity of water (or the mole fraction activity coefficient of water).

The Debye-Hückel model used in Pitzer’s equations is not the usual Debye-Hückel-charging formulation exemplified in the Davies or B-dot equations, but a different one derived by Pitzer (1973) and called the Debye-Hückel-osmotic model. The relevant equations are:

$$f(I) = -\left(\frac{4A_\phi I}{b}\right) \ln(1 + b\sqrt{I}) \quad (105)$$

$$f(I) = -2A_\phi \left(\frac{2}{b} \ln(1 + b\sqrt{I}) + \frac{\sqrt{I}}{(1 + b\sqrt{I})} \right) \quad (106)$$

The Debye-Hückel parameter A_ϕ is related to the more familiar $A_{\gamma,10}$ by:

$$A_\phi = \frac{2.303A_{\gamma,10}}{3} \quad (107)$$

The parameter b is assigned a constant value of 1.2 (Pitzer, 1973). Theoretically, this is the product aB_γ ; thus the hard core diameter at 25°C is effectively fixed at a value of about 3.65Å (and somewhat different values at other temperatures). Differences in the hard core diameters of various ions in solution are not explicitly accounted for (this is the case also in the Davies equation). However, the interaction coefficient terms of the equation effectively compensate for this. A very important feature of the Debye-Hückel-osmotic model is that it, like the Debye-Hückel-charging model, is consistent with the Debye-Hückel limiting law:

$$\log \gamma_i \rightarrow -A_{\gamma,10} z_i^2 \sqrt{I} \quad \text{as } I \rightarrow 0 \quad (108)$$

3.5.2. Solutions of Electrolytes

In a pure solution of aqueous neutral electrolyte MX , the following combinations of interaction coefficients are observable:

$$B_{MX}(I) = \lambda_{MX}(I) + \left| \frac{z_X}{2z_M} \right| \lambda_{MM}(I) + \left| \frac{z_M}{2z_X} \right| \lambda_{XX}(I) \quad (109)$$

$$C_{MX}^\phi = 3 \left(\left| \frac{z_X}{z_M} \right|^{\frac{1}{2}} \mu_{MMX} + \left| \frac{z_M}{z_X} \right|^{\frac{1}{2}} \mu_{MXX} \right) \quad (110)$$

For example, the osmotic coefficient for such a solution can be written in the form (Pitzer, 1973):

$$\begin{aligned} \phi - 1 = & \frac{|z_M z_X|}{2} (If(I) - f(I)) \\ & + \left(\frac{2\nu_M \nu_X}{\nu_{MX}} \right) B_{MX}^\phi(I) m_{MX} + \left(\frac{2(\nu_M \nu_X)^{\frac{3}{2}}}{\nu_{MX}} \right) C_{MX}^\phi m_{MX}^2 \end{aligned} \quad (111)$$

Appearing in this equation is B_{MX}^ϕ , which is given by:

$$B_{MX}^{\phi}(I) = B_{MX}(I) + IB'_{MX}(I) \quad (112)$$

Here $B'_{MX}(I)$ is the derivative of $B_{MX}(I)$ with respect to the ionic strength.

The ionic strength dependence of B_{MX}^{ϕ} was defined by Pitzer (1973) to take the following form:

$$B_{MX}^{\phi}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha\sqrt{I}} \quad (113)$$

where α was assigned a constant value of 2.0. $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$, along with C_{MX}^{ϕ} , are parameters whose values are determined by fitting experimental data, such as for the osmotic coefficient. Corresponding to the above equation is:

$$B_{MX}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha\sqrt{I}) \quad (114)$$

where:

$$g(x) = \left(\frac{2}{x^2}\right)(1 - (1+x)e^{-x}) \quad (115)$$

Pitzer and Mayorga (1974) proposed a description for B_{MX}^{ϕ} in the case of 2:2 electrolytes that is based on an additional fitting parameter:

$$B_{MX}^{\phi}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1\sqrt{I}} + \beta_{MX}^{(2)} e^{-\alpha_2\sqrt{I}} \quad (116)$$

Here α_1 is assigned a value of 1.4 and α_2 one of 12.0 and $\beta_{MX}^{(2)}$ is the additional fitting parameter. Corresponding to this is:

$$B_{MX}(I) = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha_1\sqrt{I}) + \beta_{MX}^{(2)} g(\alpha_2\sqrt{I}) \quad (117)$$

We consider first the exponential function in eqs (113) and (117). This is shown in Figure 2 for the three commonly used values of α . At zero ionic strength, this function has a value of unity. Thus, $B_{MX}^{\phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}$ or $B_{MX}^{\phi} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} + \beta_{MX}^{(2)}$. The magnitude of each term containing $\beta_{MX}^{(1)}$ or $\beta_{MX}^{(2)}$ decreases exponentially as the ionic strength increases, approaching zero as the ionic strength approaches infinity (a limit which is not of physical interest). Most of the decay takes place in the very low ionic strength range. Thus, the terms in $\beta_{MX}^{(1)}$ and $\beta_{MX}^{(2)}$ are important parts of the model, even in dilute solutions.

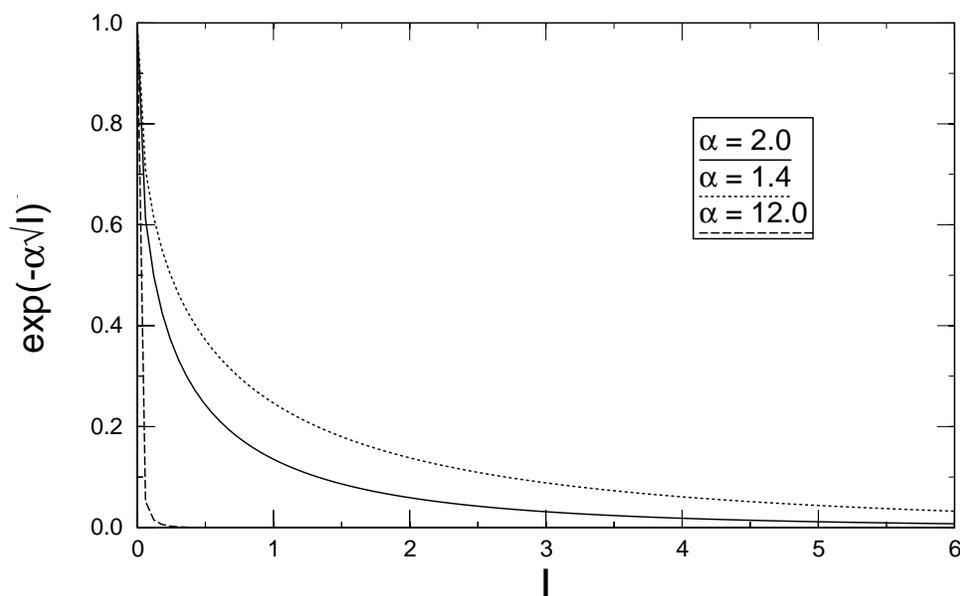


Figure 2. Behavior of the exponential function governing the ionic strength dependence of second-order interactions among cations and anions.

The function $g(x)$ is shown in Figure 3 for the three commonly used α values. It resembles the above exponential function, though it does not decay quite so rapidly. This function may be expanded as follows:

$$g(x) = 1 - 2\left(\frac{2x}{3!} - \frac{3x}{4!} + \frac{4x^2}{5!} - \frac{5x^3}{6!} + \dots\right) \quad (118)$$

This shows that $g(x) = 1$ at $x = 0$ ($I = 0$). Thus, at zero ionic strength, $B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}$ or $B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} + \beta_{MX}^{(2)}$. It can be shown that $g(x)$ approaches zero as x (and I) approach infinity.

The development thus far shows that there are two major categories of interaction coefficients. The λ_{ij} and the μ_{ijk} in terms of which the theoretical equations were originally derived are what we will call the primitive interaction coefficients. The observable combinations of these, such as $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}^{ϕ} , are what we will call the observable interaction coefficients. This latter kind of interaction coefficient represents the model data that are reported for the various systems for which Pitzer's equations have been fit to experimental data.

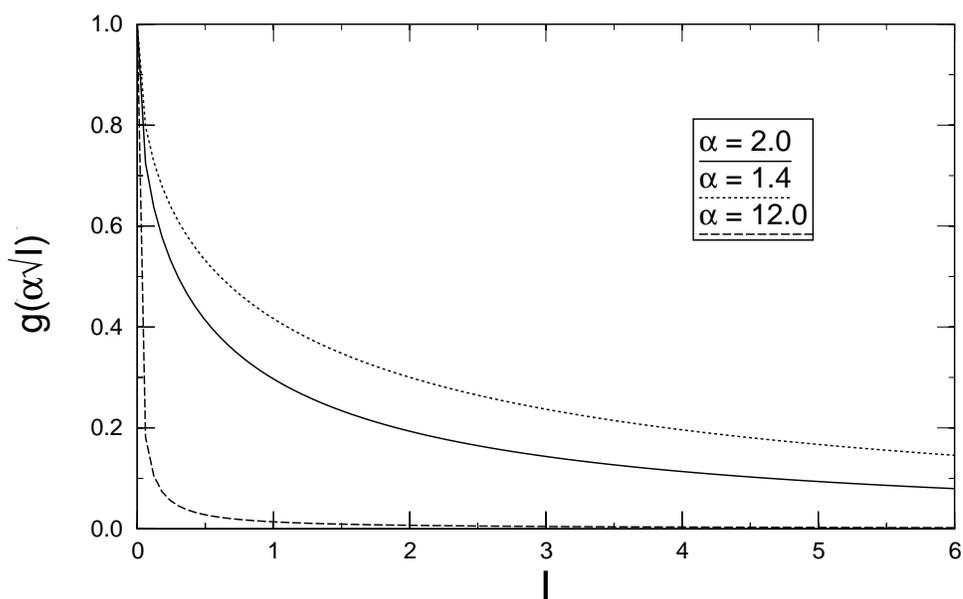


Figure 3. Behavior of the $g(x)$ function governing the ionic strength dependence of second-order interactions among cations and anions.

It is possible to rewrite the equations for $\ln \gamma_i$ and $\ln a_w$ in complex mixtures in terms of the observable interaction coefficients. An example of such equations was suggested by Pitzer (1979) and adopted with changes in notation by Harvie, Møller, and Weare (1984). These equations are much more complex than the original form written in terms of the primitive interaction coefficients. They have been incorporated into computer codes, such as that of Harvie, Møller, and Weare (1984), PHRQPITZ (Plummer et al., 1988), and SOLMINEQ.88 (Perkins et al., 1990). As noted in the previous section, there is no unique way to construct equations for single-ion activity coefficients. Furthermore, direct usage of such equations constitutes implicit adoption of a corresponding pH scale. In the case of the single-ion activity coefficient equation suggested by Pitzer, this could be termed the “Pitzer” scale.

The equations for $\ln \gamma_i$ and $\ln a_w$ which are evaluated in EQ3/6 are those written in terms of the primitive interaction coefficients. The set of these which is used is not the generalized theoretical set, which is not obtainable for the reasons discussed previously, but a practical set that is obtained by mapping the set of reported observable interaction coefficients using a set of equations that contain arbitrary conventions. These mapping equations imply a pH scale. We will show that the conventions chosen here match those suggested by Pitzer (1979), so this implied pH scale is identical to his.

The basic guides to choosing such mapping conventions are pleasing symmetries and the desirability of minimizing the number of conventional primitive interaction coefficients with non-zero values. In the case of the second order coefficients, both of these considerations suggest the following definitions:

$$\lambda_{MM}(I) = 0 \quad (119)$$

$$\lambda_{XX}(I) = 0 \quad (120)$$

$$\lambda_{MX}(I) = B_{MX}(I) \quad (121)$$

Analogous to the formulas used to describe B_{MX} , one may write:

$$\lambda_{MX}(I) = \lambda_{MX}^{(0)} + \lambda_{MX}^{(1)}g(\alpha\sqrt{I}) \quad (122)$$

or:

$$\lambda_{MX}(I) = \lambda_{MX}^{(0)} + \lambda_{MX}^{(1)}g(\alpha_1\sqrt{I}) + \lambda_{MX}^{(2)}g(\alpha_2\sqrt{I}) \quad (123)$$

From the principle of corresponding terms, it follows that the corresponding mapping equations are:

$$\lambda_{MM}^{(n)} = 0 \quad \text{for } n = 0, 2 \quad (124)$$

$$\lambda_{XX}^{(n)} = 0 \quad \text{for } n = 0, 2 \quad (125)$$

$$\lambda_{MX}^{(n)} = \beta_{MX}^{(n)} \quad \text{for } n = 0, 2 \quad (126)$$

Evaluation of the equations for $\ln \gamma_i$ and $\ln a_w$ also requires the ionic strength derivatives of the λ_{ij} coefficients. These are given by:

$$\lambda'_{MX}(I) = \lambda_{MX}^{(1)}g'(x)\left(\frac{\alpha}{2\sqrt{I}}\right) \quad (127)$$

or:

$$\lambda'_{MX}(I) = \lambda_{MX}^{(1)}g'(x)\left(\frac{\alpha_1}{2\sqrt{I}}\right) + \lambda_{MX}^{(2)}g'(x)\left(\frac{\alpha_2}{2\sqrt{I}}\right) \quad (128)$$

where $g'(x)$ is the derivative of $g(x)$ (with respect to x , not I), given by

$$g'(x) = -\left(\frac{4}{x^3}\right)\left(1 - e^{-x}\left(1 + x + \frac{x^2}{2}\right)\right) \quad (129)$$

The principle of pleasing symmetry suggests the following mapping equations for dealing with the C_{MX}^ϕ parameter:

$$\mu_{MMX} = \frac{1}{6} \left| \frac{z_M}{z_X} \right|^{\frac{1}{2}} C_{MX}^{\phi} \quad (130)$$

$$\mu_{MXX} = \frac{1}{6} \left| \frac{z_X}{z_M} \right|^{\frac{1}{2}} C_{MX}^{\phi} \quad (131)$$

The two μ coefficients are then related by:

$$\frac{\mu_{MMX}}{z_M} = \frac{\mu_{MXX}}{|z_X|} \quad (132)$$

These are in fact the mapping equations used in EQ3/6. However, the principle of minimizing the number of conventional primitive interaction coefficients would suggest instead mapping relations such as:

$$\mu_{MMX} = \frac{1}{3} \left| \frac{z_M}{z_X} \right|^{\frac{1}{2}} C_{MX}^{\phi} \quad (133)$$

$$\mu_{MXX} = 0 \quad (134)$$

Note that with this set of mapping relations, a different pH scale would be implied.

In mixtures of aqueous electrolytes with a common ion, two additional observable combinations of interaction coefficients appear (Pitzer, 1973; Pitzer and Kim, 1974):

$$\theta_{MM'}(I) = \lambda_{MM'}(I) - \left(\frac{z_{M'}}{2z_M} \right) \lambda_{MM}(I) - \left(\frac{z_M}{2z_{M'}} \right) \lambda_{M'M'}(I) \quad (135)$$

and:

$$\psi_{MM'X} = 6\mu_{MM'X} - \left(\frac{3z_{M'}}{z_M} \right) \mu_{MMX} - \left(\frac{3z_M}{z_{M'}} \right) \mu_{M'M'X} \quad (136)$$

Here M and M' are two cations and X is the anion, or M and M' are two anions and X is the cation. From previously adopted mapping conventions, it immediately follows that the corresponding mappings are given by:

$$\lambda_{MM'}(I) = \theta_{MM'}(I) \quad (137)$$

$$\mu_{MM'X} = \frac{1}{6} \left(\psi_{MM'X} + \left(\frac{3z_{M'}}{z_M} \right) \mu_{MMX} + \left(\frac{3z_M}{z_{M'}} \right) \mu_{M'M'X} \right) \quad (138)$$

In the original formulation of Pitzer's equations (Pitzer, 1973), the $\theta_{MM'}$ coefficient is treated as a constant. It was later modified by Pitzer (1975) to take the following form:

$$\theta_{MM'}(I) = {}^S\theta_{MM'} + {}^E\theta_{MM'}(I) \quad (139)$$

$\theta_{MM'}(I)$ corresponds to the Φ_{ij} of Harvie, Møller, and Weare (1984). The first term is a constant and accounts for short-range effects (this is the θ_{ij} of Harvie, Møller, and Weare). The second term, which is the newer part, is entirely theoretical in nature and accounts for higher-order electrostatic effects. Only the ${}^S\theta_{MM'}$ part is obtained by fitting. Corresponding to this is the equation:

$$\lambda_{MM'}(I) = {}^S\lambda_{MM'} + {}^E\lambda_{MM'}(I) \quad (140)$$

The relevant mapping relation is then:

$${}^S\lambda_{MM'} = {}^S\theta_{MM'} \quad (141)$$

The ${}^E\lambda_{MM'}(I)$ part is obtainable directly from theory (Pitzer, 1975):

$${}^E\theta_{MM'} = \left(\frac{z_M z_{M'}}{4I}\right) \left(J(x_{MM'}) - \frac{J(x_{MM})}{2} - \frac{J(x_{M'M'})}{2} \right) \quad (142)$$

where:

$$J(x) = \frac{1}{x} \int_0^{\infty} \left(1 + q + \frac{q^2}{2} - e^q \right) y^2 dy \quad (143)$$

in which:

$$q = -\left(\frac{x}{y}\right) e^{-y} \quad (144)$$

and:

$$x_{ij} = 6z_i z_j A^\phi \sqrt{I} \quad (145)$$

The derivative of ${}^E\lambda_{MM'}(I)$ is given by:

$$\begin{aligned}
{}^E\lambda'_{MM'}(I) &= -\left(\frac{{}^E\lambda(I)}{I}\right) \\
&+ \left(\frac{z_M z_{M'}}{8I^2}\right) \left(x_{MM'} J'(x_{MM'}) - \frac{x_{MM} J'(x_{MM})}{2} - \frac{x_{M'M'} J'(x_{M'M'})}{2}\right)
\end{aligned} \tag{146}$$

Expansion of $J(x)$ gives (Pitzer, 1975):

$$J(x) = -\left(\frac{x^2}{6}\right)(\ln x + 0.419711) + \dots \tag{147}$$

Application of L'Hospital's rule shows that $J(x)$ goes to zero as x goes to zero (hence also as the ionic strength goes to zero). $J(x)$ is a monotonically increasing function. So is $J'(x)$, which approaches a limiting value of 0.25 as x goes to infinity. The function $J(x)$ and its derivative are approximated in EQ3/6 by a Chebyshev polynomial method suggested by Harvie and Weare (1980). This method is described in detail by Harvie (1981, Appendix B, in which $J(x)$ is referred to as $J_0(x)$); this method is also described in the review by Pitzer (1987, p. 131-132).

Pitzer (1979) showed that substitution of the observable interaction coefficients into the single-ion activity coefficient equation gives the following result for cation M :

$$\begin{aligned}
\ln \gamma_M &= z_M^2 f^{\lambda'} + 2 \sum_a m_a [B_{Ma} + (\Sigma m z) C_{Ma}] + \\
&2 \sum_c m_c \theta_{Mc} + \sum_c \sum_a m_c m_a [z_M^2 B'_{ca} + z_M C_{ca} + \Psi_{Mca}] + \\
&\frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} [z_M^2 \theta'_{aa'} + \Psi_{Maa'}] + \frac{z_M}{2} \sum_c \sum_{c'} m_c m_{c'} \theta'_{cc'} + \\
&z_M \left\{ \sum_c \frac{m_c \lambda_{cc}}{z_c} - \sum_a \frac{m_a \lambda_{aa}}{|z_a|} + \frac{3}{2} \sum_c \sum_a m_c m_a \left(\frac{\mu_{cca}}{z_c} - \frac{\mu_{caa}}{|z_a|} \right) \right\}
\end{aligned} \tag{148}$$

Here a denotes anions, c denotes cations, and:

$$f^{\lambda'} = \frac{f}{2} \tag{149}$$

$$C_{MX} = \frac{C_{MX}^{\phi}}{2\sqrt{|z_M z_X|}} \tag{150}$$

$$\Sigma m z = \sum_c m_c m_c \tag{151}$$

(The single-ion equation for an anion is analogous). As pointed out by Pitzer, the unobservability of single-ion activity coefficients in his model lies entirely in the last term (the fourth line) of the equation and involves the primitive interaction coefficients λ_{cc} , λ_{aa} , μ_{cca} , and μ_{caa} . His suggested conventional single-ion activity coefficient equation is obtained by omitting this part. This requires the affected primitive interaction coefficients to be treated exactly as in the previously adopted mapping equations. This approach could in fact have been used to derive them.

In theory, the relevant data required to evaluate Pitzer's equations for complex mixtures of relatively strong aqueous electrolytes can all be obtained from measurements of the properties of pure aqueous electrolytes (giving the observable interaction coefficients $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$, and C_{MX}^{ϕ}) and mixtures of two aqueous electrolytes having a common ion (${}^S\theta_{MM'}$ and $\psi_{MM'X}$).

There is one peculiarity in this fitting scheme in that ${}^S\theta_{MM'}$ is obtainable from more than one mixture of two electrolytes having a common ion, because this parameter does not in theory depend on that ion. Thus, the value adopted may have to be arrived at by simultaneously considering the experimental data for a suite of such mixtures.

3.5.3. Solutions of Electrolytes and Nonelectrolytes

In general, it is necessary to consider the case of solutions containing nonelectrolyte solute species in addition to ionic species. Examples of such uncharged species include molecular species such as $O_{2(aq)}$, $CO_{2(aq)}$, $CH_{4(aq)}$, $H_{2S(aq)}$, $C_2H_5OH_{(aq)}$, and $SiO_{2(aq)}$; strongly bound complexes, such as $HgCl_{3(aq)}$ and $UO_2CO_{3(aq)}$; and weakly bound ion pairs such as $CaCO_{3(aq)}$ and $CaSO_{4(aq)}$. The theoretical treatment of these kinds of uncharged species is basically the same. There are practical differences, however, in fitting the models to experimental data. This is simplest for the case of molecular neutral species. In the case of complexes or ion pairs, the models are complicated by the addition of corresponding mass action equations.

The treatment of solutions of electrolytes using Pitzer's equations is quite standardized. In such solutions, there is one generally accepted relation for describing single-ion activity coefficients, though it may be expressed in various equivalent forms. Thus, in such solutions there is only one implied "Pitzer" *pH* scale. Also, the set of parameters to be obtained by regressing experimental measurements is well established. Unfortunately, this is not the case for the treatment of solutions containing both electrolytes and nonelectrolytes.

Harvie, Møller, and Weare (1984) used Pitzer's equations to construct a model of all of the major components of seawater at 25°C. They modified the equations for electrolyte systems to include some provision for neutral species-ion interactions. Additional modification was made by Felmy and Weare (1986), who extended the Harvie, Møller, and Weare model to include borate as a component. The Felmy and Weare equation for the activity of water (obtained from their equation for the osmotic coefficient) is:

$$\begin{aligned}
\ln a_w = & -\frac{\sum m}{\Omega} - \frac{2}{\Omega} \left(\frac{If-f}{2} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \right. \\
& + \sum_c \sum_{c' > c} m_c m_{c'} \left(\Phi_{cc'}^\phi + \sum_a m_a \Psi_{aa'c} \right) \\
& + \sum_a \sum_{a' > a} m_a m_{a'} \left(\Phi_{aa'}^\phi + \sum_c m_c \Psi_{cc'a} \right) \\
& \left. + \sum_n \sum_c m_n m_c \lambda_{nc} + \sum_n \sum_a m_n m_a \lambda_{na} + \sum_n \sum_c \sum_a m_n m_c m_a \zeta_{nca} \right) \quad (152)
\end{aligned}$$

In this equation, c denotes a cation and a an anion, and the following definitions are introduced:

$$Z = \sum_i |z_i| m_i \quad (153)$$

$$\Phi_{ij}^\phi = {}^S \theta_{ij} + {}^E \theta_{ij}(I) + I {}^E \theta'_{ij}(I) \quad (154)$$

The first three lines are equivalent to the mixture formulation given by Pitzer (1979). The fourth line (last three terms) is the new part. Here n denotes a neutral species, λ_{nc} and λ_{na} are second order interaction coefficients describing neutral species-ion interactions, and ζ_{nca} is an observable third order coefficient. These new interaction coefficients are treated as constants. The terms in λ_{nc} and λ_{na} were introduced by Harvie, Møller, and Weare (1984) to treat the species $CO_{2(aq)}$. The term in ζ_{nca} was put in by Felmy and Weare (1986) and is a third order interaction coefficient. It was necessary to include it in the equations to account for interactions involving the species $B(OH)_{3(aq)}$.

The corresponding single-ion equation for cation M takes the following form:

$$\begin{aligned}
\ln \gamma_M = & z_M^2 F + \sum_a m_a [2B_{Ma} + ZC_{Ma}] \\
& + \sum_c m_c \left(2\Phi_{Mc} + \sum_a m_a \Psi_{Mca} \right) \\
& + \sum_a \sum_{a' > a} m_a m_{a'} \Psi_{Maa'} + |z_M| \sum_c \sum_a m_c m_a C_{ca} \\
& + 2 \sum_n m_n \lambda_{nM} + \sum_n \sum_a m_n m_a \zeta_{naM} \quad (155)
\end{aligned}$$

Here Φ_{ij} is the θ_{ij} of the earlier notation and:

$$F = \frac{f}{2} + \sum_c \sum_a m_c m_a B'_{ca} + \sum_c \sum_{c' > c} m_c m_{c'} \Phi'_{cc'} + \sum_a \sum_{a' > a} m_a m_{a'} \Phi'_{aa'} \quad (156)$$

The first three lines are equivalent to Pitzer's suggested single-ion activity coefficient equation. The fourth line (last two terms) is the new part. The corresponding equation for anions is analogous. The corresponding equation for the N -th neutral species is:

$$\ln \gamma_N = 2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na} + \sum_c \sum_a m_c m_a \zeta_{Nca} \quad (157)$$

To deal with the fact that the λ_{nc} and λ_{na} are only observable in combination, Harvie, Møller, and Weare (1984) adopted the convention that:

$$\lambda_{N, H^+} = 0 \quad (158)$$

These equations were presented for the modeling of specific systems, and are not completely general. They are missing some terms describing interactions involving neutral species. A set of complete equations is given by Clegg and Brimblecombe (1990). Their equation for the activity coefficient of a neutral solute species is:

$$\begin{aligned} \ln \gamma_N = & 2 \sum_n m_n \lambda_{Nn} + 2 \sum_c m_c \lambda_{Nc} + 2 \sum_a m_a \lambda_{Na} \\ & + 6 \sum_n \sum_c m_n m_c \mu_{Nnc} + 6 \sum_n \sum_a m_n m_a \mu_{Nna} \\ & + 3 \sum_c m_c^2 \mu_{Ncc} + 3 \sum_a m_a^2 \mu_{Naa} + 6 \sum_c \sum_a m_c m_a \mu_{Nca} \\ & + 6 \sum_c \sum_{c' > c} m_c m_{c'} \mu_{Ncc'} + 6 \sum_a \sum_{a' > a} m_a m_{a'} \mu_{Naa'} \\ & + 3 \sum_n m_n^2 \mu_{Nnn} + 6 \sum_{n \neq N} m_N m_n \mu_{NNn} + 6 \sum_{n \neq N} \sum_{n' \neq N} m_n m_{n'} \mu_{Nnn'} \end{aligned} \quad (159)$$

This is a complete and general representation of the activity coefficient of a neutral species in terms of all possible second order and third order primitive interaction coefficients. The first line of this equation contains the same terms in λ_{nc} and λ_{na} as appear in the Felmy-Weare equation. This line is augmented by an addition term which describes second order interactions among neutral species (and which was also pointed out by Pitzer, 1987). The third line in this equation is

equivalent to the term in ζ_{Nca} that appears in the Felmy-Weare equation. Clegg and Brimblecombe (1990) have pointed out that this observable interaction coefficient is related to the corresponding primitive interaction coefficients by the relation:

$$\zeta_{NMX} = 6\mu_{NMX} + \frac{3|z_X|}{z_M}\mu_{NMM} + \frac{3z_M}{|z_X|}\mu_{NXX} \quad (160)$$

The second, fourth, and fifth lines consist of terms not found in the Felmy-Weare equation.

In a solution of a pure aqueous nonelectrolyte, the activity coefficient of the neutral species takes the form:

$$\ln \gamma_N = 2m_N\lambda_{NN} + 3m_N^2\mu_{NNN} \quad (161)$$

This activity coefficient is directly observable. Hence the two interaction coefficients on the right hand side are also observable. In a study of the solubility of aqueous ammonia, Clegg and Brimblecombe (1989) found that the term including μ_{NNN} was significant only for concentrations greater than 25 molal (a solution containing more ammonia than water). They therefore dropped this term and reported model results only in terms of λ_{NN} . Similarly, Barta and Bradley (1985) found no need for a μ_{NNN} term to explain the data for pure solutions of $CO_{2(aq)}$, $H_2S_{(aq)}$, and $CH_{4(aq)}$, and no such term was apparently required by Felmy and Weare (1986) to explain the data for $B(OH)_{3(aq)}$. Pitzer and Silvester (1976) report a significant μ_{NNN} term for undissociated phosphoric acid. This result now appears somewhat anomalous and has not been explained. The bulk of the available data, however, suggest that the μ_{NNN} term is generally insignificant in most systems of geochemical interest and can be ignored without loss of accuracy.

This result suggests that in more complex solutions, terms in λ_{NN} , μ_{NNN} , $\mu_{N'N'}$, and $\mu_{NN'N'}$ can also often be ignored. While there may be solutions in which the full complement of these terms are significant, one could argue that they must be so concentrated in nonelectrolyte components that they have little relevance to the study of surface waters and shallow crustal fluids (though some deep crustal fluids are rich in CO_2). Furthermore, one could argue that to address such solutions, it would be more appropriate to use a formalism based on a different kind of expansion than the one used in the present treatment (see Pabalan and Pitzer, 1990).

In an aqueous solution consisting of one nonelectrolyte and one electrolyte, the activity coefficient of the neutral species takes the form:

$$\begin{aligned} \ln \gamma_N = & 2m_N\lambda_{NN} + 2(m_M\lambda_{NM} + m_X\lambda_{NX}) \\ & + 6m_N(m_M\mu_{NNM} + m_X\mu_{NNX}) + m_Mm_X\zeta_{NMX} + 3m_N^2\mu_{NNN} \end{aligned} \quad (162)$$

Three new terms appear. The resemblance of the term in λ_{NM} and λ_{NX} to a traditional Setchenow term has been pointed out by various workers (e.g., Felmy and Weare, 1986; Pitzer, 1987). Work reported by Clegg and Brimblecombe (1989, 1990) for a number of such systems containing am-

monia showed that the most important of the three new terms were the second (λ_{NM} , λ_{NX}) term and the third (μ_{NNM} , μ_{NNX}) term. They defined these using the following conventions:

$$\lambda_{N, Cl^-} = 0 \quad (163)$$

$$\mu_{N, N, Cl^-} = 0 \quad (164)$$

Note that the first of these conventions conflicts with the corresponding convention adopted by Harvie, Møller, and Weare (1984), though it matches that proposed by Pitzer and Silvester (1976) in a study of the dissociation of phosphoric acid, a weak electrolyte. Clegg and Brimblecombe found that in one system, the use of the fourth (ζ_{NMX}) term was also required, though the contribution was relatively small. No use was required of the last (μ_{NNN}) term, as was shown by fitting the data for pure aqueous ammonia.

There seems to be some disagreement in the literature regarding the above picture of the relative significance of the (μ_{NNM} , μ_{NNX}) term versus that of the ζ_{NMX} term, although the seemingly contradictory results involve nonelectrolytes other than ammonia. We have noted above that Felmy and Weare (1986) used a ζ_{NMX} term to explain the behavior of boric acid-electrolyte mixtures. It is not clear if they considered the possibility of a (μ_{NNM} , μ_{NNX}) term. Pitzer and Silvester (1976) found no apparent need to include a (μ_{NNM} , μ_{NNX}) term or a ζ_{NMX} term to explain the thermodynamics of phosphoric acid dissociation in electrolyte solutions. The data on aqueous silica in electrolyte solutions of Chen and Marshall (1981), discussed by Pitzer (1987), require a ζ_{NMX} term, but no (μ_{NNM} , μ_{NNX}) term. A similar result was obtained by Barta and Bradley (1985) for mixtures of electrolytes with $CO_{2(aq)}$, $H_2S_{(aq)}$, and $CH_{4(aq)}$. Simonson et al. (1987) interpret data for mixtures of boric acid with sodium borate and sodium chloride and of boric acid with potassium borate and potassium chloride exclusively in terms of the first (λ_{NN}) and second (λ_{NM} , λ_{NX}) terms, using neither of the third order terms for nonelectrolyte-electrolyte interactions.

The (μ_{NNM} , μ_{NNX}) term can only be observed (and hence is only significant) when the concentrations of both the nonelectrolyte and the electrolyte are sufficiently high. In contrast, evaluating the ζ_{NMX} term requires data for high concentrations of the electrolyte, but low concentrations of the nonelectrolyte will suffice. Some nonelectrolytes, such as aqueous silica, are limited to low concentrations by solubility constraints. Thus, the results of Chen and Marshall (1981) noted by Pitzer (1987) are not surprising. In the case of more soluble nonelectrolytes, the range of the available experimental data could preclude the evaluation of the (μ_{NNM} , μ_{NNX}) term. This may be why Pitzer and Silvester (1976) reported no need for such a term to describe the data for mixtures of electrolytes with phosphoric acid and why Barta and Bradley (1985) found no need for such a term for similar mixtures of electrolytes with $CO_{2(aq)}$, $H_2S_{(aq)}$, and $CH_{4(aq)}$. The data analyzed by Felmy and Weare (1986) correspond to boric acid concentrations of about one molal, which may not be high to observe this term (or require its use). In the case of Simonson et al. (1987), who also looked at mixtures of electrolytes and boric acid, the need for no third order terms describing nonelectrolyte-electrolyte interactions is clearly due to the fact that the concentrations of boric acid were kept low to avoid the formation of polyborate species.

The equations for solutions containing nonelectrolytes can be considerably simplified if the model parameters are restricted to those pertaining to solutions of pure aqueous nonelectrolytes and mixtures of one nonelectrolyte and one electrolyte. This is analogous to the usual restriction in treating electrolyte solutions, in which the parameters are restricted to those pertaining to solutions of two electrolytes with a common ion. Furthermore, it seems appropriate as well to drop the terms in μ_{NNN} . The equation for the activity coefficient of a neutral electrolyte in electrolyte-
nonelectrolyte mixtures then becomes:

$$\begin{aligned} \ln \gamma_N = & 2m_N \lambda_{NN} + 2 \left(\sum_c m_c \lambda_{Nc} + \sum_a m_a \lambda_{Na} \right) \\ & + 6m_N \left(\sum_c m_c \mu_{NNc} + \sum_a m_a \mu_{NNa} \right) + \sum_c \sum_a m_c m_a \zeta_{Nca} \end{aligned} \quad (165)$$

The reduction in complexity is substantial. In the context of using Pitzer's equations in geochemical modeling codes, this level of complexity is probably quite adequate for dealing with nonelectrolytes in a wide range of application.

If a higher level of complexity is required, the next step is probably to add in terms in μ_{NNN} and λ_{NN} . The first of these has been discussed previously and is obtained from data on pure aqueous nonelectrolytes. The second must be obtained from mixtures of two aqueous electrolytes (one could argue that this is also analogous to the treatment of electrolytes). This higher level of complexity may suffice to deal with at least some CO_2 -rich deep crustal fluids and perhaps other fluids of interest in chemical engineering. However, an even higher level of complexity would probably be best addressed by a formalism based on an alternate expansion, as noted earlier.

The observability and mapping issues pertaining to the remaining parameters may be dealt with as follows. In the case of λ_{NN} , no mapping relation is required because this parameter is directly observable. The same is true of μ_{NNN} and λ_{NN} , if the higher level of complexity is required.

The λ_{NM} and λ_{NX} , and μ_{NNM} and μ_{NNX} , are only observable in combinations, but can be dealt with by adopting the following respective conventions:

$$\lambda_{N,J} = 0 \quad (166)$$

$$\mu_{N,N,J} = 0 \quad (167)$$

where J is a reference ion ($J = H^+$ as suggested by Felmy and Weare, 1986; $J = Cl$ as suggested by Pitzer and Silvester, 1976, and Clegg and Brimblecombe, 1989, 1990). In any data file used to support code calculations, the choice of reference ion must be consistent. This may require the recalculation of some published data.

The ζ_{NMX} parameter is observable and can be mapped into primitive form by adopting the following conventions:

$$\mu_{NMM} = 0 \quad (168)$$

$$\mu_{NXX} = 0 \quad (169)$$

$$\mu_{NMX} = \frac{\zeta_{NMX}}{6} \quad (170)$$

These relations are analogous to those defined for the C_{MX}^ϕ parameter.

The above conventions correspond well with the current literature on the subject. However, the treatment of the λ_{NM} and λ_{NX} , and μ_{NNM} and μ_{NNX} , though valid and functional, still stands out in that it is not analogous to, or a natural extension of, the conventions which have been universally adopted in the treatment of electrolyte solutions. The logical extension, of course, is to define observable interaction coefficients to represent the primitive coefficients which can only be observed in combination, and to then follow Pitzer (1979) in determining exactly which parts of the theoretical equations constitute the non-observable part. The conventions would then be defined so as to make these parts have zero value.

The suggested process can be shown to be consistent with the above mapping conventions for all the other coefficients treated above, including ζ_{NMX} . However, the process which worked so nicely for electrolytes fails to work for λ_{NM} - λ_{NX} , and μ_{NNM} - μ_{NNX} . We will demonstrate this for the case of the λ_{NM} - λ_{NX} . Application of the above equation to the case of an aqueous mixture of a neutral species (N) and a neutral electrolyte (MX) immediately shows that the corresponding observable combination of primitive interaction coefficients is given by:

$$L_{NMX} = |z_X|\lambda_{NM} + z_M\lambda_{NX} \quad (171)$$

In such a system, the activity coefficient of the neutral species can be written as:

$$\ln \gamma_N = \frac{2}{z_M + |z_X|} \nu_{MX} L_{NMX} m_{MX} \quad (172)$$

In the manner of Pitzer (1979), one can show that the relevant term in the single-ion activity coefficient for cation M expands in the following manner:

$$2 \sum_n m_n \lambda_{nM} = 2 \sum_n m_n \frac{L_{nMX'}}{|z_{X'}|} - 2 \sum_n m_n \frac{z_M}{|z_{X'}|} \lambda_{nX'} \quad (173)$$

where X' is some reference anion. When X' is Cl^- , we have the convention proposed by Pitzer and Silvester (1976) and followed by Clegg and Brimblecombe (1989, 1990). The first term on the right hand side is the relevant observable part; the second term is the non-observable part. Following the logic of Pitzer (1979), we could set the second term to zero. This would have the effect of defining the following mapping relations:

$$\lambda_{nX'} = 0 \quad (174)$$

$$\lambda_{NM} = \frac{L_{NMX}}{|z_X|} \quad (175)$$

Although this makes the relevant non-observable part vanish in the single-ion activity coefficient equation for all cations, it forces the complementary part in the corresponding equation for anions to not vanish, as we will now show. The relevant part of the anion equation gives the following analogous result:

$$2 \sum_n m_n \lambda_{nX} = 2 \sum_n m_n \frac{L_{nM'X}}{z_{M'}} - 2 \sum_n m_n \frac{|z_X|}{z_{M'}} \lambda_{nM'} \quad (176)$$

where M' is some reference cation. As before, the second term on the right hand side is the non-observable part. Using the above mapping equation for λ_{NM} , this can be transformed to:

$$2 \sum_n m_n \lambda_{nX} = 2 \sum_n m_n \frac{L_{nM'X}}{z_{M'}} - 2 \sum_n m_n \frac{z_X}{z_{M'} z_X} L_{nM'X} \quad (177)$$

Thus, under the conventions defined above, the non-observable part of the single-ion activity coefficient equation for anions does not vanish.

There are alternatives, but none are particularly outstanding. For example, one could reverse the situation and make analogous conventions so that the non-observable part of the anion equation vanishes, but then the non-observable part of the cation equation would not vanish. When M' is H^+ , we have the convention proposed by Felmy and Weare (1986). One could also try a symmetrical mapping, based on the following relation:

$$\lambda_{NM} = \frac{z_M}{|z_X|} \lambda_{NX} \quad (178)$$

This would lead to the following mapping relations:

$$\lambda_{NM} = \frac{z_M}{(z_M + |z_X|)} L_{NMX} \quad (179)$$

$$\lambda_{NX} = \frac{|z_X|}{(z_M + |z_X|)} L_{NMX} \quad (180)$$

Unfortunately, this would lead to a non-vanishing non-observable part in the equations for both cations and anions.

3.5.4. Temperature and Pressure Dependence

Pitzer's equations were originally developed and applied to conditions of 25°C and atmospheric pressure (e.g., Pitzer and Kim, 1974). The formalism was subsequently applied both to activity coefficients under other conditions and also to related thermodynamic properties which reflect

the temperature and pressure dependence of the activity coefficients (see the review by Pitzer, 1987).

The first effort to extend the Pitzer formalism to high temperature was a detailed study of the properties of aqueous sodium chloride (Silvester and Pitzer, 1977). In this study, the data were fit to a complex temperature function with up to 21 parameters per observable interaction coefficient and which appears not to have been applied to any other system. In general, the early efforts concerning the temperature dependence of the activity coefficients focused mainly on estimating the first derivatives of the observable interaction coefficient parameters with respect to temperature (e.g., Silvester and Pitzer, 1978). The results of the more detailed study of sodium chloride by Silvester and Pitzer (1977; see their Figures 4, 5, and 6) suggest that these first derivatives provide an extrapolation that is reasonably accurate up to about 100°C.

In more recent work, the temperature dependence has been expressed in various studies by a variety of different temperature functions, most of which require only 5-7 parameters per observable interaction coefficient. Pabalan and Pitzer (1987) used such equations to develop a model for the system $Na-K-Mg-Cl-SO_4-OH-H_2O$ which appears to be generally valid up to about 200°C. Pabalan and Pitzer (1988) used equations of this type to build a model for the system $Na-Cl-SO_4-OH-H_2O$ that extends to 300°C. Greenberg and Møller (1989), using an elaborate compound temperature function, have constructed a model for the $Na-K-Ca-Cl-SO_4-H_2O$ system that is valid from 0-250°C. More recently, Spencer, Møller, and Weare (1990) have used a more compact equation to develop a model for the $Na-K-Ca-Mg-Cl-SO_4-H_2O$ system at temperatures in the range -60 to 25°C.

The pressure dependence of activity coefficients has also been looked at in the context of the Pitzer formalism. For descriptions of recent work, see Kumar (1986), Connaughton, Millero, and Pitzer (1989), and Monnin (1989).

3.5.5. Practical Aspects

In practice, the matter of obtaining values for the observable interaction coefficients is more complicated. Not all models based on Pitzer's equations are mutually consistent. Mixing reported data can lead to inconsistencies. For the most part, differences in reported values for the same coefficient are functions of the exact data chosen for use in the fitting process, not just whose data, but what kind or kinds of data as well. Some older reported values for the mixture parameters (e.g., Pitzer, 1979) are based on fits not employing the ${}^E\theta_{MM}$ formalism, which has become firmly entrenched in more recent work.

Some differences in the values of reported Pitzer parameters are due to minor differences in the values used for the A^ϕ Debye-Hückel parameter (e.g., 0.39 versus 0.392; see Plummer et al., 1988, p. 3, or Plummer and Parkhurst, 1990). The general problem of minor discrepancies in this and other limiting law slope parameters has been looked at in some detail by Ananthaswamy and Atkinson (1984). Recently, Archer (1990) has also looked at this problem and proposed a method for adjusting reported Pitzer coefficients for minor changes in Debye-Hückel parameters without resorting to refitting the original experimental data.

There has also been some occasional modification of the basic activity coefficient equations themselves. For example, in treating the activity coefficients of alkali sulfate salts at high temperature, Holmes and Mesmer (1986a, 1986b) changed the recommended value of the α parameter from 2.0 to 1.4. Also Kodytek and Dolejs (1986) have proposed a more widespread usage of the $\beta_{MX}^{(2)}$ parameter, based on the empirical grounds that better fits can be obtained for some systems. The usage of this parameter was originally restricted to the treatment of 2:2 electrolytes (Pitzer and Mayorga, 1973).

The formal treatment of speciation in the solutions (assumptions of which species are present) can also lead to different models. Association phenomena were first recognized in the Pitzer formalism in order to deal with phosphoric acid (Pitzer and Silvester, 1976) and sulfuric acid (Pitzer, Roy, and Silvester, 1977). In general, ion pairs have been treated formally as non-existent. An exception is in the model of Harvie, Møller, and Weare (1984), who employ three ion pair species: $CaCO_{3(aq)}$, $MgCO_{3(aq)}$, and $MgOH^+$.

Components which form strong complexes have received relatively little attention in the Pitzer formalism, presumably because of the much greater experimental data requirements necessary to evaluate the greater number of parameters associated with the greater number of species. However, Millero and Byrne (1984) have used Pitzer's equations to develop a model of activity coefficients and the formation of lead chloro complexes in some concentrated electrolyte solutions. Huang (1989) has also recently looked at some examples of complex formation in the context of the Pitzer formalism. However, because strong complexing can not be represented even mathematically by the interaction coefficient formalism without taking explicit account of the associated chemical equilibria, and because such models are more difficult to develop, the practical application of the Pitzer formalism remains limited mostly to systems of relatively strong electrolytes, molecular nonelectrolytes, and a few weak nonelectrolytes.

3.5.6. Pitzer's Equations in EQ3/6: Current Status

The present treatment of Pitzer's equations in EQ3/6 is somewhat limited, particularly in regard to some of the advances that have been made with these equations in the past few years. These limitations have to do with the state of the existing data files which support the use of Pitzer's equations, the treatment of the temperature dependence of the interaction coefficients, and the treatment of neutral solute species.

The **hmw** data file is an implementation of the model of Harvie, Møller, and Weare (1984). This model is restricted to 25°C. The **pit** data file is based mostly on the data summarized by Pitzer (1979). These data include the first order temperature derivatives of the interaction coefficients. The nominal temperature range of this data file is 0-100°C. These data are not based on the currently universally accepted $E\theta$ formalism introduced by Pitzer (1975).

EQ3/6 uses or ignores the $E\theta$ formalism, depending on the value of a flag parameter on the data file. The temperature dependence, if any, is handled by using first and second order temperature derivatives of the interaction coefficients, which are expected for use at temperatures other than 25°C. The code permits a $\beta_{MX}^{(2)}$ parameter to be specified on the data file for any electrolyte. The

α parameters are also provided on the data file for each electrolyte. Thus, non-standard values can be employed if desired.

The temperature dependence is presently limited to a representation in terms of a second-order Taylor's series in temperature. This requires the presence on the supporting data file of first and second temperature derivatives (see the EQPT User's Guide, Daveler and Wolery, 1992). No provision has yet been made for the more sophisticated representations proposed for example by Pabalan and Pitzer (1987) or Spencer, Møller, and Weare (1990).

EQ3/6 is presently quite limited in terms of the treatment of nonelectrolyte components by means of Pitzer's equations. This limitation is expressed in the structure of the data files and the mapping relations presently built into the EQPT data file preprocessor. These are presently set up to deal only with electrolyte parameters. However, it is possible to enter λ_{NN} , $\lambda_{NN'}$, λ_{NM} , and λ_{NX} parameters as though they were $\beta_{MX}^{(0)}$ parameters. The λ_{NM} and λ_{NX} parameters that are part of the model of Harvie, Møller, and Weare (1984) are included on the **hmw** data file in this manner.

The present version of EQPT can not handle the ζ_{MNX} interaction coefficient; however.

The means of storing and representing interaction coefficient data in EQ3/6 deserves some comment. There is a natural tendency to represent λ_{ij} by a two-dimensional array, and μ_{ijk} by a three-dimensional array. However, arrays of this type would be sparse (for example, $\lambda_{ij} = 0$ for many i, j), and many of the entries would be duplicates of others ($\lambda_{ij} = \lambda_{ji}$, etc.). Therefore, the λ_{ij} are represented instead by three parallel one-dimensional arrays. The first contains the λ_{ij} values themselves, the second contains indices identifying the i -th species, and the third identifies the j -th species. The treatment is analogous for μ_{ijk} , which only requires an additional array to identify the k -th species. These arrays are constructed from data listed on the **data0** data files. Coefficients which must be zero by virtue of the mapping relations or other conventions are not included in the constructed arrays. Also, the storage scheme treats for example λ_{ij} and λ_{ji} as one coefficient, not two.