A Chemical Equilibrium Model for Natural Waters

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Abstract. This paper reviews the present status of the Pitzer chemical equilibrium model, which can be used to characterize the one-atmosphere activity coefficients of ionic and non-ionic solutes in natural waters as a function of temperature and ionic strength. The model considers the ionic interactions of the major seasalt ions (H, Na, K, Mg, Ca, Sr, Cl, Br, OH, HCO_3, $B(OH)_4$, HSO_4, SO_4, CO_3, CO_2, $B(OH)_3$, H_2O) and is based on the 25 °C model of Weare and co-workers. The model has been extended by a number of workers so that reasonable estimates can be made of the activity coefficients of most of the major seasalt ions from 0 to 250 °C. Recently coefficients for a number of solutes that are needed to determine the dissociation constants of the acids from 0 to 50 °C (H_3CO_3, $B(OH)_3$, H_2O, HF, HSO_4^-, H_3PO_4, H_2S, NH_4^+ etc.) have been added to the model. These results have been used to examine the carbonate system in natural waters and determine the activity of inorganic anions that can complex trace metals. The activity and osmotic coefficients determined from the model are shown to be in good agreement with measured values in seawater. This model can serve as the foundation for future expansions that can examine the activity coefficient and speciation of trace metals in natural waters. At present this is only possible from 0 to 50 °C over a limited range of ionic strengths (<1.0) due to the limited stability constants for the formation of the metal complexes. The future work needed to extend the Pitzer model to trace metals is discussed.

Key words: Activity coefficients, activity, ions

1. Introduction

Interactions between ions in natural waters can have a major effect on the rates of redox processes (Millero, 1990a,b), on mineral solubility (Harvie et al., 1984) and biochemical availability (Anderson and Morel, 1982). A quantitative treatment of these effects requires an appropriate, self-consistent model describing the variation of activity coefficients with ionic strength, temperature and composition. One would also like to know the form or speciation of metals in natural waters of different composition. The estimation of the activity coefficients of ions in natural waters can be determined by using the ion pairing or specific interaction models. The recent progress made in using these models to estimate the activity of ionic solutes and speciation of metals is briefly discussed below.

The most popular method used to account for the ionic interactions in natural waters is the ion pairing model. This model has been used by a number of workers to determine the speciation of ions in natural waters (Sillen, 1961; Garrels and

Thompson, 1962; Dyrssen et al., 1968; Ingri et al., 1967; Truesdell and Jones, 1969; Morel and Morgan, 1972; Atkinson et al., 1973; Dyrssen and Wedborg, 1974; Whitfield, 1975a,b; Millero, 1975; Whitfield, 1979; Dickson and Whitfield, 1981; Millero and Schreiber, 1982; Turner et al., 1981; Turner and Whitfield, 1987; Byrne et al., 1988). The use of the ion pairing model to estimate the activity coefficients of the major components of natural waters was pioneered by Garrels and Thompson (1962) and extended by Dickson and Whitfield (1981) and Millero and Schreiber (1982). These latter studies allow one to estimate reliable activity coefficients for a number of major and minor ions to 1 m. A number of computer codes are available to aid in determining the speciation of elements in natural waters (e.g., Perrin and Sayce, 1967; Ingri et al., 1967; Morel and Morgan, 1972; van Breeman, 1973; Atkinson et al., 1973; Crerar, 1975; Knowles and Wakeford, 1978; Westall et al., 1976; Nordstrom and Ball, 1984). Although these programs are useful in rapidly calculating the speciation in natural waters, they are generally limited to 25 °C and low ionic strengths by their limited data. The ion pairing model can presently be used to estimate the activity coefficients of the major and minor components (Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+}, Ba^{2+}, F^-, Cl^-, Br^-, OH^-, NO_3^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, $B(OH)_4^-$, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) of natural waters at 25 °C and below 1 m (Dickson and Whitfield, 1981; Millero and Schreiber, 1982; Turner et al., 1981). Byrne et al. (1988) extended these calculations from 0 to 50 °C for a number of metals. Millero and Hawke (1992) have added the divalent metals (Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}) to the major ion pairing model of Millero and Schreiber (1982). Equations are given for estimating the effect of ionic strength on the activity coefficients of free ions and the stability constants that can be easily adapted to a computer code. These equations make it possible to estimate the speciation of metals in natural waters at 25 °C to ionic strengths below 1 m. These speciation calculations are limited due to the lack of reliable stability constants valid over a wide range of temperature and ionic strength. Extension to higher ionic strengths and other temperatures is complicated by the requirement for experimental data for the large number of ion pairs −50 in the case of seawater. The Pitzer model (1991) for seawater requires stability constants for only 7 ion complexes (HSO_4^-, HF, MgF^+, CaF^+, $MgOH^+$, $MgCO_3$, $CaCO_3$). Stability constants at temperatures other than 25 °C are not readily available. Reliable extensions to higher ionic strength are difficult due to the lack of activity coefficients for ion pairs of various charge types.

The specific interaction model as formulated by Pitzer (1973) has made a large impact on our ability to estimate the activity of ionic and nonionic solutes in natural waters. The model was first used by Whitfield (1975a,b) to estimate the activity coefficients of a number of ions in a simple seawater solutions (NaCl + $MgSO_4$). This followed directly from the use of the specific interaction model (Leyendekkers, 1972; Whitfield, 1973), as formulated by Guggenheim (1935), to estimate the activities of the major sea salts. Weare and co-workers (Harvie and Weare, 1980; Harvie et al., 1984; Felmy and Weare, 1986; Møller, 1988; Greenberg and Møller, 1989; Spencer et al., 1990) and others (Millero, 1982; Pabalan

and Pitzer, 1987; Clegg and Whitfield, 1991,1995; Millero and Roy, 1997) have extended the model for the major components of seawater. The present model can be used to make reliable estimates of the activity coefficients of the major components (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, OH^-, SO_4^{2-}) of natural waters over a wide range of temperatures (0–250 °C) to high ionic strengths (<6 m). The extension of these models to trace metals has been made for solutions of chloride and sulfate solutions (Whitfield, 1975a,b) at 25 °C. The speciation of divalent (Millero and Hawke, 1992; Millero et al., 1995) and trivalent metals (Millero, 1992; Millero et al., 1995) with OH^-, HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, and HPO_4^{2-} has been added to the model at 25 °C. More recently, Campbell et al. (1993) have developed a Pitzer model for the major sea salts that considers the ionic interactions of H, Na, K, Mg, Ca, Sr, Cl, Br, OH, HSO_4, SO_4, H_2O from 0 to 50 °C and ionic strengths from 0 to 2 m. Clegg and Whitfield (1995) have also developed a major seawater model that they use to examine the dissociation of ammonia over the same temperature range. In our earlier work (Millero, 1982; Millero, 1983; Thurmond and Millero, 1982; Millero and Thurmond, 1983; Hershey and Millero, 1986; Hershey et al., 1986, 1988, 1989; Millero et al., 1987; 1989), we have used the Pitzer equations to examine the dissociation of acids in NaCl solutions with and without added divalent cations and in seawater at 25 °C. We have used these measurements to determine Pitzer parameters for the interaction of Mg^{2+} and Ca^{2+} with a number of acid anions (F^-, OH^-, HCO_3^-, CO_3^{2-}, HS^-, $B(OH)_4^-$, HSO_3^-, SO_3^{2-}, F^-, TRIS). The extension of the Pitzer model for divalent (Millero et al., 1995) and trivalent metals (Millero, 1992) has been made at 25 °C. In a recent paper (Millero and Roy, 1997), the Pitzer ionic interaction model has been extended to include the components needed to evaluate the carbonate system in natural waters from $I = 0$ to 6 m and 0 to 50 °C. This model will be discussed in the present paper and ways to extend the model for divalent and trivalent metals as a function of temperature will be outlined.

As first suggested by Whitfield (1975a,b) the combination of the ion pairing and Pitzer models can strengthen our ability to make reliable estimates of activity coefficients and to determine the speciation of metals in natural waters over a wide range of conditions. In recent years we have attempted (Millero and Schreiber, 1982; Millero, 1981, 1982, 1983, 1984, 1985, 1986, 1990a,b; Millero and Thurmond, 1983; Millero and Byrne, 1984; Hershey and Millero, 1986; Hershey et al., 1986; Millero et al., 1987; Hershey et al., 1988; Hershey et al., 1989; Millero et al., 1989; Millero and Roy, 1997) to continue the joining of these two models. From this work it is clear that the Pitzer and ion pairing models are complementary for some of the strong cation-anion interactions. For example, the Pitzer model allows the prediction of mineral solubilities and geochemical precipitation sequences, while the ion pairing model allows the prediction of chemically reactive trace metal species in solution. In this paper we will review the present status of our version of the Pitzer model and give the parameters that can be used to estimate activity coefficients for ions from 0 to 50 °C to ionic strengths of 6 m.

2. Model for the Major Components of Natural Waters

The ionic interactions affecting the non ideal behavior of an ion i in an electrolyte solution are related to the stoichiometric or total activity coefficient, $\gamma_T(i)$, which is related to the activity, a_i, and stoichiometric or total (T) concentration, $[i]_T$, by

$$a_i = \gamma_T(i)[i]_T. \tag{1}$$

The value of $\gamma_T(i)$ is controlled by the composition of the natural water at a given temperature and pressure. For ions that can form complexes with the components of the solution (e.g., $H^+ + SO_4^{2-} \rightarrow HSO_4^-$) it is necessary to know the fraction of free (F) or uncomplexed form of the ion given by

$$\alpha_H = [H^+]_F/[H^+]_T. \tag{2}$$

The desired total activity coefficient is thus given by

$$\gamma_T(H^+) = \alpha_H \gamma_F(H^+) \tag{3}$$

where $\gamma_F(H^+)$ is the activity coefficient of H^+ in the media due to the interactions of H^+ with the major components (Cl^-, etc.) of the solution. The value of α_H can be determined from

$$\alpha_H = 1/(1 + [SO_4^{2-}]/K^*_{HSO_4} + [F^-]/K^*_{HF}) \tag{4}$$

where $K^*_{HSO_4}$ and K^*_{HF} are the dissociation constants for HSO_4^- and HF in the ionic media and $[SO_4^{2-}]$ and $[F^-]$ are the concentrations of sulfate and fluoride not complexed to H^+ (at high pH this is the same as the total sulfate and fluoride in the solution). The values of the dissociation constants can be estimated from the thermodynamic values (K_{HSO_4} and K_{HF})

$$K^*_{HSO_4} = K_{HSO_4}(\gamma_{HSO_4}/\gamma_H \gamma_{SO_4}) \tag{5}$$

$$K^*_{HF} = K_{HF}(\gamma_{HF}/\gamma_H \gamma_F) \tag{6}$$

where the activity coefficients γ_i are the values in the ionic media.

   The activity coefficients of ions can be estimated in an electrolyte solution by using various extensions of the Debye–Hückel equation (Davies, 1962; Kielland, 1937). More reliable estimates can be made by using the specific interaction model that uses parameters derived from experimental measurements made at the same ionic strength (Guggenheim, 1935; Pitzer, 1973). The general equation is

$$\ln \gamma_i = D.H. + \Sigma_{ij} m_i m_j B^\gamma_{ij} + \Sigma_{ijk} m_i m_j m_k C^\gamma_{ijk} \tag{7}$$

where D.H. is some form of the Debye–Hückel limiting law. The B^γ_{ij} and C^γ_{ijk} parameters are related to the binary (ions i and j) and ternary (ions i, j and k) interactions and can be a function of ionic strength. The Pitzer equations for estimating

the activity coefficients of ions in mixed electrolyte solutions are given in detail in the Appendix. The activity coefficient of a cation (M) in a mixed electrolyte

$$
\begin{aligned}
\ln \gamma_M = {} & Z_M^2 f^\gamma + 2\Sigma_a m_a (B_{M_a} + EC_{M_a}) + Z_M^2 R + Z_M S + \Sigma_c m_c (2\Theta_{Mc} \\
& + \Sigma_a m_a \Psi_{Mca}) + \Sigma_a \Sigma_{a'} m_a m_{a'} \Psi_{aa'M} \\
& + \Sigma_c m_c 2^E \Theta_{M_c} + Z_M^2 R_1 + Z_M^2 R_2
\end{aligned}
\tag{8}
$$

can be attributed to five contributions:

1. The Debye–Hückel term ($Z_M^2 f^\gamma$) is the limiting law which is only a function of ionic strength.
2. The interaction parameters of M with the major anions (a) in the solution ($2\Sigma_a m_a (B_{M_a} + EC_{M_a})$) are determined from binary solutions of Ma.
3. The interaction parameters of M with the major cations (c) ($\Sigma_c m_c 2\Theta_{Mc}$) are determined from ternary solutions ($Ma + ca$).
4. The triplet interaction parameters of M with the major cations and anions ($\Sigma_c m_c \Sigma_a m_a \Psi_{Mca}$ and $\Sigma_a \Sigma_{a'} m_a m_{a'} \Psi_{aa'M}$) are determined from ternary solutions ($Ma + ca$).
5. The media terms for the major components ($Z_M^2 R + Z_M S$) are determined from binary mixtures of the major components of the solution.
6. The higher order electrical terms ($\Sigma_c m_c 2^E \Theta_{M_c} + Z_M^2 R_1 + Z_M^2 R_2$) for the interactions of ions of different charge (Mg-Na) are a function of ionic strength.

As shown elsewhere (Millero, 1982) for the trace components (H^+, Cu^{2+}, etc.) of the solution only the major cation interaction parameters (2, 3, 4) are needed to make reasonable estimates of the "trace" activity coefficients (Millero, 1982). The trace components of the solution do not contribute significantly to the media terms. Although this simplifies the estimation of the activity coefficients of trace constituents, many trace constituents form strong interactions with the major (SO_4^{2-}) and minor components (OH^-, CO_3^{2-}, etc.) and cannot be accounted for using reasonable values for the interaction parameters. To correct for these strong interactions one must consider the formation of an ion pair between the cation and anion. This leads to parameters for the ion pairs that are model dependent.

At a given temperature the model requires the interaction terms β_{MX}^0, β_{MX}^1, β_{MX}^2, C_{MX}^ϕ for all the electrolytes (MX) that make up the solution. These parameters account for the binary interactions of the individual components of each electrolyte ($M - M$, $X - X$, and MX) in the mixture (Pitzer and Mayorga, 1973, 1974). The values of β_{MX}^0, β_{MX}^1, β_{MX}^2, C_{MX}^ϕ for the major components of natural waters are available at 25 °C and are tabulated elsewhere (Pitzer, 1991). The Pitzer activity coefficient parameters for a number of electrolytes important in natural systems (HCl, NaCl, KCl, NaOH, MgCl₂, CaCl₂, Na₂SO₄, K₂SO₄, MgSO₄, CaSO₄) are known (Møller, 1988; Greenberg and Møller, 1989; Spencer et al., 1990; Pabalan and Pitzer, 1987) over a wide range of temperatures (0–250 °C) and have been fitted to equations of the form (Pabalan and Pitzer, 1987)

$$P(T) = q_1 + q_2(1/T - 1/T_R) + q_3 \ln(T/T_R) + q_4(T - T_R)$$
$$+ q_5(T^2 - T_R^2) \tag{9}$$

or

$$P(T) = q_1(T/2 + 298^2/2T - 298) + q_2(T^2/6 + 298^3/3T - 298^2/2)$$
$$+ q_3(T^3/12 + 298^4/4T - 298^3/3) + q_4(T^4/20$$
$$+ 298^5/5T - 298^4/4) + q_5(298 - 298^2/T) + q_6 \tag{10}$$

and (Møller, 1988; Greenberg and Møller, 1989)

$$P(T) = a_1 + a_2T + a_3/T + a_4 \ln T + a_5/(T - 263) + a_6T^2$$
$$+ a_7/(680 - T) + a_8/(T - 227) \tag{11}$$

where P is β_{MX}^0, β_{MX}^1 or C_{MX}^ϕ and T_R is a reference temperature (298.15 K) and a_i and q_i are adjustable parameters given in the Appendix. As will be discussed later the Pitzer coefficients for weakly soluble electrolytes are frequently determined from solubility and emf measurements of weak acids in ionic solutions. Data over a more limited temperature range (0–50 °C) are frequently (Simonson et al., 1987a,b; 1988) fit to equations of the form (Appendix)

$$\beta_{MX}^0(T) = a(T - T_R) + b(T - T_R)^2. \tag{12}$$

One can make reasonable estimates of activity coefficients over smaller ranges of temperature (0–50 °C) by using thermodynamic data. The integration of the heat capacity and enthalpies of electrolytes at a reference temperature (25 °C) can be used (Millero, 1979a) to estimate the effect of temperature on the osmotic and activity coefficients. Heat capacity and enthalpy data at 25 °C have been shown (Millero, 1979a) to provide reasonable estimates of activity coefficients from 0 to 75 °C and 0 to 2 m. From the definition of the effect of temperature on the coefficients used to fit the enthalpies (Silvester and Pitzer, 1978) and heat capacities (Criss and Millero, 1996), the effect of temperature on the activity coefficient parameters can be determined by

$$\beta^{(0)L} = \partial \beta^{(0)}/\partial T \tag{13}$$

$$\beta^{(0)J} = \partial^2 \beta^{(0)}/\partial T^2 + (2/T)(\partial \beta^{(0)}/\partial T). \tag{14}$$

The integration of these equations between T_R (298.15) and T gives

$$\beta^{(0)} = \beta_R^{(0)} + q_2(1/T - 1/T_R) + q_5(T^2 - T_R^2) \tag{15}$$

where

$$q_2 = (\beta^{(0)J}/3)T_R^3 - T_R^2\beta_R^{(0)L}) \tag{16}$$

$$q_5 = \beta^{(0)J}/6. \tag{17}$$

Similar equations can be derived for $\beta^{(1)}$ and C^ϕ (Appendix). The values of $\beta^{(0)J}$ recently determined by Criss and Millero (1996, 1998) can be combined with literature values of $\beta_R^{(0)}$ and $\beta_R^{(0)L}$ (Pitzer, 1991) to derive equations that can be used to estimate osmotic and activity coefficients of the electrolytes as a function of temperature. As found in earlier work (Millero, 1979a), the 25 °C enthalpy and heat capacity data can yield reasonable estimates for the activity coefficients from 0 to 50 °C (Criss and Millero, 1996).

The interactions of like charged ions ($M - N$ and $X - Y$) are related to mixing parameters (Θ_{MN} and Θ_{XY}) which are determined (Pitzer and Kim, 1974; Pitzer, 1975; Harvie and Weare, 1980) from solubility or activity measurements on ternary solutions ($MX + NX$ and $MX + MY$). The values of Θ_{ij} and Ψ_{ijk} terms are usually determined from regression analysis of experimental data from simple ternary systems for which the pure electrolyte parameters are known (Pitzer, 1991). For a ternary mixture $MX - NX$, where M and N are cations and X is a common anion the values of Θ_{ij} and Ψ_{ijk} are determined from

$$(\ln \gamma_{MX} - \ln \gamma_{MX}^0)/m_N = \Theta_{MN} + \frac{1}{2}(m_M + m_X)\Psi_{MNX} \tag{18}$$

where γ_{MX}^0 is the activity coefficient of MX calculated using only the pure electrolyte parameters and γ_{MX} is the experimental activity coefficient. The values of Θ_{MN} and Θ_{XY} are assumed to be independent of the common ion (X or Y and M or N) (called Young's second rule). Triplet interactions ($M - N - X$ and $M - X - Y$) that may occur in these mixtures are accounted for by the addition of the parameters Ψ_{MNX} and Ψ_{MXY}. It should be pointed out that the Θ_{MN} and Ψ_{MNX} terms are normally not large and do not contribute much in dilute solutions (Millero, 1982). The values of Θ_{MN} and Ψ_{MNX} are model dependent since they require known values of $\beta_{MX}^0, \beta_{MX}^1, \beta_{MX}^2, C_{MX}^\phi, \beta_{NX}^0, \beta_{NX}^1, \beta_{NX}^2, C_{NX}^\phi$ and depend on the experimental data used for their evaluation (activity or solubility). It is thus important to take care in mixing the parameters determined by various workers.

For dilute solutions the activity of neutral solutes (N) in electrolyte solutions are determined from the ratio of the solubility in a salt solution (S) and water (S^0)

$$\gamma_N = S^0/S. \tag{19}$$

The ionic strength dependence is frequently expressed by the Setchenow equation

$$\ln \gamma_N = kI. \tag{20}$$

Since most solutes are "salted out", the activity coefficient of neutral solutes are greater than one or k is positive. Due to the limited data available for some neutral solutes, it is necessary to use salting coefficients in NaCl solutions to estimate the

activity coefficients (this may involve a second order dependence of $\ln \gamma_N$ on I). If no data are available for a given solute, it is necessary to use another compound of similar structure as a model. The Pitzer interaction parameters needed to calculate the activity coefficient of a non-electrolyte in a mixed electrolyte solution include terms for the interaction of N with the cations ($2\Sigma_c m_c \lambda_{Nc}$) and anions ($2\Sigma_a m_a \lambda_{Na}$) in the solution (see Appendix). For a concentrated solution a second order term is needed to account for the interactions of N with cations and anions ($\Sigma_a m_c m_a \zeta_{Nca}$).

For a solution containing the major components of seawater (Na^+, Mg^{2+}, Cl^-, and SO_4^{2-}) one needs to know 13 binary parameters (β^0_{NaCl}, β^1_{NaCl}, C^ϕ_{NaCl}; $\beta^0_{Na_2SO_4}$, $\beta^1_{Na_2SO_4}$, $C^\phi_{Na_2SO_4}$; $\beta^0_{MgCl_2}$, $\beta^1_{MgCl_2}$, $C^\phi_{MgCl_2}$; $\beta^0_{MgSO_4}$, $\beta^1_{MgSO_4}$, $\beta^2_{MgSO_4}$, $C^\phi_{MgSO_4}$) and 6 ternary parameters (Θ_{NaMg}, Θ_{ClSO_4}, Ψ_{NaMgCl}, Ψ_{NaMgSO_4}, Ψ_{ClSO_4Na}, Ψ_{ClSO_4Mg}). The addition of the other major seawater components (K^+, Ca^{2+}, Sr^{2+}, HCO_3^-, Br^-, CO_3^{2-} and F^-) requires more parameters, but they do not contribute much to the media term of the Pitzer equation. A review of the development of the Pitzer models presently available and used in our laboratory is discussed below.

3. The MIAMI Ionic Interaction Model

Most of the computer codes used for the major components of seawater are based on the 25 °C model of Harvie et al. (1984) which accounts for the interactions of the major cations and anions (H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, OH^-, HCO_3^-, CO_3^{2-}, CO_2). This model includes the formation of a number of ion pairs (HSO_4^-, $MgOH^+$, $MgCO_3$, and $CaCO_3$). Many of the binary terms (β^0_{MX}, β^1_{MX}, C^ϕ_{MX}) and higher order interaction terms (Θ_{ij}, Ψ_{ijk}) used in the model were determined from solubility measurements. Felmy and Weare (1986) have added the borate system ($B(OH)_4^-$, $B(OH)_3$) to this 25 °C model. The model includes the formation of $MgB(OH)_4^+$ and $CaB(OH)_4^+$ ion pairs. We (Millero, 1982) have added some of the major (Sr^{2+}, F^-, Br^-) and minor (Li^+, Rb^{2+}, Cs^+, NH_4^+, Ba^{2+}, Mn^{2+}) components to this 25 °C using available (Pitzer, 1979; 1991) and estimated parameters. It should be pointed out that our model only calculates activity and osmotic coefficients while the models of Weare and co-workers can be used to examine the solubility of minerals in natural waters. Our model 25 °C was successfully used to estimate the pK of a number of acids in seawater (Millero, 1983). The 25 °C Harvie et al. (1984) model had some major flaws due to the limited data available to account for the interactions of HSO_4^- with Na^+, Mg^{2+}, K^+ and Ca^{2+} and Mg^{2+} and Ca^{2+} with HCO_3^-, $B(OH)_4^-$ and CO_3^{2-}. New experiment measurements of the dissociation constants at 25 °C of carbonic (Millero and Thurmond, 1983) and boric acid (Hershey et al., 1986) in Na-Mg-Cl solutions have led to more reliable parameters for the interaction of Mg^{2+} with HCO_3^-, CO_3^{2-}, and $B(OH)_4^-$. Measurements were also made in Na-Mg-Cl solutions to derive interaction parameters for the TRIS (Millero et al., 1987), sulfide (Hershey et al., 1988), sulfite (Millero et al., 1989) and phosphate (Hershey et al., 1989) systems. Our present 25 °C program contains parameters for major seasalt cations (Na, K, Mg, Ca, Sr) and anions (Cl,

SO_4, CO_3, HCO_3, Br, F, $B(OH)_4$) and neutral solutes (CO_2, $B(OH)_3$, HF, NH_3, H_3PO_4, H_2S, SO_2). It also contains seventeen minor cations (H, Li, Rb, Cs, NH_4, Ba, Mn, Fe, Co, Ni, Cu, Zn, UO_2, Be, Cd, Pb, MgOH) and nineteen minor anions (HSO_4, HS, OH, IO_3, ClO_3, ClO_4, BrO_3, CNS, NO_2, NO_3, H_2PO_4, HPO_4, PO_4, H_2AsO_4, $HAsO_4$, AsO_4, HSO_3, SO_3, Acetate). Recently we have added divalent and trivalent ions (Millero, 1992; Millero et al., 1995) to our 25 °C model.

Pabalan and Pitzer (1987) extended the temperature range (25–250 °C) for the Na-K-Mg-Cl-OH system using available thermodynamic data (Table A2). This was followed shortly by a paper by Møller (1988) which determined the parameters for the Na-Ca-Cl-SO_4 system from 25 to 250 °C (Table A1). It should be pointed out that although the binary parameters for these models are similar, the higher order terms are model dependent. One should, thus, be careful in joining the two models. Greenberg and Møller (1989) extended the Møller (1988) model to lower temperatures (0–250 °C) and Spencer et al. (1990) provided a 0–25°C model for the Na-K-Ca-Mg-Cl-SO_4 system (Table A1). Campbell et al. (1993) developed a 0–50°C model for the H-Na-K-Mg-Ca-Sr-Cl-Br-OH-HSO_4-SO_4 system to examine the activity coefficient of HCl in seawater. Clegg and Whitfield (1995) have developed a similar model that has been used to examine the dissociation of ammonia in seawater from 0 to 40 °C. These latter studies lacked reliable parameters for the interaction of HSO_4^- with Na^+, K^+, Mg^{2+}, and Ca^{2+} from 0 to 25 °C. These parameters are now available from emf measurements of HCl in HCl-Na_2SO_4, HCl-K_2SO_4, and HCl-$MgSO_4$ mixtures (Pierrot et al., 1997; Pierrot et al., 1998) from 0 to 50 °C. More recently Millero and Roy (1997) have extended the MIAMI model that includes the major sea salt model (H-Na-K-Mg-Ca-Sr-Cl-F-OH-HCO_3-$B(OH)_4$-HSO_4-SO_4-CO_3-CO_2-$B(OH)_3$) from 0 to 50 °C. This model has been shown (Millero and Roy, 1997) to provide reliable pK's for all the acids needed to characterize the carbonate system in natural waters (H_2CO_3, $B(OH)_3$, H_2O, HF, HSO_4^-, H_3PO_4, H_2S, NH_4^+) from 0 to 40 °C. The development of the parameters used in our present model (Millero and Roy, 1997) is outlined below.

4. Binary Interaction Parameters for the Major Cations and Anions (β_{MX}^0, β_{MX}^1, β_{MX}^2, C_{MX}^ϕ)

A summary of the sources of the binary interaction parameters used in our model is given below. Although our model contains parameters valid from 0 to 250 °C for some of the major seasalts (Pabalan and Pitzer, 1987; Møller, 1988; Greenberg and Møller, 1989), our model is only valid from 0 to 50 °C. The coefficients are given in the Appendix. A brief summary of the parameters selected for our model is given below.

4.1. H-X TERMS

The parameters selected for HCl were those determined by Campbell et al. (1993) and are valid from 0 to 100 °C and to 4 m. The H, SO_4 and H, HSO_4 parameters were taken from Pierrot and Millero (1997) and are valid from 0 to 250 °C. The HBr parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C.

4.2. Na-X TERMS

The parameters for NaCl are taken from the work of Møller (1988) and are valid from 0 to 250 °C (Table A1). The Na_2SO_4 are taken from Hovey et al. (1993) and are valid from 0 to 100 °C. The $NaHSO_4$ parameters are taken from Pierrot and Millero (1997) and are valid from 0 to 250 °C. The NaOH parameters are taken from Pabalan and Pitzer (1987) and are valid from 0 to 250 °C. The $NaHCO_3$ and Na_2CO_3 parameters are taken from Peiper and Pitzer (1982) and are valid from 0 to 50 °C. The NaBr parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The $NaB(OH)_4$ parameters are taken from the Simonson et al. (1987a) and are valid from 0 to 50 °C. The NaF parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The NaH_2PO_4, Na_2HPO_4, and Na_3PO_4 parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The NaHS parameters are taken from the work of Hershey et al. (1988) and are valid from 0 to 50 °C.

4.3. K-X TERMS

The parameters for KCl and K_2SO_4 parameters are taken from the work of Greenberg and Møller (1989) and are valid from 0 to 250 °C. The $KHSO_4$ parameters are taken from Pierrot and Millero (1998) and are valid from 0 to 50 °C. The KOH parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The $KHCO_3$ parameters are taken from Roy et al. (1983) and are valid from 5 to 45 °C. The K_2CO_3 parameters are taken from Simonson et al. (1987b) and are valid from 5 to 95 °C. The KBr parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The $KB(OH)_4$ parameters are taken from the Simonson et al. (1987a) and are valid from 0 to 50 °C. The KF parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer,

1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The KH_2PO_4 parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The parameters for K_2HPO_4 and K_3PO_4 are only available at 25 °C (Pitzer and Mayorga, 1973). The KHS parameters are taken from the work of Hershey et al. (1988) and are valid from 5 to 25 °C.

4.4. Mg-X TERMS

The $MgCl_2$ and $MgSO_4$ parameters were taken from Pabalan and Pitzer (1987) and are valid from 0 to 250 °C. The $Mg(HSO_4)_2$ parameters are taken from Pierrot and Millero (1998) and are valid from 0 to 50 °C. The $Mg(HCO_3)_2$ parameters are recalculated using the results of Millero and Thurmond (1983) and are only valid at 25 °C. The $MgBr_2$ parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The $Mg(B(OH)_4)_2$ parameters are taken from Simonson et al. (1988) and are valid from 5 to 55 °C. The $Mg(HS)_2$ parameters are taken from Hershey et al. (1988) and are valid at 25 °C.

4.5. Ca-X TERMS

The $CaCl_2$ and $CaSO_4$ parameters were taken from Greenberg and Møller (1989) and are valid from 0 to 250 °C (Table A1). The $Ca(HSO_4)_2$, $Ca(OH)_2$, and $Ca(HCO_3)_2$ parameters are taken from Harvie et al. (1984) and are only valid at 25 °C. The $CaBr_2$ parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1996) which are valid from 0 to 50 °C. The $Ca(B(OH)_4)_2$ parameters are taken from Simonson et al. (1988) and are valid from 5 to 55 °C. The $Ca(HS)_2$ parameters are taken from Hershey et al. (1988) and are only valid at 25 °C.

4.6. Sr-X TERMS

The $SrCl_2$ and $SrBr_2$ parameters are an extension of the 25 °C results (Pitzer and Mayorga, 1973) using enthalpy (Silvester and Pitzer, 1978) and heat capacity data (Criss and Millero, 1998) which are valid from 0 to 50 °C. The $SrSO_4$, $Sr(HSO_4)_2$, $Sr(OH)_2$, $Sr(HCO_3)_2$ and $Sr(B(OH)_4)_2$ parameters are equated to the values for Ca^{2+} salts.

4.7. MgOH-Cl TERMS

The MgOH, Cl parameters are taken from Harvie et al. (1984) and are only valid at 25 °C.

5. Parameters for the Interactions of Cation-Cation, Anion-Anion and Triplet Interactions (Θ_{MN}, Ψ_{MNX})

Values of these terms for the major sea salts at 25 °C are available, but only a limited amount of data is available as a function of temperature (Pabalan and Pitzer, 1987; Møller, 1988; Greenberg and Møller, 1989) (Table A10). Since the effect of temperature on Θ_{MN} and Ψ_{MNX} is not very large, it can be neglected from 0 to 50 °C without serious errors. Higher order interaction terms ($^E\Theta_{ij}$ and $^E\Theta'_{ij}$) that account for the electrostatic effect of mixing unsymmetrical ions of the same charge (Na^+-Mg^{2+}) are a function of the ionic strength and can be evaluated from the approximation equations (Pitzer, 1975; 1991). These higher order interaction terms do not always improve the fit of the experimental data and thus are not always used. Care should therefore be taken, when selecting Θ and Ψ terms, to incorporate the unsymmetrical mixing terms appropriately. For the major seasalt ions, most of the parameters have been determined as a function of temperature, some to 50 °C and others to 250 °C. As far as the minor components are concerned only a few Θ and Ψ parameters are known and they are only valid at 25 °C. The sources of the values of Θ_{ij} and Ψ_{ijk} for cation-cation and anion-anion interactions used in our model are discussed below and are given in the Appendix.

5.1. H-M INTERACTIONS

The Θ_{H-Na}, Θ_{H-Mg}, Θ_{H-Ca} and Θ_{H-Sr} interaction terms are known (Campbell et al., 1993; Roy et al., 1980; 1982a; 1986) from 0 to 50 °C. The $\Theta_{MgOH-Mg}$ interaction parameter at 25 °C is taken from Harvie et al. (1984). The triplet interaction terms Ψ_{H-M-Cl} are available for M = Na (Pierrot and Millero, 1997), Mg (Roy et al., 1980), Ca (Roy et al., 1982a) and Sr (Roy et al., 1986) from 0 to 50 °C and M = K at 25 °C (Harvie et al., 1984). The values of $\Psi_{H-Na-SO_4}$ are available from 0 to 50 °C (Pierrot and Millero, 1997). The values of Ψ_{H-K-SO_4} (Harvie et al., 1984) and Ψ_{H-K-Br} (Pitzer and Kim, 1974) are only available at 25 °C.

5.2. Na-M INTERACTIONS

The values of Θ_{Na-K}, Θ_{Na-Ca}, $\Psi_{Na-K-Cl}$, $\Psi_{Na-K-SO_4}$, $\Psi_{Na-Ca-Cl}$ and $\Psi_{Na-Ca-SO_4}$ parameters are known from 0 to 250 °C (Møller, 1988; Greenberg and Møller, 1989). The values of $\Psi_{Na-K-Br}$ (Pitzer and Kim, 1974), $\Psi_{Na-K-HCO_3}$ and $\Psi_{Na-K-CO_3}$ (Harvie et al., 1984) are available at 25 °C. Values of Θ_{Na-Mg}, Θ_{K-Mg}, $\Psi_{Na-Mg-Cl}$, and $\Psi_{K-Mg-Cl}$ are available from 25 to 250 °C (Pabalan and Pitzer, 1987). The values of Θ_{Na-Sr}, and $\Psi_{Na-Sr-Cl}$ are valid at 25 °C (Pitzer and Kim, 1974). It should

be pointed out that the binary terms for NaCl and KCl used in the studies by Møller (1988) and Greenberg and Møller (1989) and Pabalan and Pitzer (1987) are slightly different and their combined use may lead to errors at high concentrations.

5.3. K-*M* INTERACTIONS

The values of Θ_{K-Mg}, and $\Psi_{K-Mg-Cl}$ parameters are known from 5 to 250 °C (Pabalan and Pitzer, 1987). The values of Θ_{K-Ca} and $\Psi_{K-Ca-Cl}$ parameters are known from 0 to 250 °C (Møller, 1988; Greenberg and Møller, 1989). It should be pointed out that since the binary values of KCl used in these two studies are slightly different, the combined use of these parameters might lead to some differences at high concentrations. We have assumed that the $\Theta_{K-Sr} = \Theta_{Na-Sr}$, and $\Psi_{K-Sr-Cl} = \Psi_{Na-Sr-Cl}$ values.

5.4. Mg-Ca INTERACTIONS

The values of Θ_{Mg-Ca}, $\Psi_{Mg-Ca-Cl}$, and $\Psi_{Mg-Ca-SO_4}$ are only available at 25 °C (Harvie et al., 1984).

5.5. Cl-*X* INTERACTIONS

The values of Θ_{Cl-SO_4}, Ψ_{Cl-SO_4-Na}, Ψ_{Cl-SO_4-K} and Ψ_{Cl-SO_4-Ca} values are available from 0 to 250 °C (Møller, 1988; Greenberg and Møller, 1989). The values of Ψ_{Cl-SO_4-Mg} are only valid at 25 °C. The values of Θ_{Cl-HCO_3}, Θ_{Cl-CO_3}, Ψ_{Cl-HCO_3-Na}, and Ψ_{Cl-CO_3-Na} (Roy et al., 1982b; Peiper and Pitzer, 1982) are reliable from 0 to 60 °C. The values of Θ_{Cl-HSO_4} and $\Psi_{Cl_4-HSO_4-Na}$ at 25 °C are taken from Harvie et al. (1984). The 25 °C values of $\Theta_{Cl-F} = 0.01$ and $\Psi_{Cl-F-Na} = 0.0023$ have been calculated from the measurements of Clegg and Brimblecombe (1988). The values of $\Theta_{Cl-B(OH)_4}$ and $\Psi_{Cl-B(OH)_4-Na}$ from 0 to 45 °C have been determined from Owen and King (1943) and Hershey et al. (1986). The values of $\Psi_{Cl-B(OH)_4-Mg} = -0.235$ and $\Psi_{Cl-B(OH)_4-Ca} = -0.8$ have been determined from Hershey et al. (1986) and Simonson et al. (1987) and are only valid at 25 °C. The Θ_{Cl-OH} and $\Psi_{Cl-OH-Na}$ from 0 to 50 °C have been determined from Harned and Owen (1958). The values of $\Psi_{Cl-OH-K}$ and $\Psi_{Cl-OH-Ca}$ at 25 °C are taken from Harvie et al. (1984). The $\Theta_{Cl-H_2PO_4}$, Θ_{Cl-HPO_4}, Θ_{Cl-PO_4}, $\Psi_{Cl-H_2PO_4-Na}$, Ψ_{Cl-HPO_4-Na}, and Ψ_{Cl-PO_4-Na} at 25 °C have been taken from Hershey et al. (1989). The $\Theta_{Cl-H_2AsO_4}$, $\Theta_{Cl-HAsO_4}$, Θ_{Cl-AsO_4}, $\Psi_{Cl-H_2AsO_4-Na}$, $\Psi_{Cl-HAsO_4-Na}$, and Ψ_{Cl-AsO_4-Na} at 25 °C have been taken from Millero (1983). The Θ_{Cl-SO_3} and Ψ_{Cl-SO_3-Na} at 25 °C have been taken from Millero et al. (1989).

5.6. SO_4-X INTERACTIONS

The values of $\Theta_{SO_4-HCO_3}$, $\Theta_{SO_4-CO_3}$, $\Psi_{SO_4-HCO_3-Na}$, $\Psi_{SO_4-CO_3-Na}$ and $\Psi_{SO_4-HCO_3-Mg}$ valid at 25 °C are from Harvie et al. (1984). The values of $\Theta_{SO_4-B(OH)_4}$ and $\Psi_{SO_4-B(OH)_4-Na}$ at 25 °C is taken from Felmy and Weare (1986). The $\Theta_{SO_4-HSO_4}$ and $\Psi_{SO_4-HSO_4-Na}$ values are valid from 0 to 200 °C (Pierrot and Millero, 1997). The $\Psi_{SO_4-HSO_4-K}$ value at 25 °C is taken from Harvie et al. (1984). The values of Θ_{SO_4-OH}, $\Psi_{SO_4-OH-Na}$ and Ψ_{SO_4-OH-K} at 25 °C are taken from Harvie et al. (1984).

5.7. X–Y INTERACTIONS

The anion-anion binary and ternary terms of a number of minor interactions are used in the model. The values of Θ_{OH-CO_3} and Ψ_{OH-CO_3-Na} at 25 °C are taken from Harvie et al. (1984). The values of Θ_{OH-Br}, $\Psi_{OH-Br-Na}$ and $\Psi_{OH-Br-K}$ at 25 °C are taken from Pitzer and Kim (1974).

6. Parameters for the Interactions of Neutral Solutes with Ions (λ_{Nc}, λ_{Na}, ζ_{Nca})

The interaction parameters for neutral acids (CO_2, NH_3, $B(OH)_3$, HF, H_2S, and H_3PO_4) and ion pairs ($MgCO_3$ and $CaCO_3$) are needed to determine the activity coefficients in ionic media. The activity coefficient of non-electrolytes (N) in mixed electrolyte solutions is determined from

$$\ln \gamma_N = \Sigma_c m_c (2\lambda_{Nc}) + \Sigma_a m_a (2\lambda_{Na}) + \Sigma_c \Sigma_a m_c m_a \zeta_{Nca}. \qquad (21)$$

The values of λ_{Nc}, λ_{Na} and ζ_{Nca} for the interactions of non-electrolytes (N) with various cations ($c = Na^+$) and anions ($a = Cl^-$) (Pitzer, 1991; Harvie and Weare, 1980) used are reviewed below. By assigning the $\lambda_{NCl} = 0$ it is possible to divide the parameters into ionic components that can be conveniently determined from the salting coefficients for salts.

6.1. CO_2-M-X

The neutral interaction parameters λ_{CO_2Na}, λ_{CO_2Cl} and ζ_{CO_2NaCl} valid from 0 to 50 °C were taken from the work of Peiper and Pitzer (1982). These NaCl parameters were selected since they are consistent with the emf measurements of Roy et al. (1982b, 1983). The other neutral interaction parameter for CO_2-K-Cl, CO_2-Mg-Cl, CO_2-Ca-Cl, CO_2-Na-SO_4, CO_2-K-SO_4, and CO_2-Mg-SO_4 valid from 0 to 100 °C are taken from He and Morse (1993). The 25 °C CO_2-Ca-SO_4 neutral interaction parameter was also taken from He and Morse (1993).

6.2. $B(OH)_3$-M-X

The neutral $B(OH)_3$-Na-Cl, $B(OH)_3$-K-Cl, $B(OH)_3$-Mg-Cl, $B(OH)_3$-Ca-Cl interaction parameters were taken from Felmy and Weare (1986) and Simonson et al. (1987b) and are valid from 0 to 50 °C. The 25 °C values of the $B(OH)_3$-Na-SO_4 and $B(OH)_3$-K-SO_4 parameters were taken from Felmy and Weare (1986).

6.3. ACID-M-X

The neutral interaction parameters for H_3PO_4 are only available at 25 °C for the NaCl system (Pitzer and Silvester, 1978). The 25 °C parameters for NH_3-Na-Cl, NH_3-K-Cl, NH_3-Mg-Cl, NH_3-Ca-Cl, NH_3-Na-SO_4, NH_3-K-SO_4, NH_3-Mg-SO_4, and NH_3-Ca-SO_4 interactions were taken from Clegg and Brimblecombe (1989). The 25 °C neutral parameters for H_2S-Na-Cl were taken from Hershey et al. (1988). The neutral parameters for $\lambda_{HFNa} = 0.011 \pm 0.002$ and $\lambda_{HFCl} = 0$ have been determined from the pK_{HF} measurements in NaCl of Clegg and Brimblecombe (1988).

7. Correction for the Formation of Ion Complexes

As discussed above some ions like F^-, OH^-, and CO_3^{2-} can complex with the major cations Mg^{2+} and Ca^{2+}. To correct the activity coefficients of minor ions (H^+, F^-, OH^-, CO_3^{2-}, HPO_4^{2-} and PO_4^{3-}), it is necessary to know the stability constants for the formation of the complexes in the ionic media (K_{MX}^*). For the formation of MX from M^+ and X^- the values of K_{MX}^* at any ionic strength (K_{MX}^*) are determined from

$$K_{MX}^* = K_{MX}(\gamma_M \gamma_X / \gamma_{MX}) \tag{22}$$

where K_{MX} is the infinite dilution value and γ_M, γ_X, and γ_{MX} are the activity coefficients of the free ions (M, X) and the ion pair (MX). The γ values of the ions (OH^-) and charged ion pairs ($MgOH^+$) can be determined using the Pitzer equations (Equation (8)). The values of neutral ion pairs (γ_{MX}) must be determined from experimental measurements of K_{MX}^* in various ionic media (Millero and Schreiber, 1982; Millero, 1982). If reliable stability constants in water are known, one can estimate γ_{MX} from measurements of K_{MX}^* at an ionic strength. The values of γ_{MX} determined in this way are dependent upon the model used to estimate the values of γ_M and γ_X. For some ion pairs (HSO_4^-, HF, $MgOH^+$, $MgCO_3$, $CaCO_3$) data is available for their formation as a function of temperature (Millero and Roy, 1997). The activity coefficient of $MgCO_3$ at 25 °C has been determined from the measurements of Millero and Thurmond (1983). The 25 °C values of γ_{CaCO_3} have been taken form Harvie et al. (1984). The Pitzer interaction parameters for MgF^+ with Cl^- ($\beta^{(0)} = 0.2871$, $\beta^{(1)} = 0.4538$ and $C^\phi = -0.0370$) have been calculated from the measurement of Clegg and Brimblecombe (1988). Parameters for CaF^+ have been similarly determined from the measurements of

Elgquist (1970). The 25 °C parameters for estimating the activity coefficients of MgB(OH)$_4^+$ and CaB(OH)$_4^+$ have been determined from pK$_{HB}$ measurements in Na-Mg-Cl and Na-Ca-Cl solutions (Hershey et al., 1986; Simonson et al., 1987b). The measurements of Hershey et al. (1986) of pK$_2$ for H$_3$PO$_4$ in Na-Mg-Cl solutions at 25 °C have been used to determine the Pitzer parameters for γ_{MgHPO_4}. The parameters for MgPO$_4^-$ and CaPO$_4^-$ in NaCl have been determined from the measurements of pK$_3$ for the same acid (Millero, 1982; Millero and Roy, 1997).

8. Thermodynamic Constants

The thermodynamic constants for the dissociation of acid in water used in the model have been fit to equations of the form (Millero, 1979b; 1995)

$$\ln K = A + B/T + C \ln T + DT. \tag{23}$$

The values of the parameters A, etc. are given in Table I. The equation is valid from 0 to 50 °C for all of the acids and to higher temperatures for some.

The thermodynamic association constants for the formation of ion pairs used in the model have been fit to the equation

$$pK = A + B/T + CT \tag{24}$$

where the coefficients are given in Table II.

9. Reliability of the Model

The reliability of the model in natural waters can be examined by comparing the calculated activity and osmotic coefficients with the values determined by direct measurements. This can best be done for seawater solutions where reliable measurements are available as a function of temperature (0 –40 °C) and ionic strength (0–0.8 m). A comparison of the measured (Millero and Leung, 1976) and calculated osmotic coefficients are shown in Figure 1. The differences are all within 0.0035 over the entire range of temperature (0–30 °C) and salinity (5–40). Calculations of the osmotic coefficients for artificial seawater (Rush and Johnson, 1966) over a wider range of ionic strength are shown in Figure 2. Again the differences are all within 0.004 to high ionic strengths ($I = 5$ m) and only slightly higher (0.008) up to $I = 7$ m.

The activity coefficients calculated by the model from 0 to 40 °C in seawater are given in Table III. It should be pointed out that these ionic values come directly from the model and are not absolute. To make comparisons with the values measured or determined by other models one must adjust them to a common scale using non-thermodynamic assumptions ($\gamma(K^+) = \gamma(Cl^-)$, $\gamma(Na^+) = \gamma(Cl^-)$, etc.). The values for most of the ions have large changes between 0 to 20 °C, but do not change much above 25 °C.

Table I. Coefficients for the thermodynamic constants for the dissociation of acids and solubility of gases in water fit to Equation (23).

Acid	A	B	C	D	Reference
HF	−12.641	1590.2			(1)
H_2S	225.8375	−13275.324	−34.64354		(2)
H_2O	148.9802	−13847.26	−23.6521		(3)*
$B(OH)_3$	148.0248	−8966.901	−24.4344		(4) (5)*
HSO_4^-	141.411	−4340.704	−23.4825	0.016637	(6)
NH_4^+	−0.25444	−6285.33		0.0001635	(7)
H_2CO_3	290.9097	−14554.21	−45.0575		(8)*
HCO_3^-	207.6548	−11843.79	−33.6485		(9)*
H_2SO_3	554.963	−16700.1	−93.67	0.1022	(10)
HSO_3^-	−358.57	5477.1	65.31	−0.1624	(10)
H_3PO_4	115.54	−4576.7518	−18.453		(11)
$H_2PO_4^-$	172.1033	−8814.715	−27.927		(12)
HPO_4^{2-}	−18.126	−3070.75			(13)
CO_2	−60.2409	9345.17	18.7533		(14)
SO_2	−142.679	8988.76	19.8967	−0.0021	(10)
Aragonite	303.5363	−13348.09	−48.7537		(15)
Calcite	303.1308	−13348.09	−48.7537		(15)

* Refit by Millero (1979b).
(1) Dickson and Riley (1979a). (2) Millero et al. (1988). (3) Harned and Owen (1958). (4) Owen (1934). (5) Manov et al. (1944). (6) Clegg et al. (1994). (7) Bates and Pinching (1949). (8) Harned and Davis (1943). (9) Harned and Scholes (1941). (10) Goldberg and Parker (1985). (11) Bates (1951). (12) Bates and Acree (1943). (13) Sillen and Martell (1964). (14) Weiss (1974). (15) Mucci (1983).

Comparison of the measured and calculated activity coefficients for various ions at 25 °C can be made for seawater. The sequence used to determine the measured values are outlined below:

$\gamma(H^+)$ from $\gamma_\pm(HCl)$ assuming $\gamma(Cl^-) = 0.666$
$\gamma(Na^+)$ from $\gamma_\pm(NaCl)$ assuming $\gamma(Cl^-) = 0.666$
$\gamma(K^+)$ from $\gamma_\pm(KCl)$ assuming $\gamma(Cl^-) = 0.666$
$\gamma(NH_4^+)$ from K_{NH_4}, $\gamma(H^+)$ and $\gamma(NH_3) = 0.99$
$\gamma(OH^-)$ from K_W, $\gamma(H^+)$ and $(H_2O) = 0.981$
$\gamma(HCO_3^-)$ from $K_{H_2CO_3}$, $\gamma(H^+)$ and $\gamma(CO_2) = 1.16$
$\gamma(CO_3^{2-})$ from K_{HCO_3}, $\gamma(H^+)$ and $\gamma(HCO_3^-)$
$\gamma(Ca^{2+})$ from $\gamma_\pm(CaCO_3)$ determined from Ksp(Calcite) and Ksp(Aragonite)
$\gamma(Mg^{2+})$ was estimated from single ion activity measurements
$\gamma(SO_4^{2-})$ from $\gamma_\pm(CaSO_4)$ determined from Ksp(CaSO_4)

Table II. Coefficients for the formation of ion pairs in water fitted to Equation (24)[a]

Ion pair	A	B	C
$MgOH^+$	3.87	−501.6	
MgF^+	3.504	−501.6	
CaF^+	3.014	−501.6	
$MgCO_3$	1.028		0.0066154
$CaCO_3$	1.178		0.0066154
$SrCO_3$	1.028		0.0066154
$MgH_2PO_4^+$	1.13		
$CaH_2PO_4^+$	1.0		
$MgHPO_4$	2.7		
$CaHPO_4$	2.74		
$MgPO_4^-$	5.63		
$CaPO_4^-$	7.1		

[a]Millero and Roy (1997).

$\gamma(Sr^{2+})$ from $\gamma_\pm(SrSO_4)$ determined from Ksp($SrSO_4$)
$\gamma(B(OH)_4)^-)$ from K_{HB}, $\gamma(H^+)$ and $\gamma(B(OH)_3) = 1.01$
$\gamma(F^-)$ from K_{HF}, $\gamma^F(H^+) = 0.760$ and $\gamma(HF) = 1.01$
$\gamma(HS^-)$ from K_{H_2S}, $\gamma(H^+)$, and $\gamma(H_2S) = 1.11$
$\gamma(HSO_4^-)$ from K_{HSO_4}, $\gamma^F(H^+) = 0.760$, and $\gamma(SO_4^{2-})$
$\gamma(HSO_3^-)$ from $K_{H_2SO_3}$, $\gamma(H^+)$ and $\gamma(SO_2) = 1.04$
$\gamma(SO_3^{2-})$ from K_{HSO_3}, $\gamma(H^+)$ and $\gamma(HSO_3^-)$
$\gamma(H_2PO_4^-)$ from $K_{H_3PO_4}$, $\gamma(H^+)$, and $\gamma(H_3PO_4) = 1.08$
$\gamma(HPO_4^{2-})$ from $K_{H_2PO_4}$, $\gamma(H^+)$, and $\gamma(H_2PO_4^-)$
$\gamma(PO_4^{3-})$ from K_{HPO_4}, $\gamma(H^+)$, and $\gamma(HPO_4^{2-})$

The results determined in this manner (Table IV) indicate that the model can be used to predict values for the activity coefficients that are in good agreement with the measured values.

Comparisons over a wider range of temperature can be made for only a few ions (H^+, Cl^-, NH_4^+, OH^-, HCO_3^-, CO_3^{2-}, $B(OH)_4^-$). The most extensive and reliable measurement are for the mean activity coefficient for HCl in seawater. Emf measurements have been made in artificial seawater with (Khoo et al., 1977a; Dickson, 1990b; Campbell et al., 1993) and without SO_4^{2-} (Khoo et al., 1977a). The mean activity coefficient of HCl can be determined from the ionic values using

$$\gamma_\pm(HCl) = (\gamma_H \gamma_{Cl})^{0.5}. \tag{25}$$

Since the H^+ in the solution can form a complex with sulfate and fluoride, it is necessary to correct the activity coefficient for this reaction. If the concentrations

Table III. Activity coefficients of some ions predicted by our model at different temperatures.

Ion	0 °C	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
H^+	0.687	0.664	0.641	0.615	0.588	0.559	0.528	0.495	0.462
Li^+	0.737	0.733	0.729	0.725	0.721	0.717	0.713	0.709	0.704
Na^+	0.625	0.630	0.634	0.637	0.638	0.639	0.639	0.639	0.638
K^+	0.590	0.592	0.594	0.595	0.596	0.596	0.595	0.595	0.594
Rb^+	0.583	0.586	0.588	0.590	0.591	0.592	0.592	0.593	0.592
Cs^+	0.531	0.535	0.538	0.541	0.543	0.544	0.546	0.546	0.547
NH_4^+	0.588	0.592	0.595	0.597	0.599	0.601	0.602	0.604	0.604
$MgOH^+$	0.918	0.913	0.908	0.903	0.898	0.892	0.887	0.881	0.876
Mg^{2+}	0.222	0.218	0.215	0.211	0.207	0.203	0.199	0.195	0.191
Ca^{2+}	0.203	0.206	0.205	0.203	0.200	0.198	0.195	0.191	0.188
Sr^{2+}	0.203	0.201	0.199	0.197	0.195	0.193	0.190	0.187	0.184
F^-	0.313	0.314	0.316	0.318	0.319	0.321	0.322	0.324	0.325
Cl^-	0.684	0.688	0.690	0.691	0.692	0.692	0.692	0.691	0.690
Br^-	0.709	0.712	0.715	0.716	0.717	0.718	0.718	0.717	0.716
I^-	0.753	0.755	0.757	0.758	0.759	0.759	0.758	0.757	0.755
OH^-	0.312	0.304	0.296	0.288	0.281	0.273	0.266	0.259	0.253
HS^-	0.691	0.691	0.690	0.689	0.688	0.687	0.686	0.684	0.682
NO_2^-	0.660	0.656	0.653	0.650	0.647	0.643	0.640	0.636	0.632
NO_3^-	0.604	0.611	0.617	0.622	0.627	0.630	0.633	0.635	0.636
HCO_3^-	0.592	0.593	0.594	0.594	0.595	0.596	0.596	0.596	0.597
HSO_4^-	1.062	0.999	0.941	0.889	0.842	0.799	0.761	0.726	0.694
HSO_3^-	0.818	0.801	0.785	0.769	0.754	0.739	0.725	0.711	0.698
$B(OH)_4^-$	0.386	0.391	0.394	0.397	0.398	0.399	0.398	0.396	0.392
$H_2PO_4^-$	0.537	0.537	0.536	0.536	0.535	0.534	0.533	0.532	0.531
$H_2AsO_4^-$	0.819	0.816	0.812	0.807	0.803	0.799	0.795	0.790	0.786
$Acetate^-$	0.672	0.668	0.665	0.661	0.657	0.653	0.649	0.645	0.641
SO_4^{2-}	0.120	0.118	0.116	0.114	0.112	0.110	0.107	0.105	0.102
SO_3^{2-}	0.161	0.153	0.145	0.138	0.131	0.125	0.118	0.112	0.107
CO_3^{2-}	0.052	0.050	0.049	0.047	0.045	0.043	0.042	0.040	0.039
HPO_4^{2-}	0.060	0.060	0.060	0.059	0.059	0.059	0.058	0.058	0.057
$HAsO_4^{2-}$	0.113	0.111	0.109	0.106	0.104	0.102	0.099	0.097	0.094
PO_4^{3-}	3.3E-5	3.0E-5	2.9E-5	2.8E-5	2.6E-5	2.5E-5	2.5E-5	2.4E-5	2.3E-5
AsO_4^{3-}	9.9E-4	9.5E-4	9.0E-4	8.6E-4	8.2E-4	7.8E-4	7.3E-4	6.9E-4	6.5E-4
CO_2	1.208	1.197	1.188	1.179	1.171	1.162	1.153	1.143	1.134

Table IV. Comparison of measured and calculated activity coefficients of ions in seawater at 25 °C and $S = 35$ (based on $\gamma_{Cl} = 0.666$)

Ion	Measured	Calculated	Δ	Reference
H^+	0.590	0.581	0.009	Khoo et al. (1977a)
	0.589		0.008	Dickson (1990b); Campbell et al. (1993)
Na^+	0.668	0.664	0.004	Johnson and Pytkowicz (1981)
	0.670		0.006	Gieskes (1966)
	0.678		0.014	Platford (1965)
K^+	0.625	0.619	0.006	Whitfield (1975)
NH_4^+	0.616	0.624	−0.005	Khoo et al. (1977b)
	0.592		0.032	Johansson and Wedborg (1980)
Mg^{2+}	0.240	0.219	0.021	Thompson (1966)
Ca^{2+}	0.203	0.214	−0.011	Mucci (1983)
	0.180		−0.034	Culberson et al. (1978)
Sr^{2+}	0.190	0.208	−0.018	Culberson et al. (1978)
F^-	0.296	0.309	−0.013	Culberson et al. (1970)
Cl^-	0.666	0.666	0	Assigned value
OH^-	0.255	0.263	−0.008	Millero (1995)
	0.242		−0.021	Hansson (1972)
	0.254		−0.009	Culberson and Pytkowicz (1973)
	0.254		−0.009	Dickson and Riley (1979a)
HS^-	0.617	0.661	−0.044	Yao and Millero (1995)
HCO_3^-	0.570	0.574	−0.004	Mehrbach et al. (1973)
	0.587		0.013	Hansson (1973)
	0.586		0.012	Goyet and Poisson (1989)
	0.583		0.009	Roy et al. (1993)
HSO_4^-	0.782	0.770	0.012	Dickson (1990b)
$B(OH)_4^-$	0.390	0.384	0.006	Dickson (1990a)
	0.419		0.035	Hansson (1973)
	0.398		0.014	Byrne and Kester (1974)
	0.351		−0.033	Millero et al. (1993)
$H_2PO_4^-$	0.453	0.514	−0.061	Yao and Millero (1995)
	0.492		−0.022	Dickson and Riley (1979b)
	0.352		−0.162	Kester and Pytkowicz (1967)
SO_4^{2-}	0.104	0.102	0.002	Khoo et al. (1977)
	0.101		−0.001	Culberson et al. (1970)
	0.112		0.010	Whitfield (1975)
	0.121		0.019	Platford and Dafoe (1965)
	0.121		0.019	Culberson et al. (1978)
CO_3^{2-}	0.039	0.040	−0.001	Mehrbach et al. (1973)
	0.039		−0.001	Hansson (1973)
	0.037		−0.003	Roy et al. (1993)
	0.037		−0.003	Goyet and Poisson (1989)
HPO_4^{2-}	0.043	0.054	−0.011	Yao and Millero (1995)
PO_4^{3-}	0.00002	0.00002	0	Yao and Millero (1995)

Comparison of the Measured and Calculated Osmotic Coefficients of Seawater
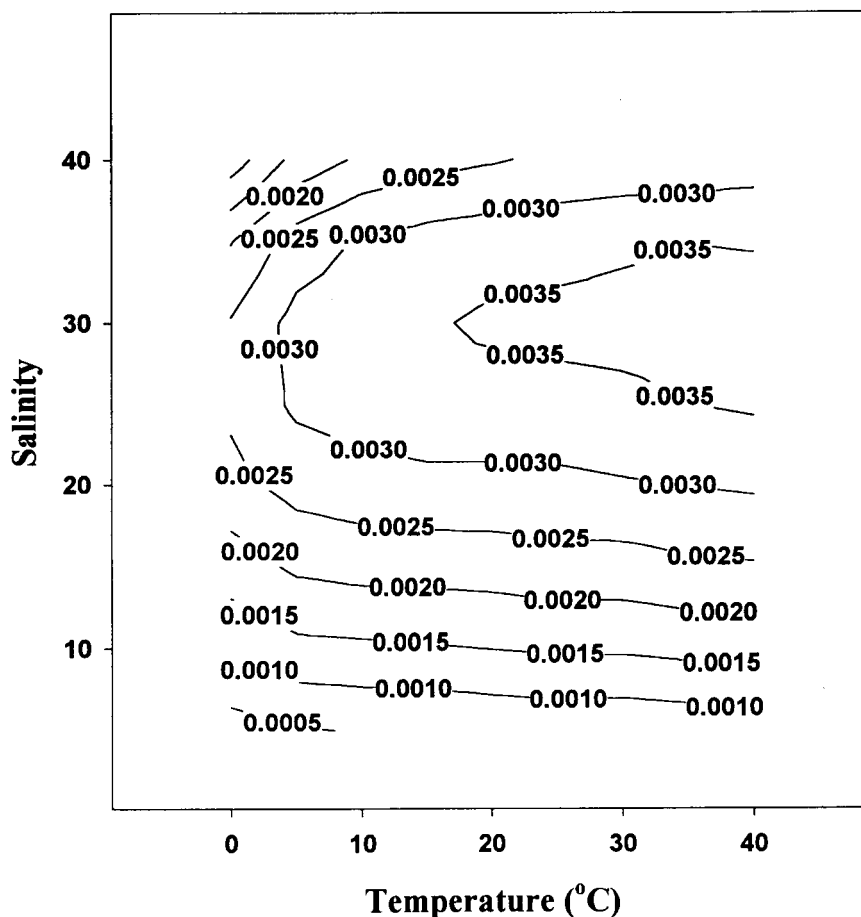
Figure 1. Comparison of the measured and calculated osmotic coefficients of seawater.

of the proton are high this requires iteration. Since this is not the case for most natural waters, one can avoid this complication and correct for the formation of the complexes using the relationship

$$\gamma_H = \gamma_H^* / (1 + [SO_4^{2-}]/K_{HSO_4}^*) + [F^-]/K_{HF}^*) \tag{26}$$

where the γ_H^* is the value calculated without sulfate and fluoride terms. A comparison of the measured (Campbell et al., 1993) and calculated mean activity coefficients of HCl in seawater with sulfate is shown in Figure 3. The deviations

Comparison of the measured and calculated osmotic coefficients of seawater at 25°C.
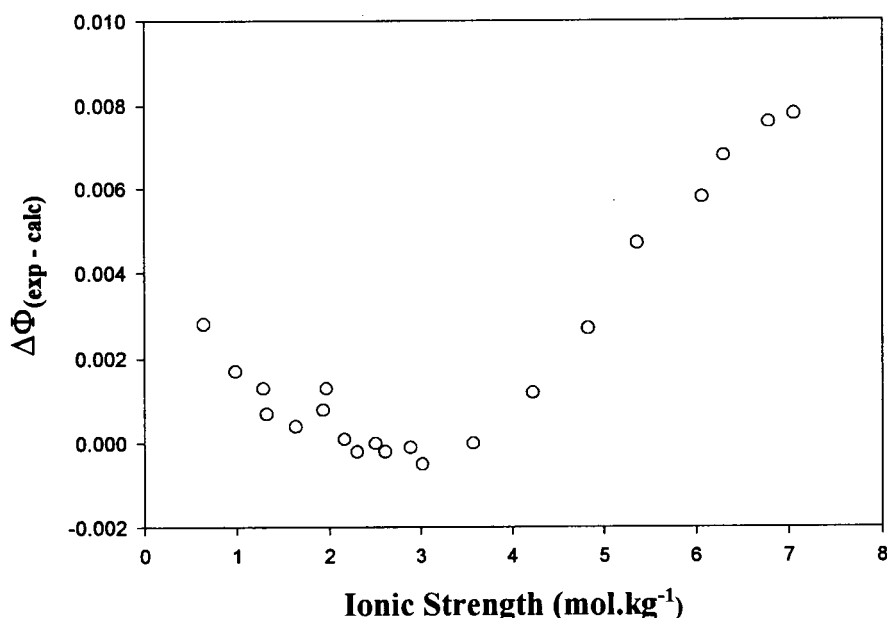
Figure 2. Comparison of the measured and calculated osmotic coefficients of seawater at 25 °C.

are generally within 0.005 with the exception of the 40 °C data that is reproduced within ± 0.01 units.

As shown elsewhere (Millero and Roy, 1997) the model yields reliable dissociation constants for the ionization of acids in seawater from 0 to 50 °C. Comparisons of the measured and calculated values of the pK for a number of acids in seawater at 25 °C are shown in Table V. The differences are quite reasonable and demonstrate the reliability of the model. The average errors from 0 to 40 °C for the acids (Millero and Roy, 1997) given in Table VI are close to the experimental error for most of the acids. It is interesting to note that the calculated pK_1 and pK_2 for carbonic acid are in better agreement with the measurements of Mehrbach et al. (1973) at 25 °C in accord with our earlier Pitzer model (Millero, 1982).

10. Future of the Model

The present model provides reliable activity coefficients for all the major components of seawater from 0 to 50°C. It also has been shown to provide reliable estimates of the pK of acids in seawater from 0 to 50°C (Millero and Roy, 1997). We presently are expanding the model to include divalent and trivalent metals

$\gamma^{tr}_{HCl}(\text{exp.}) - \gamma^{tr}_{HCl}(\text{calc.})$ in seawater .
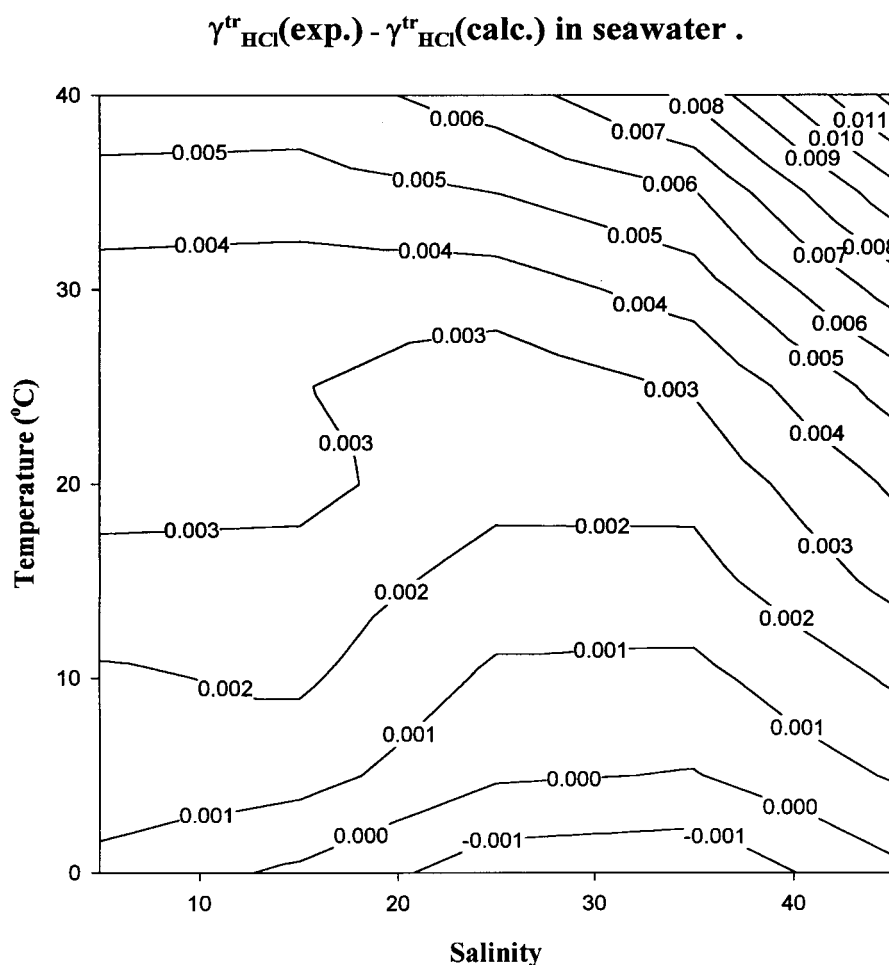
Figure 3. $\gamma^{tr}_{HCl}(\text{exp.})-\gamma^{tr}_{HCl}(\text{cac.})$ in seawater.

from 0 to 50 °C using enthalpy and heat capacity data. A number of workers have started to derive Pitzer coefficients for the interactions of actinides with the major inorganic anions of natural waters (Novak et al., 1997). The model needs new measurements for the stability constants for the complex formation of OH^-, CO_3^{2-}, etc. with divalent and trivalent metals in NaCl solutions over a wide range of temperature (0 to 50 °C) and ionic strength (0–6 m) to derive Pitzer coefficients of ion pairs. This fundamental data is needed to examine the competition of inorganic and organic ligands for trace metal in natural waters. Extensions of the model for the minor anions of natural waters at the present time are difficult due to the lack of reliable activity coefficient data for Na, K, Mg and Ca salts over a wide range of temperatures. The pK measurements of He and Morse (1993) can be used to

Table V. Comparison of measured and calculated values of pK* (total scale) in seawater at 25 °C and S = 35

Acid		Measured[a]	Calculated	Δ	Reference
H_2CO_3	pK_0	1.547	1.546	0.001	Weiss (1974)
	pK_1	5.837	5.832	0.005	Mehrbach et al. (1973)
		5.850		0.018	Hansson (1973)
		5.849		0.017	Dickson and Millero (1987)
		5.846		0.014	Goyet and Poisson (1989)
		5.847		0.015	Roy et al. (1993)
	pK_2	8.955	8.954	0.001	Mehrbach et al. (1973)
		8.942		−0.012	Hansson (1973)
		8.945		−0.009	Dickson and Millero (1987)
		8.919		−0.035	Goyet and Poisson (1989)
		8.915		−0.039	Roy et al. (1993)
NH_4^+		9.256	9.235	0.021	Yao and Millero (1995)
H_2O		13.211	13.218	−0.007	Millero (1995)
H_2S	pK_1	6.510	6.533	−0.023	Millero et al. (1988)
HF		2.611	2.552	0.059	Dickson and Riley (1979a)
H_2SO_3	pK_1	1.58	1.477	0.103	Millero et al.(1989)
	pK_2	6.13	6.159	−0.029	Millero et al.(1989)
$B(OH)_3$		8.582	8.596	−0.014	Dickson (1990a)
H_3PO_4	pK_1	1.591	1.605	−0.014	Yao and Millero (1995)
	pK_2	5.955	6.003	−0.048	Yao and Millero (1995)
	pK_3	8.783	8.746	0.037	Yao and Millero (1995)
HSO_4^-		0.983	0.993	−0.010	Dickson (1990b)
Calcite		6.367	6.397	−0.030	Mucci (1983)
Aragonite		6.186	6.221	−0.035	Mucci (1983)

[a] Most are from the equations summarized by Millero (1995) and Yao and Millero (1995).

extend the carbonate model to 100 °C. More measurements of this kind are needed to extend the model to higher temperatures for other acids.

Acknowledgements

Appendix: The Pitzer Equations for Estimating the Activity Coefficients of Solutes in Natural Waters

The Pitzer (1991) equations used to estimate the osmotic coefficient (Φ) and the activity coefficients (γ) of cations (M), anions (X) and neutral solutes (N) in a mixed electrolyte solution are given by

$$
\begin{aligned}
\Phi = {} & 1 + (2/\Sigma_i m_i)[f^\phi + \Sigma_c \Sigma_a m_c m_a (B^\phi_{ca} + 2EC_{ca}) \\
& + \Sigma_c \Sigma_{c'} m_c m_{c'} (\Theta_{cc'} + {}^E\Theta_{cc'} + \Sigma_a m_a \Psi_{cc'a}) \\
& + \Sigma_a \Sigma_{a'} m_a m_{a'} (\Theta_{aa'} + {}^E\Theta_{aa'} + \Sigma_c m_c \Psi_{aa'c}) \\
& + I(R_1 + R_2)]
\end{aligned}
\tag{A1}
$$

$$
\begin{aligned}
\ln \gamma_M = {} & Z_M^2 f^\gamma + 2\Sigma_a m_a (B_{Ma} + EC_{Ma}) + Z_M^2 R + Z_M S \\
& + \Sigma_c m_c (2\Theta_{Mc} + \Sigma_a m_a \Psi_{Mca}) + \Sigma_a \Sigma_{a'} m_a m_{a'} \Psi_{aa'M} \\
& + \Sigma_c m_c 2{}^E\Theta_{Mc} + Z_M^2 R_1 + Z_M^2 R_2
\end{aligned}
\tag{A2}
$$

$$
\begin{aligned}
\ln \gamma_X = {} & Z_X^2 f^\gamma + 2\Sigma_c m_c (B_{cX} + EC_{cX}) + Z_X^2 R + Z_X S \\
& + \Sigma_a m_a (2\Theta_{Xa} + \Sigma_c m_c \Psi_{Xac}) + \Sigma_c \Sigma_{c'} m_c m_{c'} \Psi_{cc'X} \\
& + \Sigma_a m_a 2{}^E\Theta_{Xa} + Z_X^2 R_1 + Z_X^2 R_2
\end{aligned}
\tag{A3}
$$

$$
\ln \gamma_N = \Sigma_c m_c (2\lambda_{Nc}) \Sigma_a m_a (2\lambda_{Na}) + \Sigma_c \Sigma_a m_c m_a \zeta_{Nca}.
\tag{A4}
$$

The values of R, S, R_1, and R_2 in Equations (A1) and (A2) are given by

$$
R = \Sigma_c \Sigma_a m_c m_a B'_{ca}
\tag{A5}
$$

$$
S = \Sigma_c \Sigma_a m_c m_a C_{ca}
\tag{A6}
$$

$$
R_1 = \Sigma_c \Sigma_{c'} m_c m_{c'}{}^E\Theta'_{cc'}
\tag{A7}
$$

$$
R_2 = \Sigma_a \Sigma_{a'} m_a m_{a'}{}^E\Theta'_{aa'}.
\tag{A8}
$$

The equivalent molality is given by $E = (1/2)\Sigma_i m_i |Z_i| = \Sigma m_c Z_c = \Sigma m_a |Z_a|$, where m_c, m_a, Z_c and Z_a are the molality and charge of cation c and anion a, respectively. The Debye–Hückel terms are given by

$$
f^\phi = -A^\phi I^{1.5}/(1 + 1.2 I^{0.5})
$$

$$
f^\gamma = -A^\phi [I^{0.5}/(1 + 1.2 I^{0.5}) + (2/1.2)\ln(1 + 1.2 I^{0.5})]
\tag{A9}
$$

where A^ϕ is given by (Møller, 1988)

$$
\begin{aligned}
A^\phi = \; & 3.6901532E\text{-}01 - 6.32100430E\text{-}04T + 9.14252359/T \\
& -1.35143986E\text{-}02\ln T + 2.26089488E\text{-}03/(T - 263) \\
& +1.92118597E\text{-}06T^2 + 4.52586464E\text{-}01/(680 - T).
\end{aligned}
\tag{A10}
$$

The second (B_{ij}) and third (C_{ij}) virial coefficients are given for 1-1, 2-1, and 3-1 electrolytes by

$$
B_{MX}^\phi = \beta_{MX}^0 + \beta_{MX}^1 \exp(-2I^{0.5})
\tag{A11}
$$

$$
B_{MX} = \beta_{MX}^0 + (\beta_{MX}^1/2I)[1 - (1 + 2I^{0.5})\exp(-2I^{0.5})]
\tag{A12}
$$

$$
B_{MX}' = (\beta_{MX}^1/2I^2)[-1 + (1 + 2I^{0.5} + 2I)\exp(-2I^{0.5})]
\tag{A13}
$$

$$
C_{MX} = C_{MX}^\phi/(2|Z_M Z_X|^{0.5}).
\tag{A14}
$$

For 2-2 electrolytes the coefficients are given by

$$
B_{MX}^\phi = \beta_{MX}^0 + \beta_{MX}^1 \exp(-1.4I^{0.5}) + \beta_{MX}^2 \exp(-12I^{0.5})
\tag{A15}
$$

$$
\begin{aligned}
B_{MX} = \; & \beta_{MX}^0 + (\beta_{MX}^1/0.98I)[1 - (1 + 1.4I^{0.5})\exp(-1.4I^{0.5})] \\
& +(\beta_{MX}^2/72I)[1 - (1 + 12I^{0.5})\exp(-12I^{0.5})]
\end{aligned}
\tag{A16}
$$

$$
\begin{aligned}
B_{MX}' = \; & (\beta_{MX}^1/0.98I^2)[-1 + (1 + 1.4I^{0.5} + 0.98I)\exp(-1.4I^{0.5})] \\
& +(\beta_{MX}^2/72I)[-1 - (1 + 12I^{0.5} + 72I)\exp(-12I^{0.5})]
\end{aligned}
\tag{A17}
$$

The Pitzer parameters described above are determined from fitting of measured osmotic or mean activity coefficient of electrolytes (MX) to the equation (Pitzer and Mayorga, 1973)

$$
\begin{aligned}
\ln \gamma_{MX} = \; & Z_M Z_X f^\gamma + m[2m_M m_X/(m_M + m_X)]B_{MX} \\
& +m^2[2(m_M m_X)1.5/(m_M + m_X)]C_{MX}
\end{aligned}
\tag{A18}
$$

The ${}^E\Theta_{ij}$ and ${}^E\Theta_{ij} = \mathrm{d}({}^E\Theta_{ij})/\mathrm{d}I$ are higher order terms which arise for unsymmetrical mixing of ions of the same sign. These higher order terms for mixing two cations c and c' are given by (Pitzer, 1975)

$$
{}^E\Theta_{ij} = Z_c Z_{c'}/4I[J_0(X_{cc'}) - \frac{1}{2}J_0(Xcc) - \frac{1}{2}J_0(X_{c'c'})]
\tag{A19}
$$

$${}^{E}\Theta'_{ij} = Z_c Z_{c'}/8I^2 [J_1(X_{cc'}) - \tfrac{1}{2} J_1(X_{cc}) - \tfrac{1}{2} J_1(X_{c'c'})] \tag{A20}$$

where

$$X_{cc'} = 6A^\phi Z_c Z_{c'} I^{0.5}. \tag{A21}$$

The functions $J_0(X)$ and $J_1(X)$ are given by the integrals (Pitzer, 1975)

$$J_0(X) = X/4 - 1 + (1/X) \int_0^\infty [1 - \exp(-(X/y)e^{-y})]y^2 \, dy \tag{A22}$$

$$\begin{aligned} J_1(X) = {} & X/4 - 1 + (1/X) \\ & \times \int_0^\infty [1 - (1 + (X/y)e^{-y}) \exp(-(X/y)e^{-y})]y^2 \, dy. \end{aligned} \tag{A23}$$

These integrals can be evaluated numerically. The method used in our model is outlined by Pitzer (1991).

Table A1. Parameters for Equation (14) from Møller (1988) and Greenberg and Møller (1989) valid from 0 to 250 °C

Parameter	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
β^0_{NaCl}	1.43783204E01	5.6076740E01	−4.22185236E2	−2.51226677E0	0.0	−2.61718135E-6	4.43854508	−1.70502337
β^1_{NaCl}	−4.83060685E-1	1.40677470E-3	1.19311989E2	0.0	0.0	0.0	0.0	−4.23433299
C^ϕ_{NaCl}	−1.00588714E-1	−1.80529413E-5	8.61185543E0	1.2488095E-2	0.0	3.41172108E-8	6.83040995E-2	2.93922611E-1
β^0_{KCl}	2.67375563E1	1.00721050E-2	−7.58485453E2	−4.70624175	0.0	−3.75994338E-6	0.0	0.0
β^1_{KCl}	−7.41559626	0.0	3.22892989E2	1.16438557	0.0	0.0	0.0	−5.94578140
C^ϕ_{KCl}	−3.30531334	−1.29807848E-3	9.12712100E1	5.864450181E-1	0.0	4.95713573E-7	0.0	0.0
$\beta^0_{K_2SO_4}$	4.07908797E1	8.26906675E-3	−1.418242998E3	−6.74728848	0.0	0.0	0.0	0.0
$\beta^1_{K_2SO_4}$	−1.31669651E1	2.35793239E-2	2.06712592E3	0.0	0.0	0.0	0.0	0.0
$C^\phi_{K_2SO_4}$	−1.88E-2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\beta^0_{CaCl_2}$	−9.41895832E1	−4.04750026E-2	2.34550368E3	1.70912300E1	−9.22885841E-1	1.51488122E-5	−1.39082000E0	0.0
$\beta^1_{CaCl_2}$	3.4787	−1.5417E-2	0.0	0.0	0.0	3.1791E-5	0.0	
$C^\phi_{CaCl_2}$	1.93056024E1	9.77090932E-3	−4.28383748E2	−3.57996343	8.82068538E-2	−4.62270238E-6	9.91113465	0.0
$\beta^0_{CaSO_4}$ [a]	0.15	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\beta^1_{CaSO_4}$	3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$\beta^2_{CaSO_4}$	−1.29399287E2	4.00431027E-1	0.0	0.0	0.0	0.0	0.0	0.0
$C^\phi_{CaSO_4}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] $CaSO_4$, $SrSO_4$ and $CaSO_3$ have been equated to $CaSO_4$.

Table A2. Parameters for Equation (9) and (10) from Pabalan and Pitzer (1987) valid from 25 to 200 °C.

Parameter	q_1	q_2	q_3	q_4	q_5	q_6
$\beta^0_{MgCl_2}$	0.57606	−9.31654E-04	5.93915E-07			
$\beta^1_{MgCl_2}$	2.60135	−0.0109438	2.60169E-05			
$C^\phi_{MgCl_2}$	0.059532	−2.49949E-04	2.41831E-07			
$\beta^0_{MgSO_4}$	−1.0282	8.4790E-03	−2.33667E-05	2.1575E-08	6.8402E-04	0.21499
$\beta^1_{MgSO_4}$	−2.9596E-01	9.4564E-04	0	0	1.1028E-02	3.3646
$\beta^2_{MgSO_4}$	−13.764	0.12121	−2.7642E-04	0	−0.21515	−32.743
$C^\phi_{MgSO_4}$	4.2164E-01	−3.5726E-03	1.0040E-05	−9.3744E-09	−3.5160E-04	2.7972E-02

Table A3. NaX coefficients for $P = a + b(T - 298.15) + c(T - 298.15)^{2(1)}$

Parameter	a	b	c	Range (°C)	Reference
$\beta^0_{NaHSO_4}$	0.544	−1.8478E-3	5.3937E-5	0–250	(a)
$\beta^1_{NaHSO_4}$	0.3826401	−1.8431E-2			
$C^\phi_{NaHSO_4}$	0.003905				
$\beta^0_{NaHCO_3}$	0.028	1.0E-1	5.082E-21	0–50	(b)
$\beta^1_{NaHCO_3}$	0.044	1.1E-3	−3.88E-21		
$C^\phi_{NaHCO_3}$	0				
$\beta^0_{Na_2SO_4}$	6.536438E-3	30.197349	−0.20084955	0–100	(c)
$\beta^1_{Na_2SO_4}$	0.8742642	70.014123	0.2962095		
$C^\phi_{Na_2SO_4}$	7.693706E-3	4.5879201	0.019471746		
$\beta^0_{Na_2CO_3}$	0.0362	1.79E-3	1.694E-21	0–50	(b)
$\beta^1_{Na_2CO_3}$	1.51	2.05E-3	1.626E-19		
$C^\phi_{Na_2CO_3}$	0.0052				
$\beta^0_{NaB(OH)_4}$	−0.051	5.264E-3		0–50	(d)
$\beta^1_{NaB(OH)_4}$	0.0961	−1.068E-3			
$C^\phi_{NaB(OH)_4}$	0.01498	−1.57E-3			
β_{NaHS}	0.366	−67.5[2]		0–50	(e)
β^1_{NaHS}	0				
C^ϕ_{NaHS}	−0.0127				
β^0_{NaCNS}	0.1005	0.00078		10–40	(f), (g)
β^1_{NaCNS}	0.3582	0.002			
C^ϕ_{NaCNS}	−0.0303				
$\beta^0_{Na_2SO_3}$	5.88444	−1730.55[1]		5–25	(h)
$\beta^1_{Na_2SO_3}$	−19.4549	6153.78[1]			
$C^\phi_{Na_2SO_3}$	−1.2355	367.07[1]			
$\beta^0_{NaHSO_3}$	4.3407	−1248.66[1]		5–25	(h)
$\beta^1_{NaHSO_3}$	−13.146	4014.8[1]			
$C^\phi_{NaHSO_3}$	−0.9565	277.85[1]			

[1] For Na_2SO_4, the equation is $P = a + b(1/T - 1/298.15) + c \ln(T/298.15)$ and $\alpha = 1.7$.
[2] Coefficient for $(1/T)$ instead of $(T - 298.15)$.
(a) Pierrot and Millero (1997, 1998). (b) Peiper and Pitzer (1982) (c) Hovey et al (1993). (d) Simonson et al. (1988) (e) Hershey et al. (1988). (f) Pitzer and Mayorga (1973) (g) Silvester and Pitzer (1978) (h) Millero et al. (1989).

Table A4. KX coefficients for $P = a + b(T - 298.15) + c(T - 298.15)^2$.

Parameter	a	b	c	Range (°C)	Reference
$\beta^0_{KHCO_3}$	−0.0107	0.001		5–45	(a)
$\beta^1_{KHCO_3}$	0.0478	0.0011	6.776E-21		
$C^\phi_{KHCO_3}$	0				
$\beta^0_{K_2CO_3}$	0.1288	1.1E-3	−5.1E-6	5–95	(b)
$\beta^1_{K_2CO_3}$	1.433	4.36E-3	2.07E-5		
$C^\phi_{K_2CO_3}$	0.0005				
$\beta^0_{KB(OH)_4}$	0.1469	2.881E-3		0–50	(c)
$\beta^1_{KB(OH)_4}$	−0.0989	−6.876E-3			
$C^\phi_{KB(OH)_4}$	−0.05643	−9.56E-4			
β^0_{KHS}	1.017	−251.04[1]		5–25	(d), (e)
β^1_{KHS}	0				
C^ϕ_{KHS}	−0.033				
$\beta^0_{KH_2PO_4}$	−0.0678	6.045E-4		0–50	(f), (g)
$\beta^1_{KH_2PO_4}$	−0.1042	0.00286			
$C^\phi_{KH_2PO_4}$	0	−1.011E-4			
β^0_{KCNS}	0.0416	6.87E-4		10–40	(f), (g)
β^1_{KCNS}	0.2302	0.0037			
C^ϕ_{KCNS}	−0.00252	4.3E-06			

[1] Coefficient for $(1/T)$ instead of $(T\text{-}298.15)$.

(a) Roy et al. (1983). (b) Simonson et al. (1987a). (c) Simonson et al. (1988). (d) Hershey et al. (1988). (e) Millero (1995). (f) Pitzer and Mayorga (1973). (g) Silvester and Pitzer (1978).

Table A5. MgX and CaX coefficients for $P = a + b(T - 298.15) + c(T - 298.15)^2$.

Parameter	a	b	c	Range (°C)	Reference
$\beta^0_{MgBr_2}$	0.432675	−5.62E-05		0–50	(a), (b)
$\beta^1_{MgBr_2}$	1.75275	3.8625E-03			
$C^\phi_{MgBr_2}$	0.003124				
$\beta^0_{Mg(B(OH)_4)_2}$	0.623	6.496E-3		5–55	(c)
$\beta^1_{Mg(B(OH)_4)_2}$	0.2515	−0.01713			
$\beta^2_{Mg(B(OH)_4)_2}$	−11.47	0	−3.24E-03[1]		
$C^\phi_{Mg(B(OH)_4)_2}$	0				
$\beta^0_{Mg(ClO_4)_2}$	0.496125	5.2275E-4		10–40	(a), (b)
$\beta^1_{Mg(ClO_4)_2}$	2.0085	4.5E-3			
$C^\phi_{Mg(ClO_4)_2}$	0.009578	−3.5267E-4			
$\beta^0_{CaBr_2}$	0.3816	−5.2275E-04		10–40	(a), (b)
$\beta^1_{CaBr_2}$	1.61325	6.0375E-03			
$C^\phi_{CaBr_2}$	−0.002572				
$\beta^0_{Ca(B(OH)_4)_2}$	−0.4462	5.393E-3		5–55	(c)
$\beta^1_{Ca(B(OH)_4)_2}$	−0.868	−0.0182			
$\beta^2_{Ca(B(OH)_4)_2}$	−15.88	0	−2.858E-03[1]		
$C^\phi_{Ca(B(OH)_4)_2}$	0				
$\beta^0_{Ca(ClO_4)_2}$	0.451125	8.295E-4		10–40	(a), (b)
$\beta^1_{Ca(ClO_4)_2}$	1.7565	5.0775E-3			
$C^\phi_{Ca(ClO_4)_2}$	−0.005001	−3.0918E-4			

[1] Coefficient for $(T - 303.15)^2$ and not $(T - 298.15)^2$.
(a) Pitzer and Mayorga (1973). (b) Silvester and Pitzer (1978). (c) Simonson et al. (1987b) .

Table A6. SrX coefficients for $P = a + b(T - 298.15) + c(T - 298.15)^2$.

Parameter	a	b	c	Range (°C)	Reference
$\beta^0_{SrBr_2}$	0.33113	3.2775E-4		10–40	(a), (b)
$\beta^1_{SrBr_2}$	1.7115	6.5325E-3			
$C^\phi_{SrBr_2}$	0.00123				
$\beta^0_{Sr(NO_3)_2}$	0.134625	1.77E-4		10–40	(a), (b)
$\beta^1_{Sr(NO_3)_2}$	1.38	0.0124725			
$C^\phi_{Sr(NO_3)_2}$	$-$ 0.01993				
$\beta^0_{Sr(ClO_4)_2}$	0.4269	1.524E-4		10–40	(a), (b)
$\beta^1_{Sr(ClO_4)_2}$	1.56675	7.19E-4			
$C^\phi_{Sr(ClO_4)_2}$	−0.01311	−5.86E-5			
$\beta^0_{Sr(HSO_3)_2}$	0.4269	1.524E-4		10–40	(a), (b)
$\beta^1_{Sr(HSO_3)_2}$	1.56675	7.19E-4			
$C^\phi_{Sr(HSO_3)_2}$	−0.01311	−5.86E-5			
$\beta^0_{Sr(B(OH)_4)_2}$	−0.4462	5.393E-3		5–55	Equaled to Ca
$\beta^1_{Sr(B(OH)_4)_2}$	−0.868	−0.0182			
$\beta^2_{Sr(B(OH)_4)_2}$	−15.88	0	−2.858E-03[1]		
$C^\phi_{Sr(B(OH)_4)_2}$	0				

(a) Pitzer and Mayorga (1973).
(b) Silvester and Pitzer (1978).
(1) Coefficient for $(T - 303.15)^2$ and not $(T - 298.15)^2$.

Table A7. Coefficients for $P = P_R + P^J(298.15^3/3 - 298.15^2 P_R^L)(1/T - 1/298.15) + P^J(1/6)(T^2 - 298.15^2)$ (Equation (15).

Parameter	P_R	$P^J 10^5$	$P_R^L 10^4$	Range (°C)	References
β^0_{NaI}	0.1195	−1.01	8.355	0–50	(a), (b), (c)
β^1_{NaI}	0.3439	−2.54	8.28		
C^ϕ_{NaI}	0.0018	0	−0.835		
β^0_{NaBr}	0.0973	−1.3	7.692	0–50	(a), (b), (c)
β^1_{NaBr}	0.2791	−1.06	10.79		
C^ϕ_{NaBr}	0.00116	0.16405	−0.93		
β^0_{NaF}	0.215	−2.37	5.361E-4	0–50	(a), (b), (c)
β^1_{NaF}	0.2107	0	8.7E-4		
C^ϕ_{NaF}	0	0	0		
β^0_{KBr}	0.0569	−1.43	7.39	0–50	(a), (b), (c)
β^1_{KBr}	0.2122	−0.762	1.74		
C^ϕ_{KBr}	−0.0018	0.216	−0.7004		
β^0_{KF}	0.08089	−1.39	2.14	0–50	(a), (b), (c)
β^1_{KF}	0.2021	0	5.44		
C^ϕ_{KF}	0.00093	0	0.595		
β^0_{KOH}	0.1298	−0.946	9.914[1]	0–50	(a), (c)
β^1_{KOH}	0.32	−2.59	11.86[1]		
C^ϕ_{KOH}	0.0041	0.0638	−0.944[1]		
β^0_{KI}	0.0746	−0.748	9.914	0–50	(a), (b), (c)
β^1_{KI}	0.2517	−1.8	11.86		
C^ϕ_{KI}	−0.00414	0	−0.944		
$\beta^0_{NaClO_3}$	0.0249	−1.56	10.35	0–50	(a), (b), (c)
$\beta^1_{NaClO_3}$	0.2455	−2.69	19.07		
$C^\phi_{NaClO_3}$	0.0004	0.222	9.29		
$\beta^0_{KClO_3}$	−0.096	15.1	19.87	0–50	(a), (b), (c)
$\beta^1_{KClO_3}$	0.2841	−27	31.8		
$C^\phi_{KClO_3}$	0	−19.1	0		
$\beta^0_{NaClO_4}$	0.0554	−0.611	12.96	0–50	(a), (b), (c)
$\beta^1_{NaClO_4}$	0.2755	−6.35	22.97		
$C^\phi_{NaClO_4}$	−0.00118	0.0562	−1.623		
$\beta^0_{NaBrO_3}$	−0.0205	−6.5	5.59	0–50	(a), (b), (c)
$\beta^1_{NaBrO_3}$	0.191	5.45	34.37		
$C^\phi_{NaBrO_3}$	0.0059	2.5	0		

Table A7. Continued

Parameter	P_R	$P^J 10^5$	$P^L_R 10^4$	Range (°C)	References
$\beta^0_{KBrO_3}$	-0.129	9.17	5.59[2]	0–50	(a), (c)
$\beta^1_{KBrO_3}$	0.2565	-20.2	34.37[2]		
$C^\phi_{KBrO_3}$	0	-26.6	0[2]		
$\beta^0_{NaNO_3}$	0.0068	-2.24	12.66	0–50	(a), (b), (c)
$\beta^1_{NaNO_3}$	0.1783	-2.96	20.6		
$C^\phi_{NaNO_3}$	-0.00072	0.594	-2.316		
$\beta^0_{KNO_3}$	-0.0816	-0.785	2.06	0–50	(a), (b), (c)
$\beta^1_{KNO_3}$	0.0494	-8.26	64.5		
$C^\phi_{KNO_3}$	0.0066	0	3.97		
$\beta^0_{Mg(NO_3)_2}$	0.367125	-1.2322	5.15	0–50	(a), (b), (d)
$\beta^1_{Mg(NO_3)_2}$	1.58475	4.0492	44.925		
$C^\phi_{Mg(NO_3)_2}$	-0.020625	0	0		
$\beta^0_{Ca(NO_3)_2}$	0.210825	4.0248	5.295	0–50	(a), (b), (d)
$\beta^1_{Ca(NO_3)_2}$	1.40925	-13.289	91.875		
$C^\phi_{Ca(NO_3)_2}$	-0.020142	-15.435	0		
β^0_{HBr}	0.196	-0.357	-2.049	0–50	(a), (b), (c)
β^1_{HBr}	0.3564	-0.913	4.467		
C^ϕ_{HBr}	0.00827	0.01272	-0.5685		
$\beta^0_{SrCl_2}$	0.28575	-0.18367	7.1	0–50	(a), (b), (d)
$\beta^1_{SrCl_2}$	1.66725	0	28.425		
$C^\phi_{SrCl_2}$	-0.0013	0	0		
$\beta^0_{NH_4Cl}$	0.0522	-0.597	0.779	0–50	(a), (b), (c)
$\beta^1_{NH_4Cl}$	0.1918	0.444	12.58		
$C^\phi_{NH_4Cl}$	-0.00301	0.0578	0.21		
$\beta^0_{NH_4Br}$	0.0624	-0.597	0.779[3]	0–50	(a), (c)
$\beta^1_{NH_4Br}$	0.1947	0	12.58[3]		
$C^\phi_{NH_4Br}$	-0.00436	0	0.21[3]		
$\beta^0_{NH_4F}$[4]	0.1306	1.09	0.95		(a), (b), (c)
$\beta^1_{NH_4F}$[4]	0.257	0	5.97		
$C^\phi_{NH_4F}$[4]	-0.0043	0	0		

(1) Equated to KI.
(2) Equated to $NaBrO_3$.
(3) Equated to NH_4Cl.
(4) Equated to CsF.
(a) Pitzer and Mayorga (1973). (b) Silvester and Pitzer (1978). (c) Criss and Millero (1996). (d) Criss and Millero (1998).

Table A8. Coefficients for Pitzer parameters valid at 25 °C.

Salt	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^ϕ	References
SrI	0.40125	1.86		0.0027	(a)
NaNO$_2$	0.0641	0.1015		−0.0049	(a)
NaH$_2$PO$_4$	−0.0533	0.0396		0.00795	(a)
Na$_2$HPO$_4$	−0.058275	1.4655		0.02938	(a)
Na$_3$PO$_4$	0.178133	3.85133		−0.014878	(a)
NaH$_2$AsO$_4$	−0.0442	0.2895		0	(a)
KH$_2$AsO$_4$	−0.0584	0.0626		0	(a)
Na$_2$HAsO$_4$	0.030525	1.62975		0.001803	(a)
Na$_3$AsO$_4$	0.2388	3.93		−0.013778	(a)
NaAcetate	0.1426	0.3237		−0.00629	(a)
KHSO$_4$	−0.0003	0.1735		0	(b)
KNO$_2$	0.0151	0.015		0.0007	(a)
K$_2$HPO$_4$	0.02475	1.27425		0.016387	(a)
K$_3$PO$_4$	0.372933	3.972		−0.025056	(a)
K$_2$HAsO$_4$	0.1296	1.6485		−0.017819	(a)
KAcetate	0.1587	0.3251		−0.0066	(a)
Mg(HSO$_4$)$_2$	0.4746	1.729			(b)
Mg(HCO$_3$)$_2$	0.03	0.8		0	(c)
Mg(HS)$_2$	0.17	2.78		−0.033	(d)
MgI$_2$	0.4902	1.8041		0.00793	(a)
Mg(HSO$_3$)$_2$	0.35	1.22		−0.072	(e)
MgSO$_3$	−2.8	12.9	−201	0	(e)
Ca(HSO$_4$)$_2$	0.2145	2.53		0	(b)
Ca(HCO$_3$)$_2$	0.4	2.977		0	(b)
Ca(HSO$_3$)$_2$	0.2145	2.53		0	HSO$_4^-$ salt
Ca(HS)$_2$	−0.105	3.43		0	(d)
Ca(OH)$_2$	−0.1747	−0.2303		−5.72	(b)
CaI$_2$	0.43793	1.806		−0.00084	(a)
Sr(HSO$_4$)$_2$	0.2145	2.53		0	Ca^{2+} salt
Sr(HCO$_3$)$_2$	0.4	2.977		0	Ca^{2+} salt
Sr(HSO$_3$)$_2$	0.2145	2.53		0	Ca^{2+} salt
Sr(OH)$_2$	−0.1747	−0.2303		−5.72	Ca^{2+} salt
SO$_4$(NH$_4$)$_2$	0.04088	0.6585		−0.00116	(a)
MgOHCl	−0.1	1.658		0	(b)

(a) Pitzer and Mayorga (1973) (b) Harvie et al. (1984). (c) Redetermined from Thurmond and Millero (1982). (d) Hershey et al. (1988). (e) Roy et al. (1991).

Table A9. Coefficients for H-Cl[1] and H-SO$_4$[2] ion pairs.

Parameter	a	b	c	d	Range (°C)	Reference
β^0_{HCl}	1.2859	−0.0021197	−142.58770		0–50	(a)
β^1_{HCl}	4.4474	8.425698E-3	665.7882			
C^ϕ_{HCl}	−0.305156	5.16E-4	45.521540			
$\beta^0_{\text{H−SO}_4}$	0.065	0.134945	0.022374	7.2E-5	0–250	(b)
$\beta^1_{\text{H−SO}_4}$	−15.009	−2.405945	0.335839	−0.004379		
$C^0_{\text{H−SO}_4}$	0.008073	−0.113106	−0.003553	3.57E-5		
$C^1_{\text{H−SO}_4}$	−0.050799	3.472545	−0.311463	0.004037		

[1] The equation is $P = a + bT + c/T$.
[2] The equation is $P = a + (T - 328.15)10^{-3}(b + (T - 328.15)((c/2) + (T - 328.15)(d/6)))$.
(a) Campbell et al. (1993). (b) Pierrot et al. (1997, 1998).

Table A10. Coefficients for $P = a_1 + a_2/T + a_3 T + a_4(T - 298.15) + a_5(T - 298.15)^2$ describing the temperature dependence of Θ and Ψ from 0 to 150 °C.

Parameter	a_1	a_2	$a_3 10^4$	$a_4 10^4$	$a_5 10^6$	Range (°C)	Reference
$\Theta_{H,Sr}$	0.0591			4.5		0–50	(a)
$\Theta_{H,Na}$	0.03416			−2.09[1]		0–50	(b)
$\Theta_{H,K}$	0.005			−2.275			(b)
$\Theta_{H,Mg}$	0.062			3.275		0–50	(c)
$\Theta_{H,Ca}$	0.0612			3.275		0–50	(d)
$\Theta_{Na,K}$	−5.02312111E-2	14.0213141				0–250	(e)
$\Theta_{Na,Mg}$	0.07					25–250	(f)
$\Theta_{Na,Ca}$	0.05					0–250	(g)
$\Theta_{K,Mg}$	0					0–250	(f)
$\Theta_{K,Ca}$	0.1156					0–250	(e)
Θ_{Cl,SO_4}	0.07					0–250	(e)
Θ_{Cl,CO_3}	−0.053					0-60	(h), (i)
Θ_{Cl,HCO_3}	0.0359					0–60	(h), (i)
$\Theta_{Cl,B(OH)_4}$	−0.0323			−0.42333	−21.926	0–45	(1)
Θ_{CO_3,HCO_3}	0					0–60	(j)
Θ_{HSO_4,SO_4}	0					0–200	(k)
$\Theta_{OH,Cl}$	−0.05			3.125	−8.362		(2)
$\Psi_{Na,K,Cl}$	1.34211308E-2	−5.10212917				0–250	(e)
Ψ_{Na,K,SO_4}	3.48115174E-2	−8.21656777				0–250	(e)
$\Psi_{Na,Mg,Cl}$	0.0199	−9.51				25–250	(f)
$\Psi_{Na,Ca,Cl}$	−0.003					0–250	(g)
Ψ_{Na,Ca,SO_4}	−0.012					0–250	(g)
$\Psi_{K,Mg,Cl}$	0.02586	−14.27				0–250	(f)
$\Psi_{K,Ca,Cl}$	0.047627877	−27.0770507				0–250	(e)
Ψ_{K,Ca,SO_4}	0					0–250	(e)
$\Psi_{Cl,SO_4,Na}$	−0.009					0–250	(g)
$\Psi_{Cl,SO_4,K}$	−0.21248147	37.5619614	2.8469833			0–250	(e)
$\Psi_{Cl,SO_4,Ca}$	−0.018					0–250	(g)
$\Psi_{Cl,CO_3,Na}$	0.016					0–60	(h), (l)
$\Psi_{Cl,HCO_3,Na}$	−0.0143					0–60	(h), (l)
$\Psi_{Cl,B(OH)_4,Na}$	−0.0132					0–45	(1)
$\Psi_{Cl,B(OH)_4,Mg}$	−0.235					0–45	(3)
$\Psi_{Cl,B(OH)_4,Ca}$	−0.8					0–45	(3)
$\Psi_{H,Sr,Cl}$	0.0054			−2.1		0–50	(m)
$\Psi_{H,Mg,Cl}$	0.001			−7.325		0–50	(c)
$\Psi_{H,Ca,Cl}$	0.0008			−7.25		0–50	(d)
$\Psi_{HSO_4,SO_4,Na}$	0					0–200	(k)
$\Psi_{CO_3,HCO_3,Na}$	0					0–60	(j)
$\Psi_{CO_3,HCO_3,K}$	0					0–60	(j)

[1]Determined from Owen and King (1943) and Hershey et al. (1986b) data
[2]Determined from Harned and Owen (1958, 752 pp.) data.
[3]Determined from Hershey et al. (1986b) and Simonson et al.(1987b) data.
(a) Roy et al. (1986). (b) Campbell et al. (1993). (c) Roy et al. (1980). (d) Roy et al. (1982b). (e) Greenberg and Møller (1989). (f) Pabalan and Pitzer (1987). (g) Møller (1988). (h) Thurmond and Millero (1982). (i) Peiper and Pitzer (1982). (j) This study. (k) Pierrot et al. (1998). (l) Roy et al. (1983). (m) Millero (1985).

Table A11. Values of the constant Θ and Ψ in our model.valid at 25 °C.

Parameter	Value	Reference
$\Theta_{Sr,Na}$	0.07	(a)
$\Theta_{Sr,K}$	0.01	(1)
$\Theta_{Mg,Ca}$	0.007	(b)
$\Theta_{Cl,F}$	0.01	(2)
Θ_{SO_4,CO_3}	0.02	(b)
Θ_{SO_4,HCO_3}	0.01	(b)
$\Theta_{SO_4,B(OH)_4}$	−0.012	(c)
$\Theta_{HSO_4,Cl}$	−0.006	(b)
Θ_{OH,SO_4}	−0.013	(c)
$\Theta_{OH,Br}$	−0.065	(a)
$\Theta_{NO_3,Cl}$	0.016	(a)
$\Theta_{H_2PO_4,Cl}$	0.1	(d)
$\Theta_{HPO_4,Cl}$	−0.105	(d)
$\Theta_{PO_4,Cl}$	−0.59	(d)
$\Theta_{H_2AsO_4,Cl}$	0.228	(e)
$\Theta_{HAsO_4,Cl}$	0.122	(e)
$\Theta_{AsO_4,Cl}$	0.06	(e)
$\Theta_{SO_3,Cl}$	0.0991	(f)
$\Theta_{Acetate,Cl}$	−0.017	(e)
$\Psi_{Sr,Na,Cl}$	−0.015	(a)
$\Psi_{Sr,K,Cl}$	−0.015	(1)
$\Psi_{Na,K,Br}$	−0.0022	(a)
Ψ_{Na,Mg,SO_4}	−0.015	(b)
Ψ_{K,Mg,SO_4}	−0.048	(b)
$\Psi_{Mg,Ca,Cl}$	−0.012	(b)
Ψ_{Mg,Ca,SO_4}	0.024	(b)
$\Psi_{H,Na,Cl}$	0.0002	(g)
Ψ_{H,Na,SO_4}	0	(g)
$\Psi_{H,Na,Br}$	−0.012	(a)
$\Psi_{H,K,Cl}$	−0.011	(b)
Ψ_{H,K,SO_4}	0.197	(b)
$\Psi_{H,K,Br}$	−0.021	(b)
$\Psi_{H,Mg,Br}$	−0.005	(a)
$\Psi_{MgOH,Mg,Cl}$	0.028	(b)
$\Psi_{Cl,SO_4,Mg}$	−0.004	(b)
$\Psi_{Cl,HCO_3,Mg}$	−0.0196	(b)
$\Psi_{Cl,F,Na}$	0.0023	(2)
$\Psi_{SO_4,CO_3,Na}$	−0.005	(b)
$\Psi_{SO_4,CO_3,K}$	−0.009	(b)
$\Psi_{SO_4,HCO_3,Na}$	−0.005	(b)

Table A11. Continued

Parameter	Value	Reference
$\Psi_{SO_4,HCO_3,Mg}$	-0.161	(b)
$\Psi_{HSO_4,Cl,Na}$	-0.006	(b)
$\Psi_{HSO_4,SO_4,K}$	-0.0677	(b)
$\Psi_{OH,Cl,Na}$	-0.006	(c)
$\Psi_{OH,Cl,K}$	-0.006	(c)
$\Psi_{OH,Cl,Ca}$	-0.025	(c)
$\Psi_{OH,SO_4,Na}$	-0.009	(c)
$\Psi_{OH,SO_4,K}$	-0.05	(c)
$\Psi_{OH,Br,Na}$	-0.018	(a)
$\Psi_{OH,Br,K}$	-0.014	(a)
$\Psi_{NO_3,Cl,Na}$	-0.006	(a)
$\Psi_{NO_3,Cl,K}$	-0.006	(a)
$\Psi_{H_2PO_4,Cl,Na}$	-0.028	(d)
$\Psi_{H_2PO_4,Cl,K}$	-0.0105	(h)
$\Psi_{HPO_4,Cl,Na}$	-0.003	(d)
$\Psi_{PO_4,Cl,Na}$	0.110	(d)
$\Psi_{H_2AsO_4,Cl,Na}$	0	(e)
$\Psi_{HAsO_4,Cl,Na}$	0	(e)
$\Psi_{AsO_4,Cl,Na}$	0	(e)
$\Psi_{SO_3,Cl,Na}$	-0.0156	(f)

[1]Equated to Na^+ (Θ_{Sr-Na} and $\Psi_{Sr-Na-Cl}$).

[2]Determined from Clegg and Brimblecombe (1988) data.

(a) Pitzer and Kim (1974). (b) Harvie et al. (1984). (c) Felmy and Weare (1986). (d) Hershey et al. (1989). (e) Millero (1983). (f) Millero et al. (1989). (g) Pierrot et al. (1997). (h) Pitzer and Silvester (1976).

Table A12. Coefficients of neutral solutes for $P = a + bT + cT^2 + d/T + e \ln T$.

	i	j	a	b	c	d	e	Range (°C)	Reference
$\lambda_{CO_2,i}$	Na^+		−5496.38465	−3.326566	0.0017532	109399.341	1047.021567	0–90	(a)
	K^+		2856.528099	1.7670079	−0.0009487	−55954.1929	−546.074467	0–90	(a)
	Ca^{2+}		−12774.6472	−8.101555	0.00442472	245541.5435	2452.50972	0–90	(a)
	Mg^{2+}		−479.362533	−0.541843	0.00038812	3589.474052	104.3452732	0–90	(a)
	Cl^-		1659.944942	0.9964326	−0.00052122	−33159.6177	−315.827883	0–90	(a)
	SO_4^{2-}		2274.656591	1.8270948	−0.00114272	−33927.7625	−457.015738	0–90	(a)
$\zeta_{CO_2,i,j}$	H^+	Cl^-	−804.121738	−0.470474	0.000240526	16334.38917	152.3838752	0–90	(a)
	Na^+	Cl^-	−379.459185	−0.258005	0.000147823	6879.030871	73.74511574	0–90	(a)
	K^+	Cl^-	−379.686097	−0.257891	0.000147333	6853.264129	73.79977116	0–90	(a)
	Ca^{2+}	Cl^-	−166.06529	−0.018002	−0.0000247349	5256.844332	27.377452415	0–90	(a)
	Mg^{2+}	Cl^-	−1342.60256	−0.772286	0.000391603	27726.80974	253.62319406	0–90	(a)
	Na^+	SO_4^{2-}	67030.02482	37.930519	−0.0189473	−1399082.37	−12630.27457	0–90	(a)
	K^+	SO_4^{2-}	−2907.03326	−2.860763	0.001951086	30756.86749	611.37560512	0–90	(a)
	Mg^{2+}	SO_4^{2-}	−7374.24392	−4.608331	0.002489207	143162.6076	1412.302898	0–90	(a)
$\lambda_{B(OH)_3,i}$	Na^+		−0.097						(b)
	K^+		−0.14						(b)
	Cl^-		0.091						(b)
	SO_4^{2-}		0.018						(b)
$\zeta_{B(OH)_3,i,j}$	Na^+	SO_4^{2-}	0.046						(b)
$\lambda_{NH_3,i}$	Na^+		0.0175						(c)
	K^+		0.0454						(c)
	Mg^{2+}		−0.21						(c)
	Ca^{2+}		−0.081						(c)
	Sr^{2+}		−0.041						(c)
$\zeta_{NH_3,i,j}$	Ca^{2+}	Cl^-	−0.00134						(c)
$\lambda_{H_3PO_4,i}$	H^+		0.29						(d)
	K^+		−0.07						(d)
$\zeta_{H_3PO_4,i}$	Na^+	Cl^-	0						(d)
$\lambda_{SO_2,i}$	Cl^-		0						(e)
	Na^+		0.0283						(e)
	Mg^{2+}		0.085						(f)
$\lambda_{HF,i}$	Cl^-		0						(g)
	Na^+		0.011						(g)

In $\gamma_{H_2S} = (0.1554 - 0.00806I)$ I from Hershey et al. (1998).

(a) He and Morse (1993). (b) Felmy and Weare (1986). (c) Clegg and Brimblecombe (1989). (d) Silvester and Pitzer (1976). (e) Millero et al. (1989). (f) Roy et al. (1991). (g) This study from Clegg and Brimblecombe (1988) data.

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