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A Chemical Equilibrium Model for the Carbonate System in Natural Waters*

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This paper describes a chemical equilibrium model which can be used to characterize the carbonate system in natural waters from 0 to 50 °C and high ionic strengths (6 mol L^{-1}). The model considers the ionic interactions in solutions of the major sea salts ($H–Na–K–Mg–Ca–Sr–Cl–Br–OH–HCO_3–B(OH)_4–HSO_4–SO_4–CO_3–CO_2–B(OH)_3–H_2O$). The estimated activity coefficients and infinite dilution constants have been used to determine the dissociation constants of all the acids (H_2CO_3, $B(OH)_3$, H_2O, HF, HSO_4^-, H_3PO_4, H_2S, NH_4^+ *etc.*) needed to examine the carbon dioxide system in natural waters. The model is largely based on measurements of dissociation constants in NaCl solutions with small amounts of Mg^{2+}. The model predicts the activity coefficients of HCl in seawater that agree with the measured values to 0.002 from $S = 5$ to 45 and $t = 0$ to 50 °C. The model has also been used to examine the dissociation constants of acids in seawater to test its reliability. The calculated values of the dissociation constants for the ionization of carbonic and boric acids were found to be in good agreement (± 0.02 to ± 0.03 in pK) with the experimental measurements in NaCl and seawater solutions from 5 to 45 °C and $S = 10$ to 45. The model predicts the dissociation constants of the minor acids with sufficient accuracy (± 0.03 to ± 0.06) to characterize the carbonate system in brines over a wide range of temperatures (0 to 50 °C) and ionic strength (0 to 6 mol L^{-1}). These constants can be used to characterize the carbonate systems in natural brines using measurements of two carbonate parameters (pH–TA, pH, TCO_2 *etc.*).

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* Dedicated to Marko Branica on the occasion of his 65th birthday.

INTRODUCTION

Interactions between ions in natural waters have major effects on the rates of redox processes[1,2] and on mineral solubility.[3] A quantitative treatment of these effects requires an appropriate, self consistent model describing the variation of activity coefficients with ionic strength 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 an ion pairing model[4,5] and the specific interaction model.[6–10] The use of the ion pairing model to estimate activity coefficients was pioneered by Garrels and Thompson[11] and extended by Dickson and Whitfield[4] and Millero and Schreiber.[5] These latter studies allow one to estimate reliable activity coefficients for a number of major and minor ions to 1 mol L^{-1} and at 25 °C. Extension to higher ionic strength and other temperatures is complicated by the requirement for experimental data for the large number of ion pairs – 50 in the case of the major components of seawater. The Pitzer[7,8] model for the same components requires stability constants for only 6 ion pairs.[3] Stability constants at temperatures other than 25 °C are not readily available. Reliable extensions to higher ionic strength are difficult due to our lack of knowledge of the activity coefficients of the ion pairs of various charge types.

The specific interaction model as formulated by Pitzer[7,8] 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[12,13] 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,[14,15] as formulated by Guggenheim,[6] to estimate the activities of the major sea salts. Weare and co-workers[3,9,16–19] and others[6,20,21] have extended the model for the 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 to 250 °C) to high ionic strengths (<6 mol L^{-1}). The extension of these models to trace metals has been made for solutions of chloride and sulfate solutions[12,13] at 25 °C. The speciation of divalent[22,23] and trivalent metals[23,24] with OH^-, HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, and HPO_4^{2-} have been added to the model at 25 °C. More recently, we[25] 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 mol L^{-1}. Clegg and Whitfield[26] have used the Pitzer model to examine the dissociation of ammonia in seawater using the Pitzer equations. In our earlier work,[20,27–35] 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.

Recently there has been great interest in understanding the carbonate system in natural waters. The thermodynamics of the carbonate system in seawater are well characterized[36]. However, the thermodynamic data needed to characterize the carbonate system in other natural waters such as pore fluids and brines are not readily available. In the present paper we have extended the Pitzer ionic interaction model to include the components needed to evaluate the carbonate system in natural waters from $I = 0$ to 6 mol L^{-1} and 0 to 50 °C. The model can estimate all the dissociation constants needed to characterize the carbonate system in natural waters. These equilibria are discussed in the next section.

THE CARBONATE SYSTEM IN NATURAL WATERS

The carbon dioxide in the aqueous solutions is thermodynamically controlled by the following equilibria[36]

$$CO_2\ (g) \overset{K_0}{=} CO_2\ (aq) \tag{1}$$

$$CO_2 + H_2O \overset{K_1}{=} H^+ + HCO_3^- \tag{2}$$

$$HCO_3 \overset{K_2}{=} H^+ + CO_3^{2-}\,. \tag{3}$$

The parameter K_0 is the solubility coefficient of the carbon dioxide. The dissociation constants (equations 2 and 3) for the carbonic acid system do not differentiate between $CO_2(aq)$ and H_2CO_3 and is denoted by $[CO_2] =$ $= [CO_2(aq)] + [H_2CO_3]$. The fugacity of CO_2 is defined by the relationship

$$fCO_2 = [CO_2] / K_0 \tag{5}$$

where the brackets denote total concentrations. The first dissociation constant of carbonic acid is given by

$$K_1 = [H^+]\ [HCO_3^-] / [CO_2] \tag{6}$$

and the second dissociation constant is given by

$$K_2 = [H^+]\ [CO_3^{2-}] / [HCO_3^-]. \tag{7}$$

The titration alkalinity, TA, is defined as all the bases that can accept a proton at the carbonic acid end point.[37] It is used to estimate the components of the carbon dioxide system that can accept a proton. It is defined by

$$\mathrm{TA} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{B(OH)_4^-}] + [\mathrm{OH^-}] - [\mathrm{H^+}] + \mathrm{Bases} \quad (8)$$

where $[\mathrm{OH^-}]$ includes the $\mathrm{OH^-}$ bound to $\mathrm{Mg^{2+}}$ and $[\mathrm{H^+}]$ includes the $\mathrm{H^+}$ bound to $\mathrm{SO_4^{2-}}$ and $\mathrm{F^-}$. The titration alkalinity also includes minor concentrations of other bases[37] that can accept a proton

$$\mathrm{Bases} = [\mathrm{SiO(OH)_3^-}] + [\mathrm{HPO_4^{2-}}] + 2[\mathrm{PO_4^{3-}}] + [\mathrm{NH_3}] + [\mathrm{HS^-}]. \quad (9)$$

Only the alkalinity due to the components of the carbon dioxide, the carbonate alkalinity CA, is needed to characterize the system. The CA is defined by

$$\mathrm{CA} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}]. \quad (10)$$

To calculate CA from the measured TA, one must account for the contributions of $[\mathrm{B(OH)_4^-}]$, $[\mathrm{OH^-}]$, $[\mathrm{H^+}]$ and the other bases able to accept a proton. To make this correction for the major bases, one needs to consider the dissociation equilibria for boric acid, water, phosphoric, silicic, hydrogen sulfide, and ammonia in the solution.

The solubility and precipitation of calcium carbonate as aragonite and calcite also affect the carbon dioxide system. These processes are given by

$$\mathrm{CaCO_3(s)} \overset{K_{\mathrm{SP}}}{=} \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \quad (11)$$

where the solubility product of aragonite or calcite is given by

$$K_{\mathrm{SP}} = [\mathrm{Ca^{2+}}]\,[\mathrm{CO_3^{2-}}]. \quad (12)$$

The stoichiometric dissociation constants (K_{HA}) for an acid (HA) in a given ionic media needed above, are related to the thermodynamic values (K^0_{HA}) by

$$K_{\mathrm{HA}} = \{[\mathrm{H^+}]\,[\mathrm{A^-}] / [\mathrm{HA}]\} = K^0_{\mathrm{HA}}\,\{\gamma_{\mathrm{HA}} / \gamma_{\mathrm{H}} / \gamma_{\mathrm{A}}\} \quad (25)$$

where γ_i is the stoichiometric or total activity coefficients of solute i. It should be pointed out that all the bracketed species are stoichiometric concentrations (molality or mol $\mathrm{kg^{-1}}$) and disregard any complex formation or ion pairs. It is thus necessary to specify not only the pH scale[38] used in the evaluation of the dissociation constants, but their dependency on salinity, temperature and pressure.

The stoichiometric constants, K_{HA}, described above are determined using three pH scales.[38,39] The NBS (National Bureau of Standards) scale

$$pH_{NBS} = -\log a_H = -\log \{f_H[H^+]\} \tag{26}$$

where a_H is the activity of the proton and f_H is factor related to the calibration of the electrode used with NBS buffers.[39] This pH scale is not suggested for use due to the problems of using dilute solution buffers for high ionic strength solutions.[38,39]

The free scale is given by

$$pH_F = -\log [H^+]_F \tag{27}$$

where $[H^+]_F$ is the concentration of the free or uncomplexed proton. The total scale is given by

$$pH = -\log [H^+] = -\log \{[H^+]_F + [HSO_4^-] + [F^-]\} \tag{28}$$

where $[H^+]$ is the total or stoichiometric concentration of the proton given in Eq. (25). The Pitzer model provides total or stoichiometic activity coefficients and is best suited for the total proton scale. This scale can be related to the free proton scale (without fluoride and sulfate) by

$$[H^+] / [H^+]_F = \{1 + [SO_4^{2-}] / K_{HSO4} + [F^-] / K_{HF}\} \tag{29}$$

where $[SO_4^{2-}]$ and $[F^-]$ are the concentration of SO_4^{2-} and F^- not complexed with the proton (for F^- this includes free F^-, MgF^+ and CaF^+). The dissociation constants for HF and HSO_4^- are needed to relate the two scales. As discussed elsewhere,[32] we feel that if electrodes are used to determine the pH, the electrodes should be calibrated with TRIS buffers in solutions of known composition similar to the natural water of interest.

The activity coefficients needed to determine the values of K_{HA} for acids can be estimated using an ionic interaction model for a solution of known composition. These constants can then be used to characterize the carbonate system from measurements of at least two of the following pH, pCO_2, TA and TCO_2. Although it is possible to use the ion pairing model[4,5] in dilute solutions at 25 °C, the equation developed by Pitzer[7,8] provide the most reliable method that can be used to estimate the activity coefficients of ionic and nonionic solutes over a wide range of temperatures and ionic strengths. These equations are briefly described in the next section.

Pitzer Equations for Ions in Aqueous Solutions

The Pitzer equations[7,8] for the activity coefficient (γ) of cation (M) and anion (X) and neutral species (N) are given by

$$\ln \gamma_\mathrm{M} = Z_\mathrm{M}^2 f^\gamma + 2\, \Sigma_\mathrm{a} m_\mathrm{a}(B_\mathrm{Ma} + EC_\mathrm{Ma}) + Z_\mathrm{M}^2 R + Z_\mathrm{M} S$$
$$+ \Sigma_\mathrm{c} m_\mathrm{c} (2\, \Theta_\mathrm{Mc} + \Sigma_\mathrm{a} m_\mathrm{a} \Psi_\mathrm{Mca}) + \Sigma_\mathrm{a} \Sigma_\mathrm{a'} m_\mathrm{a} m_\mathrm{a'} \Psi_\mathrm{aa'M}$$
$$+ \Sigma_\mathrm{c} m_\mathrm{c}\, 2\, {}^E\Theta_\mathrm{Mc} + Z_\mathrm{M}^2 R_1 + Z_\mathrm{M}^2 R_2 \qquad (30)$$

$$\ln \gamma_\mathrm{X} = Z_\mathrm{X}^2 f^\gamma + 2\, \Sigma_\mathrm{c} m_\mathrm{c}(B_\mathrm{cX} + EC_\mathrm{cX}) + Z_\mathrm{X}^2 R + Z_\mathrm{X} S$$
$$+ \Sigma_\mathrm{a} m_\mathrm{a} (2\, \Theta_\mathrm{Xa} + \Sigma_\mathrm{c} m_\mathrm{c} \Psi_\mathrm{Xac}) + \Sigma_\mathrm{c} \Sigma_\mathrm{c'} m_\mathrm{c} m_\mathrm{c'} \Psi_\mathrm{cc'X}$$
$$+ \Sigma_\mathrm{a} m_\mathrm{a}\, 2\, {}^E\Theta_\mathrm{Xa} + Z_\mathrm{X}^2 R_1 + Z_\mathrm{X}^2 R_2\,. \qquad (31)$$

The values of R, S, R_1, and R_2 in equations 30 and 31 are given by

$$R = \Sigma_\mathrm{c} \Sigma_\mathrm{a} m_\mathrm{c} m_\mathrm{a} B'_\mathrm{ca} \qquad (32)$$

$$S = \Sigma_\mathrm{c} \Sigma_\mathrm{a} m_\mathrm{c} m_\mathrm{a} C_\mathrm{ca} \qquad (33)$$

$$R_1 = \Sigma_\mathrm{c} \Sigma_\mathrm{c'} m_\mathrm{c} m_\mathrm{c'} {}^E\Theta'_\mathrm{cc'} \qquad (34)$$

$$R_2 = \Sigma_\mathrm{a} \Sigma_\mathrm{a'}\, m_\mathrm{a} m_\mathrm{a'} {}^E\Theta'_\mathrm{aa'}\,. \qquad (35)$$

The equivalent molality is given by $E = (1/2)\Sigma_i m_i Z_i = \Sigma m_\mathrm{c} Z_\mathrm{c} = \Sigma m_\mathrm{a} Z_\mathrm{a}$, where m_c and m_a and Z_c and $Z_\mathrm{a}$are the molality and charge on cation c and anion a. The Debye-Hückel term is given by

$$f^\gamma = -A^\phi\, [I^{1/2} / (1 + 1.2\, I^{0.5}) + (2/1.2) \ln(1 + 1.2\, I^{0.5})]. \qquad (36)$$

In these equations I is the ionic strength, Z_i is the charge, m_i is the molality of cations (c) and anions (a) in the solution and the equivalent molality $E = 1/2\, \Sigma_i m_i |Z_i|$. The second ($B_{ij}$) and third ($C_{ijk}$) virial coefficients are given for 1–1, 2–1, and 3–1 electrolytes by

$$B^\phi{}_\mathrm{MX} = \beta^0_\mathrm{MX} + \beta^1_\mathrm{MX} \exp(-2\, I^{0.5}) + \beta^2_\mathrm{MX} \exp(-1.4\, I^{0.5}) \qquad (37)$$

$$B_\mathrm{MX} = \beta^0_\mathrm{MX} + (\beta^1_\mathrm{MX} / 2\, I)\, [1 - (1 + 2\, I^{0.5}) \exp(-2\, I^{0.5})] \qquad (38)$$

$$B'_\mathrm{MX} = (\beta^1_\mathrm{MX} / 2\, I^2)\, [-1 + (1 + 2\, I^{0.5} + 2\, I) \exp(-2\, I^{0.5})] \qquad (39)$$

$$C_\mathrm{MX} = C^\phi{}_\mathrm{MX} / (2 |Z_\mathrm{M} Z_\mathrm{X}|^{0.5}). \qquad (40)$$

For 2–2 electrolytes the coefficients are given by

$$B_\mathrm{MX} = \beta^0_\mathrm{MX} + (\beta^1_\mathrm{MX} / 0.98\, I)\, [1 - (1 + 1.4\, I^{0.5}) \exp(-1.4\, I^{0.5})]$$
$$+ (\beta^2_\mathrm{MX} / 72\, I)\, [1 - (1 + 12\, I^{0.5}) \exp(-12\, I^{0.5})] \qquad (41)$$

$$B'_{\mathrm{MX}} = (\beta^1_{\mathrm{MX}} / 0.98\, I^2)\,[-1 + (1 + 1.4\, I^{0.5} + 0.98\, I)\exp(-1.4\, I^{0.5})] + (\beta^2_{\mathrm{MX}} / 72\, I)\,[-1 - (1 + 12\, I^{0.5} + 72\, I)\exp(-12\, I^{0.5})]. \quad (42)$$

The values of Θ_{ij} and Ψ_{ijk} for mixtures[7,8,40,41] needed in Eqs. 30 and 31 are related to short range interactions of ions of the same charge (Na^+–Mg^{2+} or Cl^-–SO_4^{2-}) and triplet interactions (Na^+–Mg^{2+}–Cl^-). The higher order electrostatic terms ${}^E\Theta_{ij}$ and ${}^E\Theta'_{ij}$ are due to higher order interactions between ions of different charges and are functions of ionic strength.[41] The terms are zero for symmetric electrolytes (1–1, 2–2, *etc.*). Equations that can be used to calculate these terms are given elsewhere.[8,9,41]

The activity coefficient of nonelectrolytes in mixed electrolyte solutions are determined from

$$\ln \gamma_{\mathrm{N}} = \Sigma_{\mathrm{c}} m_{\mathrm{c}}(2\lambda_{\mathrm{Nc}}) + \Sigma_{\mathrm{a}} m_{\mathrm{a}}(2\lambda_{\mathrm{Na}}) + \Sigma_{\mathrm{c}}\Sigma_{\mathrm{a}}\, m_{\mathrm{c}} m_{\mathrm{a}}\, \zeta_{\mathrm{Nca}}\,. \quad (43)$$

The values of λ_{Nc} and ζ_{Nca} terms are for the interactions of nonelectrolytes ($N = CO_2$) with various cations ($c = Na^+$) and anions ($a = Cl^-$).

Parameters for the Interactions of Cations and Anions for the Model (β^0_{MX}, β^1_{MX}, β^2_{MX}, $C^\phi{}_{\mathrm{MX}}$)

The values of β^0_{MX}, β^1_{MX}, β^2_{MX}, $C^\phi{}_{\mathrm{MX}}$ for the major components of natural waters are available at 25 °C and are tabulated elsewhere.[3,8,9,42,43] The Pitzer osmotic and activity coefficient parameters are known[8,16–19,21] for a number of electrolytes (HCl, $NaCl$, KCl, $NaOH$, $MgCl_2$, $CaCl_2$, Na_2SO_4, K_2SO_4, $MgSO_4$, $CaSO_4$) important in natural system over a wide range of temperatures (0 to 250 °C) and are frequently fit to equations of the form

$$\beta^0_{\mathrm{MX}}(T) = q_1 + q_2(1/T - 1/T_{\mathrm{R}}) + q_3 \ln(T/T_{\mathrm{R}}) + q_4\,(T - T_{\mathrm{R}}) + q_5\,(T^2 - T_{\mathrm{R}}{}^2) \quad (44)$$

where T_{R} is some reference temperature (298.15) and q_i are adjustable parameters. There is a need, however, to make reasonable estimates of activity coefficients over smaller ranges of temperature (0 to 75 °C). The integration of the heat capacity and enthalpies of electrolytes at reference temperature (25 °C) can be used[44] to estimate the effect of temperature on the osmotic and activity coefficients. Heat capacity and enthalpy data at 25 °C have been shown[44] to provide reasonable estimates of activity coefficients from 0 to 75 °C and 0 to 2 mol L^{-1}. From the definition of the effect of temperature on the coefficients used to fit the enthalpies[45] and heat capacities,[46] the effect of temperature on the activity parameters can be determined

$$\beta^{(0)\mathrm{L}} = \partial\beta^{(0)\mathrm{L}}/\partial T \quad (45)$$

$$\beta^{(0)J} = \partial^2\beta^{(0)}/\partial T^2 + (2/T)(\partial\beta^{(0)}/\partial T). \tag{46}$$

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

$$\beta^{(0)} = \beta^{(0)}{}_R + a\ (1/T - 1/T_R) + b\ (T^2 - T_R{}^2) \tag{47}$$

where

$$a = (\beta^{(0)J}/3)\ T_R{}^3 - T_R{}^2\beta^{(0)L}{}_R) \tag{48}$$

$$b = \beta^{(0)J}/6 \tag{49}$$

similar equations can be derived for $\beta^{(1)}$ and C^{ϕ}. The values of $\beta^{(0)J}$ recently determined by Criss and Millero[46] can be combined with literature values of $\beta^{(0)}{}_R$ and $\beta^{(0)L}{}_R$ (Ref. 45) to derive equations that can be use to estimate osmotic and activity coefficients of the electrolytes as a function of temperature. As found in earlier work[44] the 25 °C enthalpy and heat capacity data can yield reasonable estimate for the activity coefficients from 0 to 50 °C. For example the calculated mean activity coefficients of NaCl agree with the measured values (0.003) from 0 to 75 °C and 0 to 2 mol L^{-1}.[44,46]

For many of the major seasalt ions (H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, OH^-, SO_4^{2-}) the coefficients for equation (44) are available from 0 to 250 °C[17–19,21] and extend the earlier work of Harvie *et al.*[3,9] More limited data are available from 0 to 50 °C or 100 °C for H^+,[25,26,33] HCO_3^-, CO_3^{2-}, CO_2,[47–51] $B(OH)_3$, $B(OH)_4^-$,[52,53] NH_3,[26] and H_2S, HS^-.[33] In the present paper, we have used these latter results with other literature data to obtain Pitzer parameters that can be used to characterize the carbonate system in natural waters from 0 to 50 °C. The source of the binary parameters (β^0_{MX}, β^1_{MX}, β^2_{MX}, and $C^{\phi}{}_{MX}$) for the various electrolytes and the temperature range are given in Table I. The binary terms for $MgBr_2$, $CaBr_2$, $SrCl_2$, $SrBr_2$ were taken from the 25 °C parameters given by Pitzer and Mayorga[42] and the temperature coefficients from the enthalpy data of Silvester and Pitzer[45] and heat capacity data of Criss and Millero.[46] The choice of the higher order interaction terms needed are discussed in the next section.

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

The Θ_{ij} and Ψ_{ijk} terms are related to the short range interactions of ions of the same charge and triplet interactions, respectively. Values of these terms for the major sea salts at 25 °C are available,[3,8,9,16,25,26,28,31–35] but only a limited amount of data is available as a function of temperature.[17–18,21,54–56] Higher order interaction terms (${}^E\Theta_{ij}$ and ${}^E\Theta'_{ij}$) that account for the electro-

TABLE I

Single electrolyte Pitzer parameters (β^0, β^1, β^2, C^ϕ) used in this study

Cation	Anion	Temperature range	Reference
H	Cl	0 to 100 °C	25
	SO_4	0 to 55	Clegg *et al.*
	HSO_4	0 to 55	Clegg *et al.*
	Br	0 to 50	This study
Na	Cl	0 to 250	17
	SO_4	0 to 100	Hovey *et al.* (1993)
	HSO_4	0 to 50	25
	OH	0 to 250	21
	HCO_3	0 to 50	50
	Br	0 to 50	42,45
	CO_3	0 to 50	50
	$B(OH)_4$	0 to 50	52
	F	0 to 50	42,45
	H_2PO_4	0 to 50	42,45
	HPO_4	0 to 50	42,45
	PO_4	0 to 50	42,45
	HS	0 to 50	33.
K	Cl	0 to 250	17
	SO_4	0 to 250	17
	HSO_4	25	3
	OH	0 to 50	42,45
	HCO_3	5 to 45	48
	Br	25	42,45
	CO_3	5 to 95	51
	$B(OH)_4$	0 to 50	52
	F	0 to 50	42,45
	H_2PO_4	0 to 50	42,45
	HPO_4	0 to 50	42,45
	HS	0 to 50	33
Mg	Cl	25 to 250	21
	SO_4	25 to 250	21
	HSO_4	25	25
	OH	0 to 250	21
	HCO_3	25	29
	Br	25	42,45
	CO_3	25	29
	$B(OH)_4$	5 to 55	53
	HS	25	33
Ca	Cl	0 to 250	17
	SO_4	0 to 250	17
	HSO_4	25	3
	OH	25	3
	HCO_3	25	3

TABLE I – Cont.

Cation	Anion	Temperature Range	Reference
Ca	Br	0 to 50	42,45
	CO_3	25	3
	$B(OH)_4$	25	53
	HS	0 to 50	33
Sr	Cl	0 to 50	42,45
	SO_4	25	43
	HSO_4	25	Equated to Ca^{2+} salt
	OH	25	Equated to Ca^{2+} salt
	HCO_3	25	Equated to Ca^{2+} salt
	Br	0 to 50	42,45
	CO_3	25	Equated to Ca^{2+} salt
	$B(OH)_4$	25	Equated to Ca^{2+} salt
	F	25	Equated to Ca^{2+} salt
MgOH	Cl	25	3
$MgB(OH)_4$	Cl	0 to 50	53
$CaB(OH)_4$	Cl	0 to 50	53

static 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.[8,41] The sources of the values of Θ_{ij} and Ψ_{ijk} for cation-cation and anion-anion interactions used in this study are given in Tables II and III.

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

The interaction parameters for neutral acids (CO_2, NH_3, $B(OH)_3$, H_2S, and H_3PO_4) are needed to determine the activity coefficients in ionic media. For dilute solutions the activity of neutral solutes in electrolyte solutions are determined from the ratio of the solubility in a salt solution and water

$$\gamma_N = S^0/S. \tag{50}$$

The ionic strength dependence is frequently expressed by the Satchenow equation

$$\ln \gamma_N = k\, I\,. \tag{51}$$

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

TABLE II

Cation-cation and triplet interaction parameters (Θ_{MN}, Ψ_{MNX}) used in this study

M	N	X	Temperature range	Reference
H	Na	Cl	0 to 50 °C	25
		HSO_4	25	91
	K	Cl	0 to 50	25
		SO_4	25	3
		HSO_4	25	3
	Mg	Cl	0 to 50	54
		HSO_4	25	3
	Ca	Cl	0 to 50	55
	Sr	Cl	0 to 50	56
Na	K	Cl	0 to 250	17
		SO_4	0 to 250	17
		HCO_3	25	3
		CO_3	25	3
	Mg	Cl	25 to 250	21
		SO_4	25 to 250	21
	Ca	Cl	0 to 250	17
		SO_4	0 to 250	17
	Sr	Cl	25	40
K	Mg	Cl	0 to 250	21
		SO_4	0 to 250	21
	Ca	Cl	0 to 250	17
Ca	Mg	Cl	0 to 250	21
		SO_4	0 to 250	21
Mg	MgOH	Cl	25	3

to estimate the activity coefficients (this may involve a second order dependence of ln γ_N on I). If no data are available for a given acid, it is necessary to use another acid of similar structure as a model. The source of the Pitzer neutral parameters for acids and neutral ion pairs available[3,16,26,29,31–34] at the present time are given in Table IV.

Mean Activity Coefficient of HCl in Seawater

To test the reliability of the model and its usefulness, we will examine the activity coefficients and p*K*'s for acids in NaCl (the major component of most brines) and seawater (the dominant natural water) solutions.[20,24, 57] The seawater calculations are useful in determining the reliability of the model; since direct measurements[36] have been made over a wide range of

TABLE III

Anion-anion and triplet interaction parameters (Θ_{XY}, Ψ_{MXY}) used in this study

X	Y	M	Temperature range	Reference
Cl	SO_4	Na	0 to 250 °C	17
		K	0 to 250	17
		Mg	0 to 250	21
		Ca	0 to 250	17
	HSO_4	Na	25	91
		H	25	91
	OH	Na	0 to 250	3
		K	0 to 250	2
		Ca	0 to 250	2
	HCO_3	Na	0 to 60	28
		Mg	25	29
	CO_3	Na	0 to 60	50
		K	0 to 60	50
SO_4	HSO_4	Na	25	3
		K	25	3
		Mg	25	3
	OH	Na	0 to 250	21
		K	0 to 250	21
	HCO_3	Na	25	3
		Mg	25	3
	CO_3	Na	25	3
		K	25	3
OH	CO_3	Na	25	3
		K	25	3
HCO_3	CO_3	Na	0 to 60	50
		K	0 to 60	48

temperatures (0 to 50 °C) and ionic strengths (0.1 to 1 mol L^{-1}). With this in mind, we will first examine the mean activity coefficient of HCl in seawater with and without SO_4^{2-} to examine the effect of the major seasalts on the activity of the proton. The mean activity coefficient of HCl can be determined from the ionic values (Eqs. 30 and 31) using

$$\gamma_{\pm}(\mathrm{HCl}) = (\gamma_{\mathrm{H}}\, \gamma_{\mathrm{Cl}})^{0.5} \tag{50}$$

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 of the proton are high this requires an interation. 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

TABLE IV

Neutral interaction parameters (λ_{Nc}, λ_{Nca}, ζ_{Nca}) used in this study

N	c	a	Temperature range	Reference
CO_2	Na	Cl	0 to 50°C	50
	K	Cl	0 to 100°C	49
	Mg	Cl	0 to 100°C	49
	Ca	Cl	0 to 100°C	49
	Na	SO_4	0 to 100°C	49
	K	SO_4	0 to 100°C	49
	Mg	SO_4	0 to 100°C	49
	Ca	SO_4	25	49
$B(OH)_3$	Na	Cl	0 to 50°C	16,52
	K	Cl	0 to 50°C	16,52
	Mg	Cl	0 to 50°C	16,53
	Ca	Cl	0 to 50°C	16,53
	Na	SO_4	25	16
	K	SO_4	25	16
H_3PO_4	Na	Cl	25	45
NH_3	Na	Cl	25	88
	K	Cl	25	88
	Mg	Cl	25	88
	Ca	Cl	25	88
	Na	SO_4	25	88
	K	SO_4	25	88
	Mg	SO_4	25	88
	Ca	SO_4	25	88
H_2S	Na	Cl	25	33

$$\gamma^*_{\mathrm{H}} = \gamma_{\mathrm{H}}(\mathrm{Eq.}\ 30) / (1 + [SO_4^{2-}] / K_{\mathrm{HSO4}}) + [\mathrm{F}^-] / K_{\mathrm{HF}}) \qquad (51)$$

where the asterisk is used to denote that it is corrected for the formation of HSO_4^- and HF.

We have first used the model to determine the mean activity coefficient of HCl in of artificial seawater without sulfate[58] and with sulfate.[25,59] The comparisons of the measured and calculated values of the mean activity coefficient of HCl in seawater without sulfate[58] are shown in Figure 1. The agreement is quite good with a standard deviation of 0.002 in $\gamma_\pm$(HCl) over the entire range of temperature (5 to 40 °C) and ionic strength (0.2 to 0.9 mol L^{-1}).

The extension of the seawater model to include SO_4^{2-} is not easy due to the paucity of reliable activity coefficient data for the Na^+, K^+, Mg^{2+}, Ca^{2+}, and HSO_4^- systems at temperatures other than 25 °C. As discussed elsewhere[25] the approach we used was to determine the interaction coefficients

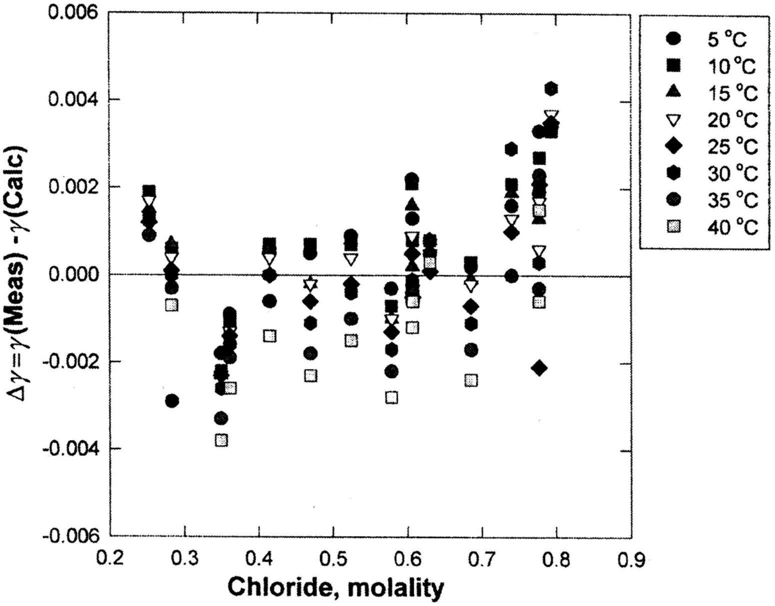

Figure 1. Comparison of the measured[58] and calculated values for the mean activity coefficient of HCl in seawater without sulfate.

between Mg-HSO_4 at 25 °C from the seawater data. This was necessary since the coefficients determined by Harvie *et al.*[3] did not yield reliable estimates for the activity coefficient of HCl in seawater with sulfate.[25] The effect of temperature on the Na-HSO_4 interaction parameters were determined from the seawater data extrapolated to zero proton concentrations. A comparison of the measured[25] and calculated mean activity coefficients of HCl with zero H^+ is shown in Figure 2. The difference are within 0.002 with the exception of one dilute point at 45 °C. This approach yields reliable mean activity coefficients of HCl with added H^+ that are in good agreement with the measured values to 0.05 mol L^{-1} H^+ with the exception of a few points at high temperatures and high concentrations of acid (see Figure 3). Since most of the natural waters have low concentrations of H^+, the errors are not important for the present study. The methods used to determine the interaction parameters of $NaHSO_4$ at temperatures from 0 to 45 °C and Mg-HSO_4 at 25 °C need further study.[26] Our preliminary analysis of new emf measurements made in HCl-$MgSO_4$ solutions yield interaction parameters that are in reasonable agreement with the estimates of Campbell *et al.*[25] As will be discussed later the estimated parameters are sufficient to determine the activity coefficients of the H^+ with sulfate over a wide range of ionic strengths.

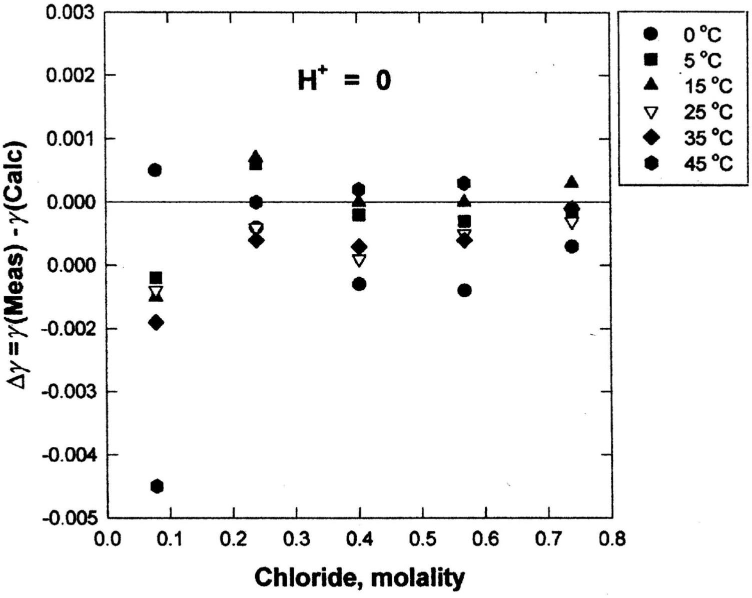

Figure 2. Comparison of the measured[25,59] and calculated values for the mean activity coefficient of HCl in seawater with sulfate (H^+ = 0).

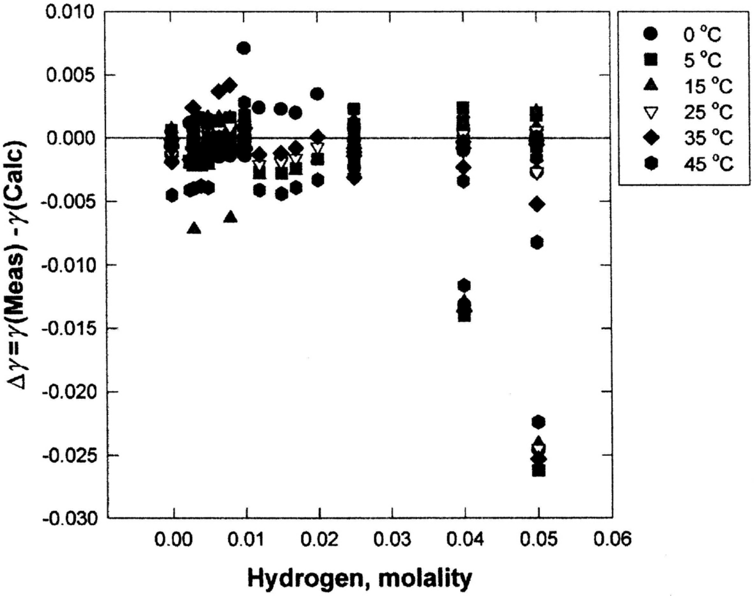

Figure 3. Comparison of the measured[25,59] and calculated values for the mean activity coefficient of HCl in seawater with sulfate as a function of the proton concentration.

Carbonic Acid Dissociation Constants

pK$_0$

To determine the first dissociation constant of carbonic acid it is necessary to know the solubility of CO_2 in the solution. Harvie *et al.*[3] have examined the solubility of CO_2 in electrolyte solutions at 25 °C and more recently He and Morse[49] have examined the solubility in seasalts from 0 to 100 °C. A comparison the predicted values of pK_0 in seawater at 25 °C using the coefficients from these two models are compared to the measured values in the Table V. The Harvie *et al.*[3] values are much lower than the measured values; while the values from He and Morse[49] are in reasonable agreement with the measured values. Since the Pitzer parameters used for the interactions of major seasalt cations with HCO_3^- and CO_3^{2-} from 0 to 50 °C used in our model are based on the solubilities of CO_2 in NaCl[60] solutions analyzed by Peiper and Pitzer,[50] we have used their salting coefficients in our model. The use of these NaCl parameters with the Harvie *et al.*[3] and He and Morse[49] parameters for the other ions gives calculated solubilities in seawater[61] that are in good agreement at 25 °C (values in parenthesis). Since the coefficients of He and Morse[49] for the other seasalts are available over a wide range of temperatures, we have used them in our further calculations. A comparison of the measured[61] and calculated values of pK_0 determined in this manner are shown in Figure 4.

TABLE V

Comparison of the measured and calculated values of pK_0 for CO_2 in seawater at 25 °C

S	pK_0(Meas)	pK_0(Calc)	
		a	b
20	1.513	1.474 (1.508)[c]	1.506 (1.510)
30	1.536	1.478 (1.531)	1.526 (1.534)
35	1.547	1.481 (1.543)	1.537 (1.546)
40	1.558	1.483 (1.554)	1.547 (1.558)

a) Harvie *et al.*[3]
b) He and Morse[49]
c) The values in parenthesis use the coefficients of NaCl from Peiper and Pitzer[50]

pK$_1$

The parameters for the first dissociation constant of carbonic acid in NaCl solutions from 5 to 45 °C are based on the earlier work of Harned and

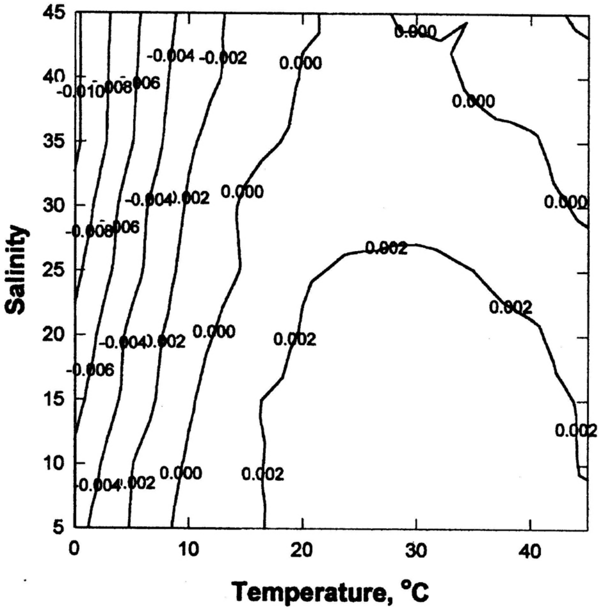

Figure 4. Comparison of the measured[61] and calculated values for pK_0 for the solubility of CO_2 in seawater.

Bonner[62] At 25 °C we have used the higher order terms determined in our earlier work.[28,29] A comparison of the measured[62,28] and calculated values of pK_1 in NaCl from 0 to 50 °C and 0.1 to 1 mol L^{-1} are shown in Figure 5. The agreement is quite good with a standard deviation of 0.005 in pK_1. As discussed elsewhere[28,29] the model predicts reliable values for pK_1 at 25 °C to 6 mol L^{-1} in NaCl and Na–Mg–Cl solutions. Since our model is limited to 50 °C we have not shown comparison of the model with the work of He and Morse.[49] From 0 to 50 °C the agree is reasonable for NaCl and KCl solutions to 3 mol L^{-1}.

The calculated values of pK_1 in seawater can be compared to the measurements of Mehrbach *et al.*,[63] Hansson,[64] Goyet and Poisson[65] and Roy *et al.*[66] Since the combined equation equations of Dickson and Millero[67] give and adequate representation of the work of Mehrbach *et al.*[63] and Hansson[64] and the combined equation of Millero[36] gives an adequate representation of Goyet and Poisson[65] and Roy *et al.*,[66] we will only show the deviations for these two equations. The results are shown in Figures 6 and 7. The calculated values are in good agreement with the measured values over the entire temperature and salinity range (standard error of 0.015 and 0.014, respectively, for the equations of Dickson and Millero[67] and Millero[36]).

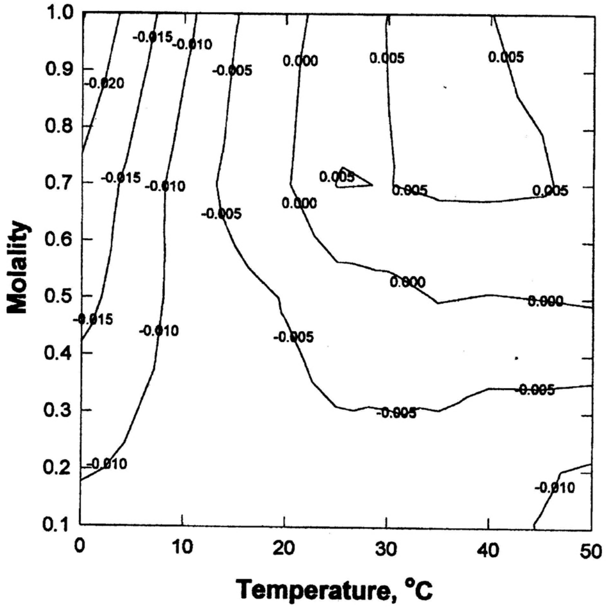

Figure 5. Comparison of the measured[71] and calculated values for pK_1 for the dissociation of H_2CO_3 in NaCl.

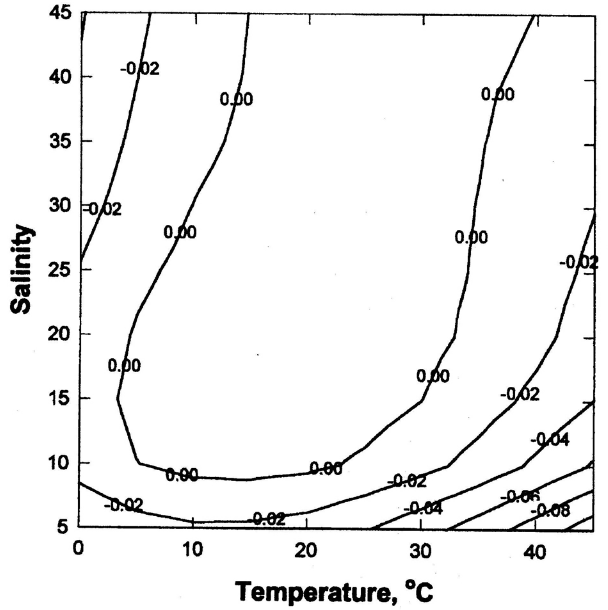

Figure 6. Comparison of the measured[67] and calculated values for pK_1 for the dissociation of H_2CO_3 in seawater.

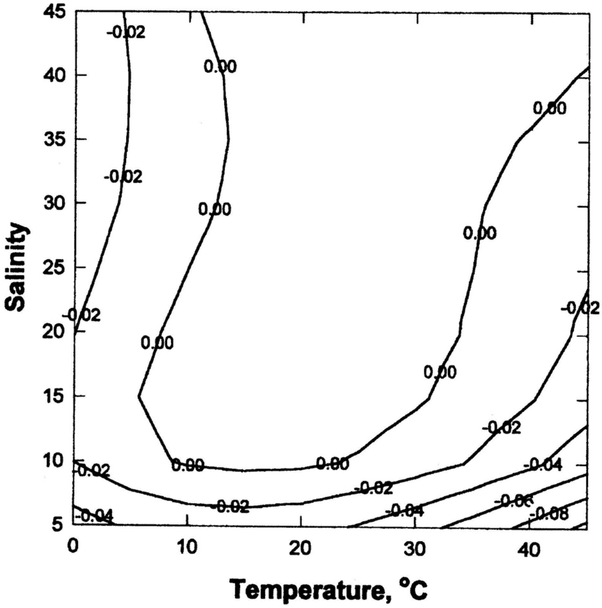

Figure 7. Comparison of the measured[36] and calculated values for pK_1 for the dissociation of H_2CO_3 in seawater.

pK_2

The parameters for the second dissociation constant of carbonic acid in NaCl solutions from 5 to 45 °C are based on the earlier work of Roy and co workers.[47] At 25 °C we have used the higher order terms determined in our earlier work.[28,29] The parameter adequately fit the measurements in NaCl and Na–Mg–Cl to 6 mol L^{-1}. The measured[36,67] values of pK_2 in seawater are compared to the calculated values in Figures 8 and 9. The calculated values are in good agreement (standard errors of 0.02 and 0.03, respectively) from 0 to 50 °C and $S = 10$ to 45. The calculated values of pK_2 are all slightly higher that the measured values over the entire temperature range.

Boric Acid Dissociation Constants

The parameters for the dissociation constant of boric acid in NaCl solutions from 5 to 45 °C are based on the earlier work of Owen and King.[68] At 25 °C we have used the higher order terms determined in our earlier work.[31] A comparison of the measured[68] and calculated values of pK_{HB} in NaCl from 0 to 50 °C and 0.1 to 3 mol L^{-1} are shown in Figure 10. The agreement is quite good with a standard deviation of 0.005 in pK_1. As discussed elsewhere,[31] the model predicts reliable values for pK_1 at 25 °C to 6 mol L^{-1} in NaCl and Na–Mg–Cl solutions.

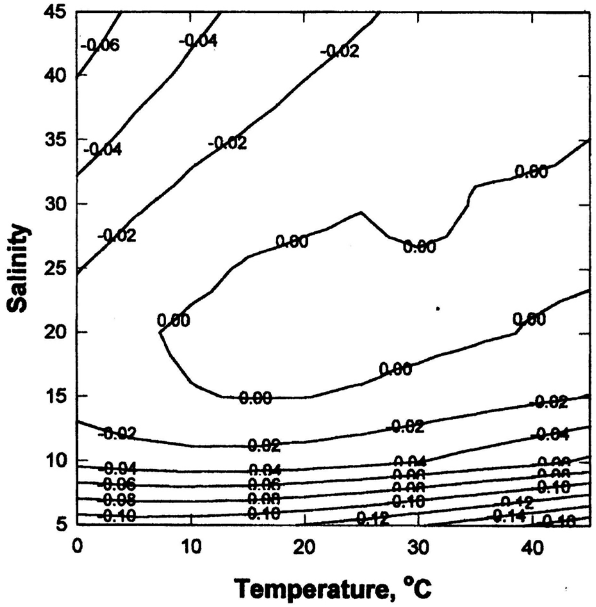

Figure 8. Comparison of the measured[67] and calculated values for pK_2 for the dissociation of H_2CO_3 in seawater.

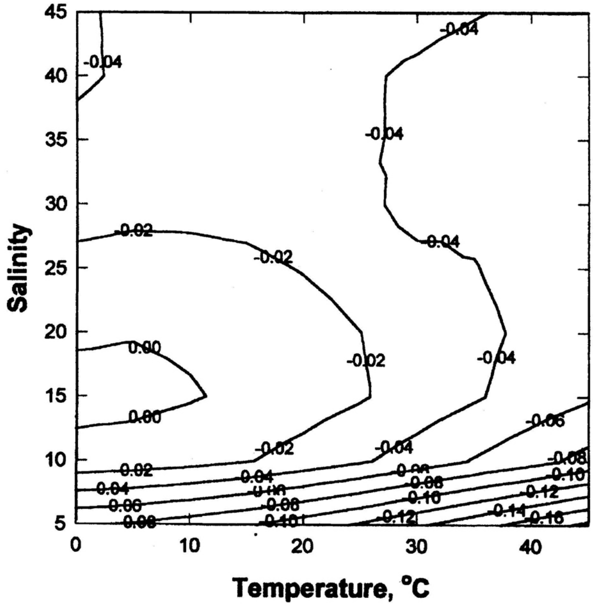

Figure 9. Comparison of the measured[36] and calculated values for pK_2 for the dissociation of H_2CO_3 in seawater.

Measurements of the dissociation of boric acid in seawater have been made by a number of workers.[64,69,70] The recent measurements of Dickson[69] are in good agreement at $S = 35$ with the work of Roy *et al.*[70] we have used his equation to compare to the calculated values from the model. The results are shown in Figure 11 and demonstrate that the model predicts reliable values (standard error 0.01 in pK_{HB}) from $S = 10$ to 45 and $t = 0$ to 50 °C.

Water Dissociation Constants

The dissociation of water in NaCl and seawater at 25 °C have been estimated using the Pitzer model in our earlier work and more recently by Clegg and Whitfield.[57] The seawater model of Harvie *et al.*[3] also gives reliable estimates of pK_W in seawater at 25 °C. The extension of the model to other temperatures in NaCl is now possible using the published parameters for HCl, NaCl and NaOH. The reliability of the model in NaCl solutions can be examined by comparing the measured Harned and Mannweiler[71] calculated from their values of $\gamma_H \gamma_{OH} / a(H_2O) = K_W/K_W^0$ from 0 to 50 °C and 0.02 to 3 mol L^{-1}. The results are shown in Figure 12 and demonstrate that the differences are within 0.005 in pK_W.

The dissociation constants for water in seawater have been made by three groups.[64,72,73] Millero[36] has recently combined these measurements

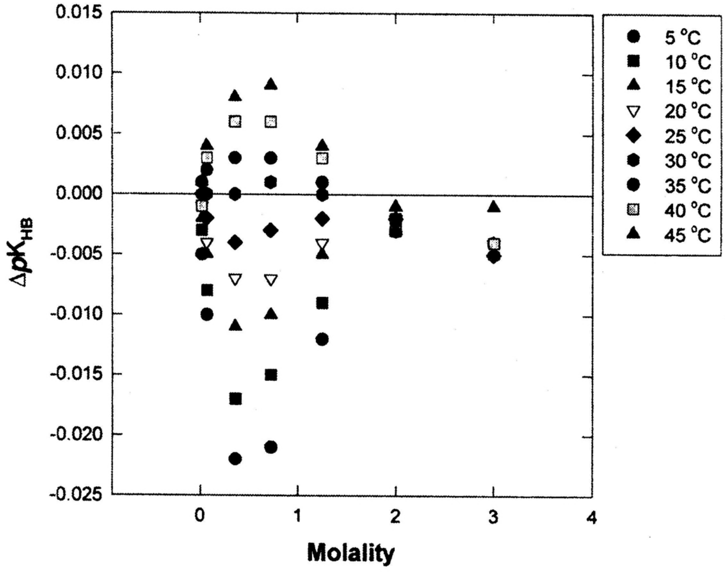

Figure 10. Comparison of the measured[68] and calculated values for pK_{HB} for the dissociation of $B(OH)_2$ in NaCl solutions.

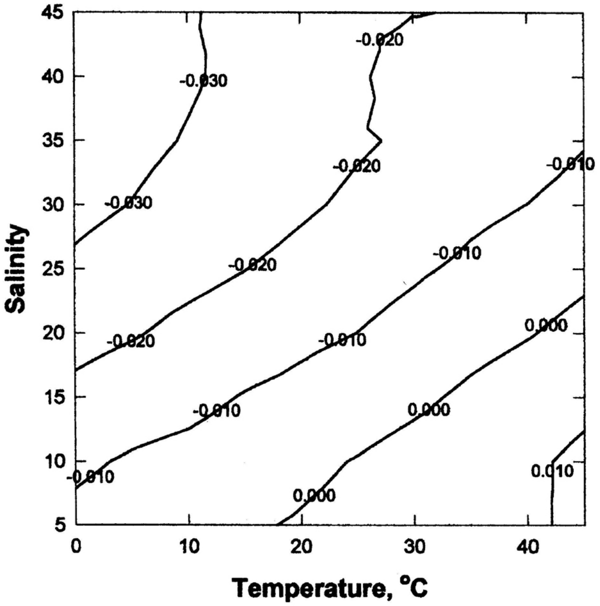

Figure 11. Comparison of the measured[69] and calculated values for pK_{HB} for the dissociation of $B(OH)_2$ in Seawater.

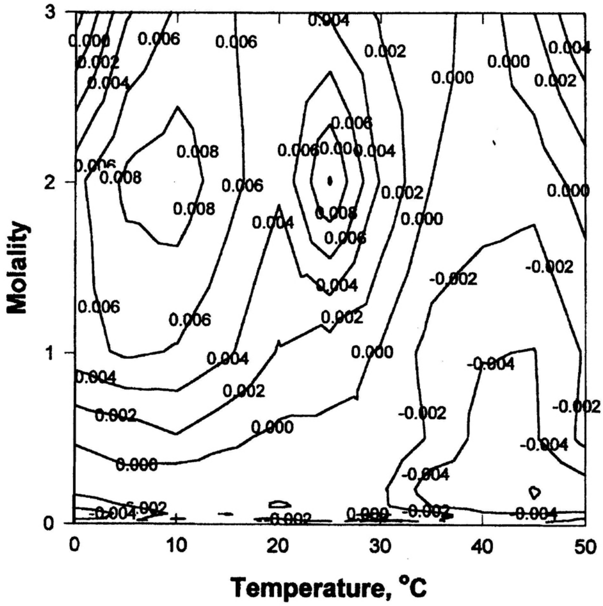

Figure 12. Comparison of the measured[71] and calculated values for pK_W for the dissociation of H_2O in NaCl solutions.

into an equation that is valid from $S = 10$ to 40 and 0 to 40 °C. A comparison with the values of pK_W from the combined measurements[36] and the calculated values are shown in Figure 13. The agreement is quite good (standard deviations of 0.005 in pK) over the entire temperature and salinity range. It should be pointed out that the seawater calculations have been corrected for the formation of MgOH using the stability constants determined by earlier workers.[3,57]

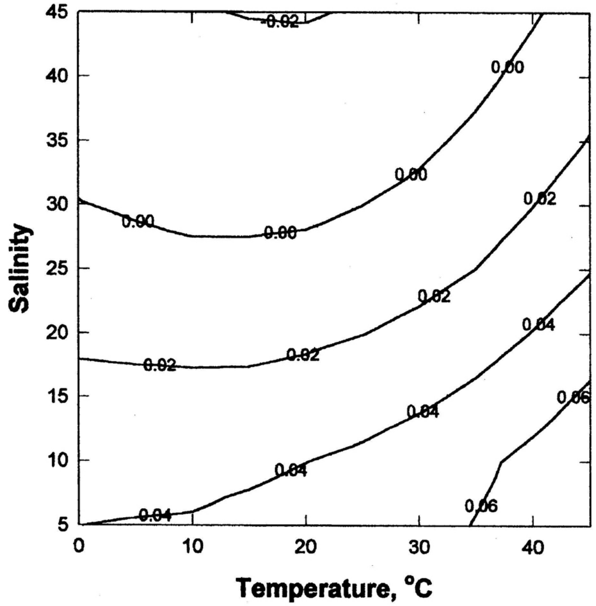

Figure 13. Comparison of the measured[36] and calculated values for pK_{HB} for the dissociation of H_2O in seawater.

Phosphoric Acid Dissociation Constants

The Pitzer equation was first applied to the phosphate system by Silvester and Pitzer[74] at 25 °C in NaCl solutions. Hershey *et al.*[35] determined higher order interaction parameters for the system at 25 °C from measurements in NaCl and Na–Mg–Cl solutions. The parameters represent the measured pK_1, pK_2 and pK_3 from 0.5 to 6 mol L^{-1} with standard deviations, respectively, of 0.04, 0.03 and 0.06. The measurements in Na–Mg–Cl of pK_1 and pK_2 have been used to determine parameter for Mg-H_2PO_4 interaction and the association constant for the formation of $MgHPO_4$ ($\log K = 2.7$) and the interaction parameter for the neutral ion pair and NaCl. Due to the limited range of the Mg (0.05 mol L^{-1}) in these solutions they may not be reliable in mixtures. This can be demonstrated by comparing the values of pK_1

TABLE VI

A comparison of the measured values for the dissociation of phosphoric acid in different media

Media	pK_1	pK_2	pK_3
NaCl	1.82	6.41	11.17
Na–Mg–Cl	1.82	6.25	–
Seawater	1.61	5.96	8.78
Calculated[a]	1.76	5.86	8.71
Calculated[b]	1.68	5.95	8.71

a) Using Mg-H_2PO_4 parameters of Hershey *et al.*[31]
b) Assuming that the Mg-H_2PO_4 parameters are the same as Mg-Cl.[42]

in NaCl, Na–Mg–Cl and seawater at the same ionic strength (Table VI). The measurements of the phosphate constants in seawater have been made by a number of workers.[75–77] Recently Yao and Millero[78] have combined these measurements into a set of equations that can be used from S = 20 to 40 and t = 5 to 25 °C. The comparisons made below are using these smooth equations.

One would expect the values of pK_1 in the Na–Mg–Cl with the same Mg concentration as seawater to be the same. At higher ionic strengths (2 to 6 mol L^{-1}) the values in Na–Mg–Cl are about 0.09 lower than in NaCl. Since the measurements shown above for Na–Mg–Cl are in reasonable agreement with the earlier measurements of Atlas *et al.*,[78] we do not think that the measurements are in error. As shown above the calculated values of the phosphate constants in seawater are not in good agreement with the measured values using the Mg–H_2PO_4 values of Hershey *et al.*[35] This cannot be attributed to the interactions with Ca which has been shown to be smaller than Mg.[20] Obviously this requires further study. In our model we have assumed that the interactions between Mg and H_2PO_4 are the same as with Cl. This yields calculated values of pK_1 and pK_2 in seawater that are in reasonable agreement with the measured values from 0 to 40 °C (see Figures 14 and 15). It should be pointed out that the calculations of pK_3 in seawater (Figure 16) have been made by correcting for the formation of Mg and Ca complexes[5] with PO_4^{3-}. This is done by determining the Pitzer parameter for the $MgPO_4^-$ and $CaPO_4^-$ ion pairs in NaCl media[20] from experimental measurements.[22–24] The calculated values of pK_3 are in good agreement with the measured values from 0 to 40 °C and salinites from 10 to 40.

Hydrogen Sulfide Dissociation Constants

In an earlier paper[80] and more recently Hershey *et al.*[33] have used the Pitzer equations to account for the interactions of HS^- with Na^+, K^+, Mg^{2+}

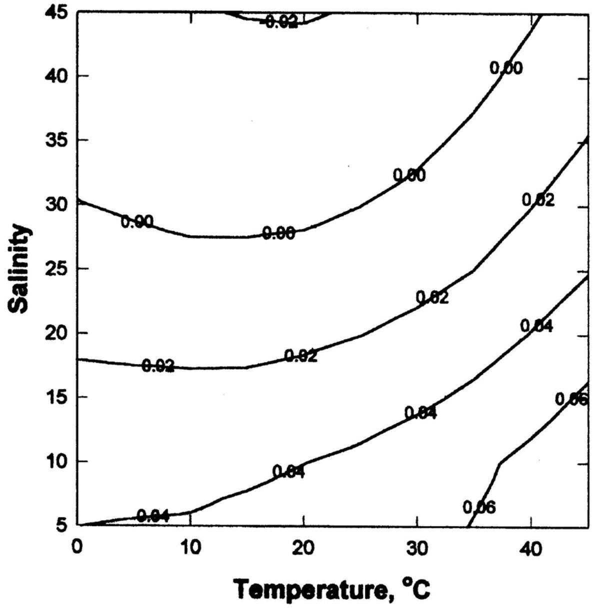

Figure 14. Comparison of the measured[36] and calculated values for pK_1 for the dissociation of H_3PO_4 in seawater.

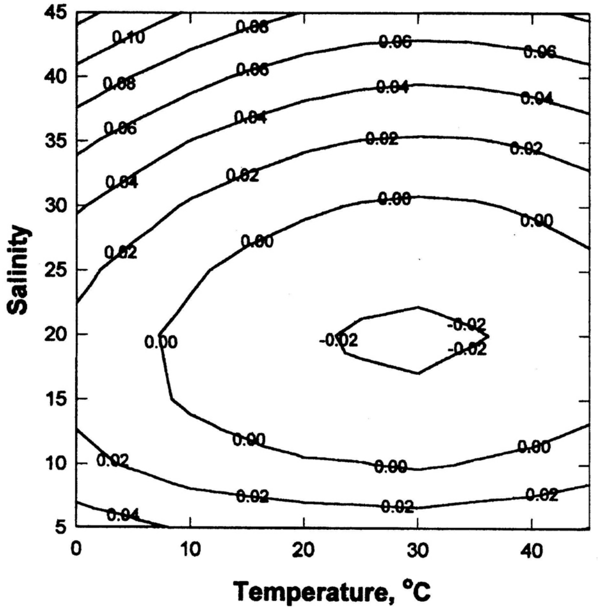

Figure 15. Comparison of the measured[78] and calculated values for pK_2 for the dissociation of H_3PO_4 in seawater.

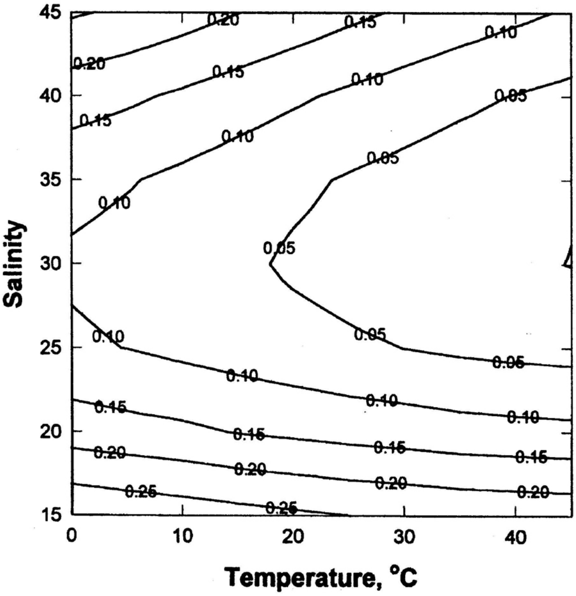

Figure 16. Comparison of the measured[78] and calculated values for pK_3 for the dissociation of H_3PO_4 in seawater.

and Ca^{2+} in NaCl media from 5 to 25 °C and I = 0.1 to 6 mol L^{-1}. The values of activity coefficient of H_2S were determined from the results[81] in NaCl at 25 °C and using the temperature coefficients in seawater are given by (to 3 mol L^{-1}). Clegg and Whitfield[57] have used these results to determine $\lambda_{Na,H_2S} = 0.0777$ and $\zeta_{H_2S,Na,Cl} = -0.00806$ at 25 °C. These workers also point out the measurements of Gamsjager and Schindler[81] are in good agreement with the more recent measurements of Barrett *et al.*[82] to 3 mol L^{-1} (above 3 mol L^{-1} the latter results are higher). The solubilities of Doubul and Riley[83] in seawater produce interaction parameters that appear to be too low.[57] The dissociation constants for H_2S have been determined by a number of workers.[84–86] Millero *et al.*[86] have summarized these results. The calculated pK_1* values of H_2S in seawater[86] from 0 to 45 °C are compared to the measured values in Figure 17. The agreement is quite reasonable with an average deviation of 0.06 in *pK.*

Ammonia Dissociation Constants

The Pitzer equation has been used to determine the dissociation constant of NH_4^+ in seawater at 25 °C in our earlier work.[20,24] This work was based on the available coefficients for the interactions of NH_4^+ with Cl^- and

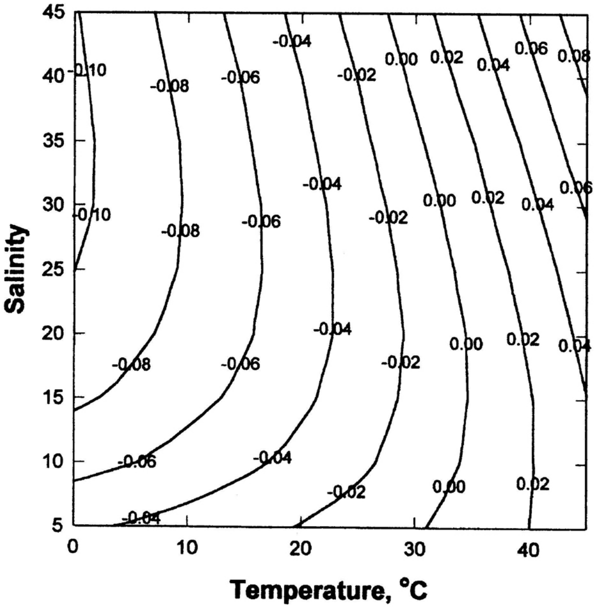

Figure 17. Comparison of the measured[78] and calculated values for pK_{H_2S} for the dissociation of H_2S in seawater.

SO_4^{2-} and estimates of the salting coefficient of NH_3 by Whitfield.[87] More recently, we have added the interactions of the major seasalts with NH_3 taken from the work of Clegg and Brimblecome.[88] Clegg and Whitfield[57] have determined Pitzer parameters for the dissociation of NH_4^+ in the major seasalts. They have shown that the model adequately predicts values for the dissociation constants for NH_4^+ in seawater from 5 to 40 °C and $S = 20$ to 45‰ that agree with the measured values of Johansson and Wedborg[89] on the average to ± 0.01 (maximum 0.03) and of Khoo *et al.*[90] to ± 0.006 in pK (maximum 0.012). Our version of the Pitzer equation has been used with the coefficients of Clegg and Brimlecome[88] to predict the dissociation constants of NH_4^+ in seawater (as formulated by Yao and Millero[78]) and the results are shown in Figure 18. The calculated results agree with the measured values with a standard error of 0.02 in pK.

Hydrogen Bisulfate Dissociation Constants

The dissociation constants for HSO_4^- are needed in natural waters to account for the amount of the proton complexed with SO_4^{2-}. As discussed above it is also useful along with the pK_{HF} to determine the free proton concentration in a solution which is needed in kinetic and speciation studies. The

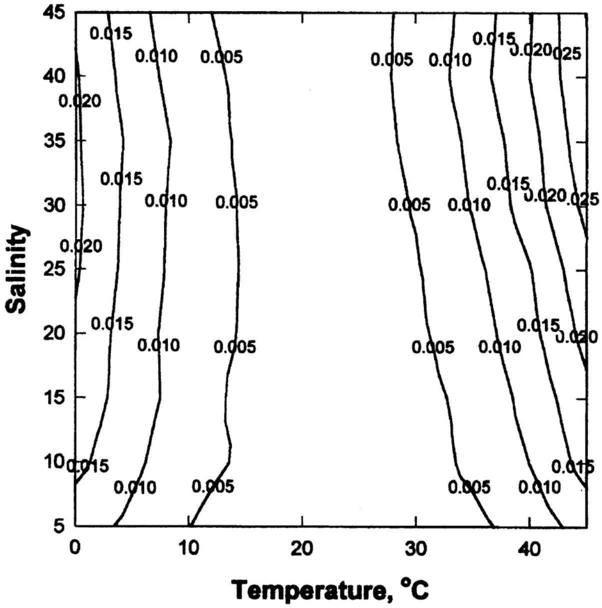

Figure 18. Comparison of the measured[78] and calculated values for pK_{NH_4} for the dissociation of NH_4^+ in seawater.

limitations in being able to determine the dissociation constants of HSO_4^- in natural waters is a lack of Pitzer parameters for the interaction of Na^+, K^+, Mg^{2+} and Ca^{2+} with HSO_4^- as a function of temperature.[92] Harvie *et al.*[3] have tabulated parameters for these interactions at 25 °C and they are used as the starting point. As discussed elsewhere[25] these parameters do not yield reliable activity coefficients of HCl in seawater. The 25 °C parameters for $NaHSO_4$ of Hovey *et al.*[91] yielded better estimates; however, it was necessary to adjust the values for the interactions of Mg^{2+} with HSO_4^- and the temperature dependence of $NaHSO_4$ between 0 to 50 °C where no direct measurements are available. This is a short fall of the present model, but as discussed above it provides reliable estimates for the activity coefficient of the H^+ in seawater.

Direct measurements of the $pK_{HSO_4^-}$ in NaCl solutions have been made by Dickson *et al.*[93] from 50 to 250 °C and $I = 0.1$ to 5 mol L^{-1}. A comparison of the extrapolated values of their model to temperatures at 0, 25 and 50 °C are shown in Table VII. The results at 25 and 50 °C are reasonable, but the extrapolations to 0 °C show large deviations at high concentrations.

A comparison the values of $pK_{HSO_4^-}$ determined by Dickson[59] from emf measurements in seawater are compared in Figure 19. The difference are all below 0.05 in pK and have a standard error of 0.05 over the entire tem-

TABLE VII

The difference between the measured and calculated values for the dissociation constant of hydrogen sulfate in NaCl solutions[a]

	$\Delta pK_{HSO_4^-}$		
m	0 °C	25 °C	50 °C
0.1	0.03	0.01	0.01
0.5	0.14	0.04	0.01
1.0	0.24	0.08	0.02
3.0	0.41	0.12	0.12
5.0	0.38	0.01	0.11

a) The measured values come from the extrapolations given by Dickson *et al.*[93]

perature and salinity range of the measurements. These calculations indicate that the model is reasonable and should provide a reasonable estimate for the effect of the formation of SO_4^{2-} on the activity coefficient of the proton in natural waters.

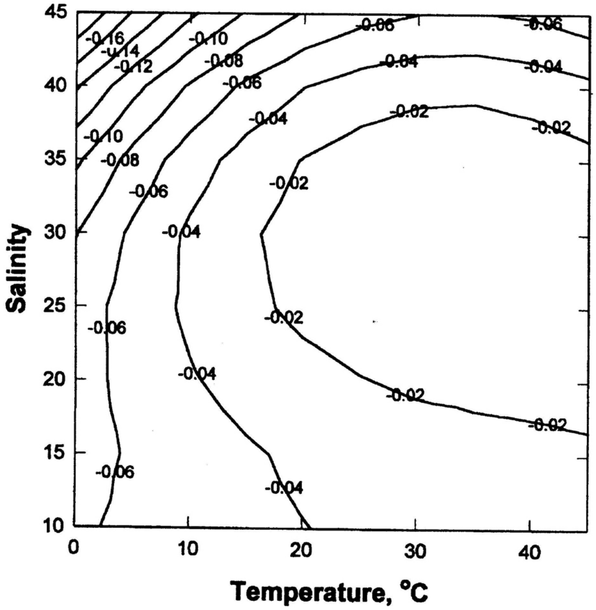

Figure 19. Comparison of the measured[59] and calculated values for $pK_{HSO_4^-}$ for the dissociation of HSO_4^- in seawater.

Hydrogen Fluoride Dissociation Constants

The dissociation of hydrogen fluoride in natural waters is needed to account for the interactions of the proton with fluoride ion. In our earlier programs,[20,24] we have used the measurements of the formation of MgF and CaF ion pairs in NaCl solutions to determine the pK_{HF} in seawater. More recently Clegg and Whitfield[57] have reexamined the interactions of F^- with Na^+, Mg^{2+}, and Ca^{2+} in natural waters. Their starting point was the measurements of the dissociation of HF in NaCl[94] from 0 to 6 mol L^{-1} at 25 °C. We have used these measured values of K_{HF}* have been compared to the values determined form the Pitzer equations using the β^0, β^1, C^ϕ coefficients referenced in Table I. As pointed out by Clegg and Whitfield[57] the activity coefficient for HF can be estimated from these measurements. We obtain a value of $\lambda_{Na,HF} = 0.011 \pm 0.002$ (assuming $\lambda_{Cl,HF} = 0$) using our version of the Pitzer program. The program yields values of log K_{HF}* that agree with the measured values to ± 0.01 in pK_{HF}* from 0 to 5 mol L^{-1}. As mentioned earlier we have accounted for the interactions of Mg^{2+} and Ca^{2+} with F^- from measurements in NaCl to 1 mol L^{-1}. More recently Clegg and Brimeblecombe[94] have determined the values of K_{MgF} in NaCl at 25 °C from 0 to 6 mol L^{-1}. The effect of ionic strength on the formation of MgF have been use to derive interaction parameter for the MgF ion pair using the Pitzer equations. The activity coefficients of Mg^{2+} and F^- in NaCl solutions can be used to estimate the activity coefficient of the ion pair MgF

$$\gamma_{MgF} = \gamma_{Mg}\, \gamma_F\, (K_{MgF} / K^*_{MgF}) \tag{52}$$

where K_{MgF} is the thermodynamic stability constant. The values of γMgF determined in this manner have been used to determine the Pitzer parameters for the MgF^+ ion pair ($\beta^0_{MF} = 0.4651$, $\beta^1_{MgF} = -1.0444$, and $C^\phi_{MgF} = -0.07203$ at 25 °C and are valid from valid from 0 to 6 mol L^{-1} NaCl and $m(Mg) = 0.06$. The activity coefficients of MgF^+ are similar to the values of other ions (Li^+, Na^+) of similar charge.[57] In our earlier analysis of the MgF and CaF systems[95] form 0.1 to 1 mol L^{-1} NaCl the activity coefficients of CaF^+ were found to be 1.14 ± 0.03 larger than the values of MgF^+. We have used this factor to estimate the activity coefficients of $CaF^+ = SrF^+$ ion pairs at higher ionic strengths. The appropriate associate constant in pure water $K_{CaF} = K_{SrF} = 10^{1.31}$ were taken from our earlier work.[5]

With these associate constants and appropriate Pitzer parameters it is possible to make reasonable estimates of the K^*_{HF} in solutions of the major seasalts over a wide range of ionic strengths (6 m) with solutions containing low concentrations of Mg (0.06). The model results can be compared to the measurements made in seawater by Culberson *et al.* (1970). The calculated value of $pK^*_{HF} = 2.52$ for $S = 35$ seawater at 25 °C is in reasonable agreement with the measured value ($pK^*_{HF} = 2.48$, Culberson *et al.*[96]). A comparison with the equation of Dickson and Riley[73] over a wider range of salinities and temperatures shows wider differences (Figure 20), but the standard errors are still reasonable (0.08). The larger decrepancies at low salinities are cause by the linear extrapolation of the results to pure water. The formation of Mg^{2+} and Ca^{2+} ion pairs with F^- cause a non linear approach to pure water. This has been discussed in our earlier[97] estimations of the pKs of acids in seawater using the ion pairing model. Simply put, the model calculations are more reliable than the extrapolations of the measurements at high concentrations to pure water.

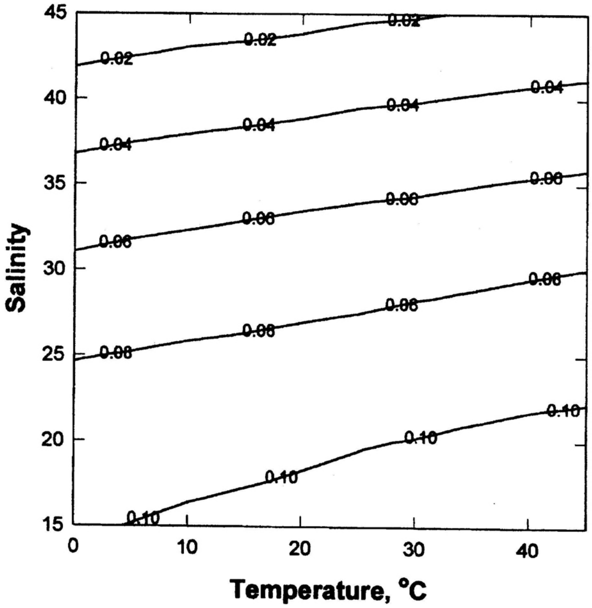

Figure 20. Comparison of the measured[36] and calculated values for pK_{HF} for the dissociation of HF in seawater.

Silicic Acid Dissociation Constants

The dissociation constant of silicic acid ($Si(OH)_4$) has not been measured in different ionic media. Measurements have been made NaCl solutions over a wide range ionic strengths (0 to 3 mol L^{-1}) and temperatures (60 to 300 °C) by Busey and Mesmer[98]. These constants at the same ionic strength of seawater can be used to determine the contribution of $Si(OH)_3O^-$ to the total alkalinity of natural waters.[36] The values these workers and others[99,100] have been combined and fitted to the equation[78]

$$\ln K_{\mathrm{Si}} = 117.40 - 8904.2/T - 19.334 \ln T + (3.5913 - 458.79/T)\, I^{0.5} + (-1.5998 + 188.74/T)\, I + (0.07871 - 12.1652/T)\, I^2 \qquad (53)$$

where the standard error is 0.02 in pK_{Si}. Hershey and Millero[101] have used the Pitzer equations to examine the pK_{Si} in NaCl solutions. However, until measurement are made in other seasalts the use of these equations over the use of Eq. (53) at the same ionic strength of the solution has little advantage.

Solubility of Calcium Carbonate

The use of the Pitzer model to estimate the solubility of $CaCO_3$ in NaCl solutions have been examined in our earlier work[102] at 25 °C. More recent measurement have been made over a wider range of temperatures by He and Morse[49] have used their carbonate model to examine the solubility from 0 to 90 °C. Since our model is similar to their model it also yields reasonable estimates of the solubility in NaCl. A more appropriate check of the model can be made by comparing the calculated solubilities of Calcite and Aragonite with the measurements of Mucci.[103] The differences shown in Figures 21 and 22 and yield calculated solubilities that are in good agreement with the measured values (0.05) from 0 to 40 °C and S = 10 to 40.

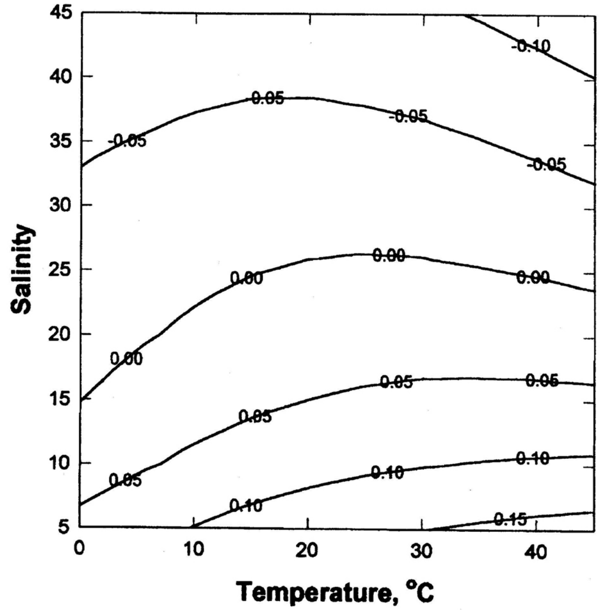

Figure 21. Comparison of the measured[101] and calculated values for pK_{Cal} for the solubility of Calcite seawater.

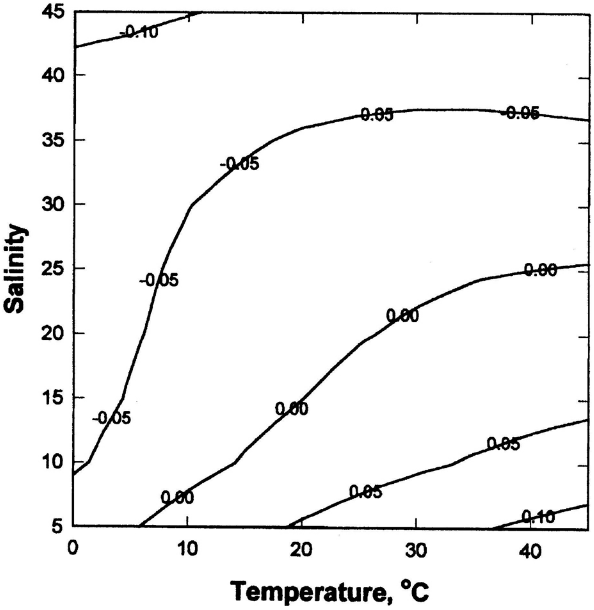

Figure 22. Comparison of the measured[101] and calculated values for pK_{Arg} for the solubility of Aragonite in seawater.

CONCLUSIONS

In this paper we have developed a chemical model that can be used to determine all the dissociation of all the acids needed to characterize the carbonate system in natural water from 0 to 50 °C and $I = 0$ to 6 mol L^{-1}. The model is based on measurements made largely in NaCl solutions with and without Mg and Ca. The model has been tested by using it to determine the p*K* of a number of acids in seawater. A summary of the differences in the measured and calculated p*K*'s for carbonic acid are shown in Table VIII; while, the results for the other acids are shown in Table IX. The results are quite reasonable and show that the model should be useful in estimating the pK of all the acids needed to characterize the carbonate system for most natural waters (0 to 50 °C and $I = 0$ to 6 mol L^{-1}).

Future work is needed to extend the model to higher temperatures. This will require new p*K* measurements in the major sea salts from 0 to 100 °C. A computer code that can be used to determine the activity coefficients of ions, the p*K* of all the acids described in this paper and solution of the calculation of the components of the carbonate system are available from the authors.

TABLE VIII

Summary of the carbonic acid calculations in seawater

Temp. Range	Salinity Range	pK_1	pK_2	Reference
5 to 30 °C	20 to 40	± 0.008	± 0.02	64
2 to 35	26 to 43	± 0.013	± 0.02	63
–1 to 40	10 to 50	± 0.014	± 0.03	65
0 to 35	20 to 43	± 0.014	± 0.02	67
0 to 45	5 to 45	± 0.016	± 0.02	66
0 to 45	5 to 45	± 0.015	± 0.02	36

TABLE IX

Summary of the calculation of the dissociation constants of acids in seawater

Acid	Temp. Range	Salinity Range	pK_{HA}	Reference
$B(OH)_3$	0 to 45 °C	5 to 45	± 0.02	69
H_2O	0 to 45	5 to 40	± 0.03	36
HF	25	20 to 40	± 0.05	73
HSO_4^-	5 to 45	5 to 45	± 0.04	59
NH_4^+	5 to 45	10 to 45	± 0.012	36, 78
H_2S	5 to 40	10 to 40	± 0.06	36, 78
H_3PO_4	5 to 40	20 to 40	± 0.05	36, 78
$H_2PO_4^-$	5 to 40	20 to 40	± 0.13	36, 78
HPO_4^{2-}	5 to 40	20 to 40	± 0.16	36, 78
Calcite	5 to 35	20 to 40	± 0.07	36, 101
Aragonite	5 to 35	20 to 40	± 0.07	36, 101

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SAŽETAK

Kemijski ravnotežni model karbonatnih sustava u prirodnim vodama

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Opisan je kemijski ravnotežni model koji se može koristiti za karakterizaciju karbonatnog sustava u prirodnim vodama od 0 do 50 °C i visokih ionskih jakosti (6 mol L^{-1}). Model razmatra ionska međudjelovanja u otopinama većinskih soli mora ($H–Na–K–Mg–Ca–Sr–Cl–Br–OH–HCO_3–B(OH)_4–HSO_4–SO_4–CO_3–CO_2–B(OH)_3–H_2O$). Za određivanje konstante disocijacije svih kiselina (H_2CO_3, $B(OH)_3$, H_2O, HF, HSO_4^-, H_3PO_4, H_2S, NH_4^+, itd.) potrebnih za ispitivanje sustava ugljikova dioksida u prirodnim vodama, korišteni su koeficijenti aktiviteta i konstante beskonačnog razređenja. Model se uglavnom temelji na mjerenjima konstanata disocijacije u otopinama natrijeva klorida s malim količinama Mg^{2+}. Model predviđa koeficijente aktiviteta HCl u morskoj vodi koji se dobro slažu s izmjerenim vrijednostima do 0.002 od $S = 5$ do 45 i $t = 0$ do 50 °C. Pouzdanost modela provjerena je određivanjem konstante disocijacije kiselina u morskoj vodi. Izračunane vrijednosti konstante disocijacije za ionizaciju karbonske i borne kiselina u dobrom su slaganju (± 0.02 do ± 0.03 u pK) s izmjerenim vrijednostima u otopinama NaCl i morskoj vodi od 5 do 45 °C i $S = 10$ do 45. Model predviđa konstante disocijacije manjinskih kiselina sa zadovoljavajućom točnošću (± 0.03 do ± 0.06) za karakterizaciju karbonatnog sustava u vodama visokog saliniteta u širokom rasponu temperature (0 do 50 °C) i ionske jakosti (0 do 6 mol L^{-1}). Te se konstante mogu koristiti za karakterizaciju karbonatnih sustava u prirodnim vodama visokog saliniteta temeljem mjerenja dva karbonatna parametra (pH–TA, pH, TCO_2).