Available online at www.sciencedirect.com
ScienceDirect
Geochimica et Cosmochimica Acta 71 (2007) 46–55
Geochimica
www.elsevier.com/locate/gca

The dissociation of carbonic acid in NaCl solutions as a function of concentration and temperature

Frank Millero *, Fen Huang, Taylor Graham, Denis Pierrot

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, USA

Received 16 May 2006; accepted in revised form 31 August 2006

Abstract

Potentiometric measurements of the stoichiometric constants for the dissociation of carbonic acid in NaCl solutions ($K_1^* = [H^+][HCO_3^-]/[CO_2]$ and $K_1^* = [H^+][CO_3^{2-}]/[HCO_3^-]$) have been made as a function of molality (0–6 m) and temperature (0–50 °C). The results have been fitted to the equations

$$pK_i^* - pK_i = A_i + B_i/T + C_i \ln T$$

The values of pK_i in pure water are taken from the literature and the adjustable parameters A_i, B_i and C_i are a function of molality

$$A_1 = 35.2911\ m^{0.5} + 0.8491\ m - 0.32\ m^{1.5} + 0.055\ m^2$$

$$B_1 = -1583.09\ m^{0.5}$$

$$C_1 = -5.4366\ m^{0.5}$$

$$A_2 = 38.2746\ m^{0.5} + 1.6057\ m - 0.647\ m^{1.5} + 0.113\ m^2$$

$$B_2 = -1738.16\ m^{0.5}$$

$$C_2 = -6.0346\ m^{0.5}$$

($\sigma = 0.013$ for pK_1^* and $\sigma = 0.020$ for pK_2^*, $N = 603$). The values determined in this study are in good agreement with the 25 °C literature values. Our results have been combined with previous measurements to derive equations that are valid from 0 to 250 °C and 0 to 5 m. This large data set has been used to determine the Pitzer parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) for the interactions of Na^+ with HCO_3^- and CO_3^{2-} from 0 to 250 °C. These results extend the carbonate system Pitzer model to hydrothermal brines containing high concentrations of NaCl.

1. Introduction

Carbonate equilibria over a wide range of ionic strength and temperature are important in a number of geochemical systems such as seawater, brines, and hydrothermal fluids. The solubility of $CaCO_3$ minerals in natural waters also require reliable dissociation constants for carbonic acid

$$CO_2 + H_2O \overset{K_1}{\Longleftrightarrow} H^+ + HCO_3^- \quad (1)$$

$$HCO_3^- \overset{K_2}{\Longleftrightarrow} H^+ + CO_3^{2-} \quad (2)$$

Measurement of the stoichiometric dissociation constants for carbonic acid

* Corresponding author. Fax: +1 305 361 4144.
E-mail address: fmillero@rsmas.miami.edu (F. Millero).

0016-7037/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.gca.2006.08.041

$$K_1^* = [H^+][HCO_3^-]/[CO_2] \quad (3)$$

$$K_2^* = [H^+][CO_3^{2-}]/[HCO_3^-] \quad (4)$$

are also important in determining the activity coefficients of HCO_3^- and CO_3^{2-} in aqueous electrolytes. The values of K_i^* are related to the thermodynamic values (K_i) by

$$K_1^* = K_1 a_{H_2O}\ \gamma_{CO_2}/\gamma_H\ \gamma_{HCO_3} \quad (5)$$

$$K_2^* = K_2 \gamma_{HCO_3}/\gamma_H\ \gamma_{CO_3} \quad (6)$$

where a_i is the activity and γ_i the activity coefficient of species i. These activity coefficients can be used to model the carbonate system in natural waters (Millero, 1982; Peiper and Pitzer, 1982; Millero and Thurmond, 1983; Harvie et al., 1984; He and Morse, 1993; Millero and Roy, 1997; Millero and Pierrot, 1998; Møller et al., 1998). The Pitzer (1991) equations are frequently used to model the ionic interactions of natural waters (Harvie and Weare, 1980; Harvie et al., 1984; Millero and Pierrot, 1998). Models are now available that can be used to estimate trace activity coefficients over a wide range of ionic strengths (0–6 m) and temperature (0–250 °C) for most of the major components of natural waters (H–Na–Mg–Ca–K–OH–Cl–HSO_4–SO_4) (Pabalan and Pitzer, 1987; Møller, 1988; Greenberg and Møller, 1989; Spencer et al., 1990; Millero and Pierrot, 1998; Christov and Møller, 2004). The addition of the carbonate system to the model at 25 °C has been made (Millero, 1982; Harvie et al., 1984), but results over a wider range of temperature are limited. Millero and Roy (1997) extended the model to include the temperature range 0–50 °C using limited data for the dissociation constants over this temperature range. He and Morse (1993) made measurements of the solubility of CO_2 and dissociation constants for carbonic acid in a number of sea salts that can be used to extend the model to 90 °C. Møller et al. (1998) have developed a carbonate model that can be used to determine solid–liquid–gas in brines to high temperatures. At high ionic strengths and moderate temperatures, reliable measurements of the dissociation constants for carbonic acid have only been made at 0, 25 and 50 °C. This limits the reliability of the model over the range of most natural waters (Millero et al., 2006).

Measurements of pK_1^* in NaCl at 25 °C as a function of concentration have been determined by a number of workers (Harned and Davis, 1943; Thurmond and Millero, 1982; He and Morse, 1993; Crea et al., 2006). The most reliable results from 0 to 50 °C for pK_1^* in NaCl to 1 m are thought to be the results of Harned and Davis (1943). He and Morse (1993) have measured pK_1^* and pK_2^* in NaCl at 0, 25, 50, 75 and 90 °C to 6 m. Roy and coworkers have made emf measurements from 5 to 45 °C in NaCl that have been used to estimate Pitzer coefficients for HCO_3^- and CO_3^{2-} (Millero and Roy, 1997). The measurements of Patterson et al. (1982, 1984) provide constants from 50 to 250 °C that we have combined with literature and our measurements from 0 to 50 °C.

In this paper, we present new measurements of the pK_1^* and pK_2^* of carbonic acid in NaCl as a function of temperature (0–50 °C) and ionic strength (0.1–6 m). We have combined these measurements with literature data (Harned and Scholes, 1941; Harned and Davis, 1943; Harned and Bonner, 1945; Thurmond and Millero, 1982; Patterson et al., 1982, 1984; He and Morse, 1993; Crea et al., 2006) to derive constants that are reliable from 0 to 250 °C and $I = 0$–6 m which is close to the solubility limit of NaCl over this temperature range. The thermodynamic values of pK_1 and pK_2 in water from 0 to 50 °C are based on the measurements of Harned and Scholes (1941) and Harned and Bonner (1945). The thermodynamic constants from 50 to 250 °C are based on the estimates of Patterson et al. (1982, 1984). Pitzer coefficients for the activity HCO_3^- and CO_3^{2-} in NaCl are determined from the combined studies. These coefficients allow us to extend the ionic interaction model for the carbonate system to high concentrations and temperatures.

2. Methods

The dissociation constants were determined from potentiometric measurements made on NaCl solutions with added Na_2CO_3 (0.002 m). This concentration of Na_2CO_3 has been shown to be appropriate to obtain reliable dissociation constants for carbonic acid in NaCl solutions (Thurmond and Millero, 1982; He and Morse, 1993; Crea et al., 2006). The NaCl was reagent grade and used without further purification. The NaCl solutions were made by weight with Milli-Q water. The concentrations of the solutions were checked by measuring the densities at 25 °C with a DMA 60 Mettler/Paar Densitometer using the density equations of Lo Surdo et al. (1982). All the solutions were equilibrated at the desired temperature in a Neslab RTE-221 constant temperature water bath to ±0.05 °C before addition to the titration vessel. The temperature in the constant temperature bath and in the cell was measured with a Guildline 9540 Digital Resistance Thermometer. The temperature inside the cell was measured before and after each titration. The values agreed to ±0.2 °C which is equivalent to an error of ±0.0018 in pK_1^* and ±0.0036 in pK_2^*. Flowing water at the desired temperature was circulated through the titration cell and around the piston delivering the HCl during an experiment. The 0.25 m HCl solutions (with added 0.45 m NaCl) were prepared with reagent grade concentrated HCl. The molality of HCl was determined coulometrically (Dickson et al., 2003).

The titration system (Millero et al., 1993) consists of a closed water jacketed plexiglass cell (200 cm^3) with a ROSS 8101 glass pH electrode and an Orion 90-02 double junction Ag/AgCl reference electrode. The titrant (~2 to 3 cm^3) is delivered with a Metrohm 665 Dosimat titrator and the emf is measured with an Orion 720A pH meter. The system is controlled by a personal computer using a National Instrument's Labwindows/CVI environment. The titration is made by adding 0.25 molar HCl (with 0.45 m NaCl) to the solution past the carbonic acid end point. A typical titration records the emf readings after

they become stable (±0.05 mV). Enough HCl is added to change the voltage by a pre-assigned increment (5 mV). This provides more data points in the range of a rapid increase in the emf near the endpoints.

The values of pK_1^* and pK_2^* were determined using a non-linear curve-fitting procedure developed in our laboratory. It is based upon the earlier work of Dyrssen et al. (1968) and Johansson and Wedborg (1982). This procedure was modified to a more "user-friendly" Excel version by Dr. Pierrot. The program determines E^*, pK_1^*, pK_2^*, TA and TCO_2 for each solution from the full titration (>60 pts). The program is similar to the one used to examine the carbonate system in seawater (Millero et al., 2006). The E^* for the electrode system is determined for each titration at a given temperature and ionic strength.

3. Results and calculations

The values of pK_1^* and pK_2^* for carbonic acid in NaCl solutions are tabulated in the Electronic Annex and shown as a function of temperature and molality in Fig. 1. The results at 0, 25 and 50 °C are compared to other workers in Figs. 2–4. The reproducibility of the values of pK_1^* and pK_2^* for the same solution are usually within ±0.005 and ±0.01, respectively. The pK_1^* and pK_2^* results at 25 °C are in good agreement with the measurements of Harned and Bonner (1945), Thurmond and Millero (1982), He and Morse (1993) and Crea et al. (2006). Our results for pK_1^*

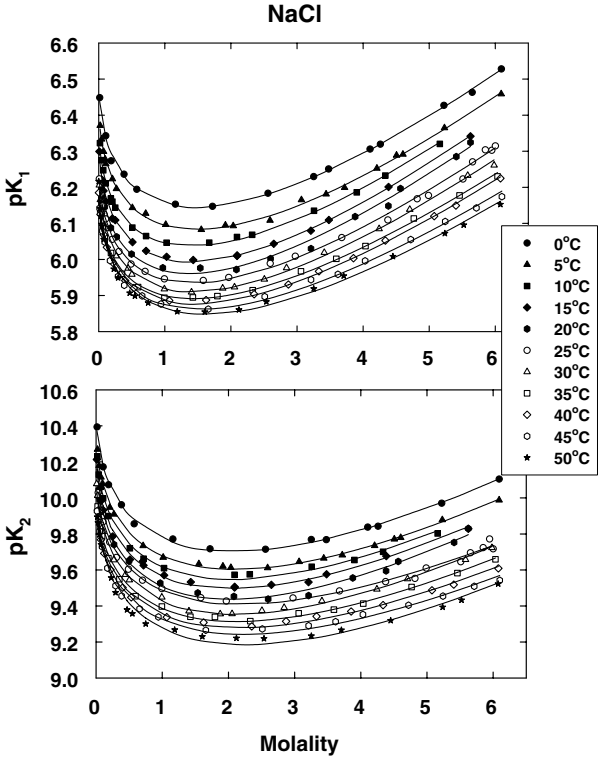

Fig. 1. The values of pK_1^* and pK_2^* for carbonic acid in NaCl as a function of molality and temperature. The curves are from the fitted results (Eqs. (10)–(13)).

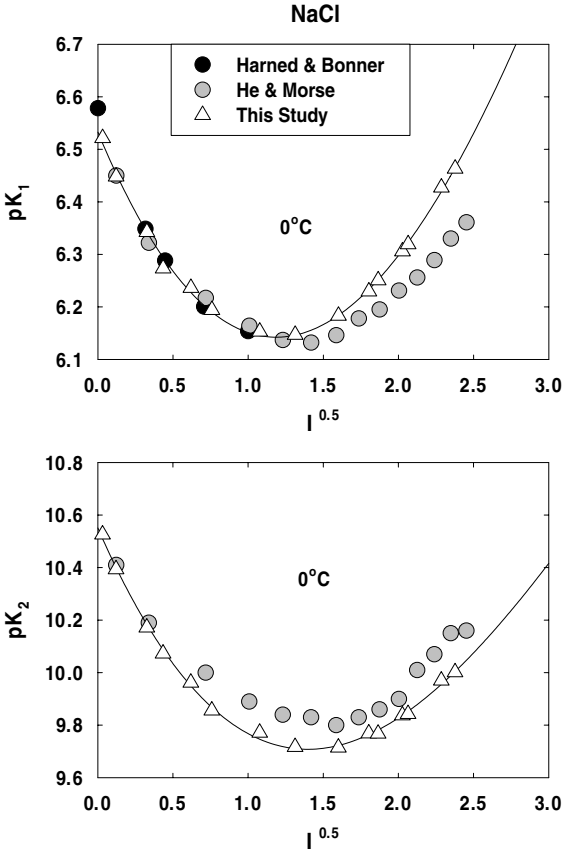

Fig. 2. A comparison of the values of pK_1^* and pK_2^* for carbonic acid at 0 °C.

and pK_2^* at 0 °C are in good agreement with the results of Harned and Davis (1943), but are higher than the results of He and Morse (1993) above a molality of 1 m. Our results at 50 °C for pK_1^* and pK_2^* are in good agreement with the results of Patterson et al. (1982, 1984). The 50 °C results of He and Morse (1993) for pK_1^* are higher than our results above 1 m.

The individual measurements at each temperature were first fitted to equations of the form

$$pK_i^* - pK_i = A\ m^{0.5} + B\ m + C\ m^{1.5} + D\ m^2 \quad (7)$$

where m is the molality (mol/kgH_2O) and the values in pure water pK_i were determined from Harned and Bonner (1945) and Harned and Scholes (1941) as refit by Peiper and Pitzer (1982) (T/K)

$$pK_1 = -114.3106 + 5773.67/T + 17.779524\ \ln\ T \quad (8)$$

$$pK_2 = -83.2997 + 4821.38/T + 13.5962\ \ln\ T \quad (9)$$

The average standard deviations for the individual temperatures are ±0.009 for pK_1^* and ±0.02 for pK_2^* ($N = 603$). All of the measurements as a function of temperature and ionic strength have been fitted to equations of the form

$$pK_i^* - pK_i = A_i + B_i/T + C_i\ \ln\ T \quad (10)$$

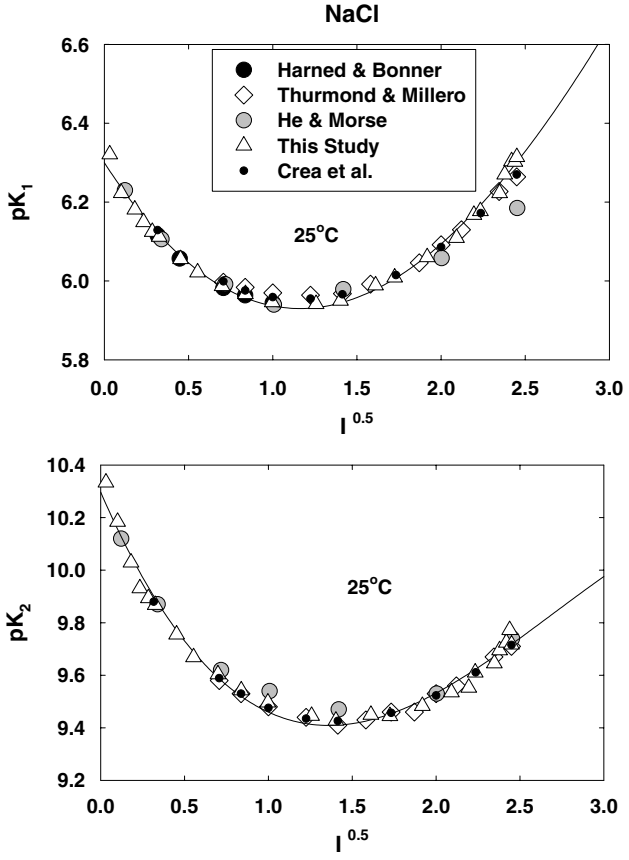

Fig. 3. A comparison of the values of pK_1^* and pK_2^* for carbonic acid at 25 °C.

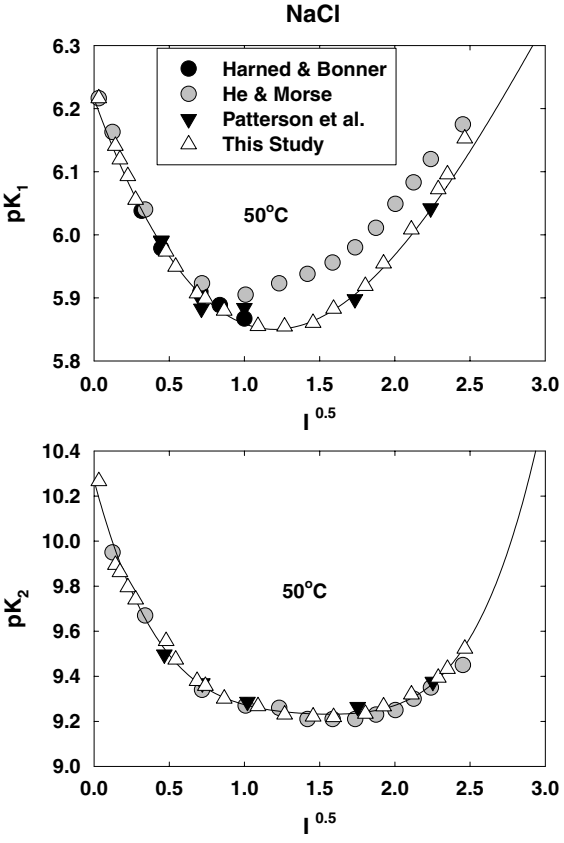

Fig. 4. A comparison of the values of pK_1^* and pK_2^* for carbonic acid at 50 °C.

The adjustable parameters have been fitted to functions of molality using the equations

$$A_i = a_0\ \mathrm{m}^{0.5} + a_1\ \mathrm{m} + a_2\ \mathrm{m}^{1.5} + a_3\ \mathrm{m}^2 \quad (11)$$

$$B_i = b_0\ \mathrm{m}^{0.5} \quad (12)$$

$$C_i = c_0\ \mathrm{m}^{0.5} \quad (13)$$

The coefficients used were arrived at by using an F-test and are shown in Table 1 along with the standard errors of the fits, $\sigma = 0.013$ for pK_1^* and $\sigma = 0.020$ for pK_2^* ($N = 603$). The differences between the measured and calculated values of pK_1^* and pK_2^* are shown in Figs. 5 and 6 as a function of temperature and molality. Most of the results are within 2σ. The errors are somewhat larger at low concentrations.

3.1. High temperature carbonate constants

The pK_1^* and pK_2^* measurements made in NaCl from 0 to 50 °C in this study can be combined with the earlier work by Patterson et al. (1982, 1984) to 250 °C. The pK_1 and pK_2 values in water from 0 to 250 °C were determined by combining the measurements of Peiper and Pitzer (1982) from 0 to 50 °C with those of Patterson et al. (1982) from 0 to 250 °C. These combined results have been fitted to the equations

$$pK_1 = -402.56788 + 11656.46/T + 72.173\ \ln T - 0.161325\ T + 7.5526\ \mathrm{E}-05\ T^2 \quad (14)$$

$$pK_2 = -122.4994 + 5811.18/T + 20.5263\ \ln T - 0.0120897\ T \quad (15)$$

with standard errors $\sigma = 0.001$ for pK_1 and $\sigma = 0.002$ for pK_2. The values of pK_1 and pK_2 are compared to the measured values of Harned and Scholes (1941), Harned and Bonner (1945), Patterson et al. (1982) and Read (1975) in Figs. 7 and 8. The agreement is quite good.

The experimental measurements of pK_1^* and pK_2^* in NaCl solutions as a function of molality (0–5 m) and temperature from 0 to 250 °C have been fitted to equation (10–13). The resulting coefficients are tabulated in Table 1 along with the standard error of the fits. The standard errors of the fits are $\sigma = 0.014$ for pK_1^* and $\sigma = 0.022$ for pK_2^* ($N = 719$ and 738, respectively).

These parameters should yield reliable values of pK_1^* and for pK_2^* in NaCl from 0 to 6 m and 0 to 250 °C. By appropriate differentiation of these equations one can calculate the effect of temperature on the free energy for the dissociation of carbonic acid in water and NaCl solutions. The thermodynamic properties (ΔG, ΔH and ΔS) for the dissociation of carbonic acid in pure water from 0 to 250 °C have been tabulated by Patterson et al. (1982, 1984).

Table 1
Coefficients for the fits of the values of pK_1^* and pK_2^* in NaCl solutions as a function of temperature and ionic strength

Coefficient		0–50 °C		0–250 °C	
		pK_1^*	pK_2^*	pK_1^*	pK_2^*
a_0	$m^{0.5}$	35.2911	38.2746	31.3616	36.88545
a_1	m	0.8491	1.6057	0.86644	1.66599
a_2	$m^{1.5}$	−0.32	−0.647	−0.33611	−0.68730
a_3	m^2	0.055	0.113	0.05888	0.12070
b_0	$m^{0.5}/T$	−1583.09	−1738.16	−1422.25317	−1669.55918
c_0	$m^{0.5}$ ln T	−5.4366	−6.0346	−4.84141	−5.83555
SD		0.013	0.020	0.023	0.033
Number		603	603	676	676

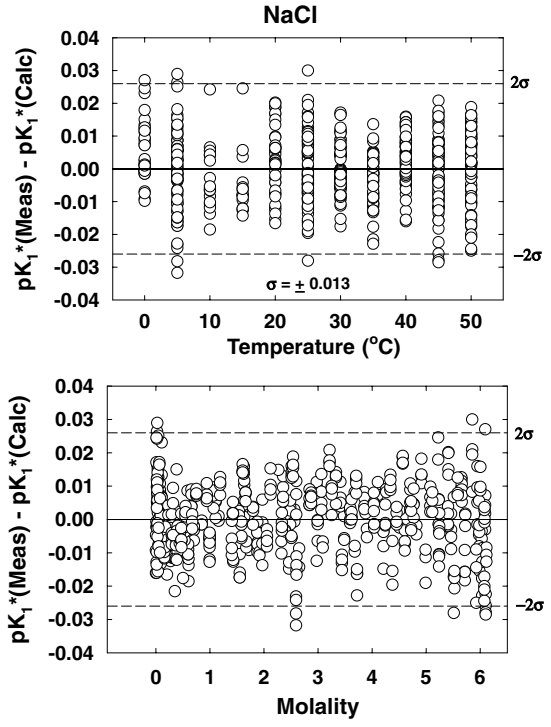

Fig. 5. The differences between the measured and calculated values of pK_1^* as a function of temperature and molality.

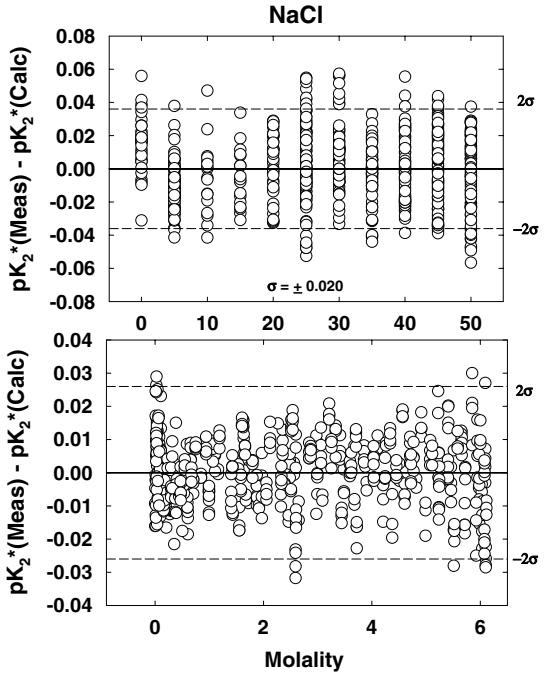

Fig. 6. The differences between the measured and calculated values of pK_2^* as a function of temperature and molality.

4. Pitzer parameters

The Pitzer coefficients for the carbonate ions can be determined from the experimentally measured values of K_1^* and pK_2^* using

$$\ln K_1 = \ln pK_1^* + \ln \gamma(H^+) + \ln \gamma(HCO_3^-) - \ln \gamma(CO_2) - \ln a(H_2O) \quad (16)$$

$$\ln\ K_2 = \ln\ pK_2^* + \ln \gamma(H^+) + \ln \gamma(CO_3^{2-}) - \ln \gamma(HCO_3^-) \quad (17)$$

Rearranging these equations one can determine the activity coefficients for HCO_3^- and CO_3^{2-} from

$$\ln \gamma(HCO_3^-) = \ln\ K_1 - \ln\ K_1^* - \ln \gamma(H^+) + \ln \gamma(CO_2) + \ln a(H_2O) \quad (18)$$

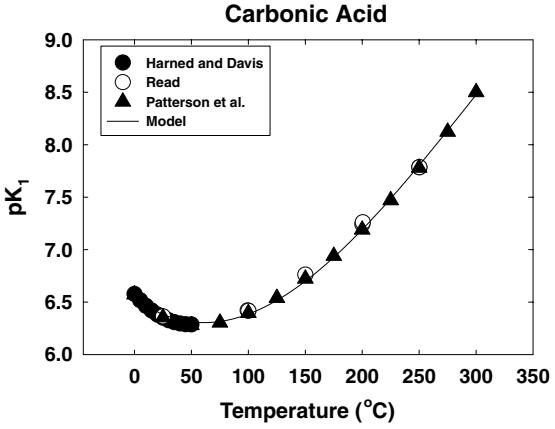

Fig. 7. Values of pK_1 for carbonic acid as a function of temperature (0–250 °C).

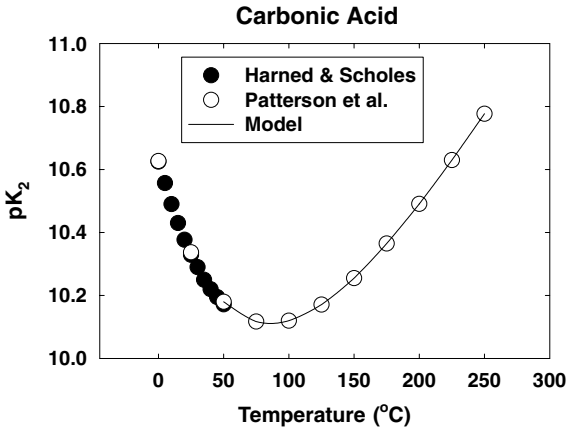

Fig. 8. Values of pK_2 for carbonic acid as a function of temperature (0–250 °C).

$$\ln \gamma(CO_3^{2-}) = \ln\ K_2 - \ln pK_2^* - \ln\ \gamma(H^+) + \ln \gamma(HCO_3^-) \quad (19)$$

The trace activity coefficients of the various ions in NaCl can be examined using the Pitzer (1991) equations

$$\ln \gamma(H^+) = f^\gamma + 2\ m_{Cl}(B_{HCl} + m_{Cl}C_{HCl}) + m_{Na}m_{Cl}(B'_{NaCl} + C_{NaCl}) + m_{Na}(2\theta_{Na-H} + m_{Cl}\ \psi_{HNaCl}) \quad (20)$$

$$\ln \gamma(HCO_3^-) = f^\gamma + 2\ m_{Na}(B_{NaHCO_3} + m_{Cl}C_{NaHCO_3}) + m_{Na}m_{Cl}(B'_{NaCl} + C_{NaCl}) + m_{Cl}(2\theta_{Cl-HCO_3} + m_{Na}\ \psi_{Cl-HCO_3-Na}) \quad (21)$$

$$\ln \gamma(CO_3^{2-}) = 4f^\gamma + 2\ m_{Na}(B_{NaCO_3} + m_{Cl}C_{NaCO_3}) + 4m_{Na}m_{Cl}B'_{NaCl} + 2m_{Na}m_{Cl}C_{NaCl} + m_{Cl}(2\theta_{Cl-CO_3} + 2\theta^E_{Cl-CO_3} + m_{Na}\ \psi_{-Na-Cl-CO_3}) \quad (22)$$

The limiting law is given by

$$f^\gamma = -A_\phi[I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2)\ \ln(1 + 1.2I^{1/2})] \quad (23)$$

$$\ln \gamma(CO_2) = 2\ m_{Na}(\lambda_{Na-CO_2} + \lambda_{Cl-CO_2}) + m_{Na}\ m_{Cl}\ \xi_{NaCl-CO_2} \quad (24)$$

$$\phi - 1 = f^\phi + m_{Na}\ B^\phi_{NaCl} + m_{Na}\ m_{Cl}\ C^\phi_{NaCl} \quad (25)$$

$$\ln a(H_2O) = -(2\ m_{NaCl}/55.51)\phi \quad (26)$$

$$f^\phi = -A_\phi[I^{0.5}/(1 + 1.2\ I^{0.5})] \quad (27)$$

$$B^\phi_{NaCl} = \beta^{(0)}_{NaCl} + \beta^{(1)}_{NaCl}\ \exp(-2I^{0.5}) \quad (28)$$

The values of B_{MX}, B'_{MX} and C_{MX} in Eqs. (20)–(22) are given by

$$B_{MX} = \beta^{(0)}_{MX} + (\beta^{(1)}_{MX}/2I)[1 - \exp(-2I^{0.5})(1 + 2I^{0.5})] \quad (29)$$

$$B'_{MX} = (\beta^{(1)}_{MX}/2I^2)[-1 + \exp(-2I^{0.5})(1 + 2I^{0.5} + 2I)] \quad (30)$$

$$C_{MX} = C^\phi_{MX}/(2|Z_M Z_X|^{0.5}) \quad (31)$$

The values of A_ϕ valid from 0 to 350 °C are given by (Møller, 1988)

$$A_\phi = 0.336901532 - 6.32100430 \times 10^{-4}T + 9.14252359/T - 1.35143986 \times 10^{-2}\ \ln T + 2.26089488 \times 10^{-3}/(T - 263) + 1.92118597 \times 10^{-6}T^2 + 45.2586464/(680 - T) \quad (32)$$

4.1. Calculations at 25 °C

The most reliable Pitzer parameters for HCl, NaCl, $NaHCO_3$, Na_2CO_3 and CO_2 are available at 25 °C. These values are tabulated in Table 2. The values for HCl and NaCl are from Pitzer and Mayorga (1973). The values of θ_{Na-H} and $\psi_{Na-H-Cl}$ are from Pitzer and Kim (1974). The values of $\beta^{(0)}_{NaHCO_3}$, $\beta^{(1)}_{NaHCO_3}$, $\beta^{(0)}_{Na_2CO_3}$, $\beta^{(1)}_{Na_2CO_3}$ and $C^\phi_{Na_2CO_3}$ are from Peiper and Pitzer (1982). These values are based on the measurements of Robinson and Macaskill (1979) for Na_2CO_3 and Harned and Davis (1943) and Roy et al. (1982) for $NaHCO_3$. The values of θ_{Cl-HCO_3}, ψ_{Cl-HCO_3-Na} and θ_{Cl-CO_3} are from Peiper and Pitzer (1982). The value of $\psi_{Cl-Na-CO_3}$ is from Thurmond and Millero (1982). The values of λ_{Na-CO_2} and $\xi_{Na-Cl-CO_2}$ to 3 m are determined from the measurements of Harned and Davis (1943) as corrected by Peiper and Pitzer (1982). They extrapolated the activity coefficents for CO_2 of Harned and Davis (1943) above 3 m to analyze the pK_1 measurements of Roy et al. (1982) to 6 m.

The values of pK_1^* and pK_2^* determined in this study and the literature (Harned and Davis, 1943; He and Morse,

Table 2
Pitzer coefficients for the carbonate system in NaCl at 25 °C

Salt	$\beta^{(0)}_{MX}$	$\beta^{(1)}_{MX}$	C^ϕ_{MX}	Reference
HCl	0.1775	0.2945	0.00080	[a]
NaCl	0.0765	0.2664	0.00127	[a]
$NaHCO_3$	0.028	0.044		[b]
			−0.01243	This study
Na_2CO_3	0.0362	1.51	0.0052	[b]

Higher order terms

I	j	k	θ_{ij}	ψ_{ijk}	
H	Na	Cl	0.036	−0.004	[c]
Cl	HCO_3	Na	0.0359	−0.0143	[b]
Cl	CO_3	Na	−0.053		[b]
				0.016	[d]

Neutral terms

λ_{Na-CO_2}	$\xi_{NaCl-CO_2}$	
0.1108	−0.0044	This study

[a] Pitzer and Mayorga (1973).
[b] Peiper and Pitzer (1982).
[c] Pitzer and Kim (1974).

1993; Thurmond and Millero, 1982; Crea et al., 2006) have been used to examine the Pitzer parameters at 25 °C. To get a reliable fit of the values of pK_1^* ($\sigma = 0.009$ for pK_1^*) the value of $C^{\phi}_{NaHCO_3} = -0.01243$ was needed along with the earlier results of Peiper and Pitzer (1982). It should be pointed out that we were not able to separate the ternary interaction parameters $\psi_{Na-Cl-HCO_3}$ and $C^{\phi}_{NaHCO_3}$. We were able to get a reliable fit of the values of pK_2^* ($\sigma = 0.028$ for pK_2^*) using the values of $\theta_{Cl-CO_3} = -0.053$ (Peiper and Pitzer, 1982) and $\psi_{Na-Cl-CO_3} = 0.016$ (Thurmond and Millero, 1982) and the other Pitzer parameters from Peiper and Pitzer (1982).

4.2. Calculations from 0 to 50 °C

The effect of temperature on the parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} for NaCl are available from 0 to 250 °C (Møller, 1988) and for HCl from 0 to 100 °C (Campbell et al., 1993) and 0 to 250 °C (Christov and Møller, 2004). The effects of temperature on the θ_{Na-H} parameter was taken from the results of Campbell et al. (1993). Peiper and Pitzer (1982) have also examined the effect of temperature on $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} for $NaHCO_3$ and Na_2CO_3 over a limited range of temperature and molality. The 0 to 50 °C measurements of Harned and Davis (1943) as readjusted by Peiper and Pitzer (1982) have been fitted using the general equations [$\sigma = 0.009$ in ln $\gamma(CO_2)$]

$$\lambda_{Na-CO_2} = -12.0230 + 576.930/T + 1.78993 \ln T \quad (33)$$

$$\xi_{Na-Cl-CO_2} = 0.00015 - 1.3368/T \quad (34)$$

using the assigned value of $\lambda_{Cl-CO_2} = 0$. The CO_2 solubility measurements of Harned and Davis (1943) were only made to 3 m. A number of other workers have determined the solubility of CO_2 in NaCl solutions (see Duan and Sun, 2003). Duan and Sun (2003) have examine most of the measurements made as a function of concentration, temperature and pressure. Others have modeled the solubility (Corti et al., 1990). The measurements of Harned and Davis (1943) are compared to the ln $\gamma(CO_2)$ measurements to 6 m by He and Morse (1993) at 0, 25 and 50 °C and the calculated values from the equations of Duan and Sun (2003) in Figs. 9–11. Although the measurements of Harned and Davis (1943) are only valid to 3 m NaCl, the extrapolated values to 6 m appear to be in reasonable agreement with the high concentration measurements of He and Morse (1993) at 25 °C. The measurements of He and Morse (1993) and the equations of Duan and Sun (2003) do not agree with the extrapolated values at 0 and 50 °C. To be consistent with the earlier work of Peiper and Pitzer (1982), we have used the values of ln $\gamma(CO_2)$ calculated from Eqs. (33) and (34) in calculations of the Pitzer parameters for $NaHCO_3$ and Na_2CO_3 from 0 to 50 °C. It should be pointed out that the derived Pitzer parameters using the extrapolated equations for $\gamma(CO_2)$ are covariant with this assumption.

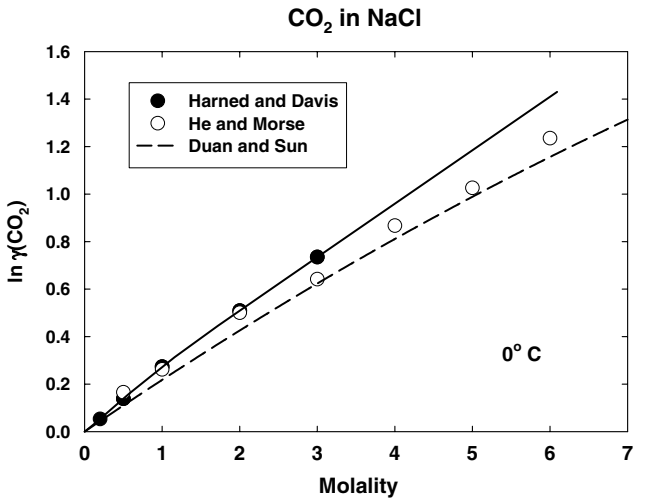

Fig. 9. Comparison of ln$\gamma(CO_2)$ in NaCl from various authors at 0 °C. The smooth curves are from the measurements of Harned and Davis (1943) (Eqs. 24, 33 and 34) and Duan and Sun (2003).

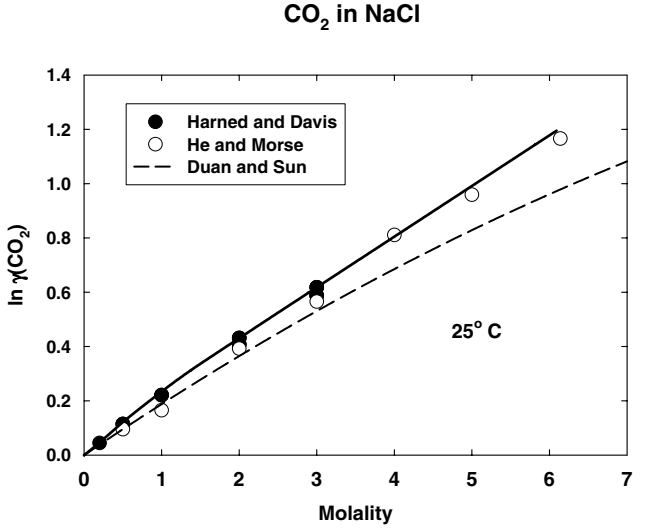

Fig. 10. Comparison of ln$\gamma(CO_2)$ in NaCl from various authors at 25 °C. The smooth curves are from the measurements of Harned and Davis (1943) (Eqs. 24, 33 and 34) and Duan and Sun (2003).

The effect of temperature for the Pitzer parameters for $NaHCO_3$ and Na_2CO_3 have been determined from our measurements of pK_1^* and pK_2^* from 0 to 50 °C. These results were fitted to the equations

$$\beta^{(0)}_{NaHCO_3}(T) = 0.028 + 5.0E-04\ (T - 298.15) + 1.80E-05\ (T - 298.15)^2 \quad (35)$$

$$\beta^{(1)}_{NaHCO_3}(T) = 0.044 + 0.0020\ (T - 298.15) - 1.80E-05\ (T - 298.15)^2 \quad (36)$$

$$C^{\phi}_{NaHCO_3}(T) = -0.01243 \quad (37)$$

$$\beta^{(0)}_{Na_2CO_3}(T) = 0.0362 + 0.0030\ (T - 298.15) + 2.840E-04\ (T - 298.15)^2 \quad (38)$$

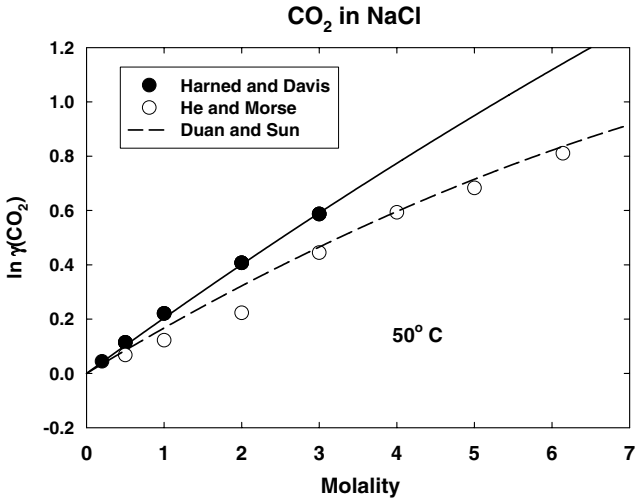

Fig. 11. Comparison of $\ln\gamma(CO_2)$ in NaCl from various authors at 50 °C. The smooth curves are from the measurements of Harned and Davis (1943) (Eqs. 24, 33 and 34) and Duan and Sun (2003).

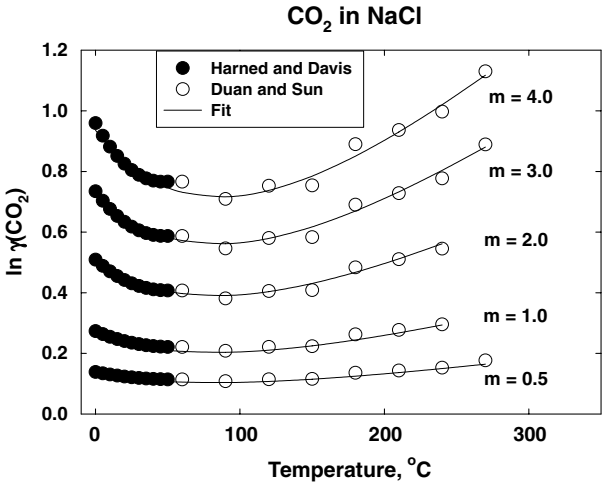

Fig. 12. The activity coefficients of CO_2 in NaCl from 0 to 250 °C.

$$\beta^{(1)}_{Na_2CO_3}(T) = 1.51 + 0.0010\ (T - 298.15) - 1.340E - 03\ (T - 298.15)^2 \quad (39)$$

$$C^{\phi}_{Na_2CO_3}(T) = 0.0052 - 5.0E - 04\ (T - 298.15) - 9.3E - 05\ (T - 298.15)^2 \quad (40)$$

The standard error of the fits using these parameters was $\sigma = 0.018$ in pK_1^* and $\sigma = 0.026$ in pK_2^*. The effect of temperature on C^{ϕ}, $\theta_{Cl\text{–}HCO_3}$ and $\psi_{Na\text{–}Cl\text{–}HCO_3}$ and $\theta_{Cl\text{–}CO_3}$ and $\psi_{Na\text{–}Cl\text{–}CO_3}$ were not needed to fit the results.

4.3. Calculations from 0 to 250 °C

By combining our pK^* measurements with the results of Patterson et al. (1982, 1984), one can determine the Pitzer coefficients for $\ln\gamma(HCO_3)$ and $\ln\gamma(CO_3)$ from 0 to 250 °C. The activity coefficients of CO_2 from 0 to 250 °C were determined from an adjustment of 0 to 50 °C and the calculated results from the equation of Duan and Sun from 50 to 250 °C (See Fig. 12). These results have be fitted to the equation ($\sigma = 0.013$)

$$\lambda_{Na\text{–}CO2} = -5.310 + 279.630/T + 0.78810\ \ln T \quad (41)$$

$$\xi_{NaCl\text{–}CO2} = 0.39750 - 19.70/T - 0.05960\ \ln T \quad (42)$$

The values of HCl and NaCl from 0 to 250 °C given in Table 3 were determined from the Pitzer coefficients from Christov and Møller (2004). The resultant Pitzer coefficients for $NaHCO_3$ and Na_2CO_3 from 0 to 250 °C are given by

$$\beta^{(0)}_{NaHCO_3}(T) = 0.028 + 0.00048\ (T - 298.15) - 3.2E - 064\ (T - 298.15)^2 - 1.0E - 08\ (T - 298.15)^3 \quad (43)$$

Table 3
Pitzer coefficients for HCl and NaCl[a]

Parameter	Constant	HCl	NaCl
$\beta^{(0)}_{MX}$	a_1	5.20980985E−02	14.3783204
	a_2	6.26911217E−04	5.60767406E−03
	a_3		−422.185236
	a_4		−2.51226677
	a_5	1.00115257E−01	
	a_6	−2.17745839E−06	−2.61718135E−06
	a_7	48.7979143	4.43854508
	a_8		−1.70502337
$\beta^{(1)}_{MX}$	a_1	2.19549623	−4.83060685E−01
	a_2	−7.77644382E−03	1.40677479E−03
	a_3		119.311989
	a_4		
	a_5	−4.06503624E−01	
	a_6	1.84693733E−05	
	a_7	−461.357568	
	a_8		−4.23433299
C^{ϕ}_{MX}	a_1		−1.00588714E−01
	a_2		−1.80529413E−05
	a_3		8.61185543
	a_4		1.24880954E−02
	a_5		
	a_6		3.41172108E−08
	a_7		6.83040995E−02
	a_8		2.93922611E−01

$Y = a_1 + a_2T + a_3/T + a_4\ \ln\ T + a_5/(T - 263) + a_6\ \ T^2 + a_7/(680 - T) + a_8(T - 227)$.

[a] Valid from 0 to 6 m, 0 to 250 °C.

$$\beta^{(1)}_{NaHCO_3}(T) = 0.044 + 0.002\ (T - 298.15) - 2.7E - 05\ (T - 298.15)^2 + 2.0E - 07\ (T - 298.15)^3 \quad (44)$$

$$C^{\phi}_{NaHCO_3}(T) = -0.01243 + 1.0E - 05\ (T - 298.15) + 8.0E - 07\ (T - 298.15)^2 \quad (45)$$

$$\beta^{(0)}_{Na_2CO_3}(T) = 0.0362 + 0.00506\ (T - 298.15) + 2.034\text{E}-04\ (T - 298.15)^2 - 3.926\text{E}-06 \times (T - 298.15)^3 + 2.197\text{E}-08\ (T - 298.15)^4 - 3.97\text{E}-11\ (T - 298.15)^5 \quad (46)$$

$$\beta^{(1)}_{Na_2CO_3}(T) = 1.51 - 0.0076\ (T - 298.15) - 9.13\text{E}-04\ (T - 298.15)^2 + 1.592\text{E}-05\ (T - 298.15)^3 - 8.59\text{E}-08\ (T - 298.15)^4 + 1.528\text{E}-10\ (T - 298.15)^5 \quad (47)$$

$$C^{\phi}_{Na_2CO_3}(T) = 0.052 - 0.00115\ (T - 298.15) - 7.1\text{E}-05\ (T - 298.15)^2 + 1.2546\text{E}-06\ (T - 298.15)^3 - 6.765\text{E}-09\ (T - 298.15)^4 + 1.199\text{E}-11\ (T - 298.15)^5 \quad (48)$$

The model predicts values of pK_1^* and pK_2^* that agree with the measured values from 0 to 250 °C and from 0 to 5 m with standard errors of 0.016 in pK_1^* and 0.026 in pK_2^*.

5. Conclusions

Measurement of the pK_1^* and pK_2^* in NaCl solutions from 0 to 250 °C have been used to determine Pitzer coefficients that can be used to determine the activity coefficients of CO_2, $NaHCO_3$ and Na_2CO_3 over a wide range of concentration. These coefficients should be useful in extending the ionic interaction model for the carbonate system in hydrothermal brines.

Acknowledgments

The authors acknowledge the support of the oceanographic section of the National Science Foundation and the National Oceanic and Atmospheric Association for supporting this study. The authors acknowledge Nancy Møller, Zhenhao Duan and the two anonymous reviewers, whose comments improved the paper.

Associate editor: David J. Wesolowski

References

Campbell, D.M., Millero, F.J., Roy, R.N., Roy, L., Lawson, M., Vogel, K., Moore, C.P., 1993. The standard potential for the hydrogen-silver, silver chloride electrode in synthetic seawater. *Mar. Chem.* **44**, 221–233.

Christov, C., Møller, N., 2004. Chemical equilibrium model of solution behavior and solubility in the H–Na–K–OH–Cl–HSO_4–SO_4–H_2O system to high concentration and temperature. *Geochim. Cosmochim. Acta* **68**, 1309.

Corti, H.R., de Pablo, J.J., Prauznitz, J.M., 1990. Phase equilibria for aqueous system containing salts and carbon dioxide. Application of Pitzer theory for electrolyte solutions. *J. Phys. Chem.* **94**, 7876–7880.

Crea, F., De Stefano, C., Gianguzza, A., Piazzese, D., Sammartano, S., 2006. Protonation of carbonate in aqueous tetraalkylammonium salts at 25 °C. *Talanta* **68**, 1102–1112.

Dickson, A.G., Afghan, J.D., Anderson, G.C., 2003. Reference materials for oceanic CO_2 analysis: a method for the certification of total alkalinity. *Mar. Chem.* **80**, 185–197.

Duan, Z., Sun, R., 2003. An improved model calculation of CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and 0 to 2000 bar. *Chem. Geol.* **193**, 257–271.

Dyrssen, D., Jagner, D., Wengelin, F., 1968. *Computer Calculations of Ionic Equilibria and Titration Procedures*. Almqvist and Wiksell, Stockholm, 250 pp..

Greenberg, J.P., Møller, N., 1989. The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na–K–Ca–Cl–SO_4–H_2O system to high concentration from 0 to 250 °C. *Geochim. Cosmochim. Acta* **53**, 2503–2518.

Harned, H.S., Scholes, S.R., 1941. The ionization constant of HCO_3^- from 0 to 50 °C. *J. Am. Chem. Soc.* **63**, 1706–1709.

Harned, H.S., Davis, R., 1943. The ionization of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions form 0 to 50 °C. *J. Amer. Chem. Soc.* **60**, 2030–2037.

Harned, H.S., Bonner, F.T., 1945. The first ionization constant of carbonic acid in aqueous solutions of sodium chloride. *J. Amer. Chem. Soc.* **67**, 1026–1031.

Harvie, C.E., Weare, J.H., 1980. The prediction of mineral solubilities in natural waters: the Na–K–Mg–Ca–SO_4–Cl–H_2O system from zero to high concentration at 25 °C. *Geochim. Cosmochim. Acta* **44**, 981–997.

Harvie, C.E., Møller, N., Weare, J.H., 1984. The prediction of mineral solubilities in natural waters: The Na–K–Mg–Ca–H–Cl–SO_4–OH–HCO_3–CO_3–CO_3–H_2O system to high ionic strengths at 25 °C. *Geochim. Cosmochim. Acta* **48**, 723–752.

He, S., Morse, J.W., 1993. The carbonic acid system and calcite solubility in aqueous Na–K–Ca–Mg–Cl–SO_4 solutions from 0 to 90 °C. *Geochim. Cosmochim. Acta* **57**, 3533–3554.

Johansson, O., Wedborg, M., 1982. On the evaluation of potentiometric titrations of seawater with hydrochloric acid. *Oceanol. Acta* **5**, 209–218.

Lo Surdo, A., Alzola, E.M., Millero, F.J., 1982. The PVT properties of concentrated aqueous electrolytes. I. Densities and apparent molal volume of NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$ solutions from 0.1 mol kg^{-1} to saturation and from 273.15 to 323.15 K. *J. Chem. Thermodyn.* **13**, 649–662.

Millero, F.J., 1982. Use of models to determine ionic interactions in the natural waters. *Thalassia Jugoslavica* **1–4**, 253–291.

Millero, F.J., Graham, T., Huang, F., Bustos, H., Pierrot, D., 2006. Dissociation constants for carbonic acid in seawater as a function of temperature and salinity. *Mar. Chem.* **100**, 80–94.

Millero, F.J., Thurmond, V., 1983. The ionization of carbonic acid in Na–Mg–Cl solutions at 25 °C. *J. Solution Chem.* **12**, 401–412.

Millero, F.J., Roy, R., 1997. A chemical model for the carbonate system in natural waters. *Croatia Chemica. Acta* **70**, 1–38.

Millero, F.J., Pierrot, D., 1998. A chemical model for natural waters. *Aquat. Geochem.* **4**, 153–199.

Millero, F.J., Zhang, J-Z., Lee, K., Campbell, D.M., 1993. Titration alkalinity of seawater. *Mar. Chem.* **44**, 153–166.

Millero, F.J., Graham, T.B., Huang, F., Bustos-Serrano, H., Pierrot, D., 2006. Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. *Mar. Chem.* **100**, 80–94.

Møller, N., 1988. The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na–Ca–Cl–SO_4–H_2O system, to high temperature and concentration. *Geochim. Cosmochim. Acta* **52**, 821–837.

Møller, N., Greenberg, J.P., Weare, J.H., 1998. Computer modeling for geothermal systems: predicting carbonate and silica scale formation, CO_2 breakout and H_2S exchange. *Transport Porous Med.* **33**, 173–204.

Pabalan, R.T., Pitzer, K., 1987. Thermodynamics of concentrated electrolyte mixtures and the prediction of mineral solubilities to high

temperature for mixtures in the system Na–K–Mg–Cl–SO_4–OH–H_2O. *Geochim. Cosmochim. Acta* **51**, 2429–2443.

Patterson, C.S., Slocum, G.H., Busey, R.H., Mesmer, R.E., 1982. Carbonate equilibria in hydrothermal systems: first ionization of carbonic acid in NaCl media to 300 °C. *Geochim. Cosmochim. Acta* **46**, 1653–1663.

Patterson, C.S., Busey, R.H., Mesmer, R.E., 1984. Second ionization of Carbonic Acid in NaCl media to 250 °C. *J. Solution Chem.* **13**, 647–661.

Peiper, J.C., Pitzer, K.S., 1982. Thermodynamics of aqueous carbonate solutions including mixtures of sodium carbonate, bicarbonate and chloride. *J. Chem. Thermodyn.* **14**, 613–638.

Pitzer, K.S., 1991. Theory: ion interaction approach: theory and data collection, 2nd ed.. In: Pitzer, K.S. (Ed.), *Activity Coefficients in Electrolyte Solutions*, Vol. 1 CRC Press, Boca Raton, Fl, pp. 75–153.

Pitzer, K.S., Mayorga, G., 1973. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem* **77**, 2300–2308.

Pitzer, K.S., Kim, J.J., 1974. Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes. *J. Amer. Chem. Soc.* **96**, 5701–5707.

Read, A.J., 1975. The first ionization constant of carbonic acid from 25 to 250 °C and to 2000 bar. *J. Sol. Chem.* **4**, 53–70.

Robinson, R.A., Macaskill, J.B., 1979. Osmotic Coefficients of awueous sodium carbonate solutions at 25 °C. *J. Solution Chem.* **8**, 35–40.

Roy, R.N., Gibbons, J.J., Trower, J.K., Lee, G.A., Hartley, J.J., Mack, J.G., 1982. The ionization of carbonic acid in solutions of sodium chloride from e.m.f measurements at 278.15, 298.15, and 318.15 K. *J. Chem. Thermodyn.* **14**, 473–482.

Spencer, R.J., Møller, N., Weare, J.H., 1990. The prediction of mineral solubilities in natural waters; a chemical equilibrium model for the Na–K–Ca–Mg–Cl–SO_4–H_2O system at temperatures below 25 °C. *Geochim. Cosmochim. Acta* **54**, 575–590.

Thurmond, V., Millero, F.J., 1982. Ionization of carbonic acid in sodium chloride solutions. *J. Solution Chem.* **11**, 447–456.