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# 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

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## Abstract

Potentiometric measurements of the stoichiometric constants for the dissociation of carbonic acid in NaCl solutions ( $K_1^* = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$  and  $K_2^* = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ ) have been made as a function of molality (0–6 m) and temperature (0–50 °C). The results have been fitted to the equations

$$\text{p}K_i^* - \text{p}K_i = A_i + B_i/T + C_i \ln T$$

The values of  $\text{p}K_i$  in pure water are taken from the literature and the adjustable parameters  $A_i$ ,  $B_i$  and  $C_i$  are a function of molality

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

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

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

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

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

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

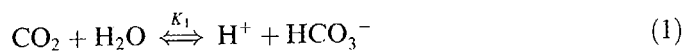
( $\sigma = 0.013$  for  $\text{p}K_1^*$  and  $\sigma = 0.020$  for  $\text{p}K_2^*$ ,  $N = 603$ ). The values determined in this study are in good agreement with the 25 °C literature values. Our results have been combined with previous measurements to derive equations that are valid from 0 to 250 °C and 0 to 5 m. This large data set has been used to determine the Pitzer parameters ( $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C^{\phi}$ ) for the interactions of  $\text{Na}^+$  with  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  from 0 to 250 °C. These results extend the carbonate system Pitzer model to hydrothermal brines containing high concentrations of NaCl.

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## 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  $\text{CaCO}_3$  minerals in natural waters also require reliable dissociation constants for carbonic acid



Measurement of the stoichiometric dissociation constants for carbonic acid

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

$$K_1^* = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2] \quad (3)$$

$$K_2^* = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (4)$$

are also important in determining the activity coefficients of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in aqueous electrolytes. The values of  $K_i^*$  are related to the thermodynamic values ( $K_i$ ) by

$$K_1^* = K_1 a_{\text{H}_2\text{O}} \gamma_{\text{CO}_2} / \gamma_{\text{H}} \gamma_{\text{HCO}_3^-} \quad (5)$$

$$K_2^* = K_2 \gamma_{\text{HCO}_3^-} / \gamma_{\text{H}} \gamma_{\text{CO}_3^{2-}} \quad (6)$$

where  $a_i$  is the activity and  $\gamma_i$  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– $\text{HSO}_4^-$ – $\text{SO}_4$ ) (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  $\text{CO}_2$  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  $\text{p}K_1^*$  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  $\text{p}K_1^*$  in NaCl to 1 m are thought to be the results of Harned and Davis (1943). He and Morse (1993) have measured  $\text{p}K_1^*$  and  $\text{p}K_2^*$  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  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  (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  $\text{p}K_1^*$  and  $\text{p}K_2^*$  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  $\text{p}K_1$  and  $\text{p}K_2$  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  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  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  $\text{Na}_2\text{CO}_3$  (0.002 m). This concentration of  $\text{Na}_2\text{CO}_3$  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/Par 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  $\pm 0.05$  °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  $\pm 0.2$  °C which is equivalent to an error of  $\pm 0.0018$  in  $\text{p}K_1^*$  and  $\pm 0.0036$  in  $\text{p}K_2^*$ . 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  $\text{cm}^3$ ) with a ROSS 8101 glass pH electrode and an Orion 90-02 double junction Ag/AgCl reference electrode. The titrant ( $\sim 2$  to 3  $\text{cm}^3$ ) 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 ( $\pm 0.05$  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  $\text{TCO}_2$  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  $\pm 0.005$  and  $\pm 0.01$ , 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  $pK_1^*$

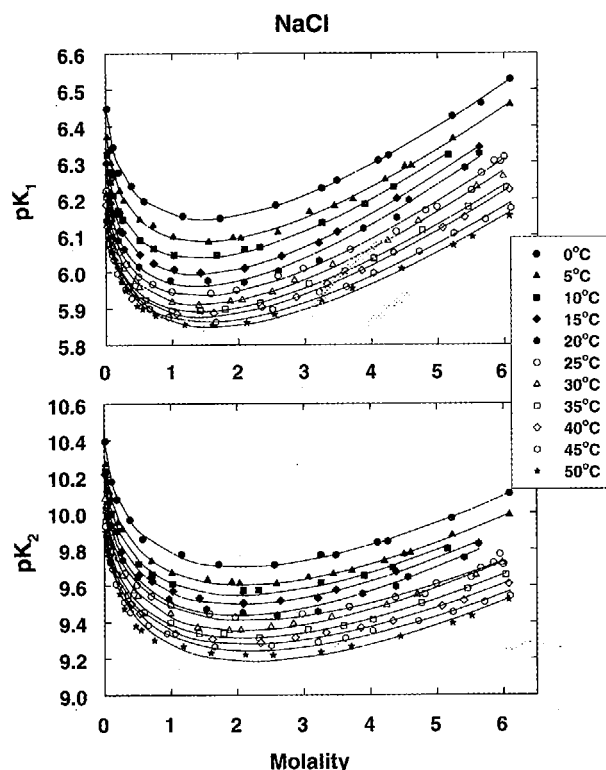


Fig. 1. The values of  $pK_1^*$  and  $pK_2^*$  for carbonic acid in NaCl as a function of molality and temperature. The curves are from the fitted results (Eqs. (10)–(13)).

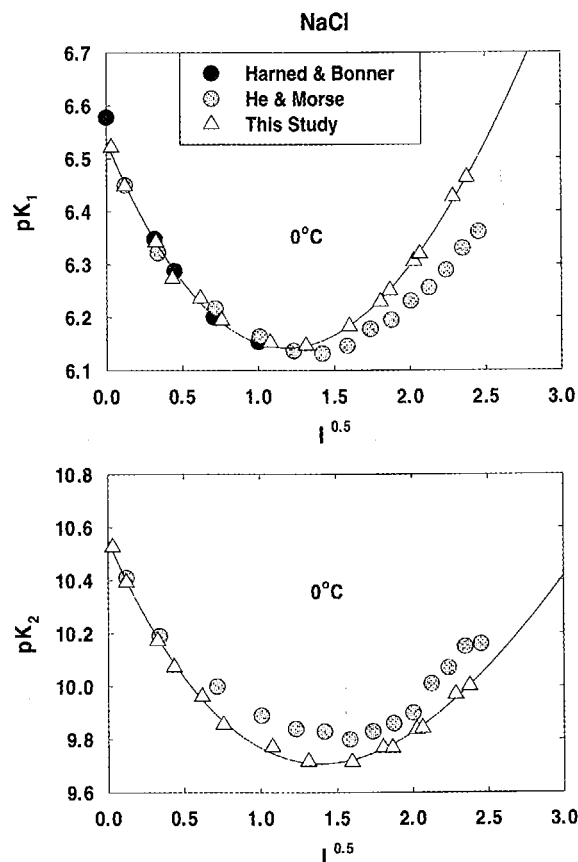


Fig. 2. A comparison of the values of  $pK_1^*$  and  $pK_2^*$  for carbonic acid at 0 °C.

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<sub>2</sub>O) 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  $\pm 0.009$  for  $pK_1^*$  and  $\pm 0.02$  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

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

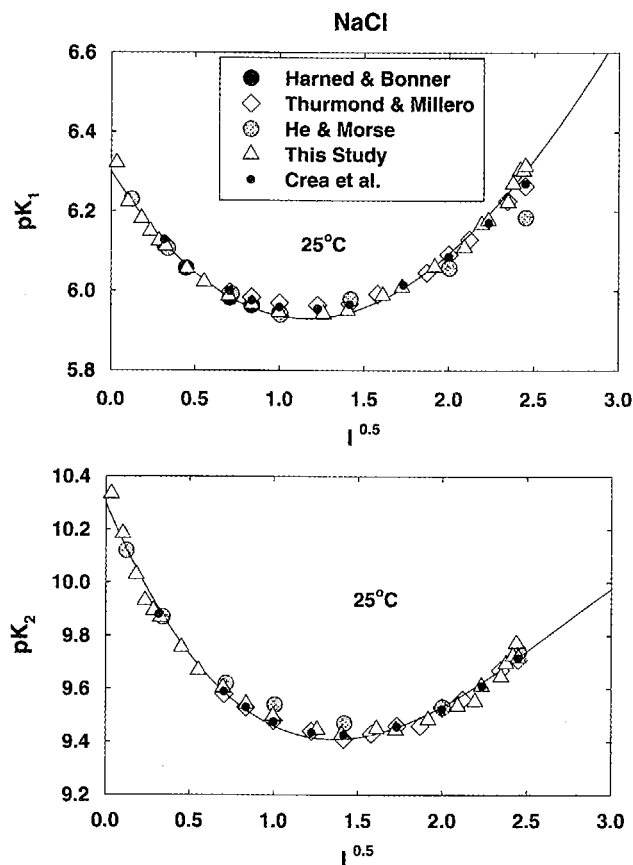


Fig. 3. A comparison of the values of  $pK_1^*$  and  $pK_2^*$  for carbonic acid at 25 °C.

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

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

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

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

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  $2\sigma$ . 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

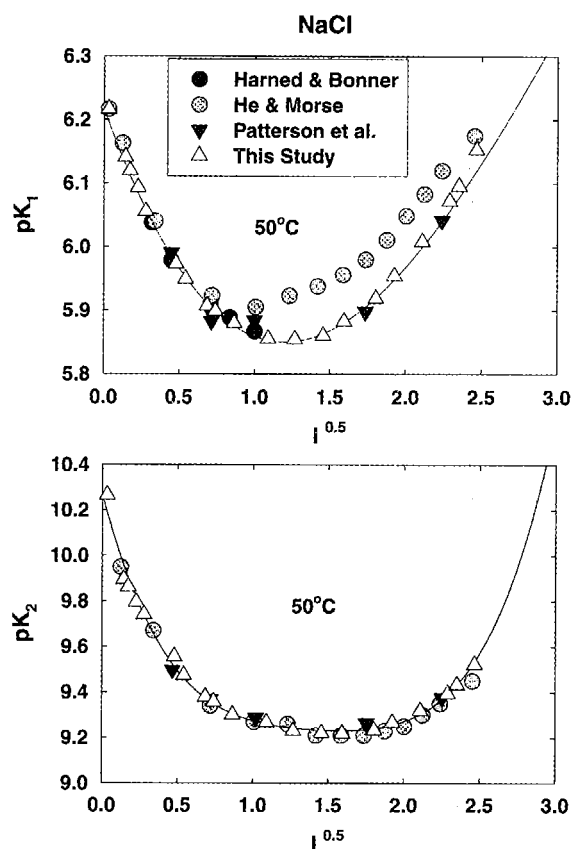


Fig. 4. A comparison of the values of  $pK_1^*$  and  $pK_2^*$  for carbonic acid at 50 °C.

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

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

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 errors 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 ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) 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

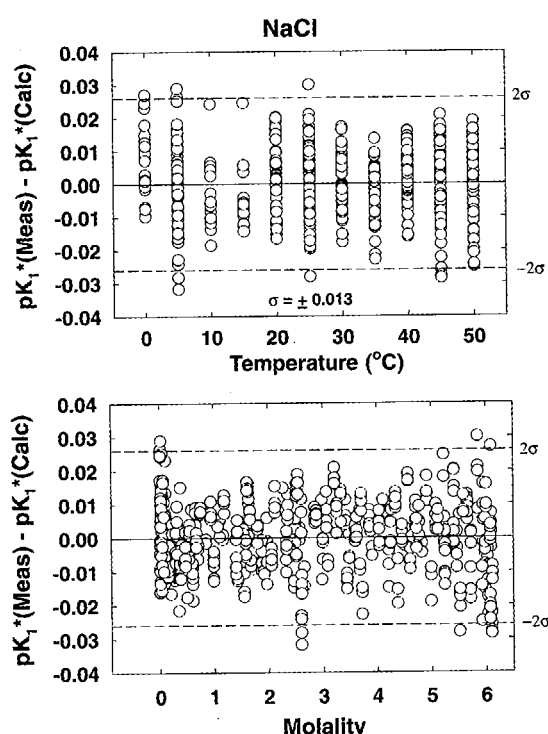


Fig. 5. The differences between the measured and calculated values of  $pK_1^*$  as a function of temperature and molality.

#### 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

$$\ln K_1 = \ln pK_1^* + \ln \gamma(\text{H}^+) + \ln \gamma(\text{HCO}_3^-) - \ln \gamma(\text{CO}_2) - \ln a(\text{H}_2\text{O}) \quad (16)$$

$$\ln K_2 = \ln pK_2^* + \ln \gamma(\text{H}^+) + \ln \gamma(\text{CO}_3^{2-}) - \ln \gamma(\text{HCO}_3^-) \quad (17)$$

Rearranging these equations one can determine the activity coefficients for  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  from

$$\ln \gamma(\text{HCO}_3^-) = \ln K_1 - \ln K_1^* - \ln \gamma(\text{H}^+) + \ln \gamma(\text{CO}_2) + \ln a(\text{H}_2\text{O}) \quad (18)$$

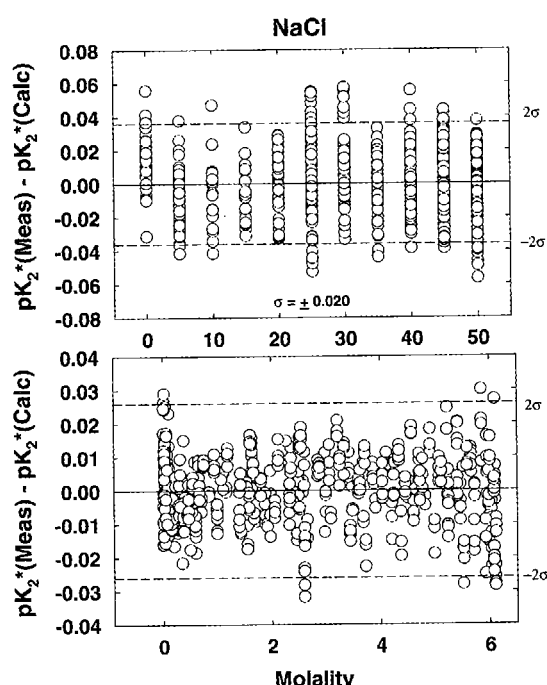


Fig. 6. The differences between the measured and calculated values of  $pK_2^*$  as a function of temperature and molality.

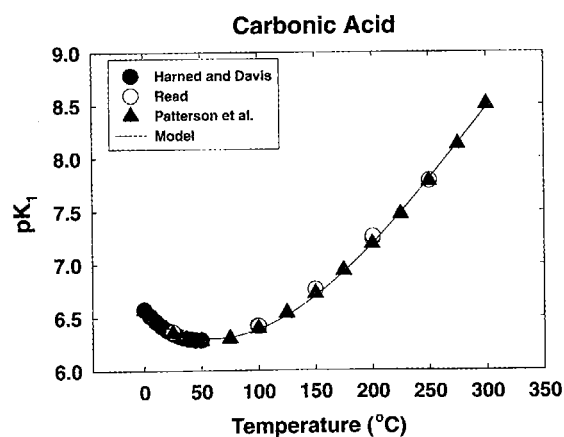


Fig. 7. Values of  $pK_1$  for carbonic acid as a function of temperature (0-250 °C).