



The values of $pK_1 + pK_2$ for the dissociation of carbonic acid in seawater

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Abstract—The values of $pK_1 + pK_2$ for the dissociation of carbonic acid have been determined in seawater as a function of temperature (0 to 45°C) and salinity (5 to 42). They were determined by the addition of NaHCO_3 to seawater stripped of CO_2 until the $\text{pH}_0 = 1/2(pK_1 + pK_2)$ was constant. The pH_0 was measured using potentiometric and spectrophotometric techniques. The values of pH_0 determined by the two methods are in good agreement (± 0.002). Our values of $1/2(pK_1 + pK_2)$ are in good agreement (0.005) with the results of Mehrbach et al. (1973) and the combined data have been fitted to the equation

$$1/2(pK_1 + pK_2) = -247.8958 + 6.564628 S - 3.322 \times 10^{-4} S^2 + 12074.50/T + 37.764148 \ln T \\ + (-290.721 S + 0.12980 S^2)/T - 0.983517 S \ln T$$

with a $\sigma = 0.0052$. Both studies indicate that the measurements of pK_2 in artificial seawater are lower than the values in real seawater. Values of the pK_1 in seawater were also determined from potentiometric titrations of seawater at a few temperatures (15 to 45°C). The results are in better agreement (0.01) with the results of Mehrbach et al. between 20 to 30°C than other workers. Our results and those of Mehrbach et al. have been combined to yield ($\sigma = 0.0056$)

$$pK_1 = -43.6977 - 0.0129037 S + 1.364 \times 10^{-4} S^2 + 2885.378/T + 7.045159 \ln T \\ \text{and } (\sigma = 0.010)$$

$$pK_2 = -452.0940 + 13.142162 S - 8.101 \times 10^{-4} S^2 + 21263.61/T + 68.483143 \ln T \\ + (-581.4428 S + 0.259601 S^2)/T - 1.967035 S \ln T$$

These studies indicate that the values of $K_1(\text{SW}) > K_1(\text{ASW})$ by ~ 0.01 and $K_2(\text{SW}) < K_2(\text{ASW})$ by ~ 0.04 near 25°C. Measurements of $pK_1 + pK_2$ and pK_1 in artificial seawater with and without boric acid show the same trends, indicating that the effect is due to interactions of boric acid with HCO_3^- and CO_3^{2-} . Further studies are needed to elucidate these interactions. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

The carbonate system in natural waters can be studied by measurements of pH, the total alkalinity (TA), the total carbonate (TCO_2) and the fugacity of CO_2 ($f\text{CO}_2$). Only two of these four parameters need to be measured to characterize the CO_2 system in solution providing that data are available for all the other acid/base species. These calculation require reliable dissociation constants for carbonic acid



The dissociation constants are defined by

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

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

where [i] are the total concentrations in mol (kg sol)⁻¹. It should be pointed out that all the constants discussed in this paper are on the seawater pH scale (pH_{SWS}), where $[\text{H}^+]_{\text{SWS}} \approx$

$[\text{H}^+]_{\text{F}} + [\text{HSO}_4^-] + [\text{HF}]$ (where the subscript F is used to denote the free proton concentration, Dickson, 1984).

Four groups have recently made measurements of pK_1 and pK_2 : Hansson (1973), Mehrbach et al. (1973), Goyet and Poisson (1989) and Roy et al. (1993). The measurements of Mehrbach et al. (1973) were made in real seawater (SW) while the other studies were made in artificial seawater (ASW). The standard errors of the fits of the measured values of pK_1 and pK_2 to functions of temperature and salinity by the authors are within 0.007 and 0.011 respectively (Table 1). Comparisons of the values of pK_1 and pK_2 at different temperatures are shown in Figure 1. The values of pK_1 are generally within $2\sigma = 0.014$, but the values of pK_2 show differences much larger than $2\sigma = 0.022$, where the standard errors are based on the fits of the authors (Table 1). Near 25°C the measurements of pK_1 in SW are 0.01 lower than the measurements in ASW; while, the measurements of pK_2 in SW are 0.04 higher than the measurements in ASW.

The present analytical precision of the measurement in the carbon dioxide system parameters (Millero et al., 2001) is ± 0.001 in pH, $\pm 4 \mu\text{mol kg}^{-1}$ in TA, $\pm 2 \mu\text{mol kg}^{-1}$ in TCO_2 and $\pm 3 \mu\text{atm}$ in $f\text{CO}_2$. To calculate the unknown parameters with the same precision as the measurements, reliable constants are needed (Millero, 1995; Lee et al., 1996). This is demonstrated in Table 2 where the effect of errors of 0.01 in pK_1 and

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Table 1. Summary of Measurements Made on the Dissociation Constants of Carbonic Acid in Seawater by Various Workers at $S = 35$ and $t = 25^\circ\text{C}$.^a

Author	Temp. (°C)	Salinity	σ (pK ₁)	σ (pK ₂)	Media
Hansson, 1973	5 to 30	20 to 40	0.007	0.009	Art. SW
Mehrbach et al., 1973	2 to 35	26 to 43	0.006	0.010	SW
Goyet & Poisson, 1989	-1 to 40	10 to 50	0.007	0.011	Art. SW
Roy et al., 1993	0 to 45	5 to 45	0.002	0.003	Art. SW

^a The standard errors in pK₁ and pK₂ are based on the original fits of the measured values to functions of temperature and salinity by the authors. The form of the equations used are similar to equation 21 (Millero, 1995).

0.04 in pK₂ are examined. With an input of pH and TA or TCO₂, one can determine the fCO₂ and TCO₂ or TA with values of pK₁ or pK₂. Since the uncertainties in pK₁ are much less than the uncertainties in pK₂, more reliable calculations of fCO₂ and TCO₂ or TA can be made using pK₁. An input of pH and TA or TCO₂ can lead to errors in the calculated values of fCO₂ of 10 μatm due to errors in pK₂. Calculations of the CO₂ parameters using an input of TA and TCO₂, fCO₂ and TCO₂ or

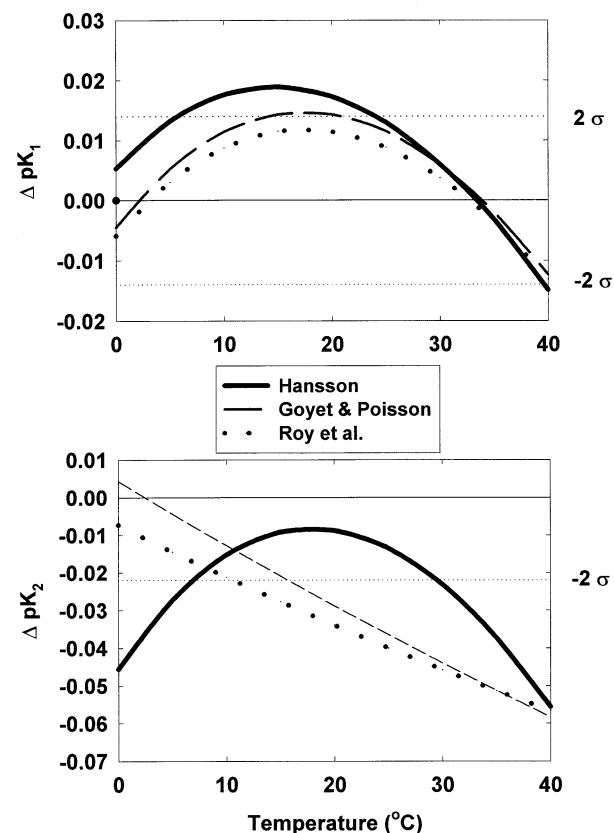


Fig. 1. A comparison of the effect of temperature on pK₁ and pK₂ at $S = 35$ of various workers to the results of Mehrbach et al., 1973 ($\Delta = \text{Others} - \text{Mehrbach}$). The dotted lines represent the 2σ error of the fits of the authors of their results to function of temperature and salinity (Table 1).

Table 2. Estimated uncertainties in the calculated CO₂ parameters due to errors of ± 0.01 in pK₁ and ± 0.04 in pK₂ or pK₂ - pK₁ (25°C and $S = 35$).^a

Errors due to an uncertainty of ± 0.01 in pK ₁				
Input	ΔpH	ΔTA μmol/kg	ΔTCO_2 μmol/kg	ΔfCO_2 μatm
pH - TA	—	—	0.0	± 10.1
pH - TCO ₂	—	0.0	—	± 10.1
pH - fCO ₂	—	± 63.0	± 57.0	—
fCO ₂ - TCO ₂	± 0.0091	± 6.0	—	—
fCO ₂ - TA	± 0.0083	—	± 5.0	—
TA - TCO ₂	± 0.0005	—	—	± 9.5

Errors due to an uncertainty of ± 0.04 in pK ₂				
Input	ΔpH	ΔTA μmol/kg	ΔTCO_2 μmol/kg	ΔfCO_2 ΔAtm
pH - TA	—	—	± 15.5	± 7.3
pH - TCO ₂	—	± 16.5	—	± 4.0
pH - fCO ₂	—	± 45.5	± 23.0	—
fCO ₂ - TCO ₂	± 0.0036	± 18.0	—	—
fCO ₂ - TA	± 0.0060	—	± 15.0	—
TA - TCO ₂	± 0.0269	—	—	± 25.6

^a The uncertainties are estimated for seawater ($S = 35$) at 25°C with values of $\text{TA} = 2300 \mu\text{mol kg}^{-1}$, $\text{TCO}_2 = 1970 \mu\text{mol kg}^{-1}$, $\text{pH} = 8.07$ and $\text{fCO}_2 = 360 \mu\text{atm}$. The uncertainties in seawater with different properties will vary somewhat from these estimates. The uncertainties of ± 0.04 in pK₂ - pK₁ are not given since they are similar to those for pK₂.

fCO₂ and TA require reliable values of pK₂ - pK₁ (Lee et al., 2000). Errors in pK₂ - pK₁ are largely due to errors in pK₂ and give uncertainties similar to those shown for pK₂ in Table 2. For example, an error of 0.04 in pK₂ - pK₁ with an input of TA and TCO₂ can lead to errors in the calculated values of fCO₂ of 26 μatm.

A number of internal consistency tests using measurements made in the laboratory (Lee et al., 1996; Leuker et al., 2000) and at sea (Wanninkhof et al., 1999; Lee et al. 2000, Millero et al., 2002) indicate that the values of pK₂ - pK₁ of Mehrbach et al. (1973) are more reliable than the results of others (Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993). The differences in the values of pK₂ - pK₁ of the studies in artificial seawater (ASW) with those determined in real seawater (SW) by Mehrbach et al. (1973) are around 0.04 (see Fig. 2) from 10 to 40°C . Since the values of pK₁ determined by all of the studies agree within 0.01 (see Fig. 1), the differences in pK₂ - pK₁ are largely due to uncertainties in pK₂ (see Fig. 1).

These comparisons point out the need to have reliable dissociation constants for carbonic acid. This paper describes some new measurements of the pK₁ + pK₂ and pK₁ in real and artificial seawater. These results extend the earlier measurements of Mehrbach et al. (1973) using improved methods and examine the effect of borate on the carbonate system. By combining our results with those of Mehrbach et al. (1973), we provide equations that we feel are appropriate for calculations of the carbonate system in the oceans. Our preliminary work indicates that borate-carbonate interactions may cause the differences in the pK₁ and pK₂ between real and artificial seawater.

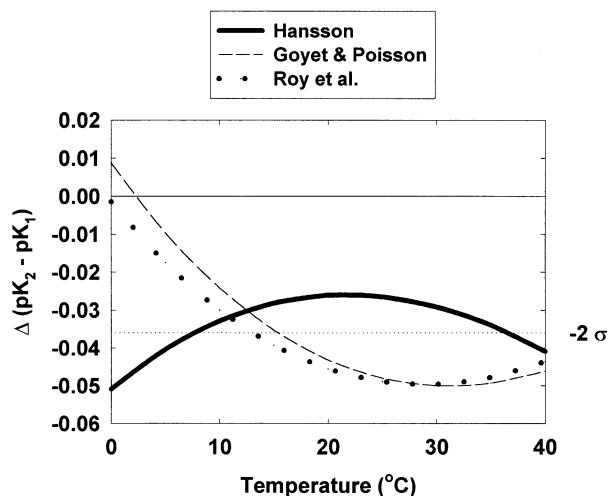


Fig. 2. A comparison of the effect of temperature on $pK_2 - pK_1$ at $S = 35$ of various workers to the results of Mehrbach et al. (1973) ($\Delta = \text{Others} - \text{Mehrbach}$). The dotted lines represent the 2σ error of the fits of the authors of their results to function of temperature and salinity (Table 1).

2. EXPERIMENTAL METHODS

The values of $pK_1 + K_2$ were determined in natural and artificial seawater using the methods of Mehrbach et al. (1973). The seawater is stripped of CO_2 after the addition of acid (HCl). The pH was then adjusted with 0.1 N NaOH within ± 0.05 pH of the equilibrium value ($\text{pH} = 1/2(\text{p}K_1 + \text{p}K_2)$). Solid NaHCO_3 was then added to the solution until a constant pH was reached. Unlike the study of Mehrbach et al. (1973), the electrode was calibrated in the sample by titrating it with HCl before the bicarbonate addition. The pH was also determined using the spectrophotometric technique with the indicator *m*-cresol purple (Clayton and Byrne, 1993). The values of pK_1 were determined in natural and artificial seawater from potentiometric titrations as described below.

3. MATERIAL AND METHODS

The seawater used in this study was Gulf Stream seawater collected off the coast of Miami. The seawater was filtered through a $0.45 \mu\text{m}$ Millipore filter before its use. The salinities of the two batches of seawater ($S = 36.2$ and $S = 35.9$) were determined with a Guildline salinometer on the Practical Salinity Scale. The salinometer was calibrated with standard seawater of known conductivity.

The artificial seawater was prepared as described by Millero (1996) according to the specifications of Goyet and Poisson (1989). Their artificial seawater solution resembles the average chemical composition of seawater better than the composition used by other authors (see Table 3).

The gravimetric salts (NaCl , Na_2SO_4 , KCl , Na_2CO_3 , NaF and KBr , all reagent grade) were dried overnight in an oven at 60°C before weighing and addition to Milli-Q water. The volumetric salts ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) were added from stock solutions of known concentrations. The concentrations of the stock solutions were determined from density measurements made with a Mettler/Par Vibrating Density Meter DMA/60 and using the equations of state for the salts (Lo Surdo et al., 1982). The density of the artificial seawater solution at 25°C was 1.023233 g/cm^3 by direct measurement, which is in reasonable agreement with real seawater (1.023343 g/cm^3) at 25°C and salinity 35 (Millero and Poisson, 1981).

The TA of the seawater was determined by titrating the sample with HCl using an automated potentiometric titration system (Millero et al., 1993). The TCO_2 of the seawater was determined from a coulometric titration system described by Johnson et al. (1993). The performance of both systems was monitored using certified reference material (CRM)

Table 3. Composition of Artificial Seawater from Various Workers and Standard Mean Chemical Composition of Seawater at $S = 35$.

Salt	Hansson ^a	Goyet & Poisson ^b	Roy et al. ^c	Real seawater ^d
NaCl	0.422000	0.409411	0.412598	0.41011
Na_2SO_4	0.028000	0.028217	0.028240	0.02824
KCl	—	0.009080	0.010208	0.00937
KBr	—	0.000823	—	0.00084
NaF	—	0.000071	—	0.00007
Na_2CO_3	—	0.001000	—	0.00026
NaHCO_3	—	—	—	0.00177
B(OH)_3	—	—	—	0.00042
MgCl_2	0.054000	0.053270	0.052815	0.05282
CaCl_2	0.010000	0.010330	0.010372	0.01028
SrCl_2	—	0.000090	—	0.00009

^a Hansson (1973).

^b Goyet and Poisson (1989).

^c Roy et al. (1993).

^d DOE (1994).

and locally prepared reference standards (RM). The reference materials indicated that the precisions were $\pm 2 \mu\text{mol/kg}$ for TA and $\pm 1 \mu\text{mol/kg}$ for TCO_2 (Mojica Prieto, 2001). The external reference was CRM Batch # 38 provided by Dr. Andrew Dickson from Scripps Institution of Oceanography, La Jolla, California. The internal reference was RM Batches 5 and 6. This is a batch of Gulf Stream seawater collected off the coast of Miami. The seawater was filtered ($0.45 \mu\text{m}$), poisoned with HgCl_2 and stored in 500 cm^3 borosilicate bottles (DOE, 1994).

The HCl (in 0.45 mol/L NaCl) used for the potentiometric titrations was prepared in a large batch and stored in 500 cm^3 borosilicate glass bottles. The concentration of the HCl was determined by coulometry (Taylor and Smith, 1959). The batch used in this study (#9601) had a concentration of $0.24892 \pm 0.00003 \text{ mol/L}$.

The NaHCO_3 used for the determination of the product K_1K_2 was reagent grade of highest purity (Aldrich A.C.S. Reagent Plus™). The purity of the NaHCO_3 can be represented by $A = \text{TCO}_2/\text{CA}$. When the bicarbonate is the only chemical species responsible for the alkalinity of the sample, the carbonate alkalinity (CA) and the total alkalinity (TA) of the solution are the same. Mehrbach et al. (1973) determined A from a comparison with a standard of KHCO_3 . In this study, the ratio A was experimentally determined by independent measurements of TA by potentiometric titration and TCO_2 by coulometry. These experiments were performed in a NaHCO_3 solution (0.002 mol/L) in NaCl media (0.7 mol/L) prepared with Milli-Q water devoid of CO_2 . The measurements resulted in $\text{CA} = 2222.0 \pm 1.7 \mu\text{mol/kg}$ and $\text{TCO}_2 = 2208.2 \pm 0.7 \mu\text{mol/kg}$. This yields a value of the ratio $A = 0.9938 \pm 0.0008$ (Mojica Prieto, 2001). The value of CA has been corrected for the blank of $10 \pm 1 \mu\text{mol kg}^{-1}$ determined in measurements of TA in 0.7 mol/L NaCl with different amounts of NaHCO_3 (Mojica Prieto, 2001). The value of $A = 1.0982$ was calculated from the pH of the NaCl media without NaHCO_3 (6.977 ± 0.002) using the equation (Mehrbach et al., 1973)

$$A = ([\text{H}^+]^2 + [\text{H}^+]\text{K}_1 + \text{K}_1\text{K}_2)/([\text{H}^+]\text{K}_1 + 2\text{K}_1\text{K}_2) \quad (5)$$

where K_1 and K_2 are the values of the carbonic acid dissociation constants in NaCl 0.7 m solutions ($\text{p}K_1 = 5.894$ and $\text{p}K_2 = 9.530$) from Thurmond and Millero (1982). This value of A was used along with the measured TA to determine the contribution of the blank to the CA and TCO_2 in the bicarbonate and calculate the errors due to the blank.

The 0.1 mol/L NaOH solution used to adjust the pH before the bicarbonate additions was prepared from J.T. Baker's Dilute-It analytical concentrate diluted with Milli-Q water that was previously purged with a CO_2 free gas. The NaOH solution was kept free of CO_2 by using an Ascarite II trap (A.H. Thomas).

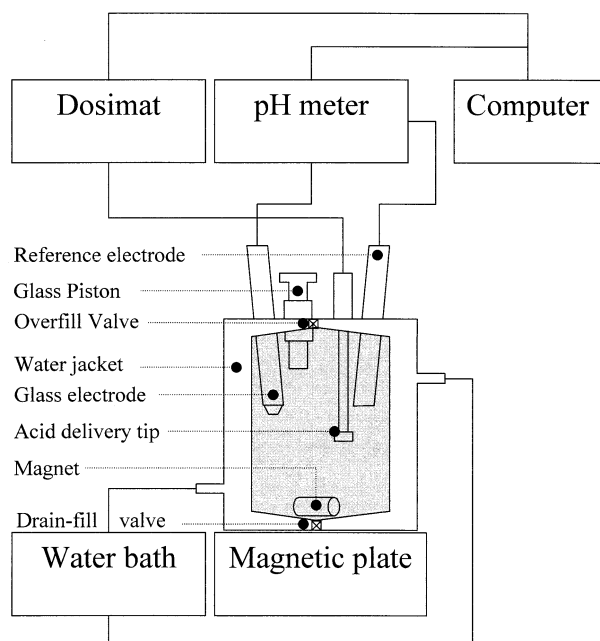


Fig. 3. The titration cell used in this study.

3.1. Electrodes

The potentiometric values of pH were determined with an Orion Ross glass electrode (8101) and a double junction Ag, AgCl electrode (8005). The outer solution of the reference electrode was filled with 0.7 m NaCl to minimize the junction potential. The emf was measured with a 720A Orion pH meter. The response and reliability of the electrodes was examined by titrating 0.7 mol/L NaCl solutions with HCl (Mojica Prieto, 2001). The pH is reproducible to ± 0.002 and the drift was less than 0.05 mV/min at a given pH.

3.2. Potentiometric Titrations

The values of pK_1 were determined using a closed cell (see Fig. 3), while the values of $1/2(pK_1 + pK_2)$ were determined in an open cell (Mojica Prieto, 2001). The volume of the closed cell (207.73 ± 0.06 cm³) was determined by comparing alkalinity titrations of Gulf Stream seawater in an open and closed cell. The volume of the cell at other temperatures was determined from titrations of seawater of known TA. The temperatures of the cell were controlled to $\pm 0.01^\circ\text{C}$ with a Neslab circulating bath. The temperature was monitored during an experiment with a Guildline platinum resistance thermometer. All of the titrations were carried out with the TA system described in detail elsewhere (Millero et al., 1993). For titrations of seawater, the program calculates TA, TCO_2 , the standard potential of the cell (E^*), the initial pH and pK_1 . Values of the emf and V_{HCl} for all of the titrations are given elsewhere (Mojica Prieto, 2001).

3.3. Coulometric Titrations

The values of TCO_2 were determined with the SOMMA (Single Operator Multiparameter Metabolic Analyzer) system. The carbon dioxide is stripped from seawater after the addition of phosphoric or hydrochloric acid, collected in an ethanalamine solution and the TCO_2 is determined by a coulometric titration (Johnson et al., 1993). The coulometric system was calibrated with certified reference material. The precision is ± 1 $\mu\text{mol/kg}$ and reproduces the CRM to ± 2 $\mu\text{mol/kg}$.

3.4. Bicarbonate Additions

The procedure used in this study for the bicarbonate addition is the following. After the alkalinity titration, the sample was purged for 15

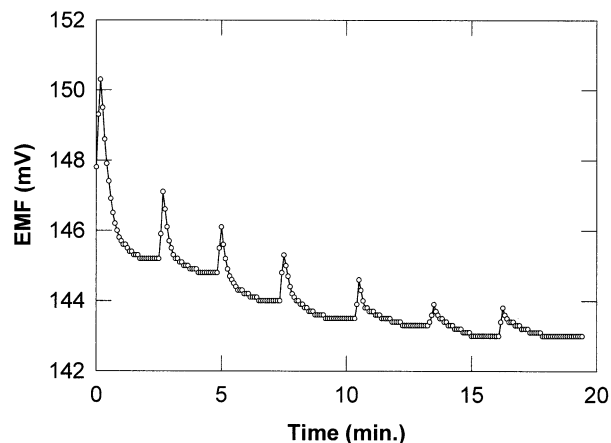


Fig. 4. The changes in the emf upon the addition of NaHCO_3 to seawater stripped of CO_2 ($S = 36.17$ and $t = 25^\circ\text{C}$).

min with N_2 to remove residual CO_2 . The titration of the sample was used to determine the initial pH, TA, TCO_2 and E^* of the electrode. The pH was adjusted with NaOH within ± 0.05 pH of the equilibrium value using a Metrohm Dosimat. The equilibration time after the addition of NaOH ranged from 15 min. at temperatures higher than 20°C to one hour at lower temperatures. Small amounts of bicarbonate were added to the sample until a steady-state pH (pH_0) was reached. The equilibration time for each addition ranged from 2 min. at temperatures higher than 25°C to 15 min. at lower temperatures. The temperature was recorded for each measurement. The pH was monitored with the same Orion pH meter used during the alkalinity titration by recording the emf after the signal became stable (± 0.05 mV). To be consistent, most of the measurements were made by approaching the equilibrium pH_0 from the acidic side. A typical experiment of bicarbonate addition is shown in Figure 4.

3.5. Absorbance Measurements

The spectroscopic measurements of the equilibrium pH upon addition of bicarbonate were performed with a Hewlett Packard UV-Visible (8453) diode array, single beam spectrophotometer. The samples were transferred to a clean and dry 30 cm³ cell with a 10 cm path length optical cell and closed with two Teflon caps. The replicates were thermally equilibrated in the water bath inside sealed plastic bags. The optical cells were placed in a thermally controlled chamber. The sample was allowed to equilibrate in the chamber and the blank was measured. Then 20 μL of a 0.008 mol/L solution of the indicator was quickly added to the sample using a Gilmont pipette. The final concentration of the indicator in the sample was approximately 5.3×10^{-6} M. Upon the addition of the dye, the cell was rotated and returned to the temperature bath to re-equilibrate before the absorbance was measured. For temperatures below 10°C , the spectrophotometric measurements became difficult because of the condensation of water on the optic cell walls. To prepare the indicator solution, 1.6176 g of the sodium salt of *m*-cresol purple from Kodak were accurately weighed. The indicator was then diluted with Milli-Q water and brought to a final volume of 500 cm³. The solution was constantly stirred until it was homogeneous. The Milli-Q water was previously purged with N_2 . The solution was transferred to a 2 mm path length optical closed cell with two Teflon caps and the absorbance of this solution was measured with a spectrophotometer. The ratio of the absorbance at $\lambda = 434$ nm and 578 nm corresponding to the absorption maxima of the acid (HI^-) and base (I^{2-}) forms of the dye respectively, was calculated after subtracting the baseline absorbance at $\lambda = 730$ nm from each of the peaks. A 1:5 (volume) hydrochloric acid solution in Milli-Q water free of CO_2 was prepared and a very small amount was added to the solution. The 2 mm cell was rinsed at least 3 times with this new solution. The absorbance was measured again and the addition of hydrochloric acid solution is repeated until the ratio is sufficiently close to unity. The indicator

solution was then transferred to a collapsible container so as to prevent any gas exchange with the atmosphere.

The spectrophotometric measurements of pH were made to increase the precision and accuracy of the pH determined by the additions of bicarbonate to the seawater sample. The spectrophotometric technique has a precision of ± 0.0005 , which is nearly an order of magnitude better than the potentiometric determination (± 0.002). The total pH_T ($\approx -\log [\text{H}^+] - \log [\text{HSO}_4^-]$) was determined from (Clayton & Byrne, 1993):

$$\text{pH}_T = \text{pK}_{\text{indicator}} + \log \left[\frac{R - 0.00692}{2.222 - 0.1331R} \right] \quad (6)$$

The value of the ratio R is given by

$$R = \frac{(A_{\lambda=578\text{nm}} - A_{\lambda=730\text{nm}})/(A_{\lambda=434\text{nm}} - A_{\lambda=730\text{nm}})}{\quad} \quad (7)$$

The dissociation constant for the m-cresol purple can be calculated from the equation (Clayton & Byrne, 1993)

$$\text{pK}_{\text{indicator}} = 1245.69/T + 3.8275 + 0.00211(35 - S) \quad (8)$$

where T is the absolute temperature (292.15 to 303.15K) and S is the salinity ($S = 30$ to 37) of the sample. The values of the $\text{pK}_{\text{indicator}}$ and pH_T are units of mol (kg soln) $^{-1}$. The calculated pH_T is corrected for the pH change resulting from addition of the dye using

$$\text{pH}_{T\text{corrected}} = \text{pH}_{\text{total}} - (7.9 - \text{pH}_{\text{total}})/150 \quad (9)$$

Lee and Millero (1995) re-determined the value of $\text{pK}_{\text{indicator}}$ at $S = 35$ from 0 to 40°C with a 0.04 mol/L TRIS buffer. The pH of the buffer was determined with an electrode of the type H_2 , Pt | AgCl, Ag. They fitted their results to the following equation:

$$\text{pK}_{\text{indicator}} = 35.9130 - 216.404/T - 10.9913 \log T \quad (10)$$

The dissociation constant is on the total proton scale and has units of molality (mol kg $^{-1}$ H $_2$ O). It is important to point out that these equations assume that molar absorption ratios are independent of temperature. In this study, we have used the combined equations of Clayton and Byrne (1993) and Lee and Millero (1995) given by [mol (kg H $_2$ O) $^{-1}$]

$$\text{pK}_{\text{indicator}} = 35.9130 - 216.404/T - 10.9913 \log T + 0.00211(35 - S) - \log (1 - 0.001005 S) \quad (11)$$

Transformation to the seawater scale was made using (Dickson and Millero, 1987; Millero, 1995):

$$\text{pH}_{\text{SWS}} = \text{pH}_T - \log \left\{ \frac{(1 + [\text{SO}_4^{2-}]/K_{\text{HSO}_4} + [\text{F}^-]/K_{\text{HF}})}{1 + [\text{SO}_4^{2-}]/K_{\text{HSO}_4}} \right\} \quad (12)$$

where $[\text{SO}_4^{2-}]$ is the total sulfate and $[\text{F}^-]$ is the total fluoride in the seawater defined in the next section (K_{HF} and K_{HSO_4} are the dissociation constants for HF and HSO_4^- respectively).

3.6. Determination of K_1

The values of K_1 were determined from a potentiometric titration of seawater with HCl. The constant was determined by a non-linear fit of the entire titration (Dickson, 1981, Johansson and Wedborg, 1982, Goyet and Poisson, 1989; Millero et al., 1993). It involves the determination of E^* , TA, TCO_2 and pK_1 by minimizing the residuals of the fit using a non-linear least square method. Since the titration of seawater does not lead to reliable values of pK_2 , it is not determined from the titrations and is fixed to the value from the fit of the values of Mehrbach et al. (1973) by Dickson and Millero (1987). The details of the methods we used in this study are given elsewhere (Mojica Prieto, 2001). All of the titrations were made on the seawater scale, $\text{pH}_{\text{SWS}} = -\log \{ [\text{H}^+] + [\text{SO}_4^{2-}]/K_{\text{HSO}_4} + [\text{F}^-]/K_{\text{HF}} \}$. The total concentrations of $[\text{SO}_4^{2-}] = (0.14/96.06)(S/1.80655)$ and $[\text{F}^-] = (6.7 \times 10^{-5}/18.9984)(S/1.80655)$ were taken from Morris and Riley (1966) and Riley (1965). The dissociation constants for HSO_4^- were taken from Dickson (1990a) and the values for HF were taken from Dickson &

Riley (1979). The values of total boron $[\text{B}]_T = (0.000232/10.811)(S/1.80655)$ were taken from Uppström (1974). The boric acid constants were taken from Dickson (1990b). The dissociation constants for water were taken from Millero (1995). All of the constants were adjusted to the seawater pH scale (Dickson and Millero, 1987; Millero, 1995).

3.7. Determination of K_1K_2

The product K_1K_2 is defined by

$$K_1K_2 = [\text{H}^+]^2[\text{CO}_3^{2-}]/[\text{CO}_2] \quad (13)$$

The carbonate alkalinity (CA) and total carbonate (TCO_2) are defined by

$$\text{CA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (14)$$

$$\text{TCO}_2 = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (15)$$

At the equilibrium pH for a solution with added NaHCO_3 , CA is equal to TCO_2 (Mehrbach et al., 1973). This gives

$$[\text{CO}_2] = [\text{CO}_3^{2-}] \quad (16)$$

and the product K_1K_2 can be determined from

$$K_1K_2 = [\text{H}^+]^2 \quad (17)$$

The equilibrium pH_0 is given by

$$\text{pH}_0 = 1/2(\text{pK}_1 + \text{pK}_2) \quad (18)$$

The ratio TCO_2/CA is given (Mehrbach et al., 1973) by

$$\text{TCO}_2/\text{CA} = A = \frac{([\text{H}^+]^2 + [\text{H}^+]K_1 + K_1K_2)/([\text{H}^+]K_1 + 2K_1K_2)}{\quad} \quad (19)$$

As discussed earlier A represents the purity of the bicarbonate used in the experiments. An error of ± 0.002 in pH leads to an error of ± 0.0004 in A, which is much smaller than an error of 0.0016 in A due to an error of 0.01 in pK_1 or an error of 0.0006 due to an error of 0.02 in pK_2 . This leads to an overall probable error of 0.0017 in A which is higher than the experimental uncertainty in the ratio A (± 0.0008) for our NaHCO_3 determined from direct measurements of TCO_2 and CA.

The value of K_1K_2 can be calculated from (Mehrbach et al., 1973):

$$K_1K_2 = (10^{-2\text{pH}_0} + [1 - A]K_110^{-\text{pH}_0})/(2A - 1) \quad (20)$$

The ratio $A = \text{TCO}_2/\text{CA}$ for the sodium bicarbonate is critical for the determination of K_1K_2 . Our error of ± 0.0008 in A can lead to errors of ± 0.007 in $1/2(\text{pK}_1 + \text{pK}_2)$ and this would propagate to errors of ± 0.015 in pK_2 . The errors in $1/2(\text{pK}_1 + \text{pK}_2)$ due to errors of 0.002 in pH (0.001) and 0.01 in pK_1 (0.001) are much smaller than those due to the errors in A.

There are several differences between the procedures used in this work and the one used by Mehrbach et al. (1973) and are listed below.

1. We made corrections for side reactions of bisulfate ion and hydrogen fluoride at the temperature and ionic strength of the solution Mehrbach et al. (1973) use values of K_{HSO_4} and K_{HF} at $S = 35$ and 25°C that are not as reliable as currently available. This causes a bias in the salinity and temperature dependence of pK_1 of as much as 0.003.
2. We determined the standard potential E^* used to calculate the pH_0 in the same solution in which the NaHCO_3 was added to the seawater. Mehrbach et al. (1973) used National Bureau of Standards buffers to calibrate their electrodes. The conversion of the NBS pH scale to the seawater scale requires a value for the apparent free hydrogen ion activity $f_{\text{H}} = a_{\text{H}}/[\text{H}^+]_{\text{SWS}}$ coefficient. Mehrbach et al. (1973) did not determine f_{H} in the solutions; they determined K_1K_2 . They determined f_{H} from their titrations while determining pK_1 at different temperatures and salinities than the solutions used to determine K_1K_2 .
4. Mehrbach et al used Lyman's (1956) values of K_{B} for the iteration procedure, which are not as reliable as recent measurements (Dick-

son, 1990b). This oversight does not have a large effect on the calculated values of pK_1 .

The experimental measurements of pH , K_1 , pK_2 and $1/2(pK_1 + pK_2)$ at various temperatures and salinities were fitted to equations of the form (Clark and Glew, 1966)

$$pK_i = A + B/T + C \ln T \quad (21)$$

where the parameters A , B and C are functions of salinity:

$$A = a_0 + a_1 S + a_2 S^2$$

$$B = b_0 + b_1 S + b_2 S^2$$

$$C = c_0 + c_1 S + c_2 S^2$$

The coefficients a_i , b_i and c_i (and thus A , B and C) for each experimental parameter (e.g., pH , pK_1) were determined by a least squares fit of the data. The coefficients needed to fit the data were determined by examining the residuals using an F-test (Mojica Prieto, 2001).

4. RESULTS AND CALCULATIONS

4.1. Determination of $pK_1 + pK_2$ in Seawater

The pH_0 was determined using potentiometric and spectrophotometric techniques in seawater as a function of salinity and temperature. The potentiometric and spectroscopic values of pH_0 are given in Tables 4 and 5. The values of pH_0 as a function of temperature and salinity were found to be a second-degree function of temperature and salinity (Mojica Prieto, 2001). The resulting equations derived from experimental values of $pH_0(\text{emf})$ and $pH_0(\text{spec})$ are given by

$$\begin{aligned} pH_0(\text{emf}) = & -279.8873 + 7.707839 S - 10.134 \times 10^{-4} S^2 \\ & + 13620.82/T + 42.479575 \ln T + (-350.238 S \\ & + 0.33069 S^2)/T - 1.149133 S \ln T \quad (22) \end{aligned}$$

$$\begin{aligned} pH_0(\text{spec}) = & -282.1204 + 8.160334 S - 5.144 \times 10^{-4} S^2 \\ & + 13646.25/T + 42.858609 \ln T + (-364.514 S \\ & + 0.18826 S^2)/T - 1.220330 S \ln T \quad (23) \end{aligned}$$

with standard errors of $\sigma = 0.004$ ($N = 91$) and $\sigma = 0.005$ ($N = 47$), respectively, for $pH_0(\text{emf})$ and $pH_0(\text{spec})$. The residuals between the measured and calculated values of pH_0 as a function of temperature and salinity are shown in Figure 5. The precision of the spectroscopic values of pH_0 is better than the potentiometric values; however, the fits are similar. This is related to errors in the spectroscopic pH due to changes during handling and re-equilibration of the temperature.

A comparison of the smoothed differences (Eqn. 22 minus Eqn. 23) between the values of $pH_0(\text{emf})$ and $pH_0(\text{spec})$ as a function of temperature and salinity are shown in Figure 6. The agreement is quite good and well within the standard error (0.005) of the individual measurements of pH_0 by the two techniques.

Since the values of $pH_0(\text{emf})$ and $pH_0(\text{spec})$ are in good agreement, the values of $1/2(pK_1 + pK_2)$ determined by the two techniques have been combined to give

$$\begin{aligned} 1/2(pK_1 + pK_2) = & -248.2121 + 6.676284 S - 3.469 \\ & \times 10^{-4} S^2 + 12088.54/T + 37.811100 \ln T \\ & + (-295.866 S + 0.13280 S^2)/T - 1.000046 S \ln T \quad (24) \end{aligned}$$

Table 5. The Values of pH_0 and $1/2(pK_1 + pK_2)$ Determined from Spectroscopic Measurements.

S	t (°C)	pH_0	$1/2(pK_1 + pK_2)$
14.993	24.932	7.640	7.581
	24.939	7.641	7.582
	24.953	7.640	7.581
	24.969	7.641	7.582
	24.969	7.641	7.582
	24.969	7.641	7.582
19.417	9.953	7.780	7.718
	9.997	7.780	7.717
	39.832	7.459	7.404
	39.859	7.465	7.409
	39.864	7.468	7.412
	19.976	24.986	7.580
24.997	25.007	7.575	7.519
	24.946	7.538	7.482
	24.950	7.536	7.480
	24.952	7.527	7.472
	24.962	7.544	7.488
	24.968	7.531	7.476
35.880	9.970	7.634	7.579
	9.997	7.640	7.583
	10.015	7.637	7.581
	20.035	7.499	7.446
	30.012	7.375	7.326
	30.014	7.380	7.331
36.178	39.940	7.261	7.217
	39.982	7.260	7.216
	24.950	7.449	7.397
	24.979	7.448	7.396
	24.983	7.447	7.395
	24.987	7.451	7.399
39.960	24.990	7.446	7.395
	24.993	7.452	7.400
	24.995	7.448	7.396
	24.996	7.449	7.397
	34.820	7.330	7.282
	34.861	7.317	7.270
39.960	34.866	7.327	7.280
	34.867	7.328	7.280
	34.879	7.323	7.276
	34.906	7.319	7.272
	34.925	7.327	7.280
	34.952	7.326	7.279
39.960	44.690	7.216	7.173
	44.912	7.222	7.178
	44.976	7.221	7.177
	9.948	7.613	7.558
	39.712	7.229	7.186
	39.865	7.230	7.188

with a standard error of $\sigma = 0.0054$ ($N = 138$). To compare our results with the work of Mehrbach et al. (1973) (see Table 6), we have determined the values of $1/2(pK_1 + pK_2)$ from their measured values of pH_0 and fitted the results to (Mojica Prieto, 2001)

$$\begin{aligned} 1/2(pK_1 + pK_2)_{\text{Mehrbach}} = & -16.7458 - 0.014695 S + 1.104 \\ & \times 10^{-4} S^2 + 2014.9/T + 3.117734 \ln T \quad (25) \end{aligned}$$

which has a standard error of $\sigma = 0.0057$ ($N = 33$) which is similar to our results. No cross terms were needed to fit the Mehrbach et al. (1973) data. This is due to the fact that they did not measure $1/2(pK_1 + pK_2)$ over a wide range of temperature and salinity. A comparison of the values of $1/2(pK_1 + pK_2)$

Table 4. The values of pH_0 and $1/2(pK_1 + pK_2)$ determined from emf measurements.

S	t(°C)	pH_0	$1/2(pK_1 + pK_2)$	
5.023	24.932	7.758	7.696	
	24.966	7.761	7.699	
	24.983	7.764	7.701	
	24.986	7.759	7.697	
	25.012	7.763	7.700	
10.010	24.963	7.689	7.629	
	24.965	7.693	7.633	
	24.975	7.690	7.630	
	24.999	7.695	7.635	
14.993	24.939	7.647	7.587	
	24.953	7.648	7.588	
	24.969	7.639	7.580	
	24.985	7.638	7.579	
	24.985	7.643	7.583	
19.417	9.953	7.780	7.718	
	9.964	7.783	7.720	
	9.997	7.787	7.724	
	10.002	7.783	7.720	
	39.832	7.468	7.412	
	39.859	7.461	7.406	
	39.864	7.465	7.409	
	39.869	7.466	7.410	
	19.976	24.935	7.575	7.519
	24.986	7.582	7.525	
25.007	7.579	7.522		
24.997	24.950	7.539	7.483	
	24.952	7.533	7.478	
	24.956	7.528	7.473	
	24.959	7.527	7.472	
	24.968	7.541	7.485	
	24.947	7.481	7.428	
	24.979	7.487	7.434	
	35.880	-0.033	7.781	7.722
	-0.011	7.782	7.723	
	-0.003	7.785	7.726	
9.970	7.639	7.583		
9.997	7.637	7.581		
10.015	7.637	7.581		
20.037	7.503	7.450		
30.012	7.374	7.326		
30.014	7.377	7.328		
39.940	7.260	7.216		
39.980	7.264	7.219		
39.982	7.261	7.217		
36.178	4.923	7.717	7.658	
	4.978	7.713	7.655	
	5.017	7.714	7.656	
	5.017	7.717	7.658	
	5.032	7.721	7.662	
	14.965	7.581	7.525	
	14.968	7.581	7.525	
	14.985	7.573	7.518	
	14.989	7.581	7.525	
	14.993	7.582	7.526	
24.950	7.445	7.393		
24.979	7.447	7.395		
24.983	7.441	7.390		
24.987	7.448	7.396		
24.988	7.451	7.399		
24.990	7.449	7.397		
24.993	7.446	7.394		
24.995	7.442	7.391		
24.996	7.447	7.395		
34.806	7.317	7.271		
36.178	34.866	7.324	7.277	
	34.867	7.328	7.280	
	34.879	7.320	7.273	

(continued)

Table 4. (Continued)

S	t(°C)	pH_0	$1/2(pK_1 + pK_2)$	
34.925	34.925	7.320	7.273	
	34.952	7.322	7.275	
	44.690	7.215	7.172	
	44.766	7.207	7.165	
	44.835	7.216	7.173	
	44.912	7.221	7.177	
	44.976	7.218	7.175	
	39.960	9.948	7.622	7.566
	9.951	7.627	7.571	
	9.983	7.612	7.557	
41.838	24.954	7.399	7.350	
	24.959	7.406	7.357	
	24.965	7.409	7.359	
	24.971	7.399	7.350	
	24.985	7.403	7.354	
	24.991	7.400	7.351	
	25.012	7.398	7.349	

determined in this study (Eqn. 24) with those determined by Mehrbach et al. (1973) (Eqn. 25) are shown in Figure 7. The differences are within 0.005 over most of the temperature and salinity range of the measurements. A comparison of our values

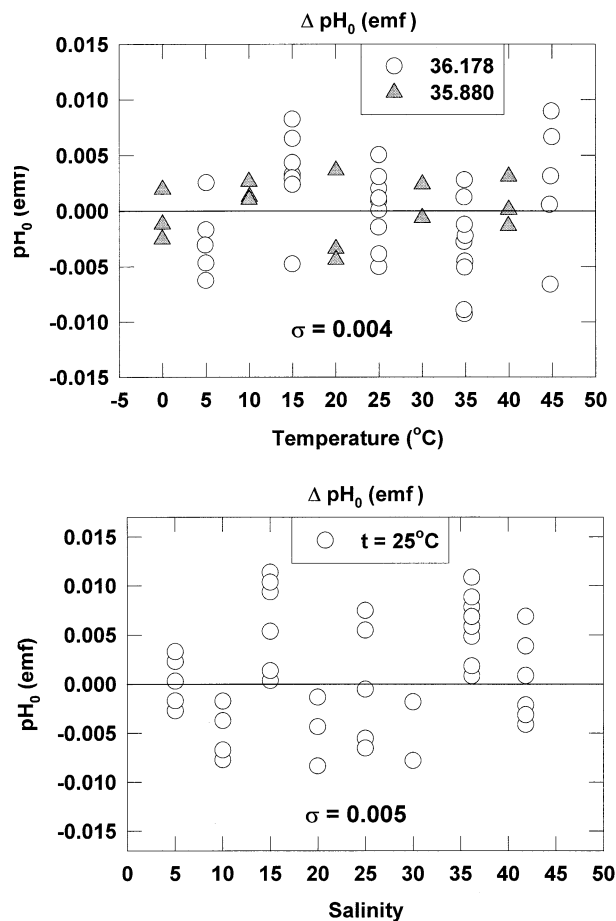


Fig. 5. The residuals between measured and calculated values of pH_0 in seawater as a function of temperature and salinity ($\Delta = \text{Meas} - \text{Calc}$).

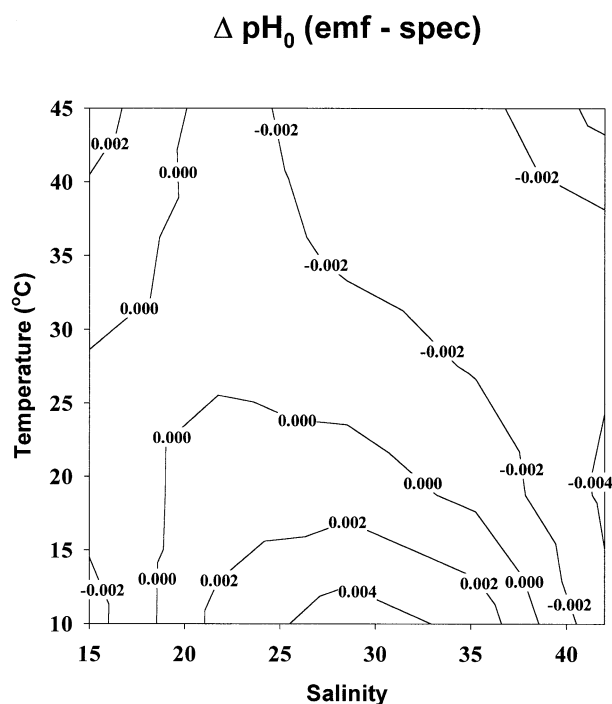


Fig. 6. A comparison of the values of pH_0 determined by potentiometric and spectrophotometric methods as a function of temperature and salinity.

of $1/2(\text{pK}_1 + \text{pK}_2)$ (Eqn. 24) with the results of other workers (Hansson, 1973; Mehrbach et al., 1973; Goyet and Poisson, 1989; Roy et al., 1993) seawater is shown in Figure 8. The differences between our work and Mehrbach et al. (1973) are all within 0.006, while the artificial seawater studies show much larger deviations especially at higher temperature. We have combined the two studies and arrived at a consensus equation

$$\begin{aligned} 1/2(\text{pK}_1 + \text{pK}_2) = & -247.8958 + 6.564628 S - 3.322 \\ & \times 10^{-4} S^2 + 12074.50/T + 37.764148 \ln T \\ & + (-290.721 S + 0.12980 S^2)/T - 0.983517 S \ln T \quad (26) \end{aligned}$$

with a standard error $\sigma = 0.0052$ ($N = 167$). This equation is valid from $S = 5$ to 43 and $t = 0$ to 45°C . We feel that this equation is the best representation of $\text{pK}_1 + \text{pK}_2$ in real seawater. The residuals of $1/2(\text{pK}_1 + \text{pK}_2)$ between our measurements and Mehrbach et al. (1973) and Eqn. 26 are shown in Figure 9. As shown in our earlier comparisons, the measured values in artificial seawater are lower than the values in real seawater. As shown in Figure 2, this is largely due to differences in pK_2 .

4.2. Determination of K_1 in Seawater

A few values of pK_1 have been determined in seawater at various temperatures (15 to 45°C) and salinities ($S = 10$ to 40). These results are given in Table 7. The values of pK_1 are a second degree function of temperature ($\sigma = 0.002$) and salinity ($\sigma = 0.005$) (Mojica Prieto, 2001). The residuals between the measured and calculated values of pK_1 as a function of temperature and salinity are shown in Figure 10. The precision is quite good (0.002 to 0.005). A comparison of our measure-

Table 6. Values of pH_0 and $1/2(\text{pK}_1 + \text{pK}_2)$ from Mehrbach et al. (1973).

t (°C)	S	$\text{pH}_{0 \text{ NBS}}$	$\text{pH}_{0 \text{ SWS}}$	$1/2(\text{pK}_1 + \text{pK}_2)$
2	26.67	7.900	7.787	7.777
		7.898	7.85	7.775
2	34.66	7.812	7.718	7.709
		7.810	7.716	7.707
		7.814	7.720	7.711
		7.818	7.724	7.715
2	41.54	7.768	7.687	7.678
		7.757	7.617	7.609
13	26.92	7.759	7.619	7.611
		7.759	7.619	7.611
13	35.2	7.689	7.567	7.558
		7.689	7.567	7.558
13	42.9	7.629	7.525	7.518
		7.629	7.525	7.518
25	19.16	7.716	7.545	7.537
		7.714	7.543	7.535
		7.711	7.540	7.532
		7.716	7.545	7.537
		7.652	7.484	7.476
		7.650	7.482	7.474
25	31.22	7.648	7.480	7.472
		7.594	7.430	7.422
		7.591	7.427	7.419
		7.593	7.429	7.421
		7.569	7.407	7.400
		7.569	7.407	7.400
25	34.9	7.567	7.405	7.398
		7.567	7.405	7.398
		7.511	7.354	7.347
		7.511	7.354	7.347
35	27.04	7.564	7.360	7.352
		7.564	7.360	7.352
35	35.01	7.494	7.287	7.281
		7.495	7.288	7.282
35	42.94	7.433	7.232	7.226
		7.433	7.232	7.226

a) The conversion of pH_{NBS} to pH_{SWS} were determined from fits of pH as a function of temperature and salinity (Mojica Prieto, 2001).

ments at $S = 36.26$ fitted to a second degree function of temperature (Mojica Prieto, 2001) with the results of other workers is shown in Figure 11. Our results are in better agreement with the seawater measurements of Mehrbach et al. (1973) than the measurements made in artificial seawater (Hansson, 1973; Goyet and Poisson, 1989; Roy et al., 1993). There appears to be a linear offset of our work with the measurements of Mehrbach et al. (1973) that we cannot fully explain at the present time. We plan to continue these measurements over a wider range of salinity and temperature in the future using flowing spectroscopic pH and pCO_2 on seawaters of known TA and TCO_2 as a function of temperature and salinity. These results should give us precise values of pK_1 that will compliment the earlier measurements of Mehrbach et al. (1973).

We have combined our limited measurements of pK_1 with the earlier work of Mehrbach et al. (1973) and fitted these values to

$$\begin{aligned} \text{pK}_1 = & -43.6977 - 0.0129037 S + 1.364 \times 10^{-4} S^2 \\ & + 2885.378/T + 7.045159 \ln T \quad (27) \end{aligned}$$

which has a standard error of 0.0056 ($N = 89$). The residuals are shown as a function of temperature and salinity in Figure 12.

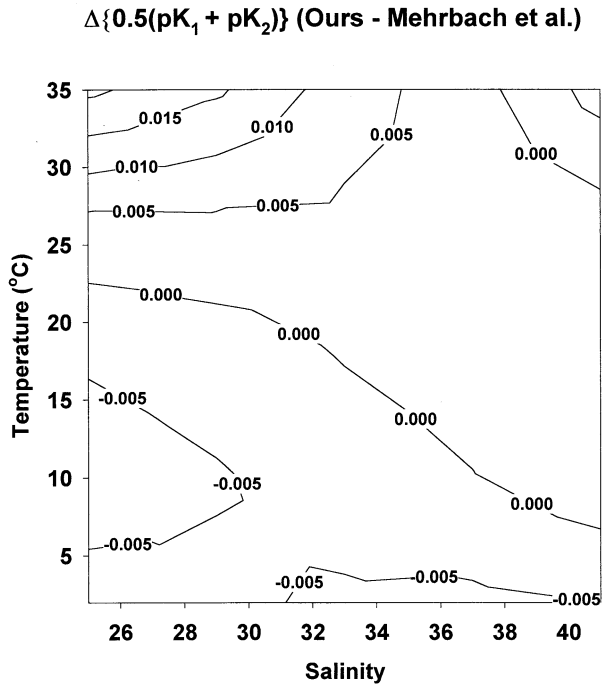


Fig. 7. A comparison of the values of $1/2(pK_1 + pK_2)$ determined in this study with the results of Mehrbach et al. (1973) as a function of temperature and salinity.

The values of pK_1 calculated from Eqn. 27 have been combined with the values of $pK_1 + pK_2$ determined in this study and by Mehrbach et al. (1973) to determine value of pK_2 . These values of pK_2 have been fitted to the equation

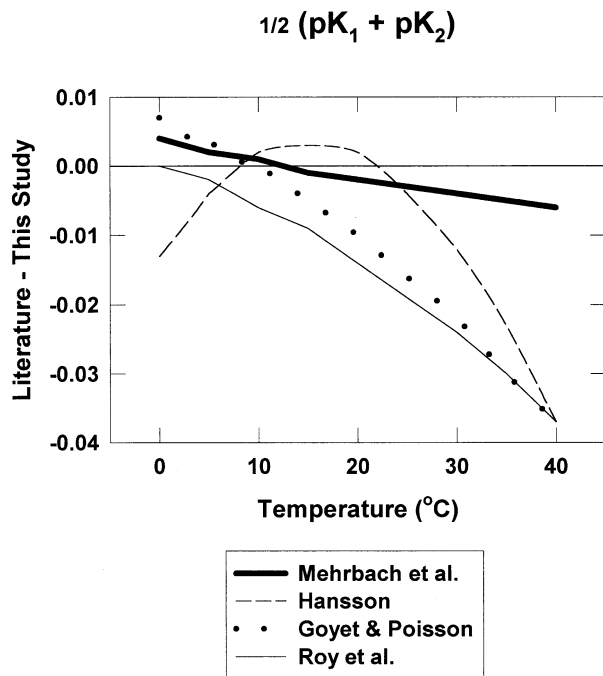


Fig. 8. Comparisons of the values of $1/2(pK_1 + pK_2)$ determined in this study with literature data (literature minus this study, Eqn. 24).

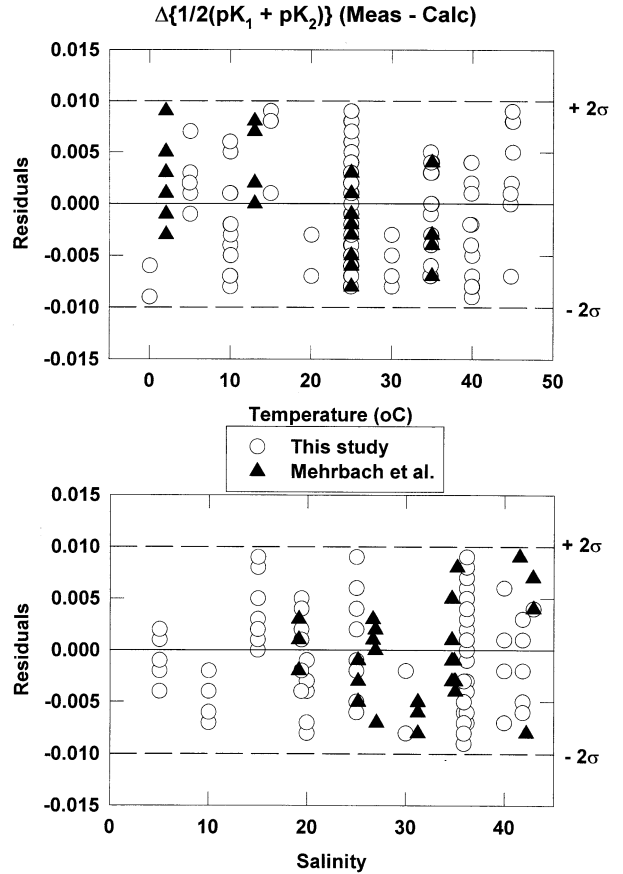


Fig. 9. The residuals between the measured and calculated values of $1/2(pK_1 + pK_2)$ as a function of temperature and salinity ($\Delta = \text{Meas} - \text{Calc}$). The dotted lines represent the 2σ errors of the fits of the results to Eqn. 26.

$$pK_2 = -452.0940 + 13.142162 S - 8.101 \times 10^{-4} S^2 + 21263.61/T + 68.483143 \ln T + (-581.4428 S + 0.259601 S^2)/T - 1.967035 S \ln T \quad (28)$$

where $\sigma = 0.010$ ($N = 167$). This equation gives a reliable representation of the pK_2 of carbonic acid in seawater.

4.3. Artificial Seawater Measurements

The values of pK_1 and $pK_2 - pK_1$ were determined in artificial seawater ($S = 34.885$) at 25°C without and with added boric acid. The values of pK_1 , pK_2 and $1/2(pK_1 + pK_2)$ are given in Table 8. The values of pK_2 have been determined by titrations of artificial seawater with added Na_2CO_3 and from measurements of K_1K_2 by the addition of bicarbonate (with and without added borate). The values of pK_1 in ASW with borate are 0.013 lower than the values in ASW without borate, while the values of pK_2 are 0.04 higher than the values without borate. These differences are in good agreement with the differences in the constants in real and artificial seawater (Figs. 1 and 2). As shown in Table 9, the values of pK_1 and pK_2 in ASW without borate are in good agreement with the values determined by Goyet and Poisson (1989) and Roy et al. (1993)

Table 7. Experimental Measurements of pK_1 in Seawater.

S	t (°C)	pK_1
36.261	14.900	5.939
		5.937
		5.935
		5.937
		5.938
36.261	24.330	5.938
		5.838
		5.837
		5.839
		5.839
36.261	34.160	5.838
		5.838
		5.758
		5.759
		5.757
36.261	45.090	5.758
		5.757
		5.756
		5.679
		5.679
10.080	24.990	5.678
		5.681
		6.000
		6.002
		6.001
16.160	24.990	6.000
		5.937
		5.940
		5.941
		5.941
19.417	24.990	5.941
		5.921
		5.915
		5.915
		5.914
24.960	24.990	5.914
		5.916
		5.889
		5.883
		5.884
29.970	24.990	5.885
		5.886
		5.860
		5.859
		5.859
36.716	24.990	5.860
		5.829
		5.830
39.960	24.990	5.826
		5.819
		5.817
		5.818
		5.818

(0.001 in pK_1 and 0.02 in pK_2). The values of pK_1 and pK_2 in ASW with borate are in good agreement with the measurements made in seawater in this study (0.002 in pK_1 and 0.02 with pK_2) and the earlier work of Mehrbach et al. (1973) (0.001 in pK_1 and 0.02 in pK_2).

This preliminary work indicates that the differences in pK_1 and pK_2 in artificial and real seawater are due to boric acid. Further work is necessary to elucidate the interactions between borate and carbonate that cause these differences.

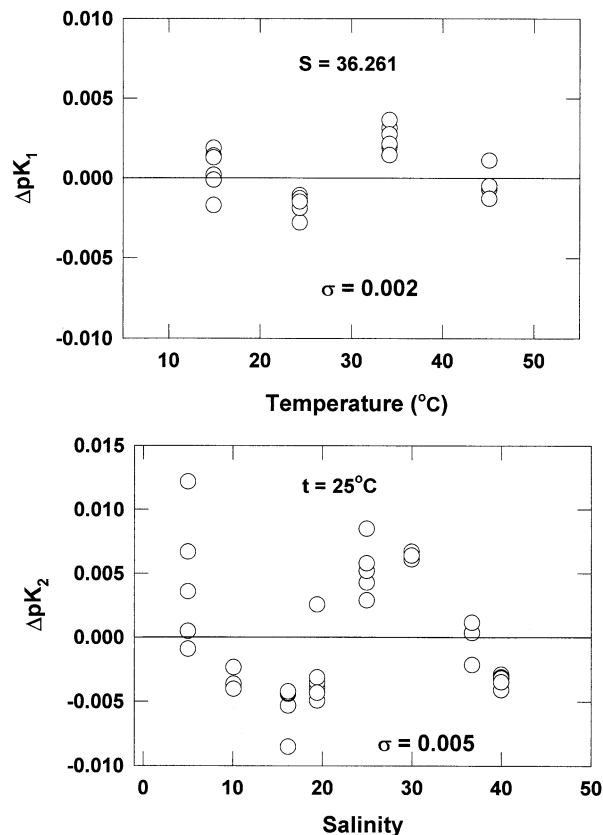


Fig. 10. The residuals between measured and calculated values of pK_1 in seawater as a function of temperature and salinity ($\Delta = \text{Meas} - \text{Calc}$).

5. DISCUSSION

The results from this study clearly demonstrate that the measured values of pK_1 and $1/2(pK_1 + pK_2)$ by Mehrbach et al. (1973) are reliable for seawater. This is in agreement with field (Wanninkhof et al., 1999; Lee et al. 2000, Millero et al., 2002) and laboratory (Lee et al. 1996, Lueker et al., 2000) measurements of the components of the CO_2 system in seawater. More importantly these results indicate that the measurements of Hansson (1973), Goyet and Poisson (1989) and Roy et al. (1993) are reliable for artificial seawater, but are not appropriate for real seawater. Our preliminary measurements at 25°C in artificial seawater without and with boric acid indicate that the differences in the results are due to boric acid that is present in real seawater. The addition of boric acid to artificial water causes the K_1 to increase and the K_2 to decrease. This can be attributed to changes in the activity coefficients of HCO_3^- and CO_3^{2-} . The stoichiometric constants are related to the thermodynamic values in water (K_1^0 and K_2^0), the activity (a_i) and the activity coefficients (γ_i) by

$$K_1 = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2] = K_1^0 a_{\text{H}_2\text{O}} \gamma_{\text{CO}_2}/\gamma_{\text{H}}\gamma_{\text{HCO}_3} \quad (29)$$

$$K_2 = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = K_2^0 \gamma_{\text{HCO}_3}/\gamma_{\text{H}}\gamma_{\text{CO}_3} \quad (30)$$

The increase in K_1 and the decrease in K_2 can be related to a decrease in $\gamma_{\text{HCO}_3^-}$ and an increase in $\gamma_{\text{CO}_3^{2-}}$. This implies that

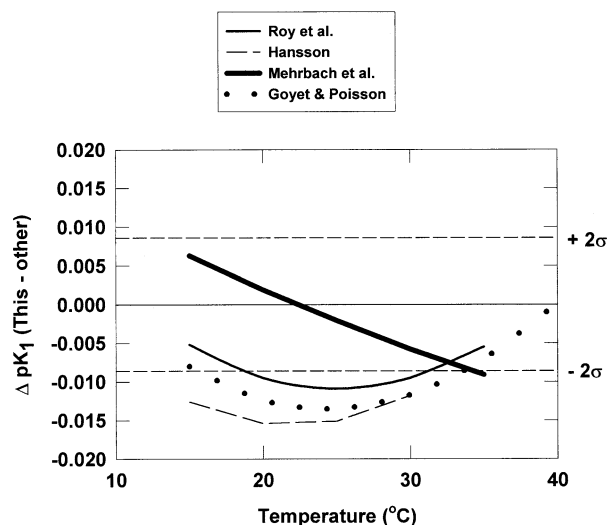
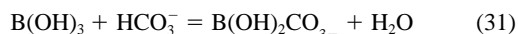


Fig. 11. A comparison of the literature values of pK_1 of various workers with those determined in this study fitted to a function of temperature (Mojica Prieto, 2001) ($S = 36.26$). The dotted lines represent the 2σ errors of the fits.

the interactions of HCO_3^- and CO_3^{2-} with $\text{B}(\text{OH})_3$ or $\text{B}(\text{OH})_4^-$ cause γ_{HCO_3} to decrease and the γ_{CO_3} to increase. A decrease in $\gamma_{\text{HCO}_3} = 0.70$ (Millero, 1996) to 0.684 can account for a decrease of 0.01 in pK_1 . This is consistent with the formation of the interaction of $\text{B}(\text{OH})_3$ with HCO_3^- suggested by McEligott and Byrne (1998). They consider the equilibrium



The interaction would lower the concentration of HCO_3^- and decrease γ_{HCO_3} consistent with the observed behavior. Unfortunately the value they found for the stability constant for the formation of $\text{B}(\text{OH})_2\text{CO}_3^-$ is not large enough to change the values of K_1 by the amount observed. Since the changes in K_2 are much larger than in K_1 , the interactions of $\text{B}(\text{OH})_3$ or $\text{B}(\text{OH})_4^-$ with CO_3^{2-} must be greater than with HCO_3^- . An increase of $\gamma_{\text{CO}_3} = 0.020$ (Millero, 1996) to 0.0215 would result in an increase of 0.03 in pK_2 (the interactions of HCO_3^- with $\text{B}(\text{OH})_3$ would account for 0.01 in the increase in pK_2). Since the formation of a complex between CO_3^{2-} and $\text{B}(\text{OH})_3$ would lower the γ_{CO_3} , this is unlikely to be the case. The increase in γ_{CO_3} is probably related to anion-anion interactions (CO_3^{2-} with $\text{B}(\text{OH})_4^-$) similar to that found for other anions (Pitzer, 1991). New studies are needed to examine these interactions in more detail.

Another puzzling thing about the effect of boric acid on K_1 and K_2 is that the effect appears to be a function of temperature. This is shown in Figure 1 where the differences in pK_1 and pK_2 are plotted versus temperature. At 0° and 30°C the values of pK_1 are in reasonable agreement. The 0.01 offsets in pK_1 just occur from 10 to 25°C . The differences in pK_2 at 0°C are quite small, but show a linear negative offset that increases with increasing temperature. These results indicate that the interaction between HCO_3^- and CO_3^{2-} with $\text{B}(\text{OH})_3$ or $\text{B}(\text{OH})_4^-$ are strong functions of temperature. This is not commonly found for anion-anion interactions (Millero, 2001).

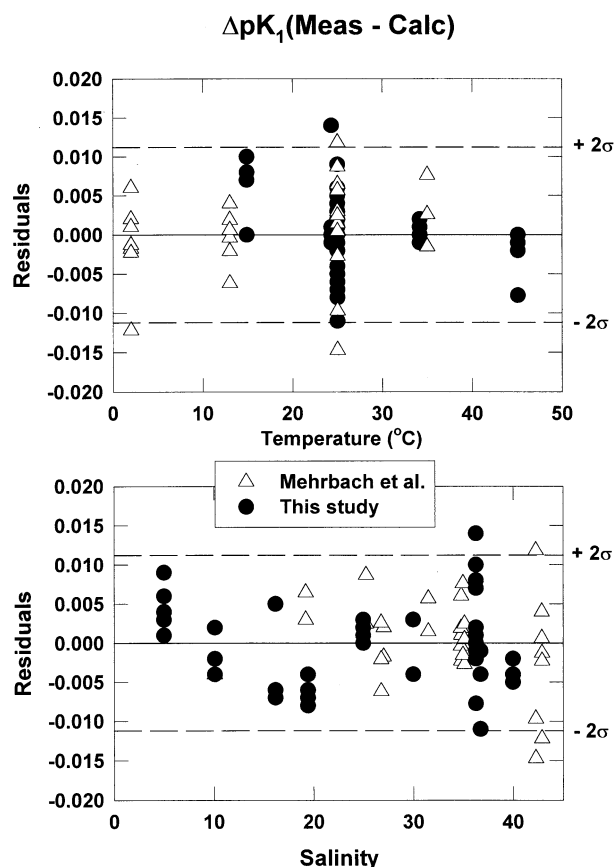


Fig. 12. The residuals between the measured and calculated values of pK_1 as a function of temperature and salinity ($\Delta = \text{Meas} - \text{Calc}$). The dotted lines represent the 2σ error of the fits of the results to Eqn. 27.

From this brief discussion, it is obvious that new measurements are needed to unravel the carbonate borate interactions that occur in seawater and perhaps in brines that have high concentrations of borate and carbonate (Felmy and Weare, 1986). For seawater calculations, the values of pK_1 and pK_2

Table 8. Values of pK_1 and pK_2 for Artificial Seawater with and without Boric Acids ($S = 34.855$ and $t = 25^\circ\text{C}$).

Constant	Without	With	Delta
pK_1	5.850 ^b 5.847 ^b 5.853 ^b	5.835 ^b 5.835 ^b 5.837 ^b	
Ave	5.850 ± 0.004	5.836 ± 0.001	-0.013
pK_2	8.88 ^a 8.91 ^b 8.90 ^b 8.91 ^b	8.94 ^a 8.93 ^b 8.95 ^b 8.94 ^b	
Ave	8.90 ± 0.01	8.94 ± 0.01	0.04
$1/2(pK_1 + pK_2)$	7.364 7.362 7.365 7.361	7.386 7.392 7.388	
Ave	7.363 ± 0.005	7.389 ± 0.005	0.054

^a Determined from measurements of $pK_1 + pK_2$ and pK_1 .

^b Determined from titrations of Na_2CO_3 .

Table 9. A comparison of the Values of pK_1 and pK_2 for Artificial Seawater with and without Boric Acids ($S = 34.855$ and $t = 25^\circ\text{C}$) with other workers.^a

Constant	Without	With	Reference
pK_1	5.849	5.836	This Study
		5.836 ^b	This Study
		5.837 ^b	Mehrbach et al.
	5.849		Goyet & Poisson
	5.847		Roy et al.
pK_2	5.850		Hansson
	8.90	8.94	This Study
		8.96 ^b	This Study
		8.96 ^b	Mehrbach et al.
	8.92		Goyet & Poisson
$1/2(pK_1 + pK_2)$	7.36	7.39	This Study
		7.40 ^b	This Study
		7.40 ^b	Mehrbach et al.
	7.38		Goyet & Poisson
	7.38		Roy et al.
	7.40	Hansson	

^a All the constants have been adjusted to the SW pH scale

^b Measurements made in real seawater.

from the earlier work of Mehrbach et al. (1973) and this study can adequately describe the thermodynamics of the carbonate system in ocean waters (Millero et al., 2002).

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