

Carbonate constants for estuarine waters

Frank J. Millero

Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science,
University of Miami, Miami, FL 33149, USA. Email: fmillero@rsmas.miami.edu

Abstract. Intensive studies have been made on the carbonate system in seawater. The thermodynamic constants needed to examine the components of the carbonate system have been developed by several authors. The thermodynamic constants for the dissociation of carbonic acid in seawater have been determined on different pH scales. The two most popular pH scales are the total scale: $[H^+]_T = [H^+]_F(1 + [SO_4^{2-}]_T/K_{H_2SO_4})$ and the seawater scale: $[H^+]_{SWS} = [H^+]_F\{1 + \beta_{H_2SO_4}[SO_4^{2-}]_T/K_{H_2SO_4} + \beta_{HF}[F^-]_T/K_{HF}\}$, where the brackets denote concentrations and the subscripts F and T are for free and total concentrations. The values of $K_{H_2SO_4}$ and K_{HF} are the dissociation constants for HSO_4^- and HF:

$$K_{H_2SO_4} = [H^+]_F[SO_4^{2-}]/[HSO_4^-]$$

$$K_{HF} = [H^+]_F[F^-]_F/[HF]_F$$

As long as the same pH scale and constants for seawater are used, one can evaluate the components of the carbonate system in seawater. Unfortunately, not all the measured and fitted constants have been made for dilute seawater, and thus cannot be used in estuarine waters. In this paper, the measured constants from $S = 1$ to 50 and $t = 0$ to 50°C have been determined on the total, seawater and free scale ($pH_F = -\log[H^+]_F$). These stoichiometric constants can now be used to examine the carbonate system in most estuarine waters.

Additional keywords: pH, scales, seawater.

Introduction

With the continued increasing concentrations of CO_2 in the atmosphere, there is increasing interest in understanding the carbonate system in natural waters (Millero 2007). Atmospheric CO_2 dissolves into the oceans and other natural waters, and this increasing flux of CO_2 into ocean waters is expected to decrease the pH (Caldeira and Wickett 2003; Orr *et al.* 2005; Royal Society 2005). Decreasing the pH of ocean waters can have large effects on the growth of calcareous and other organisms (Kleypas *et al.* 1999; Langdon and Atkinson 2005; Fabry *et al.* 2008; Guinotte and Fabry 2008) and the speciation of metals (Millero *et al.* 2009). Reliable thermodynamic dissociation constants for the carbonate system are needed to examine the components of the carbonate system in seawater. Unfortunately, these constants are reported on different pH scales, confusing many trying to understand the carbonate system. The various pH scales used are related to the ionic interactions of the proton with different components of seawater. The free scale defines the pH in terms of the free concentration of the proton in $\text{mol}(\text{kg sol})^{-1}$ (Khoo *et al.* 1977; Dickson 1984; Millero 1986):

$$pH_F = -\log[H^+]_F \quad (1)$$

This pH scale is the most useful for examining the effect of pH on thermodynamic and kinetic processes in the ocean (Millero 2001). The free pH can also be converted to the

thermodynamic definition of pH in terms of the activity of the proton ($a_H = [H^+]_F\gamma_H$, where γ_H is the activity coefficient of the proton on the free scale):

$$pH = -\log[a_H] \quad (2)$$

Estimation of the activity coefficient for the proton can be estimated using ionic interaction models (Millero and Pierrot 1998).

In seawater studies, the free, total and seawater scales have been used. The total scale includes the contribution for the formation of HSO_4^- to the proton concentration:

$$[H^+]_T = [H^+]_F(1 + [SO_4^{2-}]_T/K_{H_2SO_4}) \quad (3)$$

and the seawater scale (includes contributions for the formation of HSO_4^- and HF):

$$[H^+]_{SWS} = [H^+]_F(1 + [SO_4^{2-}]_T/K_{H_2SO_4} + [F^-]_T/K_{HF}) \quad (4)$$

Most of the experimentally measured constants in real seawater (Mehrbach *et al.* 1973; Mojica Prieto and Millero 2002; Millero *et al.* 2006) were made or can be easily converted to the

Table 1. A summary of the measurements made on the dissociation constants of carbonic acid in seawater on the seawater pH scale (pH_{SWS}) examined in the present study

Reference	Media	Salinity range	Temperature range	N ^A	N ^B
Mehrbach <i>et al.</i> (1973)	SW	19–43	2–35	30	33
Mojica Prieto and Millero (2002)	SW	12–45	5–45	55	99
Millero <i>et al.</i> (2006)	SW	0.1–50	1–50	466	458
The present study				551	590

^AThe number of measurements of pK₁.

^BThe number of measurements of pK₂.

Table 2. Coefficients for the fits of the values of pK₁ in seawater as a function of temperature, salinity and ionic strength on the pH_F, pH_T and pH_{SWS} scales

		pH _F scale	pH _T scale	pH _{SWS} scale
S ^{0.5}	a ₀	5.09247	13.4051	13.4038
S	a ₁	0.05574	0.03185	0.03206
S ²	a ₂	−9.279E-05	−5.218E-05	−5.242E-05
S ^{0.5} /T	a ₃	−189.879	−531.095	−530.659
S/T	a ₄	−11.3108	−5.7789	−5.8210
S ^{0.5} ln T	a ₅	−0.8080	−2.0663	−2.0664
s.e.		0.0055	0.0053	0.0053
Number		551	551	551

Table 3. Coefficients for the fits of the values of pK₂ in seawater as a function of temperature, salinity and ionic strength on the pH_F, pH_T and pH_{SWS} scales

		pH _F scale	pH _T scale	pH _{SWS} scale
S ^{0.5}		11.0637	21.5724	21.3728
S		0.1379	0.1212	0.1218
S ²		−3.788E-04	−3.714E-04	−3.688E-04
S ^{0.5} /T		−366.178	−798.292	−788.289
S/T		−23.288	−18.951	−19.189
S ^{0.5} ln T		−1.810	−3.403	−3.374
s.e.		0.0105	0.0108	0.0109
Number		590	590	590

pH_{SWS} scale (Dickson and Millero 1987; Millero *et al.* 2006). Rearrangement of Eqns (3) and (4) gives:

$$[\text{H}^+]_{\text{F}} = [\text{H}^+]_{\text{SWS}}(1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4} + [\text{F}^-]_{\text{T}}/\text{K}_{\text{HSO}_4}) \quad (5)$$

$$[\text{H}^+]_{\text{T}} = [\text{H}^+]_{\text{SWS}}(1 + (1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4} + [\text{F}^-]_{\text{T}}/\text{K}_{\text{HSO}_4})/(1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4})) \quad (6)$$

These equations can be used to convert the values of pH to different scales. Since most of the values for buffers used to calibrate pH electrodes in seawater are given on the pH_T scale (Dickson 1993), it is the preferred scale to use in oceanography (Dickson *et al.* 2007).

The conversion of the Mehrbach *et al.* (1973) constants from the pH_{SWS} to pH_T scale has been made by Lueker *et al.* (2000). Unlike the earlier equations of Dickson and Millero (1987) on the pH_{SWS} scale, they did not force their values into the known values for pure water (Harned and Scholes 1941; Harned and Bonner 1945). Since the limited measurements of Mehrbach *et al.* (1973) were made at salinities above 26, the constants on the pH_T scale given by Lueker *et al.* (2000) cannot be used at low salinities or in estuarine waters. In this paper, the Mehrbach *et al.* (1973) data, and more recent constants on the pH_{SWS} (Mojica Prieto and Millero 2002; Millero *et al.* 2006), have been converted to the pH_T and pH_F scales. The equations, derived from these constants, should be useful in more accurately examining the carbonate system in estuarine waters.

Calculations

As stated above, most of the measurements of the carbonic acid dissociation constants in real seawater were, or can be, determined on the pH_{SWS} scale. The relationships for the three scales given above can be used to convert the measurements on the pH_{SWS} scale to pH_F and pH_T. The dissociation constants on the pH_{SWS} scale are given by:

$$\text{K}_1(\text{SWS}) = [\text{H}^+]_{\text{SWS}}[\text{HCO}_3^-]/[\text{CO}_2] \quad (7)$$

$$\text{K}_2(\text{SWS}) = [\text{H}^+]_{\text{SWS}}[\text{CO}_3^{2-}]/[\text{HCO}_3^-] \quad (8)$$

Upon rearrangement, the substitution of [H⁺]_F in terms of [H⁺]_{SWS} gives:

$$\text{K}_1(\text{FREE}) = \text{K}_1(\text{SWS})/(1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4} + [\text{F}^-]_{\text{T}}/\text{K}_{\text{HF}}) \quad (9)$$

$$\text{K}_2(\text{FREE}) = \text{K}_2(\text{SWS})/(1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4} + [\text{F}^-]_{\text{T}}/\text{K}_{\text{HF}}) \quad (10)$$

The substitution of [H⁺]_T in terms of [H⁺]_{SWS} and rearranging gives:

$$\text{K}_1(\text{TOTAL}) = \text{K}_1(\text{SWS})\{(1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4})/(1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4} + [\text{F}^-]_{\text{T}}/\text{K}_{\text{HF}})\} \quad (11)$$

$$\text{K}_2(\text{TOTAL}) = \text{K}_2(\text{SWS})\{(1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4})/(1 + [\text{SO}_4^{2-}]_{\text{T}}/\text{K}_{\text{HSO}_4} + [\text{F}^-]_{\text{T}}/\text{K}_{\text{HF}})\} \quad (12)$$

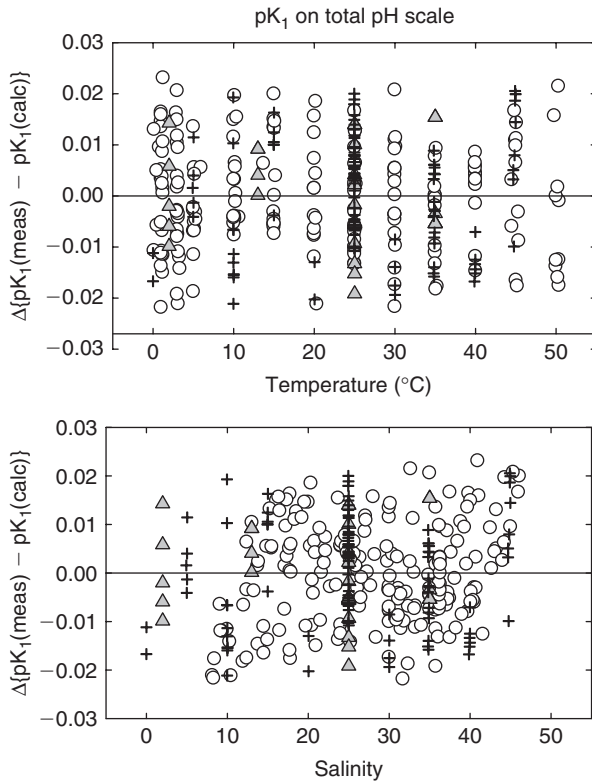


Fig. 1. The differences between the measured and calculated values of pK_1 on the total scale as a function of temperature and salinity (open circles, Millero *et al.* 2006; shaded triangles, Mehrbach *et al.* 1973; crosses, Mojica Prieto and Millero 2002).

These equations were used to convert the seawater pK_1 and pK_2 on the seawater scale to the values on the free and total scales. The values of K_{HSO_4} and K_{HF} were determined from the equations given by Dickson (1990) and Perez and Fraga (1987):

$$\begin{aligned} \ln K_{HSO_4} = & -4276.1/(T/K) + 141.328 - 23.093 \ln(T/K) \\ & + [-13\,856/(T/K) + 324.57 - 47.986 \ln(T/K)]I^{0.5} \\ & + [35\,474/(T/K) - 771.54 + 114.723 \ln(T/K)]I \\ & - 2698I^{1.5}/(T/K) + 1776I^2/(T/K) \\ & + \ln(1 - 0.001005S) \end{aligned} \quad (13)$$

$$\ln K_{HF} = 874/T - 9.68 + 0.111S^{0.5} \quad (14)$$

The ionic strength of seawater is determined from the salinity, S , using:

$$I = 19.924S/(1000 - 1.005S) \quad (15)$$

The dissociation constants used to make the conversions include the measurements of Mehrbach *et al.* (1973), Mojica-Prieto and Millero (2002) and Millero *et al.* (2006). A summary of the measurements made in these studies is given in Table 1. A total of 551 values of pK_1 and 590 values of pK_2 on the pH_{SWS} scale have been analysed using equations of the form (Millero *et al.* 2006):

$$pK_i - pK_i^0 = A_i + B_i/T + C_i \ln T \quad (16)$$

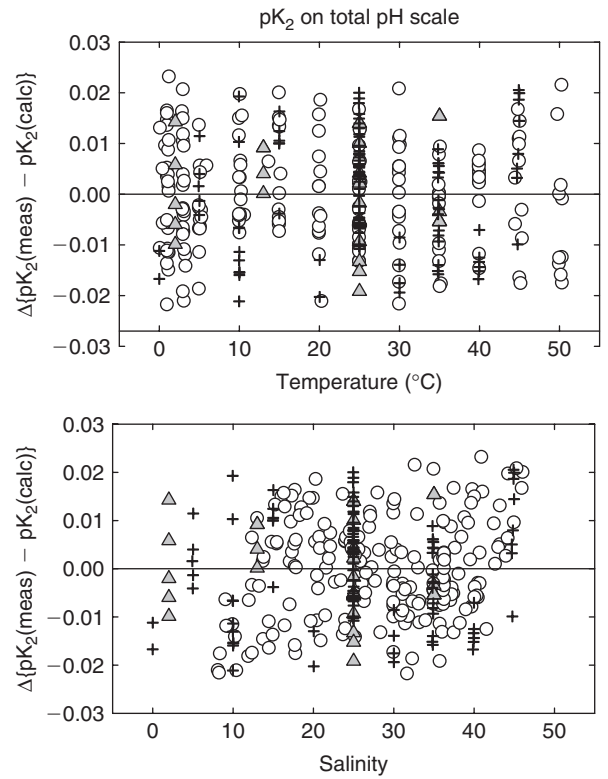


Fig. 2. The differences between the measured and calculated values of pK_2 on the total scale as a function of temperature and salinity (open circles, Millero *et al.* 2006; shaded triangles, Mehrbach *et al.* 1973; crosses, Mojica Prieto and Millero 2002).

where T is the absolute temperature and A_i , B_i and C_i are salinity dependant constants. The values of pK_i^0 in pure water are taken from Harned and Scholes (1941) and Harned and Bonner (1945), then fitted to the following equations (Millero *et al.* 2006):

$$pK_1^0 = -126.34048 + 6320.813/T + 19.568224 \ln T \quad (17)$$

$$pK_2^0 = -90.18333 + 5143.692/T + 14.613358 \ln T \quad (18)$$

The values of the adjustable parameters A_i , B_i and C_i are:

$$A_i = a_0S^{0.5} + a_1S + a_2S^2 \quad (19)$$

$$B_i = a_3S^{0.5} + a_4S \quad (20)$$

$$C_i = a_5S^{0.5} \quad (21)$$

A summary of the coefficients for all of the fits are provided in Tables 2 and 3, respectively, for pK_1 and pK_2 on all the pH scales. The standard errors of the fits for the pK_1 and pK_2 are similar for all the pH scales (0.005 for pK_1 and 0.010 for pK_2). The standard errors for the fits of pK_1 and pK_2 on the SWS scale are shown in Figs 1 and 2, with most of the deviations falling within two times the standard error of each fit.

The importance of using these equations for diluted seawater or estuarine waters is shown in Fig. 3, where the constants of pK_1 and pK_2 on the total scale of Lueker *et al.* (2000) at $S = 35$ are compared with the values determined in this study. The new

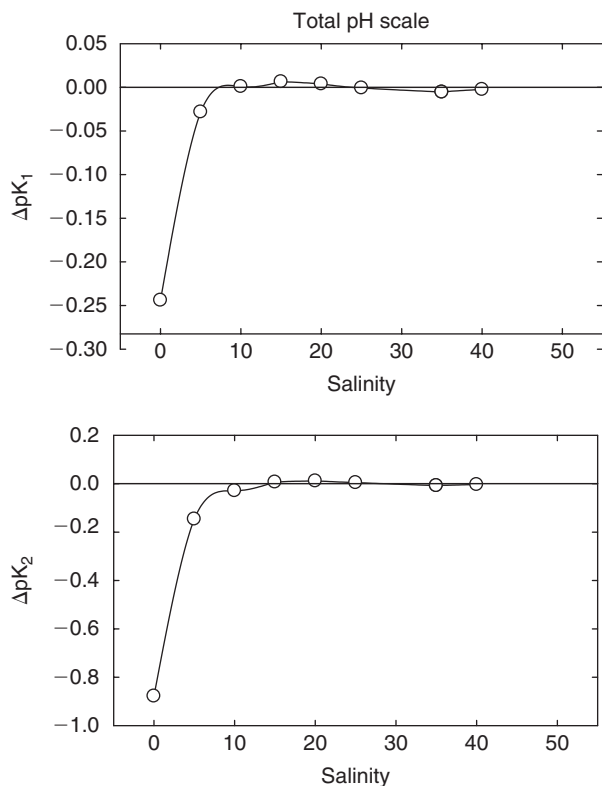


Fig. 3. The differences in the values of pK_1 and pK_2 on the total scale by Lueker *et al.* (2000) and the present study at 25°C as a function of salinity.

equations are in good agreement for salinities from 10 to 40 for pK_1 (± 0.005) and from 15 to 40 for pK_2 (± 0.008) with the equations of Lueker *et al.* (2000), but differ significantly at salinities below 10 to 15.

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