ELSEVIER

Marine Chemistry 70 (2000) 105–119

MARINE CHEMISTRY

www.elsevier.nl/locate/marchem

Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium

Timothy J. Lueker *, Andrew G. Dickson, Charles D. Keeling

Scripps Institution of Oceanography, University of California, San Diego, 341 Endurance Hall, 9500 Gilman Drive, La Jolla, CA 92093-0236, USA

Received 15 May 1999; received in revised form 14 December 1999; accepted 15 December 1999

Abstract

The partial pressure of carbon dioxide in the ocean's surface waters, precisely expressed as the fugacity (fCO_2) is determined from dissolved inorganic carbon (DIC) and total alkalinity (TA), and the first and second dissociation constants of carbonic acid, K_1 and K_2. The original measurements of K_1 and K_2 reported by Mehrbach et al. [Mehrbach, C., Culberson, C.H., Hawley, J.E., Pytkowicz, R.M., 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnol. Oceanogr. 18, 897–907] are reformulated to give equations for $\mathrm{p}K_1$ and $\mathrm{p}K_2$ ($\mathrm{p}K = -\log_{10} K$) as a function of seawater temperature and salinity, consistent with the ''total hydrogen ion'' concentration scale:

$$\mathrm{p}K_1 = 3633.86/T - 61.2172 + 9.67770 \ln T - 0.011555\, S + 0.0001152\, S^2$$

$$\mathrm{p}K_2 = 471.78/T + 25.9290 - 3.16967 \ln T - 0.01781\, S + 0.0001122\, S^2$$

By equilibrating solutions of seawater with gas mixtures of known composition, we demonstrate that the above formulations of K_1 and K_2 give calculated fCO_2 values that agree with equilibrated values to 0.07 ± 0.50% (95% confidence interval, fCO_2 up to 500 μatm). Formulations of K_1 and K_2 based on other studies resulted in calculated fCO_2 values approximately 10% lower than the measurements. Equilibrations at fCO_2 above 500 μatm yielded measured fCO_2 values higher than calculated values by on average 3.35 ± 1.22% (95% confidence interval). The cause for the fCO_2 dependence of the results is not known.

The uncertainties in $\mathrm{p}K_1$ and $\mathrm{p}K_2$ were combined with the analytical uncertainties typical of contemporary measurements of DIC and TA to reveal the expected reliability of seawater fCO_2 calculated from these parameters. For example, an

---

* Corresponding author. Tel.: +1-619-534-4230x19.
E-mail address: tlueker@ucsd.edu (T.J. Lueker).

PII: S0304-4203(00)00022-0

uncertainty of 1.0 μmol kg^{-1} in DIC and 2 μmol kg^{-1} in TA (1 standard deviation (s.d.)) will result in uncertainty of the calculated $f\mathrm{CO}_2$ of 1% or ±3.5 μatm at 350 μatm (1 s.d.).

Keywords: equilibrium constants; carbonic acid; fugacity of carbon dioxide; dissolved inorganic carbon; titration alkalinity

1. Introduction

The continuing increase of atmospheric CO_2 results in a net flux of carbon into the surface oceans. Quantifying this oceanic sink for CO_2 is vital to our understanding of the carbon cycle, especially for reducing uncertainties in predictions of the impact of future CO_2 emissions on climate (see, e.g. IPCC, 1996; Joos, 1996). The uptake of carbon by the oceans is currently being evaluated from several ocean carbon models (Orr, 1996). To calculate the net air–sea flux of CO_2, the models must determine $\Delta p\mathrm{CO}_2$, the difference between the CO_2 partial pressure in the atmosphere, and that of the surface ocean, more precisely expressed as the CO_2 fugacity ($f\mathrm{CO}_2$) (Weiss, 1974; DOE, 1994). The $f\mathrm{CO}_2$ is often computed from a knowledge of seawater temperature, salinity, and the variables dissolved inorganic carbon (DIC) and total alkalinity (TA), in part because the concentrations of DIC and TA (expressed in moles per kilogram of seawater) remain constant while seawater undergoes changes in temperature and/or pressure (see Dyrssen and Sillén, 1967). The DIC and TA are related to $f\mathrm{CO}_2$ with the first and second dissociation constants of carbonic acid in seawater K_1 and K_2. Accurate knowledge of K_1 and K_2 in seawater is a prerequisite for comparing the ocean carbon model results to direct measurements of CO_2 parameters in the oceans. Accurate values of the constants are also needed for calculating ocean inventories of anthropogenic carbon, and other aspects of ocean carbon cycle research (see, e.g. Brewer et al., 1997).

Recognizing the importance of obtaining accurate determinations of K_1 and K_2, several researchers have published measurements of these and related quantities (Hansson, 1972, 1973a,b; Mehrbach, 1973; Mehrbach et al., 1973; Millero, 1979, 1995; Plath et al., 1980; Johansson and Wedborg, 1982; Dickson and Millero, 1987, 1989; Goyet and Poisson, 1989; Roy et al., 1993). In addition, a number of investigators have examined the thermodynamic consistency of various formulations of the constants with analytical measurements made on seawater samples (Takahashi et al., 1976; Dickson, 1977; Millero et al., 1993; Stoll et al., 1993; Clayton et al., 1995; Lee, 1996; Lee and Millero, 1995; Lee et al., 1996, 1997; Murphy, 1996; Lueker, 1998; McElligot et al., 1998; Wanninkhof et al., 1999). Unfortunately, these many studies have not resulted in a consensus regarding the ‘‘best’’ choice of expressions for K_1 and K_2 as a function of salinity and temperature.

Here we demonstrate how well seawater $f\mathrm{CO}_2$ can be predicted from DIC and TA, and equations for K_1 and K_2 based on the measurements of Mehrbach et al. (1973). While more narrow in scope than some previous studies, our methods apply directly to the calculation of $f\mathrm{CO}_2$ from DIC and TA. In our laboratory the $p\mathrm{CO}_2$ of seawater was brought to a known and verified value with compressed gas mixtures calibrated in the standards laboratory of C.D. Keeling. The CO_2 concentrations in both the seawater solutions and the gases were determined with rigorously established measurement uncertainties. The results of the seawater equilibrations support the accuracy of formulations based on the measurements of Mehrbach (Mehrbach et al., 1973). Previously, Dickson and Millero (1987, 1989) adjusted the data of Mehrbach et al. (1973) to provide interpolation equations based on the $[\mathrm{H}_{\mathrm{sws}}]$ concentration scale. Here, we have readjusted Mehrbach's original data to the ‘‘total hydrogen ion’’ concentration scale to provide equations compatible with other dissociation constant formulations for important acid–base species in seawater (DOE, 1994).[1] A thorough discussion of the merits of the ‘‘total hydrogen ion’’ concentration scale for seawater studies is given elsewhere (Dickson, 1993).

We evaluated the reliability of equations based on the data of Mehrbach et al. (1973) by calculating

---

[1] Calculation of $f\mathrm{CO}_2$ using the equations for K_1 and K_2 from Dickson and Millero (1987, 1989) combined with the equations from DOE (1994) will result in an error of over 2 μatm for seawater at 25°C and 350 μatm $f\mathrm{CO}_2$.

fCO_2 from DIC, TA and K_1 and K_2, and comparing the results to the known concentrations of the gases used to equilibrate the seawater. Solutions having constant TA were equilibrated with gas mixtures having various CO_2 mole fractions over a range of temperatures. After equilibration, the CO_2 mole fraction of equilibrator gas phase ($x(CO_2)$) was measured, and compared to the fCO_2 value calculated from the DIC, TA, salinity, temperature, and the equations for K_1 and K_2. The uncertainties in the measurement of $x(CO_2)$, DIC, and TA were evaluated from replicate determinations. The measurement uncertainties allow us to evaluate the reliability in the agreement between the calculated and measured fCO_2 values. After establishing the likely errors associated with our equations for K_1 and K_2, we evaluated the potential uncertainties in fCO_2 calculated from contemporary DIC and TA measurements having well documented uncertainties. We report estimates of the uncertainties in surface ocean fCO_2 data resulting from the combined uncertainties in DIC, TA, K_1, K_2, and other necessary chemical and hydrographic data.

We begin the paper with a detailed reevaluation of the results of Mehrbach et al. (1973) and adjust them to the total hydrogen ion concentration scale. Next, the details of the seawater equilibration experiments are summarized. We also report the results of replicate analyses used to evaluate the measurement uncertainties. The equilibration results are presented as the differences between fCO_2 inferred from the equilibrator gas phase, and fCO_2 calculated using the newly formulated equations for K_1 and K_2. We conclude with an evaluation of the uncertainty of fCO_2 data calculated from measurements of DIC and TA, and address additional areas of uncertainty indicated by this and other studies.

2. Thermodynamic background

The reactions that take place when carbon dioxide dissolves in water can be represented by the following series of equilibria:

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

$$CO_2(aq) + H_2O = H_2CO_3 \tag{2}$$

$$H_2CO_3 = H^+ + HCO_3^- \tag{3}$$

$$HCO_3^- = H^+ + CO_3^{2-} \tag{4}$$

The notations (g) and (aq) refer to the state of the species, i.e. gas or aqueous solution. Unfortunately, it is difficult to distinguish between the species $CO_2(aq)$ and H_2CO_3 by analytical means. It is thus usual to lump the concentrations of $CO_2(aq)$ and H_2CO_3 together and to express this sum as the concentration of a hypothetical species, CO_2^* (this corresponds to defining the standard states for these species employing the so-called hydrate convention — Lewis and Randall, 1961).

Reactions (1), (2) and (3) are redefined in terms of this hypothetical species:

$$CO_2(g) = CO_2^*(aq) \tag{5}$$

$$CO_2^*(aq) = H^+ + HCO_3^- \tag{6}$$

The equilibrium relationships between the concentrations of these various species can then be written as:

$$K_0 = [CO_2^*]/fCO_2 \tag{7}$$

$$K_1 = [H^+][HCO_3^-]/[CO_2^*] \tag{8}$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \tag{9}$$

In these expressions, fCO_2 is the fugacity of carbon dioxide in the gas phase and brackets represent total stoichiometric concentrations of the particular chemical species enclosed, expressed in moles per kilogram solution.

3. The measurements of Mehrbach

Mehrbach et al. (1973) determined what they call the ‘‘apparent’’ dissociation constants of carbonic acid in seawater. They defined

$$K_1' = a(H^+)[HCO_3^-]/[CO_2^*] \tag{10}$$

$$K_2' = a(H^+)[CO_3^{2-}]/[HCO_3^-] \tag{11}$$

where $a(H^+)$ is defined as $10^{-pH(NBS)}$ (see Dickson, 1984) and the brackets represent total concentrations of the enclosed species in moles per kilogram of solution. All their measurements used surface seawater from the Oregon coast ($S = 31.5$) which had been filtered, and then either diluted with deionized distilled water, or concentrated by evaporation to reach the desired salinity. K_1' was estimated from a potentiometric titration of natural seawater. $K_1'K_2'$ was estimated by adding sodium bicarbonate to alkalinity free seawater until a stable pH, defined as pH^0, was observed. Assuming the relationship $\mathrm{pH}^0 = \frac{1}{2}(\mathrm{p}K_1' + \mathrm{p}K_2')$ to be valid, K_2' was evaluated from the product $K_1'K_2'$ and the K_1' determined by titration.

4. Data processing to convert to total hydrogen ion pH scale

4.1. Interpolation of pH^0 data

Although Mehrbach et al. (1973) made measurements at particular temperatures, they did not make their measurements of K_1' and of pH^0 at identical salinities. To obtain K_2', it is thus necessary to estimate K_1' at those salinities where pH^0 was measured (i.e. $K_1'K_2'$ was estimated) and hence calculate K_2' values for those temperatures and salinities (see Dickson and Millero, 1987, 1989).

Mehrbach et al. approached this problem by first fitting their measured values of K_1' and of pH^0 to interpolating functions of T and S. Values of K_2' were then calculated for a range of salinity and temperature pairs (Mehrbach et al., 1973 — Table 5). Finally, 40 of these values were selected, and an interpolating equation fitted to this (smoothed) data (resulting in the excessive number of terms used in their original interpolating equation for K_2').

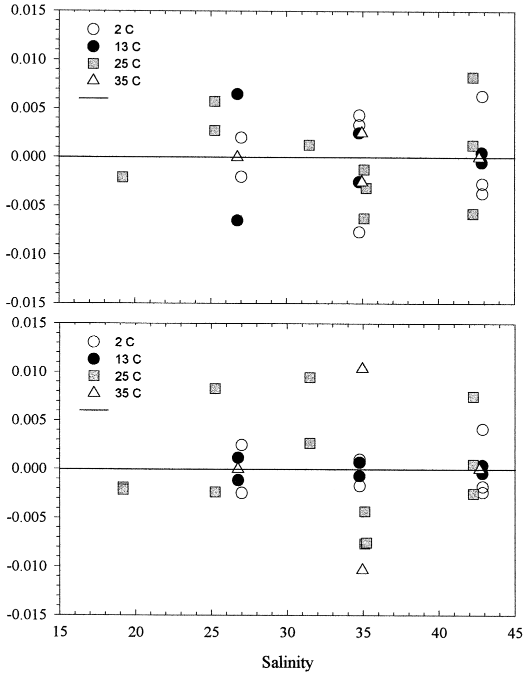


Fig. 1. Distribution of residuals around the quadratic fits listed in Table 2.

Table 1
Coefficients for quadratic interpolation functions of the form $y = a_0 + a_1S + a_2S^2$. A separate function is used at each temperature

t (°C)	$K_1' \times 10^6$	f_{H}
2.00	3.214608E − 07	6.068058E − 01
	1.168698E − 08	7.534132E − 03
	− 5.219210E − 11	− 5.250247E − 05
13.00	4.704946E − 07	6.786108E − 01
	1.143828E − 08	3.405377E − 04
	− 2.490289E − 11	5.135667E − 05
25.00	5.056381E − 07	6.635395E − 01
	1.679991E − 08	4.435003E − 04
	− 7.665929E − 11	7.826052E − 06
35.00	5.590513E − 07	7.185356E − 01
	1.910042E − 08	− 5.846244E − 03
	− 1.193293E − 10	8.783492E − 05
s[a]	0.0049	0.0043

[a] Estimated "goodness of fit"; pooled value for measurements at all temperatures.

In this work, as in Dickson and Millero (1987, 1989), the interpolation was carried out separately at each separate temperature using a quadratic function in salinity. The coefficients are given in Table 1. Values of K_2' were then calculated at the temperature and salinity at which $K_1'K_2'$ had been measured. An additional set of interpolating equations was also constructed for f_{H} (the apparent total hydrogen ion activity coefficient, see Culberson and Pytkowicz, 1973) for use in the conversion to concentration-based pH scales (next section). The quality of these fits can be seen in Fig. 1, the root mean square differences between measured and interpolated data for the whole data set are 0.0021 in $\mathrm{p}K_1'$ and 0.0024 in log f_{H}.

Table 2
Measurements of Mehrbach et al. (1973) expressed both on the original (NBS) pH scale, and on the total hydrogen ion concentration scale

t (°C)	S	$\mathrm{p}K'_{1\,(\mathrm{NBS})}$	$\mathrm{p}K'_{2\,(\mathrm{NBS})}$	$\mathrm{p}K_1$ $[\mathrm{H}]_\mathrm{T}$	$\mathrm{p}K_2$ $[\mathrm{H}]_\mathrm{T}$
2.00	26.67		9.5564		9.4504
2.00	26.67		9.5524		9.4470
2.00	27.01	6.2208		6.1152	
2.00	27.01	6.2243		6.1210	
2.00	34.66		9.4288		9.3438
2.00	34.66		9.4248		9.3399
2.00	34.66		9.4327		9.3477
2.00	34.66		9.4405		9.3556
2.00	34.78	6.1780		6.0915	
2.00	34.78	6.1778		6.0908	
2.00	34.78	6.1762		6.0956	
2.00	41.54		9.3745		9.3037
2.00	42.88	6.1373		6.0703	
2.00	42.88	6.1376		6.0711	
2.00	42.88	6.1412		6.0694	
13.00	26.76	6.1206		5.9851	
13.00	26.76	6.1192		5.9916	
13.00	26.92		9.3776		9.2464
13.00	26.92		9.3815		9.2503
13.00	34.76	6.0764		5.9614	
13.00	34.76	6.0771		5.9650	
13.00	35.20		9.2869		9.1744
13.00	35.20		9.2869		9.1744
13.00	42.85	6.0384		5.9458	
13.00	42.85	6.0388		5.9467	
13.00	42.90		9.2038		9.1116
25.00	19.16		9.3180		9.1545
25.00	19.16		9.3141		9.1506
25.00	19.16		9.3082		9.1447
25.00	19.16		9.3180		9.1545
25.00	19.19	6.0960		5.9338	
25.00	19.19	6.0959		5.9337	
25.00	25.17		9.2325		9.0733
25.00	25.17		9.2286		9.0694
25.00	25.17		9.2246		9.0655
25.00	25.25	6.0591		5.8964	
25.00	25.25	6.0539		5.8931	
25.00	31.22		9.1530		8.9984
25.00	31.22		9.1471		8.9925
25.00	31.22		9.1510		8.9964
25.00	31.49	6.0226		5.8674	
25.00	31.49	6.0195		5.8643	
25.00	34.90		9.1224		8.9707
25.00	34.90		9.1224		8.9707
25.00	34.90		9.1184		8.9667
25.00	35.10	5.9977		5.8470	
25.00	35.10	5.9963		5.8487	
25.00	35.23	5.9957		5.8462	
25.00	42.21		9.0405		8.8948
25.00	42.21		9.0405		8.8948
25.00	42.26	5.9701		5.8281	
25.00	42.26	5.9673		5.8209	
25.00	42.26	5.9661		5.8153	
35.00	26.75	6.0067		5.8117	
35.00	27.04		9.1082		8.9129
35.00	27.04		9.1082		8.9129
35.00	34.95	5.9621		5.7678	
35.00	34.95	5.9704		5.7726	
35.00	35.01		9.0083		8.8122
35.00	35.01		9.0102		8.8142
35.00	42.67	5.9367		5.7472	
35.00	42.94		8.9173		8.7281
35.00	42.94		8.9173		8.7281

4.2. Conversion between pH scales

The various pH scales for sea water can be related through the following expressions:

$$a(\mathrm{H}^+) = 10^{-\mathrm{pH(NBS)}} = f_\mathrm{H}[\mathrm{H}_\mathrm{sws}] \tag{12}$$

$$[\mathrm{H}_\mathrm{sws}] = [\mathrm{H}_f]\left(1 + S_\mathrm{T}/K(\mathrm{HSO}_4^-) + F_\mathrm{T}/K(\mathrm{HF})\right) \tag{13}$$

$$[\mathrm{H}_\mathrm{T}] = [\mathrm{H}_f]\left(1 + S_\mathrm{T}/K(\mathrm{HSO}_4^-)\right) \tag{14}$$

Converting the values of Mehrbach et al. from the NBS pH scale to the total hydrogen ion scale can be thought of as a two-step process. First, a conversion to the sea water pH scale by dividing the various apparent equilibrium constants by the appropriate values of f_H, and then conversion of this concentration scale to the total scale by correcting for the presence of fluoride ion:

$$K_\mathrm{T} = \frac{K'}{f_\mathrm{H}}\left(\frac{1 + S_\mathrm{T}/K(\mathrm{HSO}_4^-)}{1 + S_\mathrm{T}/K(\mathrm{HSO}_4^-) + F_\mathrm{T}/K(\mathrm{HF})}\right) \tag{15}$$

In converting K'_1, the value of f_H used in each case was the one determined in the original titration; to convert K'_2, the value of f_H used was obtained from the appropriate quadratic fit (Table 1).

4.3. Interpolating equations for K_1 and K_2

For convenience, the results for K_1 and K_2, reported in Table 2, have been fit using least-squares

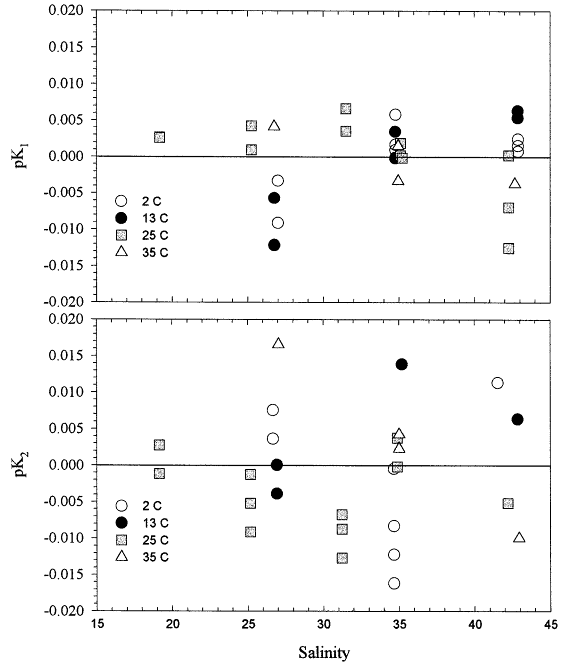


Fig. 2. Residuals of the least-squares fit of the Mehrbach data to the interpolation equations for pK_1 and pK_2.

procedures to provide the following interpolating equations:

$$\mathrm{p}K_1 = 3633.86/T - 61.2172 + 9.67770 \ln T - 0.011555\, S + 0.0001152\, S^2 \quad (16)$$

$$\mathrm{p}K_2 = 471.78/T + 25.9290 - 3.16967 \ln T - 0.01781\, S + 0.0001122\, S^2 \quad (17)$$

where T is in Kelvin and S is salinity expressed on the practical salinity scale for seawater. The root mean square deviation is 0.0055 in pK_1 and 0.0100 in pK_2. The residuals are shown in Fig. 2.

5. Gas–solution equilibrations

5.1. Introduction

Measurements of the equilibrium partitioning of carbon dioxide between seawater and a gas phase indicate the reliability of formulations for K_1 and K_2. Prior to our study, Lee (1996) and Murphy (1996) also equilibrated seawater and air to evaluate the various equations for determining K_1 and K_2. The conclusions based on those equilibration studies were decidedly mixed, and different formulations of K_1 and K_2 were recommended for use in calculating various relationships between the inorganic carbon parameters in seawater (Lee, 1996; Lee and Millero, 1995; Lee et al., 1996; Murphy, 1996). Both Lee et al. and Murphy et al. included pH measurements when interpreting their experimental results.

Our equilibration results differ from previous studies because we controlled the $f\mathrm{CO}_2$ of the system with compressed gas mixtures of known composition. We did not attempt to evaluate K_1 and K_2 directly. Instead we compare the $f\mathrm{CO}_2$ measured in the equilibrator gas phase to the known concentrations of the gas mixtures, and to the $f\mathrm{CO}_2$ calculated from DIC, TA, and the equations for K_1 and K_2. We insured the completeness of the equilibration and the reliability of the CO_2 sampling, extraction, and measurement procedures by verifying that the $f\mathrm{CO}_2$ observed at equilibrium was the value expected from the concentration of CO_2 in the gas mixtures. Replicate equilibrations of seawater solution with gas standards enabled the precision of individual CO_2 determinations to be established.

The DIC and $f\mathrm{CO}_2$ were determined using the same equipment and procedures that were employed to calibrate global ocean carbon research programs (Keeling et al., 1986, 2000; UNESCO, 1991; Dickson, 1992; Dickson et al., 2000a). TA measurements were also checked against the methods used in the analyses of certified reference materials (Dickson et al., 2000b). The results of our study are applicable to global data bases assembled under the auspices of WOCE, JGOFS, and other programs when the DIC and TA measurements were calibrated against the certified reference materials provided by A. Dickson (UNESCO, 1991; Dickson et al., 2000a).

5.2. Materials and methods

The seawater chosen for this study was collected from the Sargasso Sea (Hydrostation ''S'', 31°50′N, 64°10′W) or the North Pacific subtropical gyre (Station ALOHA, 22°45′N, 158°W). Seawater was sampled from between 2- and 25-m depths. Sample aliquots were collected in 1-l reagent style Pyrex bottles and immediately poisoned with 100 μl of saturated $HgCl_2$ solution and sealed with greased ground-glass stoppers.

Each experiment consisted of equilibration of a gas mixture with seawater, and determination of the equilibrium mole fraction of CO_2 in the gas phase, and of the DIC in the solution. The solution alkalinity (TA) was not varied, and was evaluated prior to introducing the solutions into the equilibrator, and periodically thereafter. Each seawater sample was equilibrated over a range of fCO_2 by employing several gas mixtures.

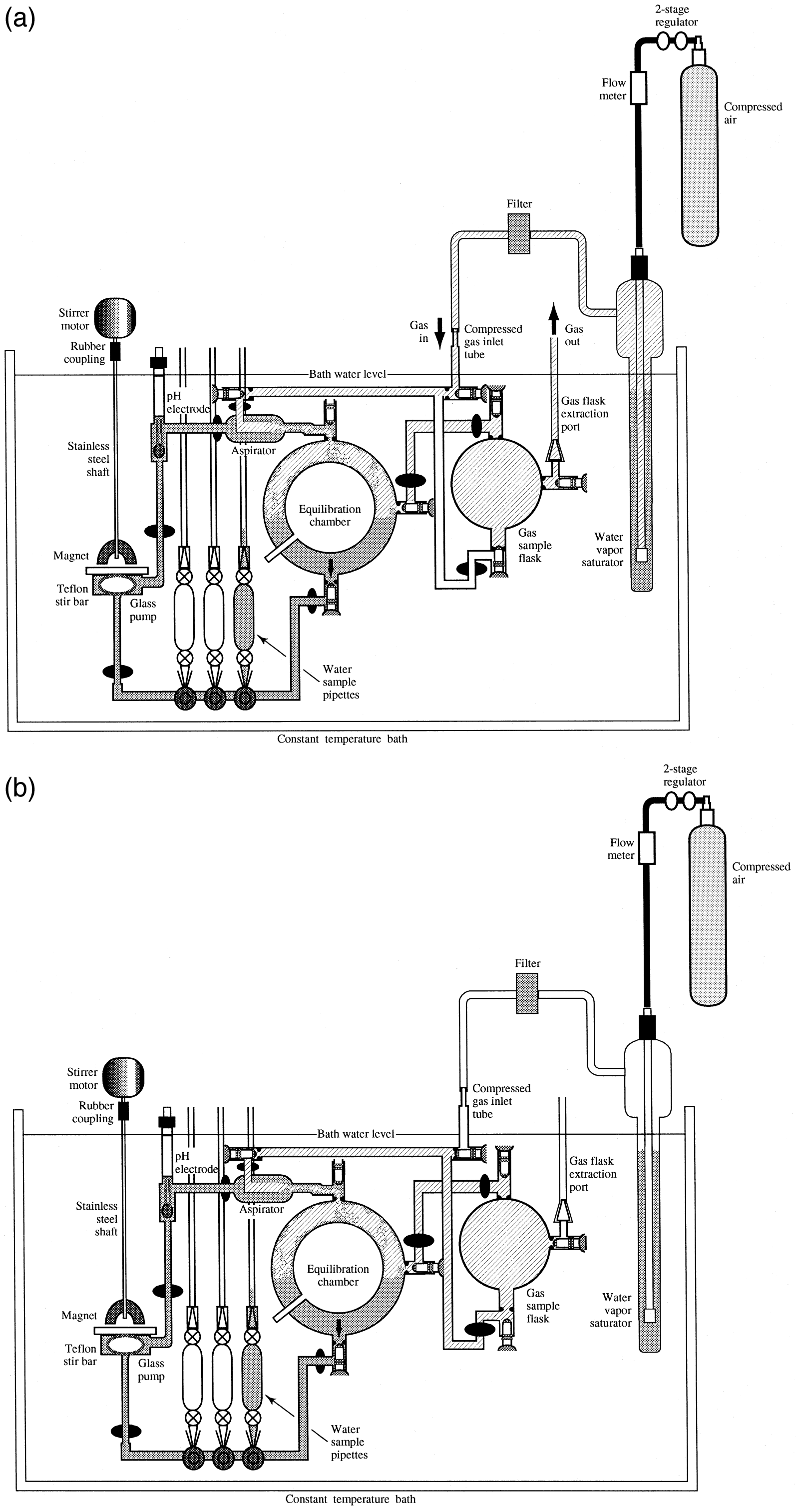
The equilibrator and vacuum extraction system were designed and built to achieve complete and stable thermodynamic equilibrium of CO_2 between the gas and solution phases in a closed system and to provide for sampling of the gas and solution without disturbing the equilibrium. The equilibrator (Fig. 3) based on a design from Benson et al. (1979) consisted of an equilibration chamber, solution pump, aspirator, gas sample flask, solution sample pipette manifold, and a pH electrode. To insure that the equilibrator was a closed system with respect to CO_2, all components, with the exception of the pump impeller (a Teflon-coated stir bar) were constructed of borosilicate glass. Stopcocks had glass plugs and double viton rubber o-rings. Components were connected with glass ball and socket joints sealed with Apiezon type-W black wax. The equilibrator was mounted on a framework constructed of 1/2-in. stainless steel rods. The Radiometer combination glass electrode (Model # GK240TC) was sealed in the equilibrator using an Ace glass o-ring seal. To control temperature, the equilibrator was immersed in a 280-l water bath. The temperature was regulated using a proportional temperature controller (YSI model 72) and monitored to a precision of 0.001°C using a platinum resistance thermometer (Hart Scientific model 1502), and to a precision of 0.01°C using mercury thermometers. The total pressure in the equilibrator was controlled by briefly venting the equilibrator to the atmospheric pressure in the laboratory. The laboratory pressure was determined to 0.1 Torr with a National Weather Service type barometer mounted in the laboratory.

Equilibration of the gas and solution was accomplished in two steps. In the first step, the fCO_2 of the solution was established by circulating either a CO_2-in-air or CO_2-in-N_2 mixture from a compressed gas cylinder through the equilibrator (Fig. 3a). In the second step, the equilibrator was closed and the gas phase circulated internally to fully equilibrate the CO_2 in the gas and solution phases (Fig. 3b). The progress of each equilibration was evaluated from changes in the emf, measured with the combination pH electrode in the solution stream, shown in Fig. 3a. The equilibration time constant, evaluated from the emf data, varied from 4 to 12 min when the equilibrator was operating in the closed configuration, and from 15 to 60 min in the flow-through configuration (Lueker, 1998). The amount of time allowed to establish equilibrium was 4 h for the gas flow-through equilibration, followed by one additional hour in the closed configuration. After fully equilibrating the phases, a sample of the gas phase and of the solution were isolated in the equilibrator. The CO_2 in the gas sample was separated from the other gases under vacuum using liquid nitrogen, and later determined manometrically. The solution aliquot was acidified and the liberated CO_2 was collected, also under vacuum with liquid nitrogen, and determined manometrically. The extraction and measurement procedures are detailed elsewhere (Lueker, 1998; Keeling et al., 2000).

The TA of the solutions was determined by potentiometric titration with HCl solution in a closed titration cell. The titration data, consisting of emf and HCl volume pairs, were processed using a nonlinear least squares minimization procedure (Dickson, 1981; DOE, 1994; Lueker, 1998). The titration results were checked by also analyzing standard and equilibrated seawater solutions with the open cell titration system used to certify seawater reference materials (Dickson et al., 2000a). The titration methodology is described in detail by Lueker (1998).

5.3. Results

For each equilibration experiment, an fCO_2 was calculated from the DIC, TA, temperature and salinity and the formulations of pK_1 and pK_2 (Eqs. (16) and (17)). In the following discussion and figures, the results are denoted ‘‘calculated fCO2’’. For the same experiment, the $x(CO_2)$ measured in the equilibrator gas phase was used to infer the equilibrium


(a)
2-stage regulator
Flow meter
Compressed air
Filter
Stirrer motor
Rubber coupling
Gas in
Compressed gas inlet tube
Gas out
Bath water level
pH electrode
Aspirator
Gas flask extraction port
Stainless steel shaft
Equilibration chamber
Magnet
Gas sample flask
Water vapor saturator
Teflon stir bar
Glass pump
Water sample pipettes
Constant temperature bath
(b)
2-stage regulator
Flow meter
Compressed air
Filter
Stirrer motor
Rubber coupling
Compressed gas inlet tube
Bath water level
pH electrode
Aspirator
Gas flask extraction port
Stainless steel shaft
Equilibration chamber
Magnet
Gas sample flask
Water vapor saturator
Teflon stir bar
Glass pump
Water sample pipettes
Constant temperature bath

fCO_2 value, denoted measured fCO_2 (Weiss, 1974) from:

$$fCO_2 = x(CO_2)\,P\exp\Big[\Big(B_{CO_2} + 2\big(1-x(CO_2)\big)^2\delta\Big)P/RT\Big] \qquad (18)$$

where $x(CO_2)$ represents the mole fraction of CO_2 in the gas, P represents the total pressure in the equilibrator, B_{CO_2} represents the 2nd virial coefficient of CO_2, δ is found from the cross-virial coefficient of the mixture CO_2 and air.

Weiss (1974) gives relationships for both B_{CO_2} and δ in cubic centimeters per mole:

$$B_{CO_2} = -1636.75 + 12.0408T - (3.27957\times10^{-2})T^2 + (3.16528\times10^{-5})T^3 \qquad (19)$$

$$\delta = 57.7 - 0.118\,T \qquad (20)$$

The differences, expressed as ΔfCO_2 (measured − calculated), were determined for each equilibration. To compare ΔfCO_2 values for equilibrations at all temperatures and CO_2 fugacities, we plot relative differences, expressed as a percentage of the measured fCO_2, in Fig. 4. The equilibrator measurement data are provided in Table 3.

The uncertainties of the ΔfCO_2 were characterized from the analytical uncertainties in measured fCO_2 DIC, and TA, and are detailed in the next section. The uncertainty of each ΔfCO_2 was estimated by propagating the errors in the measurements (Bevington, 1969):

$$\text{s.d.}\,\Delta fCO_2 = \left\{(\text{s.d.}\ fCO_2)^2 + \left(\frac{\partial fCO_2}{\partial \text{DIC}}\right)^2(\text{s.d.}\,\text{DIC})^2 + \left(\frac{\partial fCO_2}{\partial \text{TA}}\right)^2(\text{s.d.}\,\text{TA})^2\right\}^{1/2} \qquad (21)$$

The error bars shown in Fig. 4 represent ±2s.d. in ΔfCO_2.

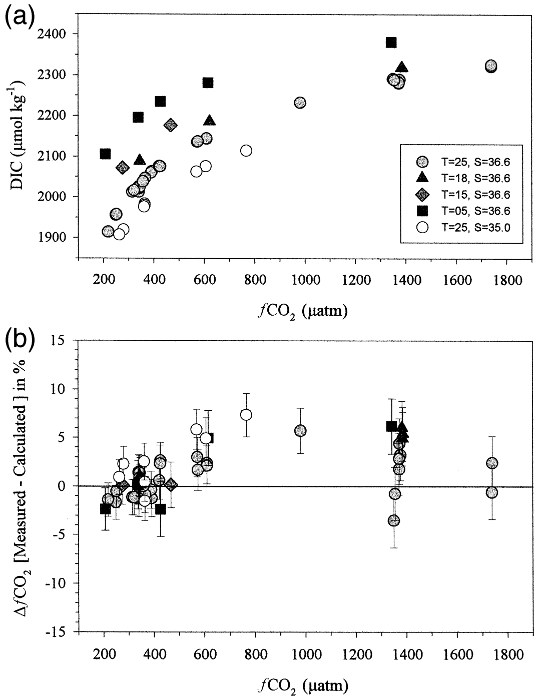


Fig. 4. (a) Equilibration experiments. Seawater samples were equilibrated at 25, 18, 15, and 5°C. (b) The differences between measured fCO_2 and fCO_2 calculated from DIC and TA. The relative differences are expressed as a percentage of the calculated fCO_2 value, in percent.

The ΔfCO_2 results in Fig. 4 show a tendency toward more positive values for equilibrations having fCO_2 above 500 μatm. Noting this apparent shift in equilibration results, we evaluated the equilibration data below and above 500 μatm separately as shown in Fig. 5a and b. Note that in doing so we have characterized the results of this study in the context of contemporary surface ocean fCO_2, typically ranging from 150 to 500 μatm (Takahashi et al., 1997). The mean relative difference for equilibrations having fCO_2 less than 500 μatm was 0.07 ± 0.50% (95% confidence interval, $n = 31$). Equilibrations having fCO_2 above 500 μatm had a mean relative difference of 3.3 ± 1.2% (95% confidence interval, $n = 21$).

Fig. 3. (a) Equilibrator operating in gas flow-through configuration is shown. The diagonal striped lines indicate the path of the gas supplied from the compressed gas cylinder. (b) Equilibrator operating in the closed gas loop configuration is shown. The diagonal striped lines indicate the path of the gas flow through the aspirator, equilibration chamber, and gas flask.

Table 3
Equilibrator data

Temperature (°C)	Salinity	DIC (μmol kg^{-1})	TA (μmol kg^{-1})	fCO$_2$ (μatm)
5.06	36.602	2195.7	2387.3	338.1
5.07	36.599	2105.3	2385.5	207.1
5.09	36.599	2382.1	2385.5	1342.5
5.10	36.599	2281.8	2385.5	615.8
5.13	36.599	2234.7	2385.5	426.2
15.06	36.602	2177.0	2387.3	467.5
15.10	36.602	2072.0	2387.3	276.1
18.03	36.546	2319.7	2383.3	1385.2
18.04	36.546	2319.1	2383.3	1385.8
18.04	36.546	2318.1	2383.3	1382.6
18.05	36.546	2089.2	2383.3	343.8
18.05	36.546	2088.6	2383.3	344.7
18.05	36.546	2088.0	2383.3	343.8
18.08	36.546	2186.4	2383.3	621.7
18.08	36.546	2185.9	2383.3	622.3
24.98	36.590	2292.0	2387.6	1349.6
24.98	36.583	1956.6	2387.6	248.1
24.99	36.590	2289.3	2387.6	1354.1
24.99	36.602	2038.8	2387.3	357.2
24.99	36.602	2137.4	2387.3	574.6
24.99	36.590	2016.8	2387.6	321.4
24.99	36.590	2326.0	2387.6	1738.5
24.99	36.590	2322.6	2387.6	1739.2
25.01	36.583	1957.6	2387.6	251.3
25.01	36.583	1915.1	2375.3	217.9
25.02	36.546	2024.3	2383.3	342.9
25.02	36.546	2025.3	2383.3	343.2
25.04	36.546	2023.8	2383.3	339.9
25.04	36.546	2281.2	2383.3	1372.0
25.04	36.546	2283.0	2383.3	1371.4
25.05	36.546	2144.5	2383.3	609.7
25.05	36.546	2026.4	2383.3	340.3
25.05	36.546	2024.5	2383.3	340.4
25.05	36.546	2013.1	2383.3	340.5
25.05	36.546	2021.6	2383.3	339.4
25.05	36.546	2284.1	2383.3	1370.5
25.05	36.546	2144.9	2383.3	609.8
25.06	36.643	2013.5	2391.5	314.0
25.06	34.966	2114.5	2299.0	767.1
25.07	36.643	2076.6	2391.5	420.6
25.07	36.643	2075.9	2391.5	425.5
25.07	36.643	2076.1	2391.5	424.9
25.07	34.966	1983.3	2299.0	364.1
25.07	34.966	1919.9	2299.0	279.9
25.07	34.966	1907.5	2299.0	262.5
25.07	34.966	2076.0	2299.0	607.0
25.07	34.966	2062.8	2299.0	569.7
25.08	36.643	2063.6	2391.5	391.7
25.08	36.643	2060.6	2391.5	388.8
25.08	36.643	2046.8	2391.5	352.4
25.08	36.643	2047.4	2391.5	365.2
25.08	36.643	2137.2	2391.5	572.1
25.08	36.643	2232.8	2391.5	981.1
25.08	36.643	2289.9	2391.5	1375.5
25.08	34.966	1980.2	2299.0	363.7
25.08	34.966	1975.9	2299.0	361.8

The ΔfCO$_2$ results in Fig. 4 correspond to fCO$_2$ calculated using Eqs. (16) and (17), based on the data of Mehrbach et al. (1973). When fCO$_2$ values are calculated using equations for K_1 and K_2 from Hansson (1973a,b), Goyet and Poisson (1989) or Roy et al. (1993), relative ΔfCO$_2$ values increase to approximately 10%, as summarized in Table 4.

5.4. Measurement uncertainties

To properly evaluate how well our equilibration data verify the use of the equations presented in this

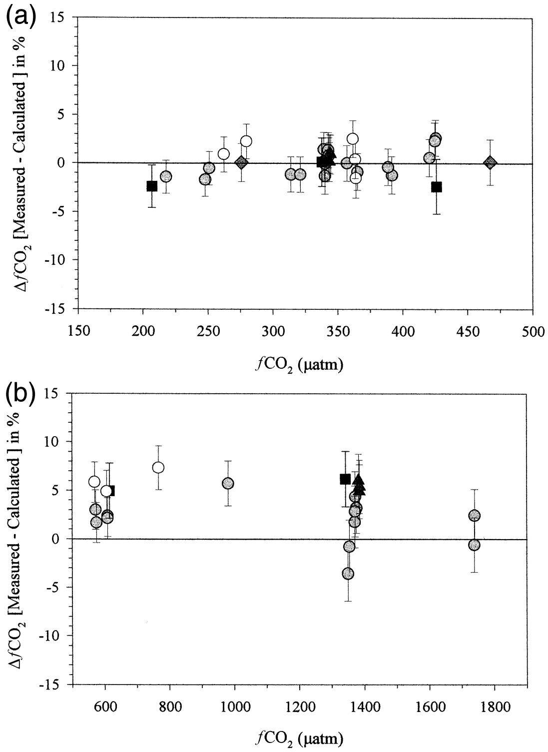


Fig. 5. (a) ΔfCO$_2$ of samples under 500 μatm. (b) ΔfCO$_2$ of samples over 500 μatm.

Table 4
The mean relative ΔfCO_2 (measured − calculated) when fCO_2 is calculated from DIC, TA, and the formulations of K_1 and K_2 from this study, Roy et al. (1993), Hansson (1973a,b) and Goyet and Poisson (1989). The constants of Hansson, and Goyet and Poisson were converted to the $[H]_T$ scale for the comparison. The 95% confidence interval is calculated according to DOE (1994)

Equations for K_1 and K_2	$fCO_2 < 500$ μatm		$fCO_2 > 500$ μatm	
	Mean ΔfCO_2 (%)	95% Confidence interval (%)	Mean ΔfCO_2 (%)	95% Confidence interval (%)
This study	0.07	0.50	3.35	1.22
Roy et al. (1993)	−10.17	0.88	−4.40	1.82
Hansson (1973a,b)	−11.13	0.68	−4.86	1.36
Goyet and Poisson (1989)	−9.22	0.99	−3.76	1.80

study, we established the magnitude of the experimental errors inherent in the calculations of ΔfCO_2. The uncertainties in each ΔfCO_2 depend on three analyses: the $x(CO_2)$ in the gas phase, the equilibrated DIC, and the TA of the equilibrator solution. Uncertainties in the equilibrator temperature, total pressure and salinity of the solution were negligible compared to the analytical uncertainties of these three CO_2 parameters (Lueker, 1998).

The uncertainty in measurements of the equilibrator gas phase $x(CO_2)$ was evaluated by comparing the amount of CO_2 extracted from the equilibrator gas phase with the $x(CO_2)$ of the gas mixtures used to establish the equilibrator fCO_2. The mean difference for 26 comparisons (gas mixture–equilibrator sample) expressed as a percentage of $x(CO_2)$ was $-0.18 \pm 0.11\%$ (95% confidence interval, $n = 26$). The s.d. of an individual equilibrator gas phase CO_2 measurement was estimated from the differences (Laitenen, 1960):

$$\mathrm{s.d.} = \left[\sum_{(1,n)} (\Delta_i)^2 / (n-1) \right]^{1/2} \tag{22}$$

The relative s.d. of the comparisons was 0.26% (Lueker, 1998). This analysis presupposes that all the error in the difference is due to measurement uncertainty in the equilibrator gas sample, and that the $x(CO_2)$ of the gas mixtures are known perfectly. This is a reasonable assumption given that the gas mixtures were determined manometrically in the laboratory of Keeling to a precision of 0.03% (Keeling et al., 1986; Lueker, 1998).

The uncertainty related to establishment of chemical equilibrium between the seawater DIC and gas mixture $x(CO_2)$ was evaluated by performing replicate equilibrations. The results of 28 DIC analyses obtained for 12 different groups of replicate equilibrations were used to compute the uncertainty of an equilibrator DIC analysis (Laitenen, 1960):

$$\mathrm{s.d.} = \left[1/(N-k) \sum_{(1,k)} \sum_{(1,n)} (\Delta_i)^2 \right]^{1/2} \tag{23}$$

where Δ represents the difference between the group mean and an individual DIC and the first sum is over 1 to n differences in each group, and the second is over k groups. N represents the total number of DIC analyses.

The s.d. of equilibrator DIC analyses was 1.15 μmol/kg based on the replicate equilibration DIC comparisons.

The uncertainty of TA measurements was evaluated using the results of repeated analyses of bicarbonate standard solutions. The results of 52 analyses using three different batches of standard solutions indicated an uncertainty of 1.17 μmol/kg (Lueker, 1998). The possibility of systematic errors in the TA measurements was examined by performing cross-checks with the TA instrumentation used to certify values for the reference materials prepared by Dickson (Dickson et al., 2000b). Several solutions were analyzed with both the closed cell instrumentation used in this study, and the open cell instrumentation of Dickson, including TA standard solutions prepared in the laboratory and seawater solutions. The cross checks indicated that the closed cell values were on average 1.17 μmol/kg lower than the open cell values (standard error 0.29 μmol/kg based on 65 analyses of five solutions, Lueker, 1998). The cause of this discrepancy is unknown. Solution aliquots were determined by weighing in both analytical systems, and both used the same HCl titrant. The seawater TA results used in this study were not corrected to agree with the results of the open cell instrumentation.

6. Discussion

6.1. Equations for pK_1 and pK_2 on the ''total hydrogen ion'' concentration scale

Our equilibration results suggest that the data reported by Mehrbach et al. should be used to derive equations for pK_1 and pK_2 *when the objective is to calculate* fCO_2 *of surface waters from DIC and TA.* It is important to note that the agreement between measured and calculated fCO_2 reflects the uncertainty in the ratio K_1/K_2, and cannot be used to evaluate either K_1 or K_2 independently.

The calculation of fCO_2 also requires the use of dissociation constants for the noncarbonate contributions to seawater alkalinity, $K(B(OH)_4^-)$, $K(H_2O)$, $K(HF)$, and $K(HSO_4^-)$. Recommended equations for these noncarbonate dissociation constants in seawater have been reported relative to the ''total hydrogen ion'' concentration scale (DOE, 1994). By reevaluating the results of Mehrbach et al. (1973) for pK_1 and pK_2 related to this concentration scale, we provide equations consistent with the noncarbonate dissociation constants recommended elsewhere (DOE, 1994; Millero, 1995).[2]

6.2. Uncertainties in the calculation of surface ocean fCO_2

Uncertainties in surface ocean fCO_2 levels calculated with K_1 and K_2 as formulated in this study will depend primarily on the quality of the DIC and TA data available. When the data are shown to be consistent with certified reference materials prepared by Dickson, data quality can be approximated from the analytical uncertainties of the measurements (Dickson, 1984, 1993).

We have characterized the reliability of fCO_2 calculated for various combinations of analytical uncertainties in DIC and TA typical of recent ocean carbon measurement programs, and summarized the results in Table 5. We denote the uncertainty in the calculated values of fCO_2 as ± 1s.d. based on the standard error of the values of K_1 and K_2 estimated from our equilibrator data, reported in Table 4, and the analytical uncertainties of the DIC and TA measurements:

$$\text{s.d calculated } fCO_2 = \left\{ \left(\frac{\partial fCO_2}{\partial K_1/K_2} \right)^2 (\text{s.d. } K_1/K_2)^2 + \left(\frac{\partial fCO_2}{\partial \text{DIC}} \right)^2 (\text{s.d. DIC})^2 + \left(\frac{\partial fCO_2}{\partial \text{TA}} \right)^2 (\text{s.d. TA})^2 \right\}^{1/2} \quad (24)$$

6.3. Apparent dependence of ΔfCO_2 on CO_2 concentration

The results of the equilibrations compared to the calculated fCO_2 data indicate agreement, within the uncertainties of the measurements, for fCO_2 up to 500 μatm. At higher fCO_2 values significant differences exist, the measured fCO_2 being larger than the calculated values by more than twice the standard error inferred from the measurements. Thus, the equations for pK_1 and pK_2 presented in this study and based on the data of Mehrbach et al. (1973) can be used with reasonable confidence at contemporary in situ levels of surface ocean pCO_2, but not at fCO_2 levels above 500 μatm.

Similar tendencies toward larger ΔfCO_2 at higher fCO_2 levels have been observed by other investigators (Lee and Millero, 1995; Lee et al., 1996, 1997; McElligot et al., 1998; Takahashi, pers. com., 1997). When the laboratory equilibrator data of Lee et al. (1996) were evaluated in a manner consistent with our results, i.e. disregarding their $[H^+]$ measurements, similar trends in ΔfCO_2 were observed (Fig. 6). Takahashi (pers. com.), observing larger ΔfCO_2

---

[2] See Dickson, 1984, 1993 for a detailed discussion of the various $[H^+]$ scales used for seawater.

Table 5
Uncertainties in calculated fCO_2 (applicable up to 500 μatm) inferred from the estimated uncertainties in the interpolation of K_1 and K_2 from Eqs. (20) and (21), and the analytical uncertainties of DIC and TA as specified in the table. The uncertainty attributed to the use of K_1 and K_2 was the standard error estimate based on the means of observed ΔfCO_2 (Table 4)

Analytical uncertainty in DIC, 1 s.d. (μmol kg^{-1})	Analytical uncertainty in TA, 1 s.d. (μmol kg^{-1})	Relative uncertainty in calculated fCO_2 1 s.d. (%)
1.0	1.0	0.7
1.0	2.0	1.0
2.0	2.0	1.3
2.0	3.0	1.6
2.0	4.0	1.9

values associated with deep water samples (elevated fCO_2 levels), suggested that the discrepancies might result from improper characterization of the alkalinity due to inorganic nutrient concentrations. We note that our measurements were all made on seawater sampled from the surface in oligotrophic gyres, and the nutrient concentrations were negligible with respect to the carbon dioxide system (Lueker, 1998). Lee et al. (1997) and McElligot et al. (1998) suggest that the dependence of ΔfCO_2 on fCO_2 values might result from inaccuracy in the formulation of K_0. In a related study, Lueker (1998) evaluated the accuracy of the formulation of K_0 at 25°C over a range of salinity. The observed deviation of the measurements from the formula recommended by Weiss (1974) was 0.6%. Though significant, this offset is not sufficiently large to cause the observed trend in ΔfCO_2 (Lueker, 1998). The cause(s) for the observed dependence of ΔfCO_2 on the fCO_2 level of seawater remains unclear. If an unknown characteristic of the carbon dioxide system in seawater is responsible, it could help to explain the often-contradictory results reported by previous investigators.

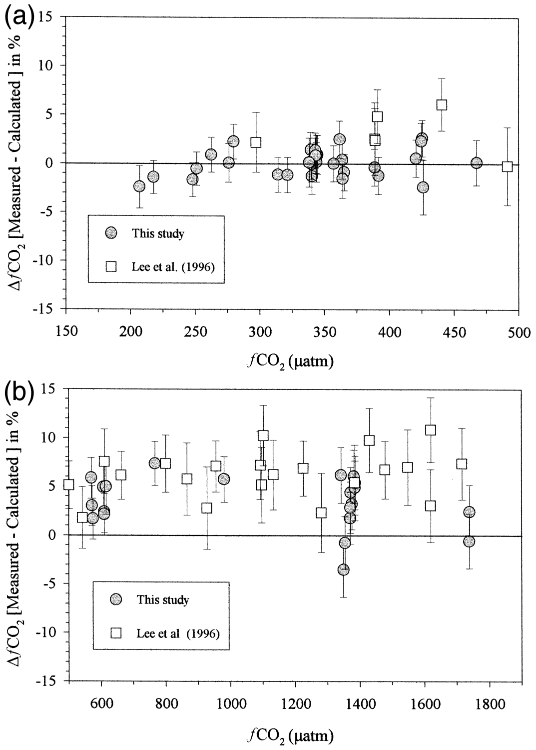


Fig. 6. (a) ΔfCO_2 for samples under 500 μatm. The data of Lee et al. (1996) are shown with the result of this study for comparison. (b) ΔfCO_2 for samples over 500 μatm.

7. Summary

The objective of our study was to provide estimates of the uncertainties resulting from the formulations of K_1 and K_2 when predicting fCO_2 from temperature, salinity, and the carbon parameters DIC and TA. We equilibrated seawater solutions with compressed gas mixtures of known composition and measured the $x(CO_2)$ in the equilibrator gas phase to confirm the completeness of the equilibration. The solution fCO_2 was calculated from the measured DIC and TA, and the difference from the observed fCO_2 reported as ΔfCO_2 (measured − calculated). The ΔfCO_2 results clearly support the use of the data of Mehrbach et al. (1973) to formulate K_1 and K_2. We reformulated the Mehrbach data to produce interpolation equations for pK_1 and pK_2 based on the ‘‘total hydrogen ion’’ concentration scale. By measuring fCO_2, DIC and TA with the same methodologies as those used to calibrate measurements of CO_2 in the atmosphere and oceans, we have confirmed that the equations are consistent with contemporary measurements of DIC and TA calibrated against certified reference materials (Keeling et al., 1986, 1999; UNESCO, 1991; Dickson, 1992; Dickson et al. 2000a,b).

When combined with high-quality DIC and TA data (having documented experimental errors), the equations for pK_1 and pK_2 reported here can be used to calculate fCO_2 with the uncertainty shown in Table 5. For DIC and TA data with analytical uncertainties of ± 1 μmol/kg and ± 2 μmol/kg (1 s.d.) respectively, calculated fCO_2 will have a relative standard deviation of approximately $\pm 1\%$, equivalent to ± 3.5 μatm at contemporary fCO_2 levels.

The ΔfCO_2 results when fCO_2 was greater than 500 μatm indicate a $3.3 \pm 1.2\%$ disparity in calculated fCO_2. Additional measurements of CO_2 equilibria in well-defined conditions should be performed to finally resolve the source of this discrepancy. By comparing results of equilibrations using solutions of known ionic composition with additional equilibrations of seawater at fCO_2 levels above 500 μatm, the source of the apparent shift in K_1/K_2 should be ascertained. Under the current circumstances, and until more consistent results are available, our ability to use thermodynamics to predict oceanic fCO_2 corresponding to future elevated atmospheric CO_2 levels remains uncertain.

Acknowledgements

This work was supported by the National Science Foundation and the Department of Energy.

References

Benson, B.B., Krause, D., Peterson, M.A., 1979. The solubility and isotopic fractionation of gases in dilute aqueous solution: I. Oxygen. J. Solution Chem. 8, 655–690.

Bevington, P.R., 1969. Data Reduction and Error Analysis for the Physical Sciences. McGraw-Hill, New York, NY, 336 pp.

Brewer, P.G., Goyet, C., Friederich, G., 1997. Direct observation of the oceanic CO_2 increase revisited. Proc. Natl. Acad. Sci. USA. 94, 8308–8313.

Clayton, T.D., Byrne, R.H., Breland, J.A., Feely, R.A., Millero, F.J., Campbell, D.M., Murphy, P.P., Lamb, M.F., 1995. The role of pH measurements in modern oceanic CO_2-system characterizations: precision and thermodynamic consistency. Deep-Sea Res., Part II 42, 411–429.

Culberson, C.H., Pytkowicz, R.M., 1973. Ionization of water in seawater. Mar. Chem. 1, 309–316.

Dickson, A.G., 1977. Some studies on acid-base behaviour in artificial seawaters. PhD Thesis, University of Liverpool.

Dickson, A.G., 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. Deep-Sea Res. 28A, 609–623.

Dickson, A.G., 1984. pH scales and proton-transfer reactions in saline media such as seawater. Geochim. Cosmochim. Acta 48, 2299–2308.

Dickson, A.G., 1992. The determination of total dissolved inorganic carbon in sea water using extraction/coulometry: the first stage of a collaborative study. Dept. of Energy rep. DOE/RL/01830T-H14, 43 pp.

Dickson, A.G., 1993. The measurement of seawater pH. Mar. Chem. 44, 131–142.

Dickson, A.G., Millero, F.J., 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. Deep-Sea Res. 34, 1733–1743.

Dickson, A.G., Millero, F.J., 1989. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media (Corrigendum). Deep-Sea Res. 36, 983.

Dickson, A.G., Anderson, G.C., Afghan, J.D., 2000a. Sea water based reference materials for CO_2 analysis: 1. Preparation and distribution. Mar. Chem, submitted for publication.

Dickson, A.G., Afghan, J.D., Anderson, G.C., 2000b. Sea water based reference materials for CO_2 analysis: 2. A method for the certification of total alkalinity. Mar. Chem., submitted for publication.

DOE, 1994. Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water. Version 2, A.G. Dickson, C. Goyet (Eds.), ORNL/CDIAC-74.

Dyrssen, D., Sillén, L.G., 1967. Alkalinity and total carbonate in sea water. A plea for $p-T$ independent data. Tellus 19, 113–120.

Goyet, C., Poisson, A., 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. Deep-Sea Res. 36, 1635–1654.

Hansson, I., 1972. An analytical approach to the carbonate system in sea water. PhD thesis, Department of Analytical Chemistry, University of Göteborg, Sweden.

Hansson, I., 1973a. The determination of the dissociation constants of carbonic acid in synthetic sea water in the salinity range of 20–40‰ and temperature range of 5–30°C. Acta Chem. Scand. 27, 931–944.

Hansson, I., 1973b. A new set of acidity constants for carbonic acid and boric acid in sea water. Deep-Sea Res. 20, 461–478.

IPCC, 1996. In: Houghton, J.T. (Ed.), Climate Change 1995: The Science of Climate Change. Cambridge Univ. Press, Cambridge, NY.

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

Joos, F., 1996. The atmospheric carbon dioxide perturbation. Europhys. News 27, 213–218.

Keeling, C.D., Guenther, P.R., Moss, D.J., 1986. An analysis of the concentration of atmospheric carbon dioxide-in-air standards: revision of 1985 Report No. 4 of the Environmental Monitoring Programme of the World Meteorological Organization, Geneva. 34 pp. and Addendum, 43 pp.

Keeling, C.D., Guenther, P.R., Emanuele, G., Lueker, T.J., Dickson, A.G., 2000. Sea water based reference materials for CO_2 analysis: 3. A method for the certification of total dissolved inorganic carbon on DIC. Mar. Chem., submitted for publication.

Laitenin, H.A., 1960. Chemical Analysis: An Advanced Text and Reference. Mcgraw-Hill, New York, NY.

Lee, K., 1996. Studies of the carbonate system in the oceans. PhD thesis, University of Miami.

Lee, K., Millero, F.J., 1995. Thermodynamic studies of the carbonate system in seawater. Deep-Sea Res. 42, 2035–2061.

Lee, K., Millero, F.J., Campbell, D.M., 1996. The reliability of the thermodynamic constants for the dissociation of carbonic acid in seawater. Mar. Chem. 55, 233–245.

Lee, K., Millero, F.J., Wanninkhof, R., 1997. The carbon dioxide system in the Atlantic Ocean. J. Geophys. Res. 102, 15693–15707.

Lewis, G.N., Randall, M., 1961. Thermodynamics. 2nd. edn. revised by Pitzer, K.S., Randall, M. McGraw-Hill.

Lueker, T.J., 1998. Carbonic acid dissociation constants determined as the ratio K_1/K_2 from the concentration of CO_2 in gas and seawater equilibrium. PhD thesis, University of California, San Diego.

McElligot, S., Byrne, R.H., Lee, K., Wanninkhof, R., Millero, F.J., Feely, R.A., 1998. Discrete water column measurement of CO_2 fugacity and pH_T in seawater: a comparison of direct measurements and thermodynamic calculations. Mar. Chem. 60, 63–73.

Mehrbach, C., 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. MS thesis, Oregon State University.

Mehrbach, C., Culberson, C.H., Hawley, J.E., Pytkowicz, R.M., 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnol. Oceanogr. 18, 897–907.

Millero, F.J., 1979. The thermodynamics of the carbonate system in seawater. Geochim. Cosmochim. Acta 43, 1651–1661.

Millero, F.J., 1995. Thermodynamics of the carbon dioxide system in the oceans. Geochim. Cosmochim. Acta 59, 661–667.

Millero, F.J., Byrne, R.H., Wanninkhof, R., Feely, R., Clayton, T., Murphy, P., Lamb, M.F., 1993. The internal consistency of CO_2 measurements in the equatorial Pacific. Mar. Chem. 44, 269–280.

Murphy, P., 1996. The carbonate system in seawater: laboratory and field studies. PhD thesis, University of Washington.

Orr, J.C., 1996. Ocean Carbon-Cycle Model Intercomparison Project (OCMIP): Phase I (1995-1997). Report #7, IGBP/GAIM.

Plath, D.C., Johnson, K.S., Pytkowicz, R.M., 1980. The solubility of calcite — probably containing magnesium — in seawater. Mar. Chem. 10, 9–29.

Roy, R.N., Roy, L.N., Vogel, K.M., Porter-Moore, C., Pearson, T., Good, C.E., Millero, F.J., Cambell, D.M., 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. Mar. Chem. 44, 249–267, (Erratum, 1996. Mar. Chem., 52: 183.).

Stoll, M.H.C., Rommets, J.W., de Baar, H.J.W., 1993. Effect of selected calculation routines and dissociation constants on the determination of total carbon dioxide in seawater. Deep-Sea Res. 40, 1307–1322.

Takahashi, T., Kaiteris, P., Broecker, W.S., Bainbridge, A.E., 1976. An evaluation of the apparent dissociation constants of carbonic acid in seawater. Earth Planet. Sci. Lett. 32, 458–467.

Takahashi, T., Feely, R.A., Weiss, R.F., Wanninkhof, R.H., Chipman, D.W., Sutherland, S.C., Takahashi, T.T., 1997. Global air–sea flux of CO_2: an estimate based on measurements of sea–air pCO_2 difference. Proc. Natl. Acad. Sci. U. S. A. 94, 8308–8313.

UNESCO, 1991. Reference materials for oceanic carbon dioxide measurements. Report of the sub-panel on standards for CO_2 measurements of the Joint Panel on Oceanographic Tables and Standards. UNESCO Tech. Pap. Mar. Sci. No. 60, 41 pp.

Wanninkhof, R., Lewis, E., Feely, R.A., Millero, F.J., 1999. The optimal carbonate dissociation constants for determining surface water pCO_2 from alkalinity and total inorganic carbon. Mar. Chem. 65, 291–301.

Weiss, R.F., 1974. Carbon dioxide in water and seawater, the solubility of a non-ideal gas. Mar. Chem. 2, 203–215.