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The recommended dissociation constants for carbonic acid in seawater

Kitack Lee,^{1,2} Frank J. Millero,³ Robert H. Byrne,⁴ Richard A. Feely,⁵ and Rik Wanninkhof¹

Abstract. A coherent representation of carbonate dissociation constants and measured inorganic carbon species is essential for a wide range of environmentally important issues such as oceanic uptake of anthropogenic CO₂ and carbon cycle depictions in ocean circulation models. Previous studies have shown varying degrees of discordance between calculated and measured CO₂-system parameters. It is unclear if this is due to errors in thermodynamic models or in measurements. In this work, we address this issue using a large field dataset (15,300 water samples) covering all ocean basins. Our field data, obtained using laboratory-calibrated measurement protocols, are most consistent with calculated parameters using the dissociation constants of *Mehrbach et al.* [1973] as refit by *Dickson and Millero* [1987]. Thus, these constants are recommended for use in the synthesis of the inorganic carbon data collected during the global CO₂ survey during the 1990s and for characterization of the carbonate system in seawater.

Introduction

The carbon dioxide system in seawater can be defined by specifying temperature, salinity, nutrient and boron concentrations, and two of the four inorganic CO₂-system parameters: pH (-log [H⁺]), total inorganic carbon (C_T), total alkalinity (A_T), and CO₂ fugacity (fCO₂). The CO₂ fugacity is expressed by the relationship, fCO₂ = [CO₂]/K₀ where K₀ is the solubility of CO₂ and [CO₂] = [CO_{2(aq)}] + [H₂CO₃]. Measurement of all four of the CO₂-system parameters allows an evaluation of the accuracy of available carbonic acid dissociation constants by the so-called "system overdetermination." Agreement between measurements and thermodynamic calculations (model closure) is fundamental to our understanding of important geochemical issues such as the determination of the calcium carbonate compensation depth and the distribution of fossil fuel CO₂ in the oceans. It is par-

ticularly important in numerical ocean circulation models where surface ocean fCO₂ is calculated from A_T and C_T fields. Different carbonate-system equilibrium models yield differences in calculated fCO₂ as large as 30 μatm.

Several determinations of carbonic acid dissociation constants have been made as a function of temperature and salinity in natural seawater [*Mehrbach et al.*, 1973] and in artificial seawater without fluoride [*Hansson*, 1973; *Goyet and Poisson*, 1989; *Roy et al.*, 1993]. *Dickson and Millero* [1987] refit the experimental datasets of *Mehrbach et al.* [1973] (referred to as MEHR-DM87) and of *Hansson* [1973]. Additional sets of constants have been created by fitting the pooled data of *Hansson* and *Mehrbach et al.* [*Dickson and Millero*, 1987], and the pooled data of *Goyet and Poisson* and *Roy et al.* [*Millero*, 1995]. Average differences in various equations for pK₁ and pK₂ are in a range of 0.001-0.008 in pK₁ and of 0.005-0.03 in pK₂ [*Millero*, 1995]. These differences are similar to the 2σ experimental precision (0.01-0.017 in pK₁ and 0.015-0.026 in pK₂) and probably are not strongly significant. However, the different equations derived from original experimental datasets yield significant differences in calculated parameters. Here we present the equations that yield the best agreement with a large field dataset.

Over the last 10 years, significant improvements have been made in the measurement of inorganic CO₂ parameters [*DOE*, 1994]. The use of certified reference material (CRM), developed by Dr. A. Dickson (Scripps Institution of Oceanography), greatly contributed to improved precision and accuracy in at-sea A_T and C_T measurements. These improvements have motivated a number of investigators to re-examine the internal consistency of the CO₂ parameters measured in the laboratory [*Lee et al.*, 1996; *Murphy*, 1996; *Lueker*, 1998] and at sea [*Millero et al.*, 1993; *Clayton et al.*, 1995; *Lee et al.*, 1997; *McElligott et al.*, 1998; *Wanninkhof et al.*, 1999; *Byrne et al.*, 1999]. These studies have resulted in conflicting conclusions regarding the optimal set of carbonic acid dissociation constants. The differing conclusions drawn from previous studies have a variety of experimental origins: (1) A_T measurement uncertainties: A_T data obtained during the U.S. JGOFS Equatorial Pacific Process Study in 1992 (EqPac92) were overestimated by about 8 μmol kg⁻¹ due to inaccurately assigned titrant concentrations. This affects the conclusions drawn by *Millero et al.* [1993]. (2) pH scale uncertainties: *McElligott et al.* [1998] noted that all four CO₂ parameters measured during the EqPac92 program would be internally consistent with the constants of MEHR-DM87 at 20°-25°C if spectroscopic pH values were increased by 0.0038. *DelValls and Dickson* [1998] determined that the pH values assigned to "tris" buffers needed to be increased by 0.0047 for all temperatures and salinities. The reported pK₂ of the indicator m-cresol purple [*Clayton and Byrne*, 1993] is based on the "tris" characterization of *Dickson* [1993] who used the reported e.m.f.

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values of *Ramette et al.* [1977]. Consequently, spectroscopic pH values obtained in the laboratory [Lee *et al.*, 1996] and in field studies [Millero *et al.*, 1993; Clayton *et al.*, 1995; Lee *et al.*, 1997] may need to be revised upward by 0.0047 pH units. (3) Limited scope of previous studies: Previous investigations of thermodynamic CO₂-system consistency often involved two or three carbon system parameters over a narrow range of temperature (t) and fCO₂, or specific ocean regions.

This work is distinct from previous studies in that it uses a large, well-calibrated field dataset covering a 5°-30°C range of temperature, a 33-37 range of salinity, and a 250-1700 μatm range of fCO₂. Field measurements were made in all major ocean basins from the equator to high latitudes. The data were obtained by many investigators over a four-year period. Laboratory measurements made over a similar range of temperature and fCO₂ are also included in this analysis. The internal consistency of all data used in this study was carefully examined on a per cruise basis: A_T and C_T data were normalized to CRM values [Dickson, 1997] and pH data were adjusted upward by 0.0047 pH units for consistency with the revised "tris" buffer characterization of *DelValls and Dickson* [1998]. This dataset, which represents our current achievable level of accuracy on a routine basis at sea and in the laboratory, is used to determine which set of carbonic acid dissociation constants is optimal for use in characterizing the oceanic CO₂-system.

Sources of Laboratory and Field Data

Laboratory measurements of all four CO₂ parameters were made on a single seawater sample (S=35) as a function of temperature (5°-35°C) and fCO₂ (300-1700 μatm). The analytical techniques and data are documented in Lee *et al.* [1996]. Field data were obtained on cruises conducted by the National Oceanic and Atmospheric Administration/Ocean-Atmosphere Carbon Exchange Study (NOAA/OACES) in the Atlantic, Indian, and Pacific Oceans (Table 1). The NOAA/OACES CO₂ dataset is unique in that all four CO₂ parameters were measured throughout the water column from the surface to 6000 m. Samples were analyzed for fCO₂ and C_T at 20°C, and for A_T and pH at 25°C except for the North Atlantic study where pH was measured at 20°C. Detailed procedures for analysis of fCO₂, pH, C_T, and A_T can be found in *DOE* [1994]. Analysis protocols differed for pH and fCO₂ measurements on different cruises. The fCO₂ of discrete samples was measured by an infrared analyzer (IR) [Wanninkhof and Thoning, 1993] on the EQPAC, A20R, and P18 cruises, and by gas chromatographic analysis with flame-ionization detection (GC-FID) after catalytic reduction of CO₂ to CH₄ [Neill *et al.*, 1997] on the I8R and P15S cruises. Spectroscopic pH measurements using the indicator m-cresol purple were made at 20°C on the A20R and at 25°C on the I8R by the University of Miami group, and at 25°C on the EQPAC, P15S, and P18 cruises by the University of South Florida group.

Results and Discussion

In this study, pH-C_T and A_T-C_T are used as input combinations to study the consistency between the measurements and the first and second carbonate dissociation constants. The pH-C_T combination can be used to assess the consistency between measurements and pK₁ parameterizations by comparing measured

Table 1. Summary of NOAA/OACES cruise data and thermodynamic consistency.

Cruise	Variable	Thermodynamic Calculations	
		Constants	
		MEHR-DM87	ROY
A20R – Atlantic Along 20°W (5°S–63°N)	ΔfCO ₂ ^A	-0.1 ± 0.8	-2.4 ± 0.8
	ΔA _T ^B	2.6 ± 3.5	-7.3 ± 4.4
	ΔfCO ₂ ^C	0.2 ± 1.0	-1.7 ± 1.2
I8R – Indian Along 80°E (43°S–10°N)	ΔfCO ₂ ^A	-0.1 ± 1.1	-1.3 ± 1.0
	ΔA _T ^B	3.8 ± 3.5	-6.4 ± 5.7
	ΔfCO ₂ ^C	2.1 ± 2.4	-4.6 ± 2.9
EQPAC – Pacific (15°S–15°N 80°W–140°W)	ΔfCO ₂ ^A	0.3 ± 1.1	-0.9 ± 1.4
	ΔA _T ^B	1.0 ± 4.9	-8.1 ± 9.5
	ΔfCO ₂ ^C	1.2 ± 2.7	-4.6 ± 4.0
P15S – Pacific Along 170°W (67°S–equator)	ΔfCO ₂ ^A	1.4 ± 1.4	0.2 ± 1.5
	ΔA _T ^B	4.2 ± 3.2	-5.6 ± 5.4
	ΔfCO ₂ ^C	3.8 ± 2.5	-2.8 ± 3.3
P18 – Pacific Along 103°W (67°S–23°N)	ΔfCO ₂ ^A	0.5 ± 0.9	-0.6 ± 1.3
	ΔA _T ^B	-2.5 ± 4.6	-12.2 ± 7.6
	ΔfCO ₂ ^C	-1.0 ± 2.8	-7.6 ± 3.0

^{A,C}ΔfCO₂ (%) = [(measured – calculated) / measured] × 100. ΔfCO₂ represents the mean of individual differences between the measured fCO₂ and fCO₂ calculated from pH-C_T (A) and A_T-C_T (C) using the constants of MEHR-DM87 and Roy *et al.* [1993].

^BΔA_T (μmol kg⁻¹) = (measured – calculated). ΔA_T represents the mean of individual differences between the measured A_T and A_T calculated from pH-C_T using the constants of MEHR-DM87 and Roy *et al.* [1993].

vs. calculated fCO₂ (Fig. 1a, 1b), and the consistency between measurements and pK₂ parameterizations by comparing measured vs. calculated A_T (Fig. 1c, 1d) [Lee *et al.*, 1996]. The A_T-C_T combination can be used to evaluate the consistency between measurements and log K₁/K₂ ratios by comparing measured fCO₂ and fCO₂ calculated from A_T-C_T (Fig. 1e, 1f). In these calculations we have used the constants of MEHR-DM87, along with equilibrium constants for other components (e.g., boric acid dissociation, solubility of CO₂, water hydrolysis, and phosphoric and silicic acid dissociation), necessary to characterize the carbonate system in seawater as recommended in *Millero* [1995]. Since the constants of MEHR-DM87 are expressed in terms of moles per kilogram of solution on the "seawater" scale [Dickson and Millero, 1987], all acid dissociation constants have been adjusted to the same scale. The effect of uncertainties in equilibrium constants on calculated parameters is discussed in the caption of Fig. 1.

Assessment of pK₁

The difference between measured fCO₂ and fCO₂ calculated from pH-C_T is strongly dependent upon the pK₁. The fCO₂ residuals in Fig. 1a and 1b show the percentage error in fCO₂ (ΔfCO₂ = [(measured fCO₂ - calculated fCO₂) / measured fCO₂] × 100) for laboratory and field data. Observations are binned into fCO₂ intervals equal to 300 μatm, and are shown as a function of sample fCO₂. The best agreement between measured and calculated fCO₂ was obtained using the constants of MEHR-DM87. The fCO₂ residuals for field measurements are mostly within ±1% over the entire fCO₂ range (Fig. 1a, 1b) and

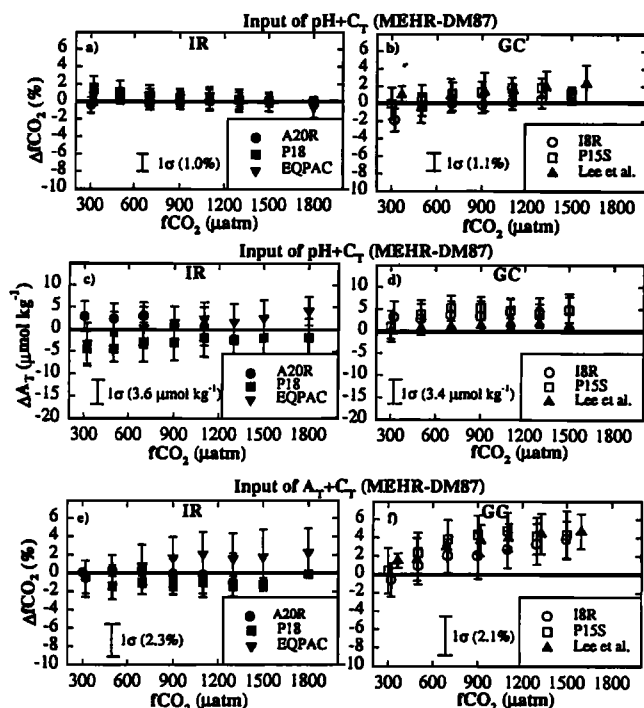


Figure 1. Comparison of laboratory [Lee *et al.*, 1996] (filled triangles) and field measurements of $f\text{CO}_2$ and A_T vs. those calculated using the constants of MEHR-DM87. (a,b) The $\Delta f\text{CO}_2$ of measured values using (a) IR (A20R, P18, EQPAC) and (b) GC-FID (I8R, P15S) vs. those calculated from pH-C_T . (c,d) The ΔA_T of measured values (c) (A20R, P18, EQPAC) and (d) (I8R, P15S) vs. those calculated from pH-C_T . (e,f) The $\Delta f\text{CO}_2$ of measured values using (e) IR (A20R, P18, EQPAC) and (f) GC-FID (I8R, P15S) vs. those calculated from $A_T\text{-C}_T$. The filled symbols are the field data (A20R, P18, EQPAC), during which discrete $f\text{CO}_2$ measurements were made using IR analysis (Fig. 1a, 1e). Open symbols are discrete $f\text{CO}_2$ measurements (I8R, P15S) using a GC-FID (Fig. 1b, 1f). Error bars represent standard deviations (1σ) of the differences in each bin. The probable error of the calculated A_T (Fig. 1c, 1d) due to uncertainties in equilibrium constants for minor components is $\pm 2.5 \mu\text{mol kg}^{-1}$ for surface water and $\pm 4.0 \mu\text{mol kg}^{-1}$ for deep water based on an uncertainty of ± 0.0042 in $\log K_B$ -boric acid; of ± 0.00015 in $\log K_0$ -solubility of CO_2 ; of ± 0.01 in $\log K_w$ -water hydrolysis; of ± 0.09 in $\text{p}K_{\text{P}_1}$ -phosphoric acid; of ± 0.03 in $\text{p}K_{\text{P}_2}$ -phosphoric acid; of ± 0.20 in $\text{p}K_{\text{P}_3}$ -phosphoric acid; of ± 0.02 in $\text{p}K_{\text{Si}}$ -silicic acid [Millero, 1995]. The assessment of the consistency between the measurements and the $\text{p}K_1$ parameterizations is independent of the uncertainties in the equilibrium constants for minor components, since calculations of $f\text{CO}_2$ from pH-C_T do not include those constants. The assessment of the consistency between the measurements and the $\text{p}K_2$ parameterizations is sensitive to these uncertainties, since these constants are needed to convert A_T to carbonate alkalinity or vice versa. These uncertainties cannot account for the non-zero slope of A_T residuals when constants other than MEHR-DM87 are used.

are of similar magnitude to those of laboratory measurements (Fig. 1b). GC-FID based field $f\text{CO}_2$ measurements are in good agreement with the laboratory measurements. The residuals for the laboratory and field data are about 3% larger using

dissociation constants other than MEHR-DM87 (Table 1). The $\text{p}K_1$ measurements of Goyet and Poisson, Hansson, and Roy *et al.* agreed to within ± 0.003 in $\text{p}K_1$ [Millero, 1995] but they differ from MEHR-DM87 by about 0.01, which is equivalent to a 3% offset in calculated $f\text{CO}_2$.

Assessment of $\text{p}K_2$

The difference between measured A_T and A_T calculated from pH-C_T strongly depends on the $\text{p}K_2$. The A_T residuals ($\Delta A_T = \text{measured } A_T - \text{calculated } A_T$ in $\mu\text{mol kg}^{-1}$) for laboratory and field data are binned and are plotted as a function of sample $f\text{CO}_2$ in Fig. 1c and 1d. The A_T residuals for laboratory and field data using the constants of MEHR-DM87 are about $\pm 3 \mu\text{mol kg}^{-1}$ (1σ) with little dependence on $f\text{CO}_2$. When the constants of Roy *et al.* and Goyet and Poisson are used, the A_T residuals are considerably larger for samples with low $f\text{CO}_2$. An adjustment of 0.03 in the $\text{p}K_2$ of Roy *et al.* would be required to produce a near zero slope in the residuals. Such an adjustment lowers the calculated A_T by about $15 \mu\text{mol kg}^{-1}$ for samples with $f\text{CO}_2 = 300 \mu\text{atm}$ and also lowers the A_T by $4 \mu\text{mol kg}^{-1}$ for samples with $f\text{CO}_2 = 1600 \mu\text{atm}$.

Assessment of the $\log K_1/K_2$ Ratio

Calculation of $f\text{CO}_2$ from $A_T\text{-C}_T$ requires a reliable $\log K_1/K_2$ ratio. The differences in the $\log K_1/K_2$ for various parameterizations range from -0.04 to $+0.06$ and are primarily caused by differences in K_2 . Measured $f\text{CO}_2$ values for samples with low $f\text{CO}_2$ ($< 500 \mu\text{atm}$) at $t = 5\text{-}30^\circ\text{C}$ are most consistent with calculations using the constants of MEHR-DM87. This is not the case at high $f\text{CO}_2$ ($> 500 \mu\text{atm}$) where $f\text{CO}_2$ residuals become greater as $f\text{CO}_2$ increases (Fig. 1f). The $f\text{CO}_2$ dependence of the residuals is apparent in two independent laboratory measurements [Lee *et al.*, 1996; Lueker, 1998], and in the field data of GC-FID based $f\text{CO}_2$ measurements (Fig. 1f). This trend is also evident irrespective of the carbonic acid dissociation constants used. This implies that the $\log K_1/K_2$ ratio calculated from these measurements varies as a function of sample $f\text{CO}_2$, which is in contradiction with our understanding of the carbonate system. The IR based $f\text{CO}_2$ measurements do not show this trend (Fig. 1e), and the apparent discrepancy in $f\text{CO}_2$ measurements at high $f\text{CO}_2$ has to be resolved before we draw firm conclusions regarding the consistency between $f\text{CO}_2\text{-}A_T\text{-C}_T$ measurements and the $\log K_1/K_2$ at high $f\text{CO}_2$. Wanninkhof *et al.* [1999] showed that surface underway $f\text{CO}_2$ measurements, made on three OACES cruises (A20R, I8R, and P18) covering a temperature range of $5\text{-}30^\circ\text{C}$ and $f\text{CO}_2$ range of $280\text{-}450 \mu\text{atm}$, are most consistent with $f\text{CO}_2$ calculated from $A_T\text{-C}_T$ data using the constants of MEHR-DM87. At low temperature, the constants of MEHR-DM87 and Roy *et al.* both give a reliable prediction of $f\text{CO}_2$, because the difference in the $\log K_1/K_2$ between Roy *et al.* and MEHR-DM87 at $t < 5^\circ\text{C}$ is significantly smaller (< 0.02) than at other temperatures. At 25°C the difference is as large as 0.05, which leads to differences in calculated $f\text{CO}_2$ of $30 \mu\text{atm}$.

Conclusions

The adjustment in the $\text{p}K_2$ of m-cresol purple suggested by DelValls and Dickson [1998] brings calculations involving pH into optimal agreement with the other CO_2 -system measurements. The constants of MEHR-DM87 are most suitable for

calculations involving pH-A_T-C_T combinations over a range of $t=0^{\circ}$ - 35° C, $S=33$ - 37 , and $f\text{CO}_2=250$ - 1700 μatm . The constants of MEHR-DM87 also yield good agreement with measurements and calculations involving $f\text{CO}_2$ -A_T-C_T combinations at low $f\text{CO}_2$. At high $f\text{CO}_2$, calculated $f\text{CO}_2$ values using the log K_1/K_2 ratio of MEHR-DM87 are less than the measured values for the laboratory and GC-FID field measurements. Definitive conclusions regarding the consistency between measurements and the log K_1/K_2 will require resolution of discrepancies in $f\text{CO}_2$ measurements at high $f\text{CO}_2$. Overall, the constants of MEHR-DM87 provide the most consistent comparisons between laboratory and field measurements over a wide range of ocean temperature, salinity, and $f\text{CO}_2$. This work suggests that the internal consistency of CO_2 -system measurements can be achieved over long periods of time by diverse teams of investigators through the use of standard reference materials.

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