

MEASUREMENT OF THE APPARENT DISSOCIATION CONSTANTS OF CARBONIC ACID IN SEAWATER AT ATMOSPHERIC PRESSURE¹

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ABSTRACT

The apparent dissociation constants of carbonic acid in seawater were determined as functions of temperature (2–35°C) and salinity (19–43‰) at atmospheric pressure by measurement of K'_1 and the product $K'_1 K'_2$. At 35‰ salinity and 25°C the measured values were $pK'_1 = 6.000$ and $pK'_2 = 9.115$; at 35‰ and 2°C the measured values were $pK'_1 = 6.177$ and $pK'_2 = 9.431$.

We have determined the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure as functions of temperature and salinity, because of discrepancies in previous published results. These constants are defined (Lyman 1956) by equations 1 and 2 (Table 1). The parentheses represent concentrations in moles per kilogram of seawater, a_{H^+} is the hydrogen ion activity defined in the NBS buffer scale (Pytkowicz et al. 1966; Pytkowicz 1969), and CO_2^* is the sum of the concentrations of molecular carbon dioxide and carbonic acid.

The use of thermodynamic dissociation constants for the calculation of CO_2 species' concentrations requires estimates of single ion activity coefficients, which are poorly known functions of temperature, salinity, pressure, and ion association. The direct determination of apparent constants in seawater obviates this problem. Apparent constants depend on temperature, pressure, ion association, and on the free concentrations of the major ions in seawater (Weyl 1961; Kester and Pytkowicz 1967). They are useful because the concentrations of the major ions are insensitive to changes in pH or to processes such as photosynthesis and the solution and precipitation of carbonates. Essentially, apparent constants can be used for processes that do not have

a sizable effect on the relative concentrations of the major ions in seawater.

The first determinations of the apparent dissociation constants of carbonic acid in seawater were made by Buch et al. (1932) and Buch (1938), by a procedure involving measurement of the alkalinity, pH, and the P_{CO_2} or total carbon dioxide. The pH (Sorensen scale) was determined with a quinhydrone electrode in the case of K'_1 and a hydrogen electrode in the case of K'_2 .

Lyman (1956) determined the apparent constants from potentiometric titrations on a single sample of seawater with a glass electrode calibrated on the NBS scale; he claimed that his method was inherently more accurate than that of Buch et al. (1932) and Buch (1938).

There is fair agreement between the K'_1 values of Buch et al. (1932) and Lyman (1956). However, Buch's (1938) values for K'_2 are as much as 20% larger than Lyman's. Edmond and Gieskes (1970) reviewed the results of Buch et al. (1932), Buch (1938, 1951), and Lyman (1956). Through a critical examination of both sets of data they derived equations for pK'_1 and pK'_2 in terms of salinity and temperature. The values of K'_1 obtained by Buch (1951) and by Lyman (1956) and K'_2 obtained by Lyman (1956) were selected as the most reliable values.

Hansson (1972) determined the apparent constants by a potentiometric titration of artificial seawater. He determined the constants by adjusting K'_1 and K'_2 until a

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Table 1. Equations from text

1. $K_1' = a_H(\text{HCO}_3^-)/(\text{CO}_2^*)$	2. $K_2' = a_H(\text{CO}_3^{2-})/(\text{HCO}_3^-)$
3. $(\text{TCO}_2)/\text{CA} = A = (a_H^2 + a_H K_1' + K_1' K_2')/(a_H K_1' + 2K_1' K_2')$	
4. $K_1' K_2' = (10^{-2\text{pH}^0} + [1 - A]K_1' 10^{-\text{pH}^0})/(2A - 1)$	
5. $F_1 = \text{TA}_0 W_0 f_H - W_a N_a f_H = a_H(W_0 + W_a)$	
6. $F_1 = (W_0 + W_a) \left[\text{TCO}_2 f_H / (1 + a_H / K_1') - a_H - T_F a_H f_H / (a_H + K_{HF}') \right. \\ \left. - T_S a_H f_H / (a_H + K_{HSO_4}') \right]$	
7. $F_2 = K_1'(W_a - W_1) = a_H(W_2 - W_a)$	
8. $F_2 = a_H(W_2 - W_a) - \frac{K_1'}{N_a} \left[\frac{(W_2 - W_a)K_2' N_a}{(W_0 + W_a)a_H} \left(1 + \frac{2a_H}{K_1'}\right) + \frac{T_B K_B'}{a_H + K_B'} \left(1 + \frac{a_H}{K_1'}\right) \right] (W_0 + W_a)$	
9. $\text{pH} = \text{pH}_b + F(E - E_b)/(2.303RT)$	
10. $\text{p}K_1' = -13.7201 + 0.031334 \times T + 3235.76/T + 1.300 \times 10^{-5} \times S \times T - 0.1032 \times S^{1/2}$	
11. $\text{p}K_2' = 5371.9645 + 1.671221 \times T + 0.22913 \times S + 18.3802 \times \log(S) - 128375.28/T \\ - 2194.3055 \times \log(T) - 8.0944 \times 10^{-4} \times S \times T - 5617.11 \times \log(S)/T + 2.136 \times S/T$	
12. $K_1' = \frac{a_w^f \text{CO}_2 K_1^0}{f_{\text{HCO}_3^-}} \left[1 + K_{\text{NaHCO}_3}^*(\text{Na}) + K_{\text{MgHCO}_3}^*(\text{Mg}) + K_{\text{CaHCO}_3}^*(\text{Ca}) \right]$	

calculated titration curve matched the experimental one. His pH scale was based on total hydrogen ion concentration. Hanson's (1972) values for K_1' are in general agreement with those of Buch et al. (1932) and of Lyman. His values for K_2' are smaller than Lyman's, the difference for 35‰ salinity being 1% at 20°C and 12% at 5°C.

Based on the intercomparison of field data obtained by a variety of techniques, Takahashi et al. (1970) suggested that Lyman's values for K_2' may be as much as 30% too low.

Disteche and Disteche (1967), Culberson et al. (1967), and Culberson and Pytkowicz (1968) extended the determination of the

constants to the pressures encountered in the deep oceans.

THEORY

Our work was done in two steps: measurement of the product $K_1'K_2'$ and measurement of K_1' . The methods used were modifications of those of Weyl (1961), Kester and Pytkowicz (1967), and Dyrssen and Sillén (1967).

Determination of $K_1'K_2'$

The ratio of total inorganic carbon, TCO_2 , to carbonate alkalinity, CA , is given by equation 3 (Table 1). If the pH of the seawater sample does not change on addition of sodium bicarbonate, then equation

4 holds where pH^0 is the steady-state pH. Thus, $K'_1K'_2$ can be determined by adding small amounts of bicarbonate until a pII is reached that remains constant on further addition of bicarbonate.

Determination of K'_1

The Gran method (Gran 1952; Dyrssen and Sillén 1967; Edmond 1970) was modified for the determination of K'_1 . Dyrssen and Sillén (1967) showed that the total alkalinity can be calculated from the Gran extrapolation line F_1 (equation 5) where

T_{A_0} = initial titration alkalinity (eq/kg-seawater);

W_0 = weight of seawater sample;

W_a = weight of acid added;

N_a = normality of acid (eq/kg-HCl);

f_{H} = activity coefficient of H^+ ;

$T_{\text{F}} = (\text{HF}) + (\text{F}^-)$ (moles/kg-seawater);

$T_{\text{S}} = (\text{HSO}_4^-) + (\text{SO}_4^{2-})$ (moles/kg-seawater);

$K'_{\text{HSO}_4} = a_{\text{H}}(\text{SO}_4^{2-})/(\text{HSO}_4^-)$.

The effects of HCO_3^- , HSO_4^- , and HF on the extrapolation line have been neglected in equation 5. If the presence of HCO_3^- , HSO_4^- , and HF is not neglected, the Gran function F_1 becomes equation 6 (Mehrbach 1973). Equation 6 shows that when $F_1 = 0$, the total initial alkalinity (contained in W_0) is equal to the equivalents of acid added. Therefore, the intercept $F_1 = 0$ of a plot of F_1 versus W_a yields W_2 , with W_2N_a being the number of equivalents of alkalinity initially present in the seawater sample.

Equations 5 and 6 are the equations of a line with a slope equal to $N_a f_{\text{H}}$. Thus in equation 6, the free hydrogen ion activity coefficient can be obtained by dividing the slope of the line by the concentration of the acid, N_a . When the corrections for HSO_4^- and HF are neglected, as in equation 5, one obtains the total hydrogen ion activity coefficient (Culbertson et al. 1970).

Dyrssen and Sillén (1967) also presented an equation equivalent to equation 7. W_1 is such that $W_1N_a = (\text{CO}_3^{2-}) + (\text{B}[\text{OH}]_4^-) + (\text{OH}^-)$ and can be obtained from a plot of F_2 versus W_a when $F_2 = 0$. Corrections must be made to equation 7 because of

borate and carbonate interference near the end point, W_1 . When these corrections are applied, equation 8 is obtained (Mehrbach 1973). In equations 6 and 8, the quantities T_{F} , T_{S} , and T_{B} were corrected for dilution by the acid titrant.

The corrections for sulfate and fluoride in equation 6 were dropped at temperatures other than 25°C , because K'_{HF} and K'_{HSO_4} were not known. At 25°C the error introduced by neglecting the corrections for sulfate and fluoride was 0.46% of the value of K'_1 .

The following iteration procedure was performed by computer for the calculation of K'_1 . Seawater of known salinity was titrated with HCl and a_{H} versus W_a was obtained. In the first iteration, approximate values of W_1 , W_2 , and K'_1 were calculated from equations 5 and 7 by a linear least squares procedure. A value of T_{CO_2} was calculated from the expression $T_{\text{CO}_2} = N_a(W_2 - W_1)$, which Edmond (1970) showed to be accurate to $\pm 0.68\%$. At 25°C the approximate values of W_1 , W_2 , K'_1 , and T_{CO_2} were then substituted into the more refined equations 6 and 8, in conjunction with Lyman's (1956) values of K'_2 and K'_{B} , and K'_{HSO_4} and K'_{HF} from Culbertson et al. (1970). At other temperatures the procedure was the same except for removal of the sulfate and fluoride corrections in equation 6. Iterations were continued until successive values of K'_1 did not differ by more than 0.5%. The correction for carbonate in F_2 was the same whether Lyman's (1956) K'_2 or ours was used, because of the small value of the correction.

EXPERIMENTAL

Titration method

Surface seawater of 31.5‰ salinity from off the Oregon coast was filtered through a $0.45\text{-}\mu$ Millipore filter and then either diluted with deionized distilled water or concentrated by evaporation to the desired salinity. For the determination of $K'_1K'_2$ we kept the buffer capacity of the seawater at a minimum by adding hydrochloric acid in an amount equivalent to the alkalinity

and then purging the solution with CO₂-free air.

For all experiments 0.2999 eq/kg-HCl was prepared from J. T. Baker's Dilute-It analytical concentrate (No. 4654). The normality of the HCl was determined by a differential potentiometric titration against primary standard Na₂CO₃. The pH of the seawater in the experiments to determine $K'_1K'_2$ was adjusted with 0.1 N NaOH prepared from Baker reagent grade sodium hydroxide (No. 3722).

The titration cell consisted of a water-jacketed beaker for constant temperature control and a rubber stopper which held a Sargent S-30080-15 C saturated calomel reference electrode with ceramic frit liquid junction, a Sargent S-30050-15 C glass electrode (Jena type U), and a thermometer. The stopper also contained a hole for placement of a syringe needle for titrations, and a glass piston and barrel. The piston receded into the barrel upon addition of solution into the cell, thus ensuring constant pressure without exchange of gases. It was similar to that used by Edmond (1970). The cell temperature was controlled with water from a constant temperature bath.

Calibration of electrodes

The potential of the glass-calomel pair was measured by an Orion 801 digital millivolt meter, standardized against a Leeds-Northrup 8687 V potentiometer. The pH was calculated from equation 9. pH_s is the pH of the standard NBS buffer (186-I-c, 186-II-c; pH 7.415 at 25°C), and E and E_s are the potentials of the electrode pair in the test solution and the buffer. R is the gas constant, F the Faraday, and T the temperature in degrees Kelvin.

The glass electrode used in these experiments was compared with a hydrogen electrode and had the theoretical slope $2.303RT/F$. In natural seawater (31.5‰ salinity) at 25°C the potential difference between the glass and hydrogen electrodes was 638.63 ± 0.10 mV (2 SD) between pH 2.4 and 8.9. The seawater was buffered with 5 mM acetic acid, 5 mM boric acid, 2.5 mM tris-(hydroxymethyl)-aminometh-

Table 2. An example of a test to determine pH^0

Temperature = 25.00°C
 Salinity = 19.17‰
 Potential of NBS pH 7.415 buffer = -44.0 mv
 Approximate cell volume = 160 ml
 Added 0.070 ml of 0.1 N NaOH to adjust the pH of the solution to the approximate value of the steady-state pH, pH^0 .

NaHCO ₃ addition number	potential
0	-62.4 mv
1	-62.0
2	-61.9
3	-61.8
4	-61.8
5	-61.8

$pH^0 = 7.716$

The salinity of the sample, corrected for dilution with 0.1 N NaOH, was 19.16‰. Each addition was approximately 8 mg NaHCO₃.

ane hydrochloride, 7.2 mM HCl, and 2.5 mM citric acid. The buffered seawater was titrated with 4 N NaOH in increments such that the pH changed about 0.25 pH units between readings.

A similar test was run in 0.5 M NaCl buffered with 5 mM boric acid, phosphoric acid, acetic acid, and hydrochloric acid. The measured glass-hydrogen electrode potential was 638.58 ± 0.13 mV (2 sigma) between pH 2.1 and 9.0. The glass-hydrogen electrode potential was 638.6 mV in NBS 7.4 buffer at 25°C.

Since the results in all three solutions were identical, within 1 SD, it appears that the response of the glass electrode does not depend on the composition or concentration of the test solution. This indicates that the asymmetry potential of the glass electrode is constant in these solutions. The constant potential difference between the glass and hydrogen electrodes implies that the glass electrode has the theoretical slope $2.303 RT/F$.

When the electrodes were calibrated as recommended by Bates (1964) in two buffers (NBS 7.415 and 4.008 at 25°C), the calculated slope was 0.9910 ± 0.0002 of the theoretical electrode slope at all temperatures between 2° and 35°C. The differ-

Table 3. Experimental results. Concentrations are moles per kilogram seawater

Temp (°C)	Salinity (‰)	$K'_1 \times 10^6$	f_H	pH^0	Temp (°C)	Salinity (‰)	$K'_1 \times 10^6$	f_H	pH^0				
2.00	26.67	0.6015 0.5966	0.770 0.774	7.900	25.00	19.16	0.8017 0.8019	0.677 0.677	7.716				
				7.898					7.714				
	27.01			7.711									
				7.716									
	34.66			19.19		7.812			25.17	7.652			
						7.810				7.650			
	34.78			25.25		0.6638			0.8727	0.813	0.677	7.648	
						0.6641						0.674	
	41.54			31.22		0.7290			0.836	7.768	0.8833	0.677	7.594
													0.7284
13.00	26.76	0.7225 0.7576 0.7599	0.827 0.718 0.731	7.757	31.49	0.9492	0.684 0.684	0.684	7.569				
									7.569				
	26.92			34.90		0.8387		0.750	7.759	0.9560	0.684	0.684	7.569
													7.567
	34.76			35.10		0.8373		0.755	7.689	1.0052	0.690	0.695	7.567
													7.689
	35.20			35.23		0.9153		0.787	7.689	1.0085	0.695	0.692	7.511
													7.511
	42.85			42.21		0.9145		0.788	7.629	1.0099	0.692	0.692	7.511
													7.511
42.90	42.26	1.0712	0.702	7.629	1.0782	0.695	0.688	7.511					
								7.511					
35.00	26.75	1.0812	0.688	7.629	0.9846	0.625	0.625	7.564					
								7.564					
	27.04				34.95	1.0912	0.624	7.494	1.0705	0.619	7.495		
												7.495	
	34.95				35.01	1.1568	0.629	7.433	1.1568	0.629	0.629	7.433	
												7.433	
42.94	42.94	1.1568	0.629	7.433	1.1568	0.629	0.629	7.433					
								7.433					

ence between the theoretical slope and the slope measured in the two buffers must be due to the calomel reference electrode, since the glass electrode was shown to have the theoretical slope. The difference is probably due to a different value of the liquid junction potential of the reference electrode in each buffer.

Determination of $K'_1K'_2$

Reagent grade NaHCO_3 (Baker No. 3506) was used in determining $K'_1K'_2$. It was compared to primary standard KHCO_3 , prepared as described by Kolthoff and

Stenger (1942). The purity of a bicarbonate sample is given by its value of TCO_2/CA . Pure bicarbonate has a value of one; a sample contaminated with carbonate has a value < 1 .

The value of TCO_2/CA for the NaHCO_3 used in our experiments was determined by comparing the value of the steady-state pH obtained with primary standard KHCO_3 to the value of the steady-state pH obtained with the NaHCO_3 , or pH^0 . Since, by definition, the primary standard's value of TCO_2/CA is exactly equal to one, its steady-state pH is equal to $1/2(\text{p}K'_1 + \text{p}K'_2)$. pH^0

Table 4. $K_1 \times 10^6$ as a function of salinity and temperature

	Salinity (‰)															
	19.00	25.00	27.00	29.00	31.00	32.00	33.00	34.00	35.00	36.00	37.00	38.00	39.00	40.00	43.00	
0	0.498	0.552	0.569	0.586	0.602	0.610	0.617	0.625	0.633	0.640	0.648	0.655	0.662	0.669	0.690	
1	0.512	0.567	0.585	0.601	0.618	0.626	0.634	0.642	0.650	0.657	0.665	0.672	0.680	0.687	0.708	
2	0.525	0.582	0.600	0.617	0.634	0.642	0.650	0.658	0.666	0.674	0.682	0.690	0.697	0.705	0.727	
3	0.539	0.597	0.615	0.633	0.650	0.658	0.667	0.675	0.683	0.691	0.699	0.707	0.715	0.722	0.745	
4	0.552	0.612	0.630	0.648	0.666	0.675	0.683	0.692	0.700	0.708	0.716	0.724	0.732	0.740	0.763	
5	0.565	0.626	0.645	0.664	0.682	0.691	0.699	0.708	0.716	0.725	0.733	0.741	0.749	0.757	0.781	
6	0.579	0.641	0.660	0.679	0.698	0.707	0.716	0.724	0.733	0.741	0.750	0.758	0.766	0.775	0.798	
7	0.592	0.655	0.675	0.695	0.713	0.722	0.732	0.740	0.749	0.758	0.767	0.775	0.783	0.792	0.816	
8	0.605	0.670	0.690	0.710	0.729	0.738	0.747	0.757	0.766	0.774	0.783	0.792	0.800	0.809	0.833	
9	0.618	0.684	0.705	0.725	0.744	0.754	0.763	0.772	0.782	0.791	0.799	0.808	0.817	0.826	0.851	
10	0.631	0.698	0.719	0.740	0.759	0.769	0.779	0.788	0.797	0.807	0.816	0.825	0.833	0.842	0.868	
11	0.643	0.712	0.733	0.754	0.774	0.784	0.794	0.804	0.813	0.822	0.832	0.841	0.850	0.859	0.885	
12	0.656	0.726	0.747	0.769	0.789	0.799	0.809	0.819	0.828	0.838	0.847	0.857	0.866	0.875	0.901	
13	0.668	0.739	0.761	0.783	0.804	0.814	0.824	0.834	0.844	0.853	0.863	0.872	0.881	0.891	0.917	
14	0.680	0.752	0.775	0.797	0.818	0.828	0.838	0.848	0.858	0.868	0.878	0.887	0.897	0.906	0.933	
15	0.692	0.765	0.788	0.810	0.832	0.842	0.853	0.863	0.873	0.883	0.893	0.902	0.912	0.921	0.949	
16	0.704	0.778	0.801	0.824	0.846	0.856	0.867	0.877	0.887	0.897	0.907	0.917	0.927	0.936	0.964	
17	0.715	0.791	0.814	0.837	0.859	0.870	0.880	0.891	0.901	0.911	0.921	0.931	0.941	0.951	0.979	
18	0.726	0.803	0.827	0.850	0.872	0.883	0.894	0.904	0.915	0.925	0.935	0.945	0.955	0.965	0.994	
19	0.737	0.815	0.839	0.862	0.885	0.896	0.907	0.918	0.928	0.939	0.949	0.959	0.969	0.979	1.008	
20	0.748	0.826	0.851	0.874	0.897	0.908	0.919	0.930	0.941	0.952	0.962	0.972	0.982	0.992	1.022	
21	0.758	0.838	0.862	0.886	0.909	0.921	0.932	0.943	0.954	0.964	0.975	0.985	0.995	1.005	1.035	
22	0.768	0.848	0.873	0.898	0.921	0.932	0.944	0.955	0.966	0.976	0.987	0.998	1.008	1.018	1.048	
23	0.778	0.859	0.884	0.909	0.932	0.944	0.955	0.966	0.977	0.988	0.999	1.010	1.020	1.030	1.060	
24	0.787	0.869	0.895	0.919	0.943	0.955	0.966	0.977	0.989	1.000	1.010	1.021	1.032	1.042	1.072	
25	0.796	0.879	0.905	0.929	0.953	0.965	0.977	0.988	0.999	1.011	1.021	1.032	1.043	1.053	1.084	
26	0.805	0.888	0.914	0.939	0.964	0.975	0.987	0.998	1.010	1.021	1.032	1.043	1.053	1.064	1.095	
27	0.813	0.897	0.923	0.949	0.973	0.985	0.997	1.008	1.020	1.031	1.042	1.053	1.064	1.074	1.105	
28	0.821	0.906	0.932	0.958	0.982	0.994	1.006	1.018	1.029	1.041	1.052	1.063	1.073	1.084	1.115	
29	0.829	0.914	0.941	0.966	0.991	1.003	1.015	1.027	1.038	1.050	1.061	1.072	1.083	1.093	1.125	
30	0.836	0.922	0.949	0.974	0.999	1.011	1.023	1.035	1.047	1.058	1.069	1.080	1.091	1.102	1.134	
31	0.843	0.929	0.956	0.982	1.007	1.019	1.031	1.043	1.055	1.066	1.077	1.089	1.100	1.110	1.142	
32	0.849	0.936	0.963	0.989	1.014	1.026	1.039	1.050	1.062	1.074	1.085	1.096	1.107	1.118	1.150	
33	0.855	0.943	0.970	0.996	1.021	1.033	1.045	1.057	1.069	1.081	1.092	1.103	1.114	1.125	1.157	
34	0.861	0.949	0.976	1.002	1.027	1.040	1.052	1.064	1.076	1.087	1.099	1.110	1.121	1.132	1.164	
35	0.866	0.954	0.981	1.008	1.033	1.045	1.058	1.070	1.082	1.093	1.105	1.116	1.127	1.138	1.170	

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is some value greater than $1/2(pK'_1 + pK'_2)$ due to contamination with carbonate. The value of $T\text{CO}_2/\text{CA}$ for our sample of NaHCO_3 was calculated from equation 3 using values of $1/2(pK'_1 + pK'_2)$, pH^0 , and K'_1 (Hawley 1973) measured in 0.72 molal NaCl . The value of $T\text{CO}_2/\text{CA}$ for the NaHCO_3 used in our experiments, as calculated from equation 3, was 0.9991 ± 0.0002 . In seawater this is equivalent to a difference of 0.012 ± 0.003 pH units between pH^0 and $1/2(pK'_1 + pK'_2)$.

We obtained pH^0 by making additions of NaHCO_3 to alkalinity-free seawater. Rapid convergence to the equilibrium pH was accomplished by adjusting the initial pH to within ± 0.05 pH of the equilibrium value with 0.1 N NaOH before adding the bicarbonate. The value for the equilibrium pH was the same when it was approached from an initial pH that was higher or lower than the equilibrium value (Table 2). To calculate $K'_1K'_2$, the measured values of pH^0 and $A (= 0.9991)$ were substituted into equation 4.

The first apparent dissociation constant, K'_1 , was determined by the modified Gran method described earlier. Hydrochloric acid (0.2999 eq/kg-HCl) was added in increments of 0.025 to 0.050 ml, depending on the salinity and the amount needed to neutralize the alkalinity. A calibrated 2-ml piston buret was used for the titrations.

RESULTS

The experimental results are given in Table 3. For purposes of interpolation, the experimental values of pK'_1 , pH^0 , and pK'_2 were fit, by a nonlinear least squares computer program, to equations which included the terms T , S , $\log(S)$, $1/T$, $\log(T)$, ST , S/T , $S^{1/2}$, $S^{1/3}$, S^2 , and $\log(S)/T$, where S is salinity in parts per thousand and T is temperature in degrees Kelvin. Coefficients not included in equations 10 and 11 were not statistically significant. Equation 10 for pK'_1 was obtained from the experimental data. Two standard deviations of the experimental points from equation 10 is 0.005 in pK'_1 or 1.2% in K'_1 . The values of K'_1 at integral values of temperature and

salinity in Table 4 were calculated from equation 10.

The experimental values of pH^0 (Table 3) were fit to an equation in the same manner as those of pK'_1 . Two standard deviations of the experimental data from the least squares equation was 0.006 in pH^0 . Values of pH^0 calculated from this equation were then substituted into equation 4 ($A = 0.9991$) and values of $K'_1K'_2$ were calculated at each temperature and salinity for which K'_1 had been calculated in Table 4. Values of K'_2 were obtained by dividing each value of $K'_1K'_2$ by the corresponding value of K'_1 . The calculated values of K'_2 are given in Table 5. Equation 11 for pK'_2 was obtained by fitting a least squares equation to 40 data points extracted from Table 5.

Tables 4 and 5 for K'_1 and K'_2 are precise to 1.2% for K'_1 and 2.0% for K'_2 . These precisions are based on 2 SD of the measured K'_1 and pH^0 from the regression equations. Equations 10 and 11 were developed to aid interpolation; they have no theoretical basis.

DISCUSSION

Apparent dissociation constants are used to describe processes, such as the solution and precipitation of carbonates, that have only slight effects on the major cation composition of seawater. From equation 1 and the definitions of stoichiometric association constants, one obtains equation 12 (Hawley 1973). In equation 12 the K^* values represent the association constants for bicarbonate association with sodium, magnesium, and calcium; the values in parentheses are the free concentrations of Na^+ , Mg^{2+} , and Ca^{2+} ; a_w is the activity of water; and K_1^0 is the thermodynamic ionization constant. The activity coefficients of molecular carbon dioxide, f_{CO_2} , and free bicarbonate ion, $f_{\text{HCO}_3^-}$, depend only on ionic strength. For the value of K'_1 to be altered, the relative concentrations of the major ions must vary or the salinity must change. Similar arguments apply to K'_2 .

In Tables 6 and 7 our values of the apparent dissociation constants are com-

Table 5. $K_s \times 10^6$ as a function of salinity and temperature

	Salinity (‰)																	
	19.00	25.00	27.00	29.00	31.00	32.00	33.00	34.00	35.00	36.00	37.00	38.00	39.00	40.00	43.00			
0	1.67	2.44	2.69	2.92	3.14	3.24	3.34	3.44	3.53	3.62	3.71	3.79	3.87	3.94	4.14			
1	1.73	2.52	2.76	3.00	3.22	3.32	3.43	3.53	3.62	3.71	3.80	3.88	3.96	4.04	4.24			
2	1.81	2.60	2.84	3.08	3.31	3.41	3.52	3.62	3.71	3.81	3.90	3.98	4.06	4.14	4.35			
3	1.88	2.68	2.93	3.17	3.40	3.51	3.61	3.72	3.81	3.91	4.00	4.09	4.17	4.25	4.47			
4	1.96	2.77	3.03	3.27	3.50	3.61	3.72	3.82	3.92	4.02	4.11	4.20	4.29	4.37	4.60			
5	2.05	2.87	3.13	3.37	3.61	3.72	3.83	3.93	4.04	4.14	4.23	4.32	4.41	4.50	4.73			
6	2.14	2.97	3.23	3.48	3.72	3.83	3.95	4.05	4.16	4.26	4.36	4.45	4.55	4.63	4.88			
7	2.23	3.08	3.34	3.60	3.84	3.96	4.07	4.18	4.29	4.39	4.49	4.59	4.69	4.78	5.03			
8	2.34	3.19	3.46	3.72	3.97	4.09	4.20	4.32	4.43	4.53	4.64	4.74	4.84	4.93	5.20			
9	2.44	3.31	3.59	3.85	4.10	4.22	4.34	4.46	4.57	4.68	4.79	4.89	4.99	5.09	5.37			
10	2.55	3.44	3.71	3.98	4.24	4.36	4.49	4.60	4.72	4.83	4.95	5.05	5.16	5.26	5.56			
11	2.67	3.57	3.85	4.12	4.38	4.51	4.64	4.76	4.88	5.00	5.11	5.22	5.33	5.44	5.75			
12	2.79	3.70	3.99	4.27	4.54	4.67	4.80	4.92	5.05	5.17	5.29	5.40	5.52	5.63	5.95			
13	2.92	3.85	4.14	4.42	4.69	4.83	4.96	5.09	5.22	5.34	5.47	5.59	5.71	5.82	6.16			
14	3.06	3.99	4.29	4.58	4.86	5.00	5.13	5.26	5.40	5.53	5.65	5.78	5.90	6.02	6.38			
15	3.19	4.15	4.45	4.74	5.03	5.17	5.31	5.45	5.58	5.71	5.85	5.98	6.11	6.23	6.61			
16	3.34	4.30	4.61	4.91	5.20	5.35	5.49	5.63	5.77	5.91	6.05	6.18	6.32	6.45	6.84			
17	3.49	4.46	4.78	5.08	5.38	5.53	5.68	5.82	5.97	6.11	6.25	6.40	6.54	6.68	7.09			
18	3.64	4.63	4.95	5.26	5.57	5.72	5.87	6.02	6.17	6.32	6.47	6.61	6.76	6.91	7.34			
19	3.80	4.80	5.12	5.44	5.76	5.91	6.07	6.22	6.38	6.53	6.69	6.84	6.99	7.14	7.60			
20	3.96	4.97	5.30	5.62	5.95	6.11	6.27	6.43	6.59	6.75	6.91	7.07	7.23	7.39	7.87			
21	4.13	5.15	5.48	5.81	6.14	6.31	6.47	6.64	6.80	6.97	7.13	7.30	7.47	7.63	8.14			
22	4.30	5.33	5.66	6.00	6.34	6.51	6.68	6.85	7.02	7.19	7.36	7.54	7.71	7.89	8.42			
23	4.47	5.51	5.85	6.19	6.54	6.71	6.89	7.06	7.24	7.42	7.60	7.78	7.96	8.14	8.70			
24	4.65	5.69	6.03	6.38	6.74	6.92	7.10	7.28	7.46	7.65	7.83	8.02	8.21	8.40	8.98			
25	4.82	5.87	6.22	6.58	6.94	7.12	7.31	7.49	7.68	7.87	8.07	8.26	8.46	8.66	9.27			
26	5.00	6.05	6.41	6.77	7.14	7.33	7.52	7.71	7.90	8.10	8.30	8.50	8.71	8.92	9.56			
27	5.18	6.23	6.59	6.96	7.34	7.53	7.72	7.92	8.12	8.33	8.54	8.75	8.96	9.18	9.85			
28	5.36	6.41	6.77	7.15	7.53	7.73	7.93	8.13	8.34	8.55	8.77	8.99	9.21	9.44	10.15			
29	5.53	6.58	6.95	7.33	7.72	7.93	8.13	8.34	8.56	8.77	9.00	9.22	9.46	9.69	10.43			
30	5.71	6.75	7.12	7.51	7.91	8.12	8.33	8.54	8.76	8.99	9.22	9.46	9.70	9.94	10.72			
31	5.88	6.92	7.29	7.68	8.09	8.30	8.52	8.74	8.97	9.20	9.44	9.68	9.93	10.19	11.00			
32	6.04	7.08	7.45	7.85	8.27	8.48	8.70	8.93	9.16	9.40	9.65	9.90	10.16	10.43	11.27			
33	6.20	7.23	7.61	8.01	8.43	8.65	8.88	9.11	9.35	9.60	9.85	10.11	10.38	10.66	11.54			
34	6.36	7.37	7.75	8.16	8.59	8.81	9.04	9.28	9.53	9.78	10.04	10.31	10.59	10.88	11.79			
35	6.50	7.51	7.89	8.30	8.73	8.96	9.20	9.44	9.69	9.96	10.22	10.50	10.79	11.09	12.04			

Table 6. Comparison of values of the first apparent dissociation constant, $K'_1 \times 10^6$, from various workers. Our values are in parentheses

Source	Salinity (%)	Temp (°C)				
		5	10	20	25	35
Lyman (1956)	35.0	0.776(0.760)*	0.832(0.842)*		1.00(1.085)*	1.07(1.158)*
Buch et al. (1932)†	21.81			0.839(0.786)		
	33.96		0.832(0.788)		1.064(0.988)	1.15(1.069)
	34.49			0.995(0.936)		
Hansson (1972)‡	35.0	0.693(0.716)	0.760(0.797)	0.897(0.941)	0.962(0.999)	

*This work's values corrected to pH scale used by Lyman (1956).

†Values recalculated by Edmond and Gieskes (1970).

‡Values adjusted to NBS pH scale.

pared with those of Buch et al. (1932) and Buch (1938) (as recalculated by Edmond and Gieskes 1970), Lyman (1956), and Hansson (1972). The difference between our values of K'_1 and those of Buch et al. (1932) averages 6.7% (range 5.6–7.8%), our values being lower in all cases. At 35‰ salinity our values for K'_1 are smaller than those of Lyman at low temperature and greater at higher temperatures, the average difference being 4.6%. Lyman's values were taken from his smoothed values and compared to values of ours recalculated to conform to his pH scale, which is based on standardization in 0.05 M potassium biphthalate (pH = 4.008 at 25°C). The necessity that the comparison of values be made on the same pH scale is discussed below. We found similar disagreement with Lyman at other salinities. Our values for

K'_1 are larger than those reported by Hansson. The average difference between the two sets of data is 4.0%.

Our values of K'_2 are smaller, in all cases, than those reported by others (Table 7). Buch's (1938) values are 26% larger than ours, Hansson's (1972) 3.4%, and Lyman's (1956) 3.2% at temperatures of 25°C and below and 13.4% at 35°C.

Part of the disagreement between the results of Buch (1938) and ours is due to the effect of ($MgOH^+$) ion pairs on the alkalinity; Buch determined K'_2 at pH 9.0, and he calculated the contribution of hydroxide ion to the total alkalinity from the ionization constant of water in NaCl solutions. Hansson (1972) showed that the ionization constant of water in seawater is four times larger than its value in NaCl. Based on Hansson's value for the ionization

Table 7. Comparison of values of the second apparent dissociation constant, $K'_2 \times 10^{10}$, of various workers. Our values are in parentheses

Source	Salinity (%)	Temp (°C)				
		5	10	20	25	35
Lyman (1956)	35.0	4.68(4.48)*	5.37(5.16)*		8.13(8.12)*	11.48(10.12)*
Buch (1938)†	25.13			6.63(4.99)		
	34.96			9.06(6.58)		
Hansson (1972)‡	35.0	4.18(4.04)	4.97(4.72)	6.79(6.59)	7.82(7.68)	

*This work's values corrected to pH scale used by Lyman (1956).

†Values recalculated by Edmond and Gieskes (1970).

‡Values adjusted to NBS pH scale.

constant of water in seawater, our calculations show that the values of Buch for K'_2 at 35‰ and 20°C are 4.5% too high.

A significant part of the disagreement in the values of K'_1 and K'_2 may be due to the difference in pH scales used. Lyman (1956) standardized on pH 4.0 buffer and Hansson's (1972) basic calibration is relative to the bicarbonate end point at a pH of about 4.5. We standardized our electrodes in pH 7.4 buffer. Since there is a difference between the theoretical slope of a glass electrode and the empirical slope determined by calibration in 7.4 and 4.0 buffers, the pH scale depends on the buffer used for calibration if the theoretical slope is used in the calculations. If we had not corrected our values to compensate for the difference between the pH scales used by us and by Lyman (1956), our values would differ from his by 4.5% in K'_1 and 18% in K'_2 .

A recent paper by Simpson and Broecker (1973) gives experimental data from which the ratio $K'_2 : K'_1$ can be calculated at 22.4°C and 36.6‰ salinity. Their value for $K'_2 : K'_1$ is 3.2% larger than ours. They neglected the effect of hydroxide ion on the alkalinity, and in their experiments the hydroxide ion concentration was about 2.6% of the total carbonate ion concentration. Their value for $K'_2 : K'_1$ would agree better with ours if they had considered the effect of hydroxide ion on the alkalinity.

We compared three "identical" Sargent calomel reference electrodes in measurements with the same glass electrodes. Changing the reference electrode changed the measured pH value by as much as 0.011 pH units, equivalent to a 2.6% variation in K'_1 and K'_2 . This effect may be one reason for the differences between the values reported by each author.

Values of the total hydrogen ion activity coefficient, $(f_{\text{H}})_T$, calculated from equation 6 are given in Table 3. Hansson's (1972) dissociation constants, which are based on the total hydrogen ion concentration, must be multiplied by $(f_{\text{H}})_T$ to be compared with constants based on the NBS pH scale. Also, his values must be slightly altered for

use in natural seawater, since his artificial seawater contained no fluoride and less sulfate than natural seawater.

Hansson (1972) compared the application of the NBS pH scale for three reference electrodes, one filled with saturated KCl, one with seawater of 35‰ salinity, and one filled with 20‰ salinity seawater. This comparison is misleading as apparent constants and the NBS pH scale should be used with the same general type of reference electrode when K' is determined and when it is applied to pH values measured in seawater. Then the arbitrariness in the definition of pH cancels between the two sets of measurements and derived values of the concentrations of carbonate species are correct. Both the NBS scale and Hansson's pH scale are conventional and must be used in a self-consistent manner.

The values of the pressure coefficients of the apparent dissociation constants of carbonic acid (Culberson and Pytkowicz 1968) were unchanged when recalculated using our values of K'_1 and K'_2 .

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