AN ABSTRACT OF THE THESIS OF

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MEASUREMENT OF THE APPARENT DISSOCIATION CONSTANTS

OF CARBONIC ACID IN SEAWATER AT

ATMOSPHERIC PRESSURE

The apparent dissociation constants of carbonic acid were determined as functions of temperature and salinity in seawater at atmospheric pressure.

There is fair agreement between my values of K'_1 and those of Buch et al. (1932), Lyman (1956), and Hansson (1971). My values, on the average, are 6.7% lower than Buch et al.'s (1932), 4.6% smaller than Lyman's (1956), and 4.0% higher than Hansson's (1972).

My values for K'_2 are smaller than those reported by other workers. They differ by 3.4% from Hansson's (1972) values, and 26% from Buch's (1938). Lyman's (1956) values are larger than mine by 3.2% at temperatures of 25°C and below, and greater by 13.4% at 35°C.

Measurement of the Apparent Dissociation
Constants of Carbonic Acid in Seawater
at Atmospheric Pressure

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Typed by Suelynn Williams for Carl Mehrbach

Men suffer want and become
Curiously ignoble; as prosperity
Made them curiously vile

But look how noble the world is,
The lonely-flowing waters,
    the secret-keeping stones,
    the flowing sky.

              Robinson Jeffers
               from "Life From the Lifeless"

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If it were not for Claudia Barton's aid in running my data through my computer program, which was written for maximum boredom of the teletype operator, the completion of this work may still have been in the future.

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TABLE OF CONTENTS

LIST OF TABLES

MEASUREMENT OF THE APPARENT DISSOCIATION CONSTANTS

OF CARBONIC ACID IN SEAWATER AT

ATMOSPHERIC PRESSURE

I. INTRODUCTION

Carbon dioxide is important to man because of its role in the carbon cycle of nature. In the photosynthetic process, the earth's flora intake carbon dioxide, respire oxygen, and produce organic compounds such as carbohydrates, proteins, and fats (Villee, 1957). These plant products are digested and assimilated by man in his routine life process.

The earth's temperature is also controlled to a large extent by carbon dioxide in the atmosphere (Keeling, 1970). Carbon dioxide is transparent to visible and ultraviolet solar radiation, which is absorbed by the earth. The earth then radiates some of the absorbed solar energy as infrared radiation. The carbon dioxide in the atmosphere absorbs much of this infrared radiation and prevents its escape from the earth's atmosphere (Broecker et al., 1971). This phenomenon is known as the greenhouse effect. It is a factor that keeps the earth's environment as warm as it is.

In our century the carbon dioxide in the earth's atmosphere has increased by 12% due to man's burning of fossil fuel (Callender, 1968). Revelle and Suess (1957) said, concerning this interaction of man with

his environment, that "human beings are now carrying out a large

scale geophysical experiment of a kind which could not have happened

in the past nor be reproduced in the future. Within a few centuries

we are returning to the air and oceans the concentrated organic carbon

stored over hundreds of millions of years." If carbon dioxide's atmos-

pheric concentration continues to increase at its present rate of accel-

eration, the temperature of the earth may rise as much as $20°C$ in the

next 100 years (Pytkowicz, 1973).

The oceans are the greatest sink for the carbon dioxide in the

atmosphere (Broecker et al., 1971). Forty percent of all the carbon

dioxide man has produced by the burning of fossil fuel already resides

in the oceans (Broecker et al., 1971). Thus the oceans are an impor-

tant natural regulator of the carbon dioxide system. Carbon dioxide

dissolves in the oceans and is utilized by plants in photosynthesis and

by plants and animals in the production of carbonates. The carbonates

dissolve in seawater or are deposited on the sea floor as sediment

(Revelle, 1965). It is also carbon dioxide that assists in the control

of the pH and composition of seawater by participating in homogeneous

and heterogeneous acid-base and exchange reactions (Stumm and

Morgan, 1970).

In order to fully understand the effect of carbon dioxide dis-

solution in seawater, it is necessary to know the concentrations of the

various carbon dioxide species (i.e., carbonic acid, molecular carbon

dioxide, carbonate and bicarbonate) in seawater. The apparent dissociation constants of carbonic acid in seawater are needed to describe the relative distribution of these species in seawater. In this work, these apparent (quasi-stoichiometric) dissociation constants of carbonic acid in seawater were determined at atmospheric pressure as functions of temperature and salinity. These constants are defined (Moberg et al., 1934) by

$$K'_1 = \frac{a_H(HCO_3^-)}{(CO_2^*)} \tag{1}$$

$$K'_2 = \frac{a_H(CO_3^=)}{(HCO_3^-)} . \tag{2}$$

The parentheses represent concentrations in moles per kilogram of seawater, a_H is the hydrogen ion activity defined in the National Bureau of Standards (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 carbon dioxide 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 of 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 which do not have a sizable effect upon 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). The first constant was defined by

$$K''_1 = \frac{a_H(HCO_3^-)}{a_{H_2CO_3}} \tag{3}$$

and the second by equation (2). Buch et al.'s (1932) and Buch's (1938) procedure involved the measurement of the alkalinity, the pH, and the pCO_2 or total carbon dioxide. The solubility of CO_2 in seawater was estimated from its solubility in sodium chloride solutions. pCO_2 was measured gasometrically, total carbon dioxide was measured by boiling the seawater after acidification, and the pH was determined with a quinhydrone electrode in the case of K''_1 and with a hydrogen electrode in the case of K'_2. The pH was referenced to the Sörensen scale.

Lyman (1956) determined the apparent constants by carrying out complete titrations on a single sample of seawater. He used a

glass electrode calibrated on the NBS scale. Lyman (1956) claimed that his method was inherently more accurate and precise than Buch et al.'s (1932) and Buch's (1938). He defined K'_1 and K'_2 by equations (1) and (2).

Edmond and Gieskes (1970) reviewed the results of Buch et al. (1932), Buch (1938), 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 K'_2 obtained by Lyman (1956) were selected as the most reliable ones for derivation of equations relating pK'_1 and pK'_2 to temperature and salinity.

Hansson (1972) determined the apparent constants by titrating borate free artificial seawater with HCl. He determined his constants by adjusting his K'_1 and K'_2 until a calculated titration curve matched his experimental one. The pH scale utilized was based upon seawater as a standard state.

Based upon the intercomparison of field data obtained from a variety of techniques, Takahashi et al. (1971) suggested that Lyman's (1956) values for K'_2 may be as much as 30% too low.

Disteche and Disteche (1967), Culberson, Kester and Pytkowicz (1967), and Culberson and Pytkowicz (1968) extended the determination of the constants to the pressures encountered in the deep oceans.

I redetermined the dissociation constants since Edmond and

Gieskes (1970) inferred that no one set of data was adequate, and since Takahashi et al. (1971) suggested that Lyman's (1956) values for K'_2 were incorrect.

II. THEORY

This work was done in two steps: the measurement of the product $K'_1 K'_2$ and of K'_1. The method used was a modification of methods developed by Weyl (1961), Kester and Pytkowicz (1967), and Dyrssen and Sillen (1967).

The following definitions and equations are used in this paper:

$$TA = (HCO_3^-) + 2(CO_3^{2-}) + N(a_H) \qquad (4)$$

where TA is the titration alkalinity and $N(a_H)$ is the concentration of ions, other than carbonic acid species, which react with the hydrogen ion.

$$CA = (HCO_3^-) + 2(CO_3^{2-}) = TA - N(a_H) \qquad (5)$$

CA is the carbonate alkalinity. Total carbon dioxide is defined as

$$TCO_2 = (CO_2^*) + (HCO_3^-) + (CO_3^{2-}) \qquad (6)$$

For the determination of $K'_1 K'_2$, I obtained the following expression from equations (1), (2), (4), (5) and (6):

$$\frac{TCO_2}{CA} = \frac{a_H^2 + K'_1 a_H + K'_1 K'_2}{K'_1 a_H + 2 K'_1 K'_2} = \frac{TCO_2}{TA - N(a_H)} \qquad (7)$$

Let y_o be the initial TCO_2 and y be the moles of sodium bicarbonate added. If the pH does not change upon addition of y to a sample of seawater then, from (7),

$$\frac{TCO_2}{CA} = \frac{y_o}{TA - N(a_H)} = \frac{y_o + y}{TA - N(a_H) + y} = 1 \qquad (8)$$

Therefore, $y_o = TA - N(a_H)$ and $a_H^2 + K'_1 a_H + K'_1 K'_2 = K'_1 a_H + 2K'_1 K'_2$, which leads to $a_H^2 = K'_1 K'_2$ or

$$pH = \tfrac{1}{2}(pK'_1 + pK'_2) \qquad (9)$$

Thus, $K'_1 K'_2$ can be determined by adding small amounts of bicarbonate until a pH is reached that remains constant upon further additions of bicarbonate.

The Gran method (Gran, 1952; Dyrssen and Sillen, 1967; Edmond and Gieskes, 1970) was modified for the determination of K'_1. After the bicarbonate endpoint in a titration of seawater with acid, TA is essentially $(HCO_3^-) - (H^+)_{total}$, with $(H^+)_{total} = (H^+)_{free} + (HF) + (HSO_4^-)$ (Culberson, Pytkowicz and Hawley, 1970). Therefore,

$$TA_o \left[\frac{W_o}{W_o + W_a} \right] - W_a \left[\frac{N_a}{W_o + W_a} \right] = \frac{TCO_2}{1 + a_H/K'_1} - \frac{a_H}{f_H} +$$

$$- \frac{T_F a_H}{a_H + K'_{HF}} - \frac{T_S a_H}{a_H + K'_{HSO_4^-}} \qquad (10)$$

where

TA_o = initial titration alkalinity (equiv/Kg-seawater)

W_o = weight of seawater sample

W_a = weight of acid added

N_a = normality of acid (equiv/Kg-HCl)

f_H = free activity coefficient of H^+

T_F = (HF) + (F$^-$)   (moles/Kg-seawater)

T_S = (HSO$_4^-$) + (SO$_4^{2-}$)   (moles/Kg-seawater)

$K'_{HF} = a_H(F^-)/(HF)$

$K'_{HSO_4^-} = a_H(SO_4^{2-})/(HSO_4^-)$.

Rearranging (10),

$$F_1 = (TA_o W_o f_H) - (W_a N_a f_H) =$$

$$= (W_o + W_a) \left[\frac{TCO_2 f_H}{1 + a_H/K'_1} - a_H - \frac{T_F a_H f_H}{a_H + K'_{HF}} - \frac{T_S a_H f_H}{a_H + K'_{HSO_4^-}} \right]$$

(11)

The corresponding uncorrected equation in Dyrssen and

Sillen (1967) is

$$F_1 = (W_o + W_a)a_H \tag{12}$$

in which the presence of residual HCO_3^- and the formation of HF and

HSO_4^- at low pH's have not been considered. It can be seen from

equation (11) that when $F_1 = 0$, the total initial alkalinity (contained in

W_o) 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 $W_2 N_a$ being the number of equivalents of alkalinity initially present in the seawater sample.

Equation (11) is an equation of a line with a slope equal to $N_a f_H$. Thus the free activity coefficient of the hydrogen ion can be obtained by dividing the slope of the line by the concentration of the acid, N_a. When the corrections for HF and HSO_4^- are neglected in equation (11), one obtains the total hydrogen ion activity coefficient, $(f_H)_T$ (Culberson, Pytkowicz and Hawley, 1970).

Dyrssen and Sillen (1967) also presented equations equivalent to the following:

$$pK'_1 = pH - \log \left[\frac{W_2 - W_a}{W_a - W_1} \right] \tag{13}$$

$$F_2 = K'_1 (W_a - W_1) = a_H (W_2 - W_a) \tag{14}$$

They expressed their equations in terms of H^+ concentration. W_1 is such that $W_1 N_a = (CO_3^{2-}) + (B(OH)_4^-) + (OH^-)$ and can be obtained from a plot of F_2 versus W_a when $F_2 = 0$. Therefore, corrections must be made to equation (14) because of borate and carbonate interference near the endpoint, W_1. When these corrections are applied, one obtains the following equation (as is shown in the Appendix I)

$$F_2 = K'_1 (W_a - W_1) = a_H (W_2 - W_a) +$$

$$- \frac{K'_1}{N_a} \left[\frac{(W_2 - W_a) K'_2 N_a}{(W_o + W_a) a_H} (1 + \frac{2a_H}{K'_1}) + \frac{T_B K'_B}{a_H + K'_B} (1 + \frac{a_H}{K'_1}) \right] (W_o + W_a)$$

$$(15)$$

In equations (11) and (15), the quantities T_F, T_S and T_B were corrected for dilution by the acid titrant.

The corrections for sulfate and fluoride were dropped in equation (11) at temperatures other than 25°C, because K'_{HF} and K'_S were not known, and because the error introduced by neglecting the corrections for sulfate and fluoride was found to be smaller than the inherent experimental error at 25°C. It was 0.46% of the value of K'_1.

The following iteration procedure was performed by computer for the calculation of K'_1 (program is given in Appendix II). 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 (12) and (14), by a linear least squares procedure. A value of TCO_2 was calculated from the expression $TCO_2 = N_a (W_2 - W_1)$, which Edmond (1970) claimed to be accurate to ± 0.68%. At 25°C the approximate values of W_1, W_2, K'_1, and TCO_2 were then plugged into the more refined equations (11) and (15), in conjunction with Lyman's (1956) values of K'_2 and K'_B, and $K'_{HSO_4^-}$ and K'_{HF} from Culberson, Pytkowicz and Hawley (1970). At all other

temperatures the procedure was the same except for the removal of the corrections for sulfate and fluoride in equation (11). Iterations were continued until successive values of the slope of F_2, which was equal to K'_1, did not differ by more than 0.5%. The correction for carbonate in F_2 was found to have the same effect whether Lyman's (1956) K'_2 or that obtained by me was employed, because of the small value of the correction.

III. EXPERIMENTAL

Surface seawater of 31.5‰ salinity from off the Oregon coast was filtered through a 0.45μ Millipore filter and then either diluted with deionized distilled water or concentrated by evaporation to obtain the desired salinity. For the determination of $\frac{1}{2}(pK'_1 + pK'_2)$, the buffer capacity of the seawater should be at a minimum. This was accomplished by adding hydrochloric acid in an amount equivalent to the alkalinity and then removing the carbon dioxide by purging the solution with carbon dioxide-free air.

The hydrochloric acid concentration used in all experiments was 0.2999 equiv/Kg-HCl, prepared from J. T. Baker's Dilute-It analytical concentrate (#4654). The normality of the HCl was determined by a differential potentiometric titration against primary standard Na_2CO_3 solution. One-tenth normal NaOH, prepared from Baker reagent grade sodium hydroxide (#3722), was used to adjust the pH of the seawater in the experiments to determine $\frac{1}{2}(pK'_1 + pK'_2)$.

The titration cell consisted of a water-jacketed beaker for constant temperature control and a rubber stopper which held a Sargent-Welch S-30080-15-C saturated calomel internal reference electrode with a ceramic frit liquid junction, a Sargent-Welch S-30050-C glass electrode, and a calibrated thermometer. The stopper also contained a hole for placement of a syringe needle for titrations, and a glass syringe

piston and barrel. The piston receded into the barrel upon addition

of solution into the cell, thus insuring constant pressure without

exchange of gases. The cell is similar to that used by Edmond (1970).

The temperature of the cell was controlled with water from an Aminco

constant temperature bath (#4-8605).

The potential of the glass-calomel pair was measured by an

Orion 801 digital millivolt meter, which was standardized against

a Leeds-Northrup 8687 volt potentiometer.

The calculation of the test solution's pH, pH_t, was made from

the following equation.

$$pH_t = pH_b + \frac{(E_t - E_b)}{2.303RT/F} \qquad (16)$$

pH_b is the pH of the standard NBS buffer (186-I-c, 186-II-c; pH 7.415

at 25°C), and E_t and E_b are the potentials of the electrode pair in the

test solution and the buffer, respectively. R is the gas constant, F is

the Faraday constant, and T is the temperature in degrees Kelvin.

The glass electrode used in these experiments was compared

with a hydrogen electrode, and it was found to have the theoretical

slope, 2.303RT/F. In natural seawater at 25°C, the potential differ-

ence between the glass and the hydrogen electrode was 638.63 mv ±

0.10 mv (two standard deviations) between pH 2 and 9. The natural

seawater (salinity 31.5‰) was buffered with 0.005M acetic acid,

0.005M boric acid, 0.0025M tris(hydroxymethyl)aminomethane

hydrochloride, 0.0072M HCl, and 0.0025M citric acid. The initial pH of the buffered seawater was 2.39. The seawater solution was then titrated with 4N NaOH in increments such that the pH was changed by approximately 0.25 pH units between readings. The final reading was taken at pH 8.87.

A similar test was run in 0.5M NaCl, buffered with 0.005M boric acid, 0.005M phosphoric acid, 0.005M acetic acid, and 0.005M hydrochloric acid. The results gave a glass-hydrogen electrode potential of 638.58 mv ± 0.13 mv (two standard deviations) between pH 2 and pH 9.

Also, the electrodes' potential difference was found to be 638.6 mv in NBS 7.4 buffer at 25°C.

Since the results in all three solutions were identical, within one standard deviation, it appears that the response of the glass electrode does not depend upon the composition or concentration of the solution in which it is used. This indicates that the glass electrode shows no assymetry potential differences from one of these solutions to another.

The constant potential difference between the glass and the hydrogen electrodes at pH's between 2 and 9 implies that the glass electrode has the same slope as that theoretically defined for the hydrogen electrode, or 2303RT/F millivolts per pH unit.

When the electrodes were calibrated as recommended by Bates

(1964) in two buffers (NBS 7.4 and NBS 185-d (pH 4.008 at 25°C)),

the slope obtained was 0.9910 ± 0.0002 of the theoretical electrode

slope at all temperatures between 2° and 35°C. The difference

between the theoretical electrode slope and the slope measured in two

buffers must be due to the calomel reference electrode, since the

glass electrode was shown to have a theoretical slope. The difference

is probably due to a different value of the liquid junction potential of

the reference electrode in each buffer.

Reagent grade $NaHCO_3$ (Baker #3506) was used to determine

$\frac{1}{2}(pK'_1 + pK'_2)$. It was referenced against primary standard $KHCO_3$,

prepared as described by Kolthoff and Stenger (1942). The purity of

a bicarbonate sample is represented by the sample's value of $TCO_2/$

CA. Pure bicarbonate has a value of one, while a sample contami-

nated with carbonate has a value less than one.

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

in 0.72 molal NaCl with primary standard $KHCO_3$ and the value of the

steady state pH obtained with the $NaHCO_3$, or pH^o. Since, by definition,

the primary standard's TCO_2/CA value is exactly equal to one, its

steady state pH is equal to $\frac{1}{2}(pK'_1 + pK'_2)$. pH^o is some value greater

than $\frac{1}{2}(pK'_1 + pK'_2)$ due to contamination with carbonate. The values

of $\frac{1}{2}(pK'_1 + pK'_2)$, pH^o, and K'_1 in 0.72 molal NaCl (Hawley and

Pytkowicz, 1973) were then substituted in the following equation,

which is merely a rearrangement of equation (7):

$$A = \frac{TCO_2}{CA} = \frac{10^{-2pH^o} + K'_1 10^{-pH^o} + 10^{-(pK'_1 + pK'_2)}}{K'_1 10^{-pH^o} + 2(10^{-(pK'_1 + pK'_2)})} \qquad (17)$$

The value of TCO_2/CA for the $NaHCO_3$ used in our experiments, as calculated from (17), was 0.9991 ± 0.0002. In seawater this is equivalent to a difference of approximately 0.012 ± 0.003 pH units between pH^o and $\frac{1}{2}(pK'_1 + pK'_2)$.

pH^o was obtained 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 unit of the equilibrium value with 0.1N NaOH before adding the bicarbonate. The same value for the equilibrium pH was obtained when it was approached from an initial pH that was higher or lower than the equilibrium value. An example of an experiment is given in Table 1.

In order to obtain $K'_1 K'_2$, pH^o and the value of A (=0.9991) calculated from equation (17) were substituted into the following equation, which is a rearrangement of equation (7):

$$K'_1 K'_2 = \frac{10^{-2pH^o} + (1 - A)K'_1 10^{-pH^o}}{(2A - 1)} \qquad (18)$$

The first apparent dissociation constant, K'_1, was determined by the modified Gran method described earlier. Hydrochloric acid (0.2999 equivalents/Kg-HCl) was added in increments of 0.025 to

Table 1: An example of a test to determine pH^o.

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 0.1N NaOH to adjust the pH of the solution to the approximated value of the steady state pH, pH^o.

$NaHCO_3$ addition number*	potential
0	-62.4 mv
1	-62.0
2	-61.9
3	-61.8
4	-61.8
5	-61.8

From equation (16), pH^o = 7.716

The salinity of the sample, corrected for dilution with 0.01N NaOH, was 19.16‰

*Each addition was approximately 8 mg $NaHCO_3$.

0.050 ml, depending upon the salinity and the amount needed to

neutralize the alkalinity. A calibrated 2 ml piston buret (Gilmont

#S1200) was used for the titrations.

IV. RESULTS

The values of K'_1 and $K'_1 K'_2$ were measured at 27, 35 and 43‰ at 2, 13, and 35°C, and at 19, 25, 31, 35 and 42‰ at 25°C. The experimental results are given in Table 2.

The experimental values of pK'_1 were fit by a nonlinear least squares computer program, to an equation 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. The equation obtained from the experimental data follows. The coefficients not included in this equation were not statistically significant.

$$pK'_1 = -1.3720058 \times 10^1 + 3.1334423 \times 10^{-2} \times T +$$

$$+ 3.2357584 \times 10^3 / T + 1.3002925 \times 10^{-5} \times S \times T +$$

$$- 1.0319833 \times 10^{-1} \times S^{1/2} \tag{19}$$

Two standard deviations of the experimental points from equation (19) is 0.005 in pK'_1 or 1.2% in K'_1. The values of K'_1 at integral values of temperature and salinity were calculated from equation (19) and placed in Table 3.

The experimental values of pH^o (given in Table 2) were fit to an equation in the same manner as those of pK'_1. The following equation

Table 2: Experimental results. Concentration unit is moles per kilogram seawater.

Temp (°C)	Salinity (‰)	$K'_1 \times 10^6$	f_H	pH^o
2.00	26.67			7.900
				7.898
	27.01	.6015	.770	
		.5966	.774	
	34.66			7.812
				7.810
				7.814
				7.818
	34.78	.6638	.802	
		.6641	.801	
		.6665	.813	
	41.54			7.768
	42.88	.7290	.836	
		.7284	.837	
		.7225	.827	
13.00	26.76	.7576	.718	
		.7599	.731	
	26.92			7.757
				7.759
	34.76	.8387	.750	
		.8373	.755	
	35.20			7.689
				7.689
	42.85	.9153	.787	
		.9145	.788	
	42.90			7.629
25.00	19.16			7.716
				7.714
				7.711
				7.716
	19.19	.8017	.677	
		.8019	.677	
	25.17			7.652
				7.650
				7.648

Table 2 (continued)

Temp (°C)	Salinity (‰)	$K'_1 \times 10^6$	f_H	pH^o
25.00	25.25	.8727	.674	
		.8833	.677	
	31.22			7.594
				7.591
				7.593
	31.49	.9492	.684	
		.9560	.684	
	34.90			7.569
				7.569
				7.567
	35.10	1.0052	.690	
		1.0085	.695	
	35.23	1.0099	.692	
	42.21			7.511
				7.511
	42.26	1.0712	.702	
		1.0782	.695	
		1.0812	.688	
35.00	26.75	.9846	.625	
	27.04			7.564
				7.564
	34.95	1.0912	.624	
		1.0705	.619	
	35.01			7.494
				7.495
	42.67	1.1568	.629	
	42.94			7.433
				7.433

Table 3: $K'_1 \times 10^6$ as a function of salinity and temperature.

Salinity (‰)

Temp (°C)	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	.498	.552	.569	.586	.602	.610	.617	.625	.633	.640	.648	.655	.662	.669	.690
1	.512	.567	.585	.601	.618	.626	.634	.642	.650	.657	.665	.672	.680	.687	.708
2	.525	.582	.600	.617	.634	.642	.650	.658	.666	.674	.682	.690	.697	.705	.727
3	.539	.597	.615	.633	.650	.658	.667	.675	.683	.691	.699	.707	.715	.722	.745
4	.552	.612	.630	.648	.666	.675	.683	.692	.700	.708	.716	.724	.732	.740	.763
5	.565	.626	.645	.664	.682	.691	.699	.708	.716	.725	.733	.741	.749	.757	.781
6	.579	.641	.660	.679	.698	.707	.716	.724	.733	.741	.750	.758	.766	.775	.798
7	.592	.655	.675	.695	.713	.722	.732	.740	.749	.758	.767	.775	.783	.792	.816
8	.605	.670	.690	.710	.729	.738	.747	.757	.766	.774	.783	.792	.800	.809	.833
9	.618	.684	.705	.725	.744	.754	.763	.772	.782	.791	.799	.808	.817	.826	.851
10	.631	.698	.719	.740	.759	.769	.779	.788	.797	.807	.816	.825	.833	.842	.868
11	.643	.712	.733	.754	.774	.784	.794	.804	.813	.822	.832	.841	.850	.859	.885
12	.656	.726	.747	.769	.789	.799	.809	.819	.828	.838	.847	.857	.866	.875	.901
13	.668	.739	.761	.783	.804	.814	.824	.834	.844	.853	.863	.872	.881	.891	.917
14	.680	.752	.775	.797	.818	.828	.838	.848	.858	.868	.878	.887	.897	.906	.933
15	.692	.765	.788	.810	.832	.842	.853	.863	.873	.883	.893	.902	.912	.921	.949
16	.704	.778	.801	.824	.846	.856	.867	.877	.887	.897	.907	.917	.927	.936	.964
17	.715	.791	.814	.837	.859	.870	.880	.891	.901	.911	.921	.931	.941	.951	.979
18	.726	.803	.827	.850	.872	.883	.894	.904	.915	.925	.935	.945	.955	.965	.994
19	.737	.815	.839	.862	.885	.896	.907	.918	.928	.939	.949	.959	.969	.979	1.008
20	.748	.826	.851	.874	.897	.908	.919	.930	.941	.952	.962	.972	.982	.992	1.022
21	.758	.838	.862	.886	.909	.921	.932	.943	.954	.964	.975	.985	.995	1.005	1.035
22	.768	.848	.873	.898	.921	.932	.944	.955	.966	.976	.987	.998	1.008	1.018	1.048
23	.778	.859	.884	.909	.932	.944	.955	.966	.977	.988	.999	1.010	1.020	1.030	1.060
24	.787	.869	.895	.919	.943	.955	.966	.977	.989	1.000	1.010	1.021	1.032	1.042	1.072
25	.796	.879	.905	.929	.953	.965	.977	.988	.999	1.011	1.021	1.032	1.043	1.053	1.084
26	.805	.888	.914	.939	.964	.975	.987	.998	1.010	1.021	1.032	1.043	1.053	1.064	1.095
27	.813	.897	.923	.949	.973	.985	.997	1.008	1.020	1.031	1.042	1.053	1.064	1.074	1.105
28	.821	.906	.932	.958	.982	.994	1.006	1.018	1.029	1.041	1.052	1.063	1.073	1.084	1.115
29	.829	.914	.941	.966	.991	1.003	1.015	1.027	1.038	1.050	1.061	1.072	1.083	1.093	1.125
30	.836	.922	.949	.974	.999	1.011	1.023	1.035	1.047	1.058	1.069	1.080	1.091	1.102	1.134
31	.843	.929	.956	.982	1.007	1.019	1.031	1.043	1.055	1.066	1.077	1.089	1.100	1.110	1.142
32	.849	.936	.963	.989	1.014	1.026	1.039	1.050	1.062	1.074	1.085	1.096	1.107	1.118	1.150
33	.855	.943	.970	.996	1.021	1.033	1.045	1.057	1.069	1.081	1.092	1.103	1.114	1.125	1.157
34	.861	.949	.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	.866	.954	.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

was obtained:

$$pH^o = 2.7320399 \times 10^3 + 8.6802262 \times 10^{-1} \times T +$$

$$+ 1.2253089 \times 10^{-1} \times S + 9.2682884 \times \log(S) +$$

$$- 6.3810229 \times 10^4/T - 1.1188611 \times 10^3 \times \log(T) +$$

$$- 4.2102212 \times 10^{-4} \times S \times T - 2.8795312 \times 10^3 \times \log(S)/T$$

$$(20)$$

Two standard deviations of the experimental data from equation (20)

is 0.006 in pH^o.

The values of pH^o from equation (20) were substituted into

equation (18), along with A (=0.9991), and values of $K'_1 K'_2$ were

calculated at each temperature and salinity for which K'_1 had been

calculated in Table 3. Values of K'_2 were obtained by dividing the

value of $K'_1 K'_2$ at each temperature and salinity by the corresponding

value of K'_1. These calculated values of K'_2 are given in Table 4.

The following equation for pK'_2 was obtained from forty data points

extracted from Table 4:

$$pK'_2 = +5.3719645 \times 10^3 + 1.6712212 \times T +$$

$$+ 2.2912927 \times 10^{-1} \times S + 1.8380222 \times 10^1 \times \log(S) +$$

$$- 1.2837528 \times 10^5/T - 2.1943055 \times 10^3 \times \log(T) +$$

$$- 8.0943679 \times 10^{-4} \times S \times T +$$

$$- 5.6171116 \times 10^3 \times \log(S)/T + 2.1364128 \times S/T \qquad (21)$$

One standard deviation of the calculated values of K'_2 extracted from

Table 4 from equation (21) is 0.0003 in pK'_2.

Table 4: $K'_2 \times 10^{10}$ as a function of temperature and salinity.

Salinity (‰)

Temp (°C)	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

Tables 3 and 4 for K'_1 and K'_2, which were developed from equations (19) and (20), are precise to 1.2% for K'_1 and 2.0% for K'_2. These precisions are based on two standard deviations of the measured K'_1 and pH^o from the regression lines, as these lines were used to generate the tables.

V. DISCUSSION

Apparent (quasi-stoichiometric) dissociation constants are useful to describe processes, such as the dissolution and precipitation of carbonates and changes in pH, which have only slight effects upon the major cation composition of seawater. From equation (1) and the definitions of stoichiometric association constants, one obtains equation (22) (Hawley and Pytkowicz, 1973)

$$K'_1 = \frac{K^{o'}_1}{a_{H_2O} f_{CO_2}} \left[1 + K^*_{NaHCO_3}(Na) + K^*_{MgHCO_3}(Mg) + K^*_{CaHCO_3}(Ca) \right]$$

(22)

In equation (22), the K^*s represent the association constants for bicarbonate association with sodium, magnesium, and calcium, the values in parentheses are the free concentrations of Na^+, Mg^{++}, and Ca^{++}, a_{H_2O} is the activity of water, and f_{CO_2} is the total carbon dioxide activity coefficient. $K^{o'}_1$, which is defined by equation (23), depends only on ionic strength:

$$K^{o'}_1 = \frac{a_{H_2O}(HCO_3^-)_{free}}{CO_2^*}$$

(23)

In equation (23), $(HCO_3^-)_{free}$ represents the free concentration of bicarbonate. In order to alter the value of K'_1 the relative concentrations of the major ions must vary or the salinity must change. Similar arguments apply to K'_2.

In Tables 5 and 6 the values of the first and second apparent dissociation constants determined in this work are compared with those of Buch et al. and Buch (1932, 1938; recalculated by Edmond and Gieskes, 1970), Lyman (1956), and Hansson (1972). The difference between my values for K'_1 and those of Buch et al. (1932) is, on the average, 6.7% (range 5.6 to 7.8%), with my values being lower in all cases. The comparison was done over the temperature range 10 to 35°C and the salinity range 21.8 to 34.5‰. At 35‰ salinity my values for K'_1 are smaller than those of Lyman (1956) at low temperature (5° and under) and greater at higher temperatures, the average difference being 4.6%. The values of Lyman's (1956) were taken from his smoothed values. They are compared to values of mine which have been recalculated to conform to his pH scale, which is based on a 0.05M potassium biphthalate (pH(NBS)=4.008 at 25°C) standardization and a theoretical electrode response. The necessity that the comparison of values be made on the same pH scale is discussed later. Similar disagreement with Lyman (1956) was found at other salinities. My values for K'_1 are larger than those reported by Hansson (1972). The difference between the two sets of data averages 4.0%.

My values of K'_2 are smaller, in all cases, than those reported by other authors (Table 6). Buch's (1938) values are 26% larger than mine, Hansson's (1972) 3.4%, and Lyman's (1956) 3.2% at temperatures

Table 5: Comparison of values of the first apparent dissociation constant from various workers. This work's values are in parentheses.

		$K'_1 \times 10^6$				
		Temp (°C)				
Source	Salinity (‰)	5	10	20	25	35
Lyman (1956)	35.0	.776(.760)*	.832(.842)*		1.00(1.085)*	1.07(1.158)*
Buch (1932)[#]	21.81			.839(.786)		
	33.96		.832(.788)		1.064(.988)	1.15(1.069)
	34.49			.995(.936)		
Hansson (1971)[±]	35.0	.693(.716)	.760(.797)	.897(.941)	.962(.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.

Table 6: Comparison of values of the second apparent dissociation constant of various workers. This work's values are in parentheses.

		$K'_2 \times 10^{10}$				
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 (1971)[±]	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.

of 25°C and below, and 13.4% at 35°C.

Part of the disagreement between the results of Buch (1938) and mine is due to the effect of $(MgOH^+)$ ion pairs on the alkalinity. Buch (1938) 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, pK_w^{sw}, is larger than its value in NaCl. I used the value of the total hydroxide activity coefficient calculated from Hansson's (1972) data at 20°C to determine the effect of the total hydroxide ion on K'_2 on Buch's (1938) measurements at 20°C. The "total hydroxide ion activity coefficient" in seawater can be calculated from the following equation.

$$(\gamma_{OH}) = \frac{K_w^o a_{H_2O}}{K_w^{sw} \rho_{sw}^2 (\gamma_H)_T} \tag{24}$$

Using $pK_w^o = 14.167$ (Harned and Owen, 1958), $pK_w^{sw} = 13.39$ (Hansson, 1972), $a_{H_2O} = 0.981$ (Robinson, 1954), $\rho_{sw} = 1.0248$ and $(\gamma_H)_T = 0.721$ $(=(f_H)_T$, this work), I calculated that at 20°C and 35‰ $(\gamma_{OH})_T = 0.216$. Substitution of $(\gamma_{OH})_T$ into Buch's (1938) equation for K'_2, indicates that his values for K'_2 at 35‰ and 20°C are 4.5% too high.

A significant part of the disagreement in the values may be due to the difference in the pH scales used by each worker. Lyman (1956)

standardized his electrodes in pH 4.0 buffer and Hansson's (1972) basic calibration is relative to the bicarbonate endpoint at a pH of about 4.5. I standardized my electrodes in pH 7.4 buffer and used a theoretical electrode response slope in my calculations.

Since there is a difference between the theoretical slope of an electrode pair and the empirical one determined by calibration in two buffers, the pH scale depends upon the buffer used for calibration of the electrode pair when a theoretical slope is used in calculations. Theoretically, the pH 7.4 and 4.0 buffers are separated by 3.4 X $(2.303RT/F)$ volts. Empirically it is found that they are separated by a value less than theory. In my case they were separated by 0.9910 X 3.4 $(2.303RT/F)$ volts. The discrepancy must be attributed to differences in the response of the reference electrode from one buffer to the other, rather than to the glass electrode, which has been shown to have a theoretical response with no assymmetry potential changes from one solution to another.

Without correction of my values to compensate for the difference between the pH scale which I used and that which Lyman (1956) used, my values would differ by 4.5% in K'_1 and 18% in K'_2.

In Table 2 the values of the total hydrogen activity coefficient, $(f_H)_T$, are given, as they are determined simultaneously with K'_1. Hansson's (1972) apparent dissociation constants, which are based on a total hydrogen ion concentration, must be multiplied by $(f_H)_T$ 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.

The pH measured with three different calomel reference electrodes and the same glass electrode varied by as much as 0.01 pH units. A 0.01 pH unit change results in differences of 2.3% in K'_1 and 4.6% in $K'_1 K'_2$. This may be one reason for differences in various workers' values.

The values of the pressure coefficients of the apparent dissociation constants of carbonic acid (Culberson and Pytkowicz, 1968) were found to be unchanged when recalculated using the values of K'_1 and K'_2 determined in this work.

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APPENDICES

APPENDIX I

DERIVATION OF F_2

Between the carbonate and the bicarbonate endpoints the titra-
tion alkalinity that remains at any point is represented by

$$\frac{(W_2 - W_a)N_a}{W_o + W_a} = (HCO_3^-) + 2(CO_3^=) + (B(OH)_4^-) \tag{25}$$

or

$$(HCO_3^-) = \frac{(W_2 - W_a)N_a}{W_o + W_a} - 2(CO_3^=) - (B(OH)_4^-) \tag{26}$$

TCO_2 is defined by equation (6). Substitution of equation (1) into
equation (6) gives:

$$TCO_2 = (HCO_3^-) + \frac{a_H(HCO_3^-)}{K'_1} + (CO_3^=) \tag{27}$$

Insertion of equation (26) into equation (27) yields:

$$TCO_2 = \frac{(W_2 - W_a)N_a}{W_o + W_a} - (CO_3^=) - (B(OH)_4^-) +$$

$$+ \frac{a_H}{K'_1} \left[\frac{(W_2 - W_a)N_a}{W_o + W_a} - 2(CO_3^=) - (B(OH)_4^-) \right] \tag{28}$$

TCO_2 can be calculated from (Edmond, 1970),

$$TCO_2 = \frac{N_a(W_2 - W_1)}{W_o + W_a} \qquad (29)$$

Equating (29) with (28), and rearranging, yields:

$$(W_2 - W_1)N_a = (W_2 - W_a)N_a + \frac{a_H}{K'_1}(W_2 - W_a)N_a +$$

$$- \left[(CO_3^=)(1 + \frac{2a_H}{K'_1}) - (B(OH)_4^-)(1 + \frac{a_H}{K'_1}) \right] (W_o + W_a)$$

$$(30)$$

From (2):

$$(CO_3^=) = \frac{K'_2(HCO_3^-)}{a_H} \qquad (31)$$

The concentration of $B(OH)_4^-$ is given by (Edmond, 1970),

$$(B(OH)_4^-) = \frac{T_B K'_B}{a_H + K'_B} \qquad (32)$$

Substitution of (31) and (32) in (30) gives the following equation:

$$(W_2 - W_1)N_a = (W_2 + W_a)N_a + \frac{a_H}{K'_1}(W_2 - W_a)N_a +$$

$$- \left[\frac{(HCO_3^-)K'_2}{a_H}(1 + 2\frac{a_H}{K'_1}) + \frac{T_B K'_B}{a_H + K'_B}(1 + \frac{a_H}{K'_1}) \right] (W_o + W_a)$$

$$(33)$$

After the carbonate endpoint and before the bicarbonate endpoint,

essentially all the alkalinity is present as bicarbonate.

$$\frac{(W_2 - W_a)N_a}{W_o + W_a} = (HCO_3^-) \tag{34}$$

This is a good approximation, and since it is used to make a small correction its error is of little consequence.

Placing (34) into (33), and rearranging, equation (15) for F_2 is derived.

$$F_2 = K'_1(W_a - W_1) = a_H(W_2 - W_a) +$$

$$- \frac{K'_1}{N_a}\left[\frac{(W_2 - W_a)K'_2 N_a}{(W_o + W_a)a_H}\left(1 + \frac{2a_H}{K'_1}\right) + \frac{T_B K'_B}{a_H + K'_B}\left(1 + \frac{a_H}{K'_1}\right)\right](W_o + W_a)$$

$$\tag{15}$$

APPENDIX II

COMPUTER PROGRAM FOR CALCULATION OF K'_1 AND f_H

```
00001:        PROGRAM MATISSE
00002:        DIMENSION V(100),E(100),F(2,100),FF(100),FX(100),
00003:       1VV(100),VX(100),Y(100),JJ(100),PH(100)
00004:        REAL M,NO,MSAVE
00005:        INTEGER A,Z,C,X,T,H,H1
00006:        WRITE(61,1000)
00007: 1000 FORMAT(' ANSWER ALL QUESTIONS THAT MAY BE ANSWERED',/,
00008:       1' YES OR NO WITH 1 FOR YES AND 0 FOR NO.',/)
00009:        ITER=-1
00010:        JINX=0
00011:        H=1
00012:        H1=0
00013:      1 WRITE(61,11)
00014:     11 FORMAT(' WHAT WAS THE WEIGHT OF SEAWATER(IN GRAMS)',/,
00015:       1' PRESENT IN THE TITRATION CELL, THE ACID CONCEN-',/,
00016:       2' TRATION(IN EQ/KG), THE ELECTRODE SLOPE(IN MV PER',/,
00017:       3' PH UNIT), THE PH OF THE BUFFER, AND THE POTENTIAL',/,
00018:       4' AT YOUR BUFFER PH(IN MV)?',/,
00019:       5' (TYPE VALUE AFTER <>, THEN RETURN CARRIAGE)',/)
00020:        WT=FFIN(60)
00021:        CONC=FFIN(60)
00022:        SL=FFIN(60)
00023:        BPH=FFIN(60)
00024:        BPOT=FFIN(60)
00025:        WRITE(61,15) WT,CONC,SL,BPH,BPOT
00026:     15 FORMAT(' ARE THE FOLLOWING VALUES CORRECT?',/,
00027:       1' WT=',F6.2,4X,' CONC=',F6.4,4X,' SL=',F5.2,/,
00028:       2' BPH=',F6.3,4X,' BPOT=',F5.1,/)
00029:        READ(60,105) A
00030:    105 FORMAT(I1)
00031:        IF(A.EQ.0) GO TO 1
00032:        WRITE(61,12)
00033:     12 FORMAT(//,' GIVE YOUR VARIABLES FOR THE VOLUME OF',/,
00034:       1' HCL, V(IN ML), AND THE POTENTIAL, E(IN MV), AT ',/,
00035:       2' THAT VOLUME OF ACID.',/,
00036:       3' HOW MANY VALUES WILL YOU GIVE?')
00037:        N=FFIN(60)
00038:        DO 50 K=1,N
00039:        V(K)=TTYIN(3H V=)
00040:     50 E(K)=TTYIN(3H E=)
00041:      4 WRITE(61,18)
00042:     18 FORMAT(//,18H ARE THE FOLLOWING,/,
00043:       116H VALUES CORRECT?,/)
00044:        DO 51 K=1,N
00045:        WRITE(61,19) K,V(K),E(K)
00046:     19 FORMAT(5X,I3,5X,3H V=,F6.3,5X,3H E=,F6.1)
00047:     51 CONTINUE
00048:        READ(60,105) Z
00049:        IF(Z.EQ.1) GO TO 321
00050:    888 WRITE(61,20)
```

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00051;    20 FORMAT(//,20H WHICH INDEX HAS THE,/,
00052;       132H INCORRECT VALUE ASSIGNED TO IT?)
00053;        J=FFIN(60)
00054;        WRITE(61,21)
00055;    21 FORMAT(/,24H GIVE THE CORRECT VALUES,/,
00056;       127H FOR V AND E FOR THAT INDEX)
00057;        V(J)=TTYIN(3H V=)
00058;        E(J)=TTYIN(3H E=)
00059;        WRITE(61,53)
00060;    53 FORMAT(20H ARE THERE ANY OTHER,/,
00061;       127H VALUES OF V AND E THAT ARE,/,
00062;       211H INCORRECT?,/)
00063;        READ(60,105) T
00064;        IF(T.EQ.1) GO TO 888
00065;        GO TO 4
00066;   321 WRITE(61,5303)
00067; 5303 FORMAT(/,' BEGINNING WITH WHICH INDEX DO YOU',/,
00068;       1' WISH F(1) TO BE CALCULATED?',/)
00069;        JOT=FFIN(60)
00070;        IF(JOT.EQ.1) JOT=2
00071;        NJOT=JOT-1
00072;     6 WRITE(61,25)
00073;    25 FORMAT(//,20H VALUES FOR F(1) ARE,/,
00074;       112H AS FOLLOWS..,/)
00075; 3426 DO 60 K=NJOT,N
00076;        PH(K)=(BPOT-E(K))/SL+BPH
00077;        IF(H1.NE.1) GO TO 3427
00078;        AH=(10.0)**(-(((BPOT-E(K))/SL)+BPH))
00079;        TF=(WT/(WT+V(K)))*SAL*6.9E-05/(1.80655*18.9984)
00080;        BICAR=(TCO2/1000.0)*FH/(1.0+AH/(10.0**(-AVGPK)))
00081;        FLORD=TF*FH*AH/(AH+(10.0**(-PKF)))
00082;        SULFT=FH*(0.14*SAL/(1.80655*96.06))*AH/
00083;       1(AH+(10.0**(-PKS)))
00084;        F(1,K)=(WT+V(K))*(AH-BICAR+FLORD+SULFT)
00085;        GO TO 3428
00086; 3427 F(1,K)=(WT+V(K))*(10.0**(-(((BPOT-E(K))/
00087;       1SL)+BPH)))
00088; 3428 IF(V(K).EQ.0.0) GO TO 777
00089;        IF(NJOT.EQ.K.AND.NJOT.GT.1) GO TO 60
00090;        IF(NJOT.NE.1) GO TO 6000
00091;        FF(K)=0.0
00092;        VV(K)=0.0
00093;        GO TO 8000
00094; 6000 FF(K)=F(1,K-1)
00095;        VV(K)=V(K-1)
00096; 8000 D=(F(1,K)-FF(K))/(V(K)-VV(K))
00097;        IF(ITER.GE.0) GO TO 60
00098;        WRITE(61,24) K,V(K),F(1,K),D,PH(K)
00099;    24 FORMAT(3H N=,I3,2X,3H V=,F6.3,2X,6H F(1)=,
00100;       1E10.3,2X,7H DF/DV=,E10.3,2X,4H PH=,F5.3)
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00101:        GO TO 60
00102:  777 IF(ITER.GE.0) GO TO 60
00103:        WRITE(61,650) K,V(K),F(1,K),PH(K)
00104:  650 FORMAT(3H N=,I3,2X,3H V=,F6.3,2X,6H F(1)=,E10.3,
00105:       121X,4H PH=,F5.3)
00106:   60 CONTINUE
00107: 1075 IF(ITER.GE.0) GO TO 1304
00108:        WRITE(61,250)
00109:  250 FORMAT(/,25H DO YOU WISH TO ELIMINATE,/,
00110:       119H ANY OF THE VALUES?,/)
00111:        READ(60,105) KOR
00112:        IF(KOR.NE.1) GO TO 1001
00113:        NU=0
00114:  254 WRITE(61,251)
00115:  251 FORMAT(38H WHICH INDEX DO YOU WISH TO ELIMINATE?,/)
00116:        NU=NU+1
00117:        NUE=0
00118:        JJ(NU)=FFIN(60)
00119:        IF(JJ(NU).LT.(NJOT+1)) NJOT=NJOT-1
00120:        DO 1113 KJL=1,NU
00121: 1113 IF(JJ(KJL).LT.JJ(NU)) NUE=NUE+1
00122:        JJ(NU)=JJ(NU)-NUE
00123:        JJNU=JJ(NU)
00124:        N=N-1
00125:        DO 252 L=JJNU,N
00126:        V(L)=V(L+1)
00127:  252 E(L)=E(L+1)
00128:        WRITE(61,253)
00129:  253 FORMAT(/,27H ARE THERE ANY OTHER VALUES,/,
00130:       123H YOU WISH TO ELIMINATE?,/)
00131:        READ(60,105) KANS
00132:        IF(KANS.EQ.1) GO TO 254
00133:        IF(H-1) 412,6
00134: 1001 WRITE(61,95)
00135:   95 FORMAT(21H BETWEEN WHICH VALUES,/,
00136:       125H OF N DO YOU WISH A LEAST,/,
00137:       231H SQUARES LINE TO BE CALCULATED?,/)
00138:        C=FFIN(60)
00139:        X=FFIN(60)
00140:        IF(H.EQ.2) GO TO 1303
00141:        IC1=C
00142:        IX1=X
00143: 1303 IC2=C
00144:        IX2=X
00145:        IF(ITER.LT.0) GO TO 1306
00146: 1304 IF(H.EQ.2) GO TO 1305
00147:        C=IC1
00148:        X=IX1
00149:        GO TO 1306
00150: 1305 C=IC2
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00151;       X=IX2
00152; 1306 NN=X-C+1
00153;       SUM=0.0
00154;       XY=0.
00155;       SXY=0.
00156;       SX=0.
00157;       SY=0.
00158;       SXS=0.
00159;       SSX=0.
00160;       DO 7 L=C,X
00161;       XY=V(L)*F(H,L)
00162;       SXY=SXY+XY
00163;       SX=SX+V(L)
00164;       SY=SY+F(H,L)
00165;       SXS=SXS+V(L)**2
00166;     7 CONTINUE
00167;       SSX=SX**2
00168;       NO=(NN)*SXS-SSX
00169;       M=((NN)*SXY-SX*SY)/NO
00170;       B=(SXS*SY-SX*SXY)/NO
00171;       DO 201 L=C,X
00172;       Y(L)=M*V(L)+B
00173;   201 SUM=SUM+(Y(L)-F(H,L))**2
00174;       SS=SUM/NN
00175;       DELTA=NN*SXS-SSX
00176;       SM=SQRT((NN*SS)/DELTA)
00177;       SB=SQRT((SS*SXS)/DELTA)
00178;       SRSS=SQRT(SS)
00179;       IF(ITER.GE.0) GO TO 1307
00180;       WRITE(61,26) M,B,SRSS,SM,SB
00181;    26 FORMAT(3H M=,E15.7,5X,3H B=,E15.7,/,
00182;      427H SAMPLE STANDARD DEVIATION=,E12.5,/,
00183;      526H SLOPE STANDARD DEVIATION=,E15.7,/,
00184;      639H ORDINATE INTERCEPT STANDARD DEVIATION=E15.7,//,
00185;      132H DO YOU WISH TO CHOOSE DIFFERENT,/,
00186;      221H VALUES OF N AND REDO,/,
00187;      313H CALCULATION?,/)
00188;       READ(60,105) KK
00189;       IF(KK.EQ.1) GO TO 1001
00190; 1307 IF(H.EQ.2) GO TO 2000
00191;       VT=-B/M
00192;       MSAVE=M
00193;       IF(ITER.GE.0) GO TO 1308
00194;   412 WRITE(61,27)
00195;    27 FORMAT(21H VALUES FOR F(2) WERE,/,
00196;      124H FOUND TO BE AS FOLLOWS:,//)
00197; 1308 DO 9 L=1,N
00198;       PH(L)=(BPOT-E(L))/SL + BPH
00199;       IF(H1.NE.1) GO TO 3530
00200;       AH=10.0**(-(((BPOT-E(L))/SL)+BPH))
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00201;        FU2=AH*(VT-V(L))
00202;        OUT=(10.0**(-AVGPK))*(WT+V(L))/CONC
00203;        CARBCK=(10.0**(-PK2))*CONC*(VT-V(L))/(AH*(WT+V(L)))
00204;        CARMULT=(1.0+2.0*AH/(10.0**(-AVGPK)))
00205;        TB=(WT/(WT+V(L)))*(0.237/10.82)*(SAL/1.80655)/1000.0
00206;        BORCK=TB*(10.0**(-PKB))/(AH+(10.0**(-PKB)))
00207;        WITHIN=(1.0+AH/(10.0**(-AVGPK)))
00208;        F(2,L)=FU2-OUT*(CARBCK*CARMULT+BORCK*WITHIN)
00209;        GO TO 3529
00210; 3530 F(2,L)=(VT-V(L))*(10.0**(-((BPOT-E(L))/
00211;      2SL+BPH)))
00212; 3529 IF(V(L).EQ.0.0) GO TO 778
00213;        IF(L.NE.1) GO TO 6001
00214;        FX(L)=0.0
00215;        VX(L)=0.0
00216;        GO TO 8001
00217; 6001 FX(L)=F(2,L-1)
00218;        VX(L)=V(L-1)
00219; 8001 DD=(F(2,L)-FX(L))/(V(L)-VX(L))
00220;        IF(ITER.GE.0) GO TO 1309
00221;        WRITE(61,80) L,V(L),F(2,L),DD,PH(L)
00222;   80 FORMAT(3H N=,I3,2X,3H V=,F6.3,2X,
00223;       16H F(2)=,E10.3,2X,7H DF/DV=,E10.3,2X,
00224;       24H PH=,F5.3)
00225; 1309 IF(F(2,L).LT.0.0.AND.FX(L).GT.0.0) GO TO 44
00226;        GO TO 9
00227;  778 IF(ITER.GE.0) GO TO 9
00228;        WRITE(61,511) L,V(L),F(2,L),PH(L)
00229;  511 FORMAT(3H N=,I3,2X,3H V=,F6.3,2X,6H F(2)=,E10.3,21X,
00230;       14H PH=,F5.3)
00231;    9 CONTINUE
00232;   44 H=2
00233;        GO TO 1075
00234; 2000 VO=-B/M
00235;        IF(ITER.GE.0) GO TO 1375
00236;        WRITE(61,29)
00237;   29 FORMAT(21H VALUES FOR PK(1) ARE,/,
00238;       130H AS FOLLOWS FOR THE PARTICULAR,/,
00239;       214H VOLUME GIVEN.,/)
00240; 1375 SUMPK=0.0
00241;        DO 99 K=C,X
00242;        PK=((BPOT-E(K))/SL+BPH-ALOG10((VT-V(K))/
00243;      1(V(K)-VO)))
00244;        SUMPK=SUMPK+PK
00245;        IF(ITER.GE.0) GO TO 99
00246;        WRITE(61,90) V(K),PK
00247;   90 FORMAT(3H V=,F6.3,4X,5H PK1=,F6.3)
00248;   99 CONTINUE
00249;        AVGPK=SUMPK/NN
00250;        TCO2=(((VT-VO)*CONC)/WT)*1000.0
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00251:          TA=((CONC*VT)/WT)*1000.0
00252:          IF(ITER.GE.0) GO TO 1376
00253:          WRITE(61,822) TCO2,TA,AVGPK
00254:      822 FORMAT(//,' TOTAL CARBON DIOXIDE=',F6.3,' MM/KG',/,
00255:         1' TOTAL ALKALINITY=',F5.3,' MEQ/KG',/,
00256:         2' AVERAGE PK=',F6.3)
00257: 1376 FH=MSAVE/CONC
00258:          IF(ITER.GE.0) GO TO 1377
00259:          WRITE(61,225) FH
00260:      225 FORMAT(' HYDROGEN ION ACTIVITY COEFFICIENT=',F5.3)
00261: 1377 IF(ITER.LT.-1) GO TO 1351
00262:          IF(H1.EQ.1) GO TO 3216
00263:          WRITE(61,281)
00264:      281 FORMAT(//,' THE FOLLOWING VALUES ARE NEEDED TO MAKE',/,
00265:         1' CORRECTIONS FOR BICARBONATE, AND CARBONATE,',/,
00266:         2' BORATE, FLORIDE, AND SULFATE NEAR TO THE RESPECTIVE',/,
00267:         3' END-POINTS (APPROXIMATE VALUES ARE NEEDED):')
00268:          WRITE(61,282)
00269:      282 FORMAT(' (1) THE SALINITY, S, OF THE SEAWATER',/,
00270:         1' (IN PARTS PER THOUSAND).',/,
00271:         2' (2) PK(2) FOR CARBONIC ACID IN SEAWATER FOR THE ',/,
00272:         3' TEMPERATURE AND SALINITY OF THE SEAWATER.',/,
00273:         4' (3) THE DISSOCIATION CONSTANT OF BORIC ACID IN ',/,
00274:         5' SEAWATER (GIVE AS -LOG(K) OR PKB).')
00275:          WRITE(61,238)
00276:      238 FORMAT(' (4) PKF(-LOG(K)) FOR HYDROFLORIC ACID',/,
00277:         1' IN SEAWATER.',/,
00278:         2' (5) PKS FOR SULFURIC ACID IN SEAWATER.')
00279:      239 SAL=TTYIN(2HS=)
00280:          PK2=TTYIN(4HPK2=)
00281:          PKB=TTYIN(4HPKB=)
00282:          PKF=TTYIN(4HPKF=)
00283:          PKS=TTYIN(4HPKS=)
00284:          WRITE(61,241) SAL,PK2,PKB,PKF,PKS
00285:      241 FORMAT(/,' ARE THE FOLLOWING VALUES CORRECT?',/,
00286:         1' SAL=',F6.3,2X,' PK2=',F6.3,2X,' PKB=',F6.3,2X,' PKF=',
00287:         2F4.2,2X,' PKS=',F4.2,/)
00288:          READ(60,105) NGO
00289:          IF(NGO.EQ.1) GO TO 242
00290:          WRITE(61,243)
00291:      243 FORMAT(' ENTER CORRECT VALUES!',/)
00292:          GO TO 239
00293:      242 H1=1
00294:          IF(JINX.EQ.0) GO TO 249
00295: 1351 WRITE(61,1301)
00296: 1301 FORMAT(/,' DO YOU WISH TO PERFORM ITERATIONS',/,
00297:         1' ON THE CORRECTED VALUES?',/)
00298:          READ(60,105) IQUEST
00299:          IF(IQUEST.EQ.0) GO TO 1311
00300:          WRITE(61,1302)
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00301;  1302 FORMAT(/,' HOW MANY ITERATIONS DO YOU WISH TO ',/,
00302;      1' PERFORM?',/)
00303;       ITER=FFIN(60)
00304;  3216 IF(ITER.GE.0) GO TO 1310
00305;  1311 WRITE(61,2312)
00306;  2312 FORMAT(//,' DO YOU WISH TO FURTHER CORRECT VALUES?',/)
00307;       READ(60,105) KWNDER
00308;       IF(KWNDER.EQ.1) GO TO 1351
00309;       GO TO 500
00310;   249 WRITE(61,813)
00311;   813 FORMAT(//, ' CORRECTED VALUES FOR F(1) ARE AS',/,
00312;      1' FOLLOWS:',/)
00313;  1310 R=1
00314;       JINX=1
00315;       IF(ITER.LT.1) GO TO 1352
00316;       WRITE(61,1353) ITER
00317;  1353 FORMAT(/,' ITERATION NUMBER ',I2)
00318;  1352 ITER=ITER-1
00319;       IF(ITER.EQ.0) GO TO 6
00320;       GO TO 3426
00321;   500 END
```

]