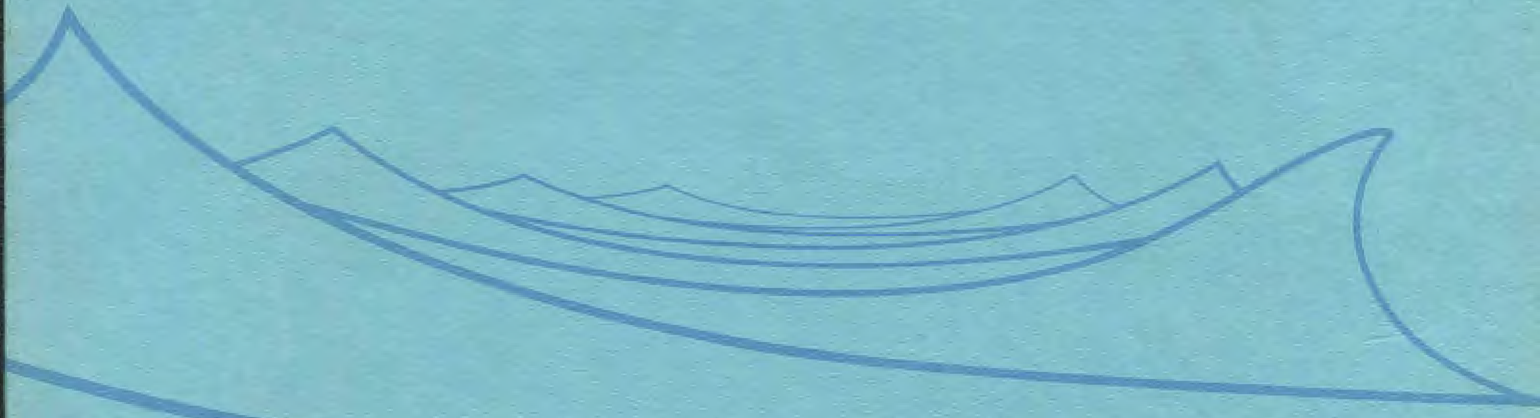

SIO REFERENCE SERIES

Laboratory Report: Seawater Equilibration Experiment No. 3

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May 1978 SIO Ref. No. 78-14

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Seawater Equilibration Experiment No. 3

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La Jolla, California

February 7, 1978

Research supported by the Oceanography Section,
National Science Foundation, NSF Grant DES74-21496.

MAY 1978 SIO REFERENCE NO. 78-14

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I. Introduction

During this extensive series of equilibrations on a single sample of seawater, occupying virtually the entire month of March, 1977, precisions of approximately one part per thousand in P_{CO_2} were consistently obtained for the first time in the history of the SIO CO_2 Project's investigations. This report presents the data of the experiment in detail and discusses experimental procedures and methods of calculation of the results.

II. Experimental Procedures

The basic procedures and apparatus used were the same as those used in the series of equilibrations on pure water-sodium bicarbonate mixtures reported in Keeling and Guenther [1977]. The equilibration vessel, as depicted in the aforementioned paper, consists of two one-liter pyrex flasks joined together by an 8 mm Westef O-ring stopcock. An identical stopcock closes off the upper, or gas bulb and a 14 mm standard taper joint allows the apparatus to be attached to the extraction vacuum line. An arm on the gas bulb can be frozen in liquid nitrogen to transfer CO_2 into the apparatus. The bottom or solution bulb contains an egg-shaped magnetic stirring bar. The apparatus was volume calibrated on 4 - 8 November, 1976 by weighing water. The total volume of the apparatus is 2188.73 cc and the gas bulb volume is 1101.26 cc.

The extraction vacuum line, also as depicted in Keeling and Guenther [1977], is a modification of the Wong [1970] extraction line.

The CO_2 is frozen in liquid nitrogen under slow pumping and then separated from residual water vapor by repeated dry ice sublimations before transfer into a sample tube. The extract is then brought to the manometer vacuum line and transferred into the appropriate manometric chamber for measurement. For details of the manometric measurement procedure see Guenther and Keeling [1976].

A. The Seawater

The experiment was performed on North Atlantic surface seawater from a single ampoule of I.A.P.S.O. standard seawater prepared by the Institute of Oceanographic Sciences, Wormley, Godalming, Surrey, England. The ampoule is from batch P70, 18/9/1975, with a specified chlorinity of 19.375°/₀₀. The collection, preparation and standardization of this seawater is described by Wilson [1975]. The collected seawater is brought to a nominal salinity of 35°/₀₀ by dilution with distilled water. Representative ampoules from the batch are then standardized by silver nitrate titration: thus the specified chlorinity. Using the standard relationship cited by Wilson [1975],

$$S°/_{oo} = 1.80655 \ Cl°/_{oo} \tag{1}$$

the salinity of batch P70 comes out to be 35.002°/₀₀

The seawater was transferred from the ampoule into the equilibrator solution bulb carefully so as to minimize loss or gain of CO_2 from the room, although this was not strictly necessary as will be seen. The solution bulb was first flushed with CO_2-free nitrogen gas for about one hour. The ampoule was then broken at both ends and the seawater allowed to flow by gravity through a glass tube into the bottom of the solution bulb. Not all of the seawater in the ampoule was transferred as the upper layer may have exchanged with the room air. The solution bulb was then sealed onto the gas bulb apparatus with Apiezen black wax while flushing the connection with nitrogen.

The amount of seawater was determined by weighing the apparatus first empty (containing air) and then with seawater (containing nitrogen and air). The uncorrected weight found was 238.080 g. This was corrected for buoyancy to 238.321 g using the densities of air, seawater and balance weights.

Just before sealing the solution bulb the seawater was poisoned with about .0009 g mercuric chloride, or about 4 mg/liter. According to R. Weiss [private communication] an amount of one mg mercuric chloride per liter of seawater is adequate. This amount of $HgCl_2$ does not affect the salinity significantly.

Fine, Wang and Millero [1974] cite the following expression for the density of seawater as a function of temperature and salinity:

$$\begin{aligned}
\sigma_T &= A_T + B_T\,\sigma_0 + C_T\,\sigma_0^2 \\
\sigma_0 &= -9.344586324 \times 10^{-2} + 0.814876577S \\
&\quad -4.8249614 \times 10^{-4}S^2 + 6.76786136 \times 10^{-6}S^3 \\
A_T &= (4.53168t - 0.545939t^2 - 1.98248 \times 10^{-3}t^3 \\
&\quad -1.438 \times 10^{-7}\,t^4)\,(t + 67.26)^{-1} \qquad (2) \\
B_T &= 1 - 4.7867 \times 10^{-3}t + 9.8185 \times 10^{-5}t^2 \\
&\quad - 1.0843 \times 10^{-6}t^3 \\
C_T &= 1.803 \times 10^{-5}t - 8.164 \times 10^{-7}t^2 + 1.667 \times 10^{-8}t^3
\end{aligned}$$

where t is in °C and S in $^\circ/_{\circ\circ}$. The specific density σ is related to the density ρ by $\sigma = (\rho - 1)\ 1000$.

Using equations (2) the density of the seawater at 20.00°C is calculated to be 1.02478 kg/liter.

Lyman and Fleming [1940] give relationships used to calculate molal quantities for seawater. The ionic strength as a function of chlorinity is given by:

$$\mu = .00147 + .03592\text{Cl}^\circ/_{\circ\circ} + .000068(\text{Cl}^\circ/_{\circ\circ})^2 \qquad (3)$$

The seawater of this experiment has a molal ionic strength of 0.7229 moles/kg water using the above relation. The weight of total salt per kilogram of seawater as a function of chlorinity is given by:

$$\Sigma = 0.073 + 1.8110\text{Cl}^\circ/_{\circ\circ} \qquad (4)$$

The weight of pure water substance per liter of seawater is obtained from (4) as:

$$\text{gH}_2\text{O/liter SW}(t^\circ c) = (1000 - \Sigma_{\text{Cl}^\circ/_{\circ\circ}}) \cdot \rho_{t^\circ C} \qquad (5)$$

A liter of the seawater of this experiment (chlorinity of 19.375$^\circ/_{\circ\circ}$ and temperature of 20.00°C) is found to contain 988.75 grams of pure water substance.

B. Degassing the Seawater

Immediately after being weighed, the equilibration vessel containing the seawater sample was attached to the extraction line, and the gas bulb was pumped to a vacuum of one millitorr or less with the stopcock connecting the bulbs closed. The solution bulb containing the seawater was then frozen in a dry ice slush. Complete freezing required about forty-five minutes. The gas in the solution bulb was then vacuum extracted in the usual way through a dry ice trap for water and through a liquid nitrogen trap for CO_2. When the solution bulb had been pumped to a vacuum near one millitorr, the connecting stopcock was again closed and the solution bulb thawed. The initial phase of this thawing must be done quickly in a bath of warm water to melt the outside layer of ice or the ice may expand and crack the vessel. After the seawater was completely thawed it was stirred briefly and then refrozen. When it was completely refrozen, the amount of gas remaining could be tested by opening the equilibrator to a portion of the vacuum line containing a vacuum gauge. These pressures were as follows: Extraction One, near atmospheric (not measured); Extraction Two, 0.8 mm Hg; Extraction Three, 60 millitorr. It was apparent throughout the remainder of the experiment that very little noncondensible gas remained in the system after this treatment.

The CO_2 trapped during the degassing procedure was transferred back into the equilibrator without measurement. It was found that no discernible water had been trapped during the degassing procedure, probably because the seawater was completely frozen before extraction. The procedure could be expedited by not freezing so completely and then transferring any water lost (and trapped) back into the equilibrator.

C. Addition of CO_2 Gas

The amount of CO_2 in the seawater equilibration system was increased by adding an aliquot of CO_2 gas at the beginning of the experiment, prior to the first equilibration. The amount added was sufficient to boost the initial pre-equilibration P_{CO_2} to greater than 16000 micro-atmospheres.

An accurate determination of the CO_2 to be added was made by running an assay on a weighed quantity of sodium carbonate. The salt was Baker Ultrex anhydrous Na_2CO_3 that had been heated to 270°C in September 1976 and since stored in a dessicater above $Mg(ClO_4)_2$. A weight of 0.144355 g of this salt was transferred into the extraction vessel attached to the extraction vacuum line. After the vessel was evacuated the salt was acidified with 0.4M H_3PO_4 and the CO_2 gas extracted and then measured manometrically in the usual way. A quantity of 1.3618×10^{-3} moles of CO_2 was found, corresponding to an assay of 99.98_8% of the Na_2CO_3.

The assay CO_2 was then transferred by sublimation into the gas bulb of the equilibration assembly before beginning the first equilibration of the experiment.

D. Running the Equilibrations

An equilibration was begun by opening the connecting stopcock between the bulbs, immersing the assembly in the constant temperature water bath and starting the (air-driven) magnetic stirrer to power the stirring bar in the solution bulb.

For the first three equilibrations (Equil. No. 3.0, 3.1 and 3.2) the solution bulb was momentarily cooled in dry ice to condense water vapor before opening the connecting stopcock so that seawater or condensed water in the stopcock region would not spurt into the evacuated gas bulb. This possibly complicating step was removed from the procedure beginning with Equil. No. 3.3. At the same time the procedure was also changed so that the water removed from the system during extraction was transferred back into the gas bulb, thus mostly equalizing the pressure differential.

The constant temperature water bath was regulated to 20.00 ± .01°C. Water cooled to about 19.5°C was flowed through a copper coil immersed in the bath for cooling purposes. Regulation was accomplished by controlling the power to a low-wattage (25W) immersed light bulb with a differential microset mercury thermoregulator having a sensitivity better than ± 0.01°C.

Temperature was measured with a Beckmann thermometer calibrated by Walt Bryan at S.I.O. in February, 1974. On 17 March 77 five other high precision thermometers were tested versus the Beckmann and found to agree very well indeed (within a few hundredths degree in the worst case). The recorded temperature was that recorded just before ending the equilibration. It differs from 20.00°C only for Equil. No. 3.9 (20.01°C)

The stirring rate could be regulated between a very slow rate and a very fast rate where much cavitation and disturbance of the surface took place. In fact until Equil. No. 3.8 a quite fast stirring rate had been used throughout the equilibration studies. This speed was such that the stirring bar at the bottom of the solution was exposed to the gas phase: a whirlpool-like funnel was formed in the center of the solution. Concern with possible supersaturation effects led to slowing the stirring rate down severely beginning with Equil. No. 3.8. The rate was on the order of only 1-2 complete revolutions of the stirring bar per second. Due to off center alignment of the stirrer, a slightly asymmetric "sloshing" was usually present as well. In any case the seawater was kept moving to eliminate diffusion effects within the solution while keeping the gas/liquid interface essentially flat. This slow rate was continued throughout the rest of the experiment apparently resulting in the great improvement in the precision of repetitive runs from Equil. No. 3.8 onward.

On repetitive equilibrations, where both the water (after Equil. No. 3.2) and the CO_2 was transferred back into the gas bulb for a rerun, an equilibration time of about fifteen hours (overnight) was considered (and shown to be) more than enough. In cases beginning farther from equilibrium, especially after the initiation of slow stirring, a time of forty hours (over two nights) was deemed necessary.

The equilibrations were ended by closing the connecting stopcock, stopping the magnetic stirrer and removing the assembly from the bath.

E. Extraction and Measurement

The equilibration assembly was attached to the extraction line using Apiezon grease, and the line was evacuated up to the gas bulb stopcock for about one hour before beginning the extraction. During the vacuum extraction the water was frozen out of the gas stream in a thimble trap cooled to dry ice temperature, and then the CO_2 was frozen out in a spherical trap cooled to liquid nitrogen temperature. The trapped CO_2 was separated from residual water vapor by two dry ice sublimations on the extraction line during transfer of the sample to a sample tube and then by three more dry ice sublimations during transfer from the sample tube into the small manometer sample column. After the extractions of Equil. No. 3.0 and 3.1 the water remaining in the extraction line was transferred to a pre-weighed, evacuated sample tube and then weighed and discarded. This amount was 0.023 grams in both cases. After Equil. No. 3.2 and subsequent equilibrations, however, the water in the line was transferred back into the gas bulb. Thus, the amount and salinity of the seawater remains constant after Equil. No. 3.2. The value of the salinity was not adjusted for the small loss of water after Equil. No. 3.0 and 3.1, about one part in five thousand. This correction would have a negligible effect on the various salinity dependent parameters. For example, the effect of a 1/5000 increase in Cl°/₀₀ on K_1 is only 1/10000.

The sizes of the extracted gas bulb samples varied over a considerable range, from about 7×10^{-4} moles to about 2×10^{-5} moles, requiring the use of three different chambers of the small manometer, the nominally 64cc, 16cc and 4cc chambers. The volume of the 4cc chamber had been calibrated directly (see Guenther [1976]). The volumes of the other two chambers were adjusted from preliminary volume ratio values by the results of the extensive set of Na_2CO_3 assays performed in the work reported by Keeling and Guenther [1977].

In all cases two separate manometric measurements were made for each CO_2 extraction. The sample was then transferred into a sample tube to be either stored or transferred back into the equilibrator gas bulb. The extraction from Equil. No. 3.0, after measurement in the manometer, was inadvertantly contaminated with room air, while frozen in liquid nitrogen and before transfer back into the equilibrator. The contamination was only brief but it is not possible to predict exactly how much CO_2 from the room may have frozen in the tube. Assuming as an upper limit a pressure of 1000 ppm CO_2 in the room air, and given a volume of 65 cc for the sample tube, an estimate of 2.7×10^{-6} moles of contamination is deduced. This is about 0.4% of the size of the extraction after Equil. No. 3.0 and about 0.2% of the amount of CO_2 added at the beginning of the experiment. The non-condensable gas from the contamination was pumped away. As it turned out, the method of calculating "backward" which is applied to the experiment makes this contamination inconsequential. Also the first six runs or so are suspect because of the fast stirring effects, as can be noted in the fact that <u>less</u> CO_2 was found in the Equil. No. 3.1 extraction after the contamination of the system with room CO_2.

F. Total CO_2 Determination

After the final Equil. No. 3.17, the total inorganic carbon remaining in the system was determined by acidifying the seawater, extracting the CO_2 evolved and measuring the amount of CO_2 in the manometer in the usual way.

A solution of approximately 0.4M H_3PO_4 was prepared on 17 September 1976 by adding 42 cc of B & A reagent grade 86% H_3PO_4 to about 1 3/4 liters commercial distilled water in a two-liter flask. The solution was boiled vigorously for about two hours, after which time there was very little or no gas apparently remaining. An assembly with a 4 mm O-ring stopcock was then blackwaxed to the flask and the stopcock closed after steam had passed through the assembly for several minutes. The 0.4M H_3PO_4 solution was thus made gas free. That very little gas was in the H_3PO_4 solution at the time of the experiment was evidenced by the "hammering" of the acid solution in its flask and by the absence of detectable non-condensable gas during the total CO_2 extraction.

About 100 cc of the H_3PO_4 solution was transferred under vacuum conditions, first into a pipette and then into the previously evacuated gas bulb of the equilibrator assembly. The acid was then flowed into the solution bulb where it was mixed well with the seawater. The evolved CO_2 gas, extracted in the usual way, was separated from water vapor, and then was measured in the manometer. The acidity of the remaining solution was checked with pH paper immediately upon disassembling the apparatus and was found to be less than pH 4, indicating that a sufficient excess of acid was present to convert all the dissolved inorganic carbon to CO_2 gas.

III. Calculations and Results

A. Table 1. Equilibration Experimental Data

The basic experimental conditions for the eighteen equilibrations are summarized in Table 1. The weight of the seawater remains constant from Equil. No. 3.2 on, reflecting the change in procedure whereby the water removed from the gas bulb during extraction was transferred back into the gas bulb rather than into a sample tube for weighing. The time of equilibration is entered to the nearest hour. The remark $\underline{CO_2}$ OUT means that the CO_2 extracted from the gas bulb after an equilibration was removed from the system, i.e. not transferred back into the gas bulb for the next equilibration. An equilibration immediately following one noted with a $\underline{CO_2}$ OUT thus began with no CO_2 in the gas bulb. Also in the remarks column is noted the change in stirring rate from fast to slow and the change in which the procedure of cooling the solution bulb prior to opening the connecting cock to begin an equilibration is discontinued.

B. Table 2. Manometric Experimental Data

The original experimental data for the measurements made on the precision constant volume manometer are presented in Table 2. In two cases, Equil. No. 3.4 and Equil No. 3.10, measurements on a single sample were made in two adjacent manometric chambers in order to check the volume ratios. In both cases the measurement in the smaller chamber is used to calculate the value for that equilibration. The meniscus corrections listed were determined on 27 September 1976. Of the listed chamber volumes, the nominally 4 cc was determined in 1974 (Guenther [1976]) with reference to calibrated plenums, and the nominally 16 cc and 64 cc chambers were determined in 1976 by a best fit of the 1976 work on Ultrex Na_2CO_3 assays.

The number of moles of CO_2 is calculated from the experimental data and the volume of the manometric chamber using the virial equation of state, as detailed in Manometer Report IV (Guenther [1976]).

An estimate of the precision of the manometric measurements can be made by calculating the relative error of a single measurement in the set of paired measurements;

$$\left(\frac{\sigma}{n}\right) = \sqrt{\frac{\Sigma\left(\frac{d}{\bar{n}}\right)_i^2}{N_a - N_f}} \tag{6}$$

where

$\frac{\sigma}{n}$ is the overall average relative sigma.

d is the deviation of an individual measurement from the mean of a pair of measurements

$\bar{n}$ is the mean of a pair of measurements

N_a is the total number of measurements

N_f is the total number of pairs, or samples

For all 22 pairs of measurements listed in Table 2 the (σ/n) is calculated to be 2.1×10^{-4} or about one part in five thousand.

C. Table 3. Calculation of P_{CO_2} and T_{CO_2}

The partial pressure of CO_2 gas in the system in atmospheres is calculated from the number of moles in the gas bulb, determined in the manometer, using the virial equation of state,

$$P_{CO_2} = \frac{n_{GB}RT}{V_{GB}} \left(1 + \frac{n_{GB}}{V_{GB}} B \right) \qquad (7)$$

where

P_{CO_2} = partial pressure of CO_2, in atmospheres

n_{GB} = number of moles of CO_2 found in gas bulb

V_{GB} = volume of gas bulb (1101.26 cc)

R = gas constant, 82.056 atm cm^3/°K mole

T = temperature, 293.16°K

B = 2nd virial coefficient, taken to be -127.98 cm^3/mole at 20°C (Sengers, et al. [1971])

The partial pressures in the experiment were low enough that the difference between the above calculation and a perfect gas calculation is only one part in fifteen thousand for the highest pressure, that in Equil. No. 3.0. A small additional departure resulting from the presence of water vapor is neglected.

The concentration of total inorganic carbon in seawater, T_{CO_2}, is calculated by a stepwise procedure with the intermediate steps tabulated in Table 3.

Dividing the weight of seawater by the density yields the volume of seawater, 232.51 ml, which is then subtracted from the total volume of the equilibrator assembly to obtain the volume of the gas phase, 1956.22 cc. The number of moles of CO_2 in the gas phase, n_{GP}, is obtained from the number of moles in the gas bulb assuming gas proportionality, i.e.:

$$n_{GP} = \frac{V_{GP}}{V_{GB}} n_{GB} \tag{8}$$

The total moles of inorganic carbon in the system is obtained directly from the total carbon determined at the end of the experiment and the individual n_{GB}'s. When an aliquot of CO_2 gas was removed from the system (CO_2 OUT) as in Equil. No. 3.17, the n_{GB} is added to the total carbon to determine the total carbon for that equilibration. Thus the entire series of equilibrations is calculated from the end back to the beginning, adding the CO_2 OUT in each case to obtain a new value for the total number of moles of carbon in the system.

The number of moles of carbon in the seawater is then obtained by subtracting the number of moles in the gas phase from the total number of moles. T_{CO_2} in mmol/kg Sw is obtained by dividing the millimoles of carbon in the seawater by the weight of seawater, .238275 kg. This weight is used for all the equilibrations, even Equil. No. 3.0 and Equil. No. 3.1, where it is one part in four thousand in error.

The molar T_{CO_2}, in mmol/liter of seawater at 20°C is obtained by multiplying the gravimetric concentration by the density. The molal T_{CO_2} in mmol/kg of water is obtained by dividing the molar T_{CO_2} by the weight, in kilograms, of pure water substance in a liter of seawater at 20°C, 0.98875 kg. This molal conversion is by the Lyman and Fleming [1940] formulation. See section II A for details.

D. Table 4. Summary of P_{CO_2} and T_{CO_2}

Results of replicate equilibrations are averaged together in this table to yield a summary of the different points in the "gas titration" of the seawater. Sigmas for the P_{CO_2} and molar T_{CO_2} numbers are obtained by the normalized (n-1) method.

E. Derivation of Expressions for Calculation of K_2 and Buffer Factor

The carbonate system in seawater can be described by the expressions for the total inorganic carbon concentration, T_{CO_2}, or

$$C = [CO_2] + [HCO_3-] + [CO_3=] \tag{9}$$

for the alkalinity,

$$A = [HCO_3-] + 2[CO_3=] + [H_2BO_3-] + [OH-] - [H+] \tag{10}$$

for the apparent equilibrium quotients,

$$K_o = [CO_2]/P \tag{11}$$

$$K_1 = [H+][HCO_3-]/[CO_2] \tag{12}$$

$$K_2 = [H+][CO_3=]/[HCO_3-] \tag{13}$$

$$K_B = [H+][H_2BO_3-]/[B(OH)_3] \tag{14}$$

$$K_w = [H+][OH-] \tag{15}$$

and for the total borate concentration,

$$B = [B(OH)_3] + [H_2BO_3-] \tag{16}$$

where brackets denote the concentration of the designated ion including possible ion pairs, $[CO_2]$ includes hydrated CO_2, $[H_2CO_3]$, and P is the partial pressure of CO_2 gas, P_{CO_2}.

Introducing the quantities,

$$X \equiv \sqrt{K_1K_2} \ / \ [H+] \tag{17}$$

$$K \equiv \sqrt{\frac{K_1}{K_2}} \tag{18}$$

$$W(X) \equiv [H_2BO_3-] + [OH-] - [H+] \tag{19}$$

and substituting from equations (11) to (16), one obtains rearrangements of (9), (10) and (19),

$$A = K_oP(KX + 2X^2) + W(X) \tag{20}$$

$$C = K_oP(1 + KX + X^2) \tag{21}$$

$$W(X) = \frac{B}{1 + \frac{\sqrt{K_1K_2}}{K_BX}} + \frac{K_WX}{\sqrt{K_1K_2}} - \frac{\sqrt{K_1K_2}}{X} \tag{22}$$

Using the above relationships,

$$2C - A = K_oP(2 + KX) - W(X) \tag{23}$$

and rearranging,

$$KX = \frac{2C - A + W(X) - 2K_oP}{K_oP} \qquad (24)$$

From equation (20),

$$X^2 = \frac{A - C - W(X) + K_oP}{K_oP} \qquad (25)$$

Squaring equation (24),

$$K^2X^2 = \frac{(2C - A + W(X) - 2K_oP)^2}{K_o{}^2P^2} \qquad (26)$$

and substituting equations (18) and (25), one obtains:

$$\frac{K_1}{K_2}\left[\frac{A - C - W(X) + K_oP}{K_oP}\right] = \frac{(2C - A + W(X) - 2K_oP)^2}{K_o{}^2P^2} \qquad (27)$$

Simplifying,

$$\frac{K_1K_o}{K_2} = \frac{(2C - A + W(X) - 2K_oP)^2}{P(A - C - W(X) + K_oP)} \qquad (28)$$

Introducing the quantities,

$$A' = A - W(X) \qquad (29)$$

$$C' = C - K_oP \qquad (30)$$

one obtains the working relationships,

$$\Phi \equiv \frac{K_1K_o}{K_2} = \frac{(2C' - A')^2}{P(A' - C')} \qquad (31)$$

and

$$X = \sqrt{\frac{A' - C'}{K_o P}} \tag{32}$$

Substituting the definition of Φ from equation (31) into equation (22) to eliminate K_2 yields

$$W(X) = \frac{B}{1 + \dfrac{K_1\sqrt{K_o}}{K_B\sqrt{\Phi}\, X}} + \frac{K_W\sqrt{\Phi}\, X}{K_1\sqrt{K_o}} - \frac{K_1\sqrt{K_o}}{\sqrt{\Phi}\, X} \tag{33}$$

Rearranging (31) and substituting (30), one obtains

$$P^2[K_o(\Phi - 4K_o)] + P[\Phi(A' - C) + 4K_o(2C - A')] - (2C - A')^2 = 0 \tag{34}$$

a quadratic equation in P. By evaluating the coefficients of P and then solving for P with the quadradic solution,

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{35}$$

one obtains a calculated value of P in terms of a given C, A and Φ.

F. Calculation of A, Φ and Buffer Factor

Programs were written for a Texas Instruments (T.I.) programmable calculator to define the seawater system using the input data of total inorganic carbon concentration, C, and the partial pressure of CO_2 gas, P. The first program calculates Φ for every paired C and P assuming an alkalinity, A. The program calculates K_oP; C' from equation (30);

$\sqrt{\Phi}$ X, using initial trial values of Φ and X; W(X) using equation (33); A' from equation (29); finally a new X using equation (32), and a new Φ, using equation (31). The program then repeats itself with the new X and Φ values, iterating until the Φ value converges to a specified degree (e.g. to a ppm). A value for Φ is obtained in this way for each of the five paired C and P values and for various values of A. The value of A found to produce the least scatter in the Φ's for the five cases is taken to be the alkalinity of the seawater.

With the alkalinity and Φ determined by the above method, another program is used to determine the buffer or Revelle factor by numerical integration. For any given C value, the corresponding P is calculated by solving for P in equation (34). The program begins in the same way as previously, calculating $K_{)}P$ (using initially a trial value of P), C', $\sqrt{\Phi}$ X (using initially a trial value of X), W(X), A', and a new X. Then the program calculates the quadratic coefficients "a, b, and c" and solves for a new value of P (see equations (34) and (35)). The program then repeats itself with the new X and P values, iterating until P converges to a specified degree. In this way values of P can be obtained for C values approximately 1% apart. Numerical integration yields the buffer or Revelle factor:

$$R = \frac{(P_1 - P_2)/\ \overline{P}}{(C_1 - C_2)/\ \overline{C}} \tag{36}$$

where $\overline{P}$ and $\overline{C}$ are the averages of P_1 and P_2 and C_1 and C_2, respectively.

G. Table 5. Values of Constants

Values of the various constants and parameters used in the calculation of Φ, A and the buffer factor are given in Table 5 along with equations for their temperature and salinity dependencies.

H. Table 6. Calculation of Φ and A

Table 6 presents the results of calculating the quantity $\Phi = K_1K_o/K_2$ for several values of A using the T.I. calculator program. Six different values of alkalinity from 2.3830 to 2.3840 m mol/liter are tried, with 2.3833 yielding the lowest scatter in Φ, about 1.5 parts per thousand, among the five experimental points. Values of parameters used are as in Table 5.

I. Table 7. Calculation of Buffer Factor

Using the Φ and A found in the first calculation, 46.758 and 2.3833 m mol/liter respectively, as shown in Table 6, the Revelle factors or buffer factors for each point, as calculated by numerical integration, are summerized in Table 7. The T.I. program calculates a P_{CO_2} for a given value of T_{CO_2}. The five experimental values of T_{CO_2} are used along with the (a) values 1% smaller than each of the points to calculate Revelle factors for each level of T_{CO_2} using equation (36) for numerical integration.

IV. Discussion

A. Precision of Replicate Equilibrations and Stirring Speed Effects

Inspection of the results summarized in Table 4 reveals the outstanding change in the precision of replicate equilibrations occurring after the institution of a slow stirring speed. Prior to that time (with Equil. No. 3.8) the precision only approached one part per thousand in equilibrations with high P_{CO_2}. Some equilibrations with CO_2 in pure water carried out prior to this experiment showed this, and Equil. Nos. 3.1, 3.2 and 3.3 in this experiment also display good precision. However, note that Equil. No. 3.0, which should have had enough time to reach equilibration, has a very different P_{CO_2}. The values obtained for Equil. No. 3.5 and No. 3.6, as compared to Equil. No's. 3.7, 3.8 and 3.9, exemplify the large scatter obtained during fast stirring. Equil. No. 3.6 had a very long equilibration time as well.

If supersaturation of CO_2 gas in the solution is occurring, one might expect the amount of supersaturation to be very sensitive to the actual stirring speed at high speeds. Equil. Nos. 3.1 to 3.5 all had the same fast rate of stirring, as well as could be managed. The magnetic stirrer is powered by an air pressure pump and all valves were left unchanged so as to keep the rate constant. For Equil. No. 3.6 the rate was increased slightly and the results can be accounted for by supersaturation. The rate was slowed down a bit for Equil. No. 3.7, and this experiment agrees well with the next two after institution of the much slower rate of stirring. It is possible that a steady-state excess of CO_2 in the seawater could be eliminated after only a slight slowing of the stirring speed if cavitation and turbulent mixing of the gas and liquid phases are substantially lessened. In any case, it is clear that fast stirring rates yield imprecise results as compared to slow rates.

A number of authors of papers dealing with gas solubility have commented on supersaturation effects. Murray and Riley [1971] claim that they checked for supersaturation by changing the rate of stirring and found no effects up to the "highest rate obtainable." However they did worry about supersaturation due to hydrostatic head by inserting the CO_2 bubbler no more than 0.5 cm below the surface of the liquid. MacInnes and Belcher [1933], however, apparently found supersaturation effects in their preliminary experiments and used only a gentle rocking motion to reach equilibration. An extensive discussion by Cady, Elsey and Berger [1922] regarding the solubility of Helium in water concludes that previous workers obtained erroneous results due to violent agitation or shaking of the water with the gas. They note that the effect of even a small increase in pressure is easily noticed in gas solubilities, and that it is much easier to get a gas into solution than it is to get it out again. In other words the steady-state supersaturation produced is not readily reversible. The results of the experiment reported herein seem to support the view that supersaturation is indeed a very important problem to worry about when equilibrating CO_2 gas with seawater.

B. Attainment of Equilibrium

There is some evidence in the results reported in Tables 3 and 4 that equilibrium is not quite reached after the first equilibration. For the three groups of equilibrations Nos. 3.11, 3.12, 3.13 and 3.14, 3.15 and 3.16, 3.17 the second run is always higher than the first on the order of one part per thousand. There are too few data to prove whether this variation is a systematic effect or just an accidental reflection of the inherent precision of the experiment. Further work should clear this up, but in any case a precision of one part per thousand in P_{CO_2} equilibration is already very satisfying.

C. Results as Presented in Tables 6 and 7 and Figures 1 and 2

The values of Φ calculated for the five experimental points using the six different values of alkalinity are plotted in Figures 1 and 2. Figure 1 shows clearly the sensitivity of Φ to a small change in A. A change of 1 part in 2000 in the value of A results in a definite shift of Φ for the five points from a downward slope to an upward slope. In Figure 2 the values of Φ for A = 2.3833 m mol/liter are plotted and compared with plots for values of A slightly smaller and slightly larger than 2.3833. Not surprisingly, the plot with the lowest scatter is also the one with the least slope.

The Revelle factors presented in Table 7 are not greatly different than factors calculated directly from data of Buch (Buch *et al.* [1932], Buch [1938] and Buch [1951]) and Lyman [1957]. These calculations are discussed in detail by Keeling [1973]. Note that the Revelle factor begins to fall in value after reaching a maximum somewhere near 2000 ppm in P_{CO_2}. A more detailed calculation of the maximum and comparisons to Lyman and Buch will be accomplished with a computer analysis elsewhere.

The calculation procedure was rerun to test the effects of changing the values of the parameters K_1 and K_B. Using Buch's value of K_1, 9.84361×10^{-7}, as calculated from the equation listed in Table 5, Φ is calculated to be 47.199 while the alkalinity giving the lowest scatter in Φ remains 2.3833 m mol/liter. The Revelle factors remain unchanged, at least to the number of significant figures shown in Table 7. An approximately 2% <u>downward</u> change in K_1, thus results in an upward change in Φ of about 1%. Calculation of K_2 from equation (31), using Lyman's value of K_1, yields a K_2 of 7.136×10^{-10}, while using Buch's value of K_1 yields a K_2 of 6.928×10^{-10} or about 3% lower. The parameter K_2, really the value determined in this experiment, is seen to be very sensitive to the chosen value of K_1.

Similarly, an approximately 2% <u>upward</u> change in the value of K_B causes Φ to come out 47.255, again about 1% higher. The effect on K_2 in this case is such that it is lowered by about 0.3%. The best value of A remains unchanged as well as the Buffer factors.

The value of K_2, 7.136×10^{-10} mole/liter, calculated from the experimental data using Lyman's K_1 and K_B, agrees fairly well with Lyman's K_2, 7.191×10^{-10}, but rather poorly with Buch's K_2, 8.626×10^{-10}.

The Lyman and Buch K_2's are calculated using the equations included in Table 5. Using Buch's K_1 as a parameter in the calculation of Φ, as discussed above, serves only to worsen the agreement with the Buch K_2.

In summary the results of the calculation procedure show that determination of K_2 by this experiment is very sensitive to the chosen alkalinity value and to the assumed value of the first ionization constant K_1. The value of K_2 is seen to be less sensitive to the value of K_B. The buffer factor is quite insensitive to either K_1 or K_B.

Table 1. Equilibration Experimental Data

quilibration No.	Date Equilibration Began	Weight Seawater (g)	Temperature (CT Bath) (°C)	Approx. Time of Equilibration (hour)	Remarks
3.0	2 Mar 77	238.321	20.00	38	Fast stirring. Solution bulb cooled in dry ice
3.1	4 Mar 77	238.298	"	63	" " " " " " " " Contaminatio
3.2	7 Mar 77	238.275	"	15	" " " " " " " "
3.3	8 Mar 77	"	"	16	" " Solution bulb no longer cooled. CO_2 OUT
3.4	9 Mar 77	"	"	14	" " CO_2 OUT
3.5	10 Mar 77	"	"	17	" "
3.6	11 Mar 77	"	"	65	" "
3.7	14 Mar 77	"	"	16	" "
3.8	15 Mar 77	"	"	16	Slow stirring
3.9	16 Mar 77	"	20.01	15	" " CO_2 OUT
3.10	17 Mar 77	"	20.00	16	" " CO_2 OUT
3.11	18 Mar 77	"	"	64	" "
3.12	21 Mar 77	"	"	15	" "
3.13	22 Mar 77	"	"	15	" " CO_2 OUT
3.14	23 Mar 77	"	"	40	" "
3.15	25 Mar 77	"	"	16	" " CO_2 OUT
3.16	26 Mar 77	"	"	40	" "
3.17	28 Mar 77	"	"	16	" " CO_2 OUT

Table 2. Manometric Experimental Data

Equilibration or Experiment Number	Volume of Chamber (cc)	Vacuum Column Height (mm)	Sample Column Height (mm)	Meniscus Correction (mm)	Temperature (°C)	Calculated Number of Moles		Remarks
						Single set	Average	
Assay 21	63.277	625.617	232.588	−.014	19.14	1.36178x10^{-3}	1.36180x10^{-3}	CO$_2$ added to seawater
	"	625.717	232.590	"	19.20	1.36183		
3.0	"	432.676	232.600	"	19.10	6.92362x10^{-4}	6.92340x10^{-4}	
	"	432.626	232.599	"	19.05	6.92318		
3.1	"	423.113	232.616	"	19.04	6.59310	6.59310x10^{-4}	
	"	423.109	232.619	"	19.03	6.59310		
3.2	"	423.204	232.612	"	19.56	6.58401	6.58438x10^{-4}	
	"	423.188	232.616	"	19.50	6.58474		
3.3	"	423.348	232.626	"	19.08	6.59995	6.60080x10^{-4}	
	"	423.426	232.634	"	19.11	6.60166		
3.4	15.973	683.008	314.078	+.024	19.89	3.21778	3.21835x10^{-4}	Value used for this equilibratio
	"	682.818	314.076	"	19.70	3.21835		
	63.277	325.784	232.568	−.014	19.55	3.21782	3.21786x10^{-4}	
	"	325.794	232.586	"	19.52	3.21789		
3.5	15.973	497.589	314.092	+.024	19.01	1.60356	1.60330x10^{-4}	
	"	497.518	314.069	"	19.03	1.60303		
3.6	"	490.831	314.091	"	18.73	1.54601	1.54608x10^{-4}	
	"	490.837	314.108	"	18.69	1.54614		
3.7	"	497.954	314.065	"	18.75	1.60851	1.60828x10^{-4}	
	"	497.908	314.078	"	18.74	1.60805		
3.8	"	498.916	314.093	"	20.19	1.60830	1.60852x10^{-4}	
	"	498.935	314.073	"	20.17	1.60875		

Table 2. Manometric Experimental Data (contd.)

quilibration or Experiment Number	Volume of Chamber (cc)	Vacuum Column Height (mm)	Sample Column Height (mm)	Meniscus Correction (mm)	Temperature (°C)	Calculated Number of Moles		Remarks
						Single set	Average	
3.9	15.973	498.559	314.126	+.024	19.85	1.60687×10^{-4}	1.60708×10^{-4}	
	"	498.578	314.090	"	19.86	1.60729		
3.10	3.7974	775.333	375.296	-.368	19.90	8.28824×10^{-5}	8.28594×10^{-5}	Value used for this equilibration
	"	775.102	375.258	"	19.92	8.28363		
	15.973	409.268	314.086	+.024	19.94	8.28585	8.28736×10^{-5}	
	"	409.328	314.108	"	19.95	8.28886		
3.11	3.7974	601.373	375.271	-.368	19.99	4.67399	4.67254×10^{-5}	
	"	601.234	375.256	"	20.01	4.67108		
3.12	"	601.318	375.277	"	19.65	4.67846	4.67943×10^{-5}	
	"	601.471	375.288	"	19.71	4.68040		
3.13	"	601.280	375.302	"	19.57	4.67851	4.67918×10^{-5}	
	"	601.388	375.288	"	19.64	4.67986		
3.14	"	519.442	375.280	"	19.38	2.98221	2.98218×10^{-5}	
	"	519.526	375.305	"	19.50	2.98214		
3.15	"	520.022	375.264	"	20.34	2.98423	2.98472×10^{-5}	
	"	520.080	375.264	"	20.36	2.98522		
3.16	"	478.123	375.328	"	20.00	2.11892	2.11936×10^{-5}	
	"	478.128	375.287	"	20.01	2.11980		
3.17	"	478.192	375.294	"	19.95	2.12144	2.12136×10^{-5}	
	"	478.268	375.274	"	20.23	2.12128		
CO_2	63.277	382.125	232.606	-.014	20.51	5.14589×10^{-4}	5.14505×10^{-4}	Total CO_2 remaining in system (after acidification)
	"	382.076	232.606	"	20.51	5.14421		

Table 3. Calculation of P_{CO_2} and T_{CO_2}

Equilibration No.	n_{GB}	P_{CO_2} (micro atmospheres)	Moles Carbon in Gas Phase	Total Moles Carbon in system	Moles Carbon in Seawater	T_{CO_2} m mol/kg Sw	T_{CO_2} m mol/ℓ at 20°C	T_{CO_2} m mol/kg H_2O
3.0	6.9234×10^{-4}	15122	1.2298×10^{-3}	1.8378×10^{-3}	6.0801×10^{-4}	2.5517	2.6149	2.6446
3.1	6.5931	14401	1.1712	1.8378	6.6668	2.7980	2.8673	2.8999
3.2	6.5844	14382	1.1696	1.8378	6.6823	2.8044	2.8739	2.9066
3.3	6.6008	14418	1.1725	1.8378	6.6531	2.7922	2.8614	2.8940
3.4	3.2184	7030.0	5.7170×10^{-4}	1.1778	6.0607	2.5436	2.6066	2.6362
3.5	1.6033	3502.2	2.8480	8.5593×10^{-4}	5.7112	2.3969	2.4563	2.4842
3.6	1.5461	3377.2	2.7464	8.5593	5.8128	2.4396	2.5000	2.5284
3.7	1.6083	3513.1	2.8569	8.5593	5.7024	2.3932	2.4525	2.4804
3.8	1.6085	3513.5	2.8572	8.5593	5.7020	2.3930	2.4523	2.4802
3.9	1.6071	3510.5	2.8548	8.5593	5.7045	2.3941	2.4534	2.4813
3.10	8.2859×10^{-5}	1810.0	1.4719	6.9522	5.4803	2.3000	2.3570	2.3838
3.11	4.6725	1020.6	8.3000×10^{-5}	6.1236	5.2936	2.2216	2.2766	2.3025
3.12	4.6794	1022.2	8.3122	6.1236	5.2924	2.2211	2.2761	2.3020
3.13	4.6792	1022.1	8.3119	6.1236	5.2924	2.2211	2.2761	2.3020
3.14	2.9822	651.43	5.2974	5.6557	5.1259	2.1513	2.2046	2.2297
3.15	2.9847	651.98	5.3019	5.6557	5.1255	2.1511	2.2044	2.2295
3.16	2.1194	462.96	3.7648	5.3572	4.9807	2.0903	2.1421	2.1665
3.17	2.1214	463.40	3.7683	5.3572	4.9804	2.0902	2.1420	2.1664
T_{CO_2}				5.14505				

Table 4. Summary of P_{CO_2} and T_{CO_2}

Equilibration No.	Average P_{CO_2} (micro atmospheres)	σ	Average T_{CO_2} (m mol/liter 20°C)	σ	Average T_{CO_2} (m mol/kg SW)	Average T_{CO_2} (m mol/kg H_2O)
3.0	15122		2.6149		2.5517	2.6446
3.1, 3.2, 3.3	14400	18, .12%	2.8675	.0062, .22%	2.7982	2.9002
3.4	7030.0		2.6066		2.5436	2.6362
3.5	3502.2		2.4563		2.3969	2.4842
3.6	3377.2		2.5000		2.4396	2.5284
3.7, 3.8, 3.9	3512.4	1.6, .05%	2.4527	.0006, .02%	2.3934	2.4806
3.10	1810.0		2.3570		2.3000	2.3838
3.11, 3.12, 3.13	1021.6	.90, .09%	2.2763	.0003, .01%	2.2213	2.3022
3.14, 3.15	651.70	.39, .06%	2.2045	.0001, .01%	2.1512	2.2296
3.16, 3.17	463.18	.31, .07%	2.1420	.0001, .003%	2.0902	2.1664

Table 5. Values of Constants and Other Parameters

Parameter	Note	Value for Cl = 19.375°/₀₀ or S = 35.002 °/₀₀ and temperature = 20.00°C (Molar units)
K_o	1	3.3206×10^{-2} moles/ℓ atm
K_1	2, 6	1.004427×10^{-6} moles/ℓ
K_B	3	1.9056×10^{-9} moles/ℓ
K_W	4	6.6834×10^{-15} (moles/ℓ)^2
B	5	4.119×10^{-4} moles/ℓ

Notes

1 The following equation represents the data of Murray and Riley [1971] as interpreted by Weiss [1974]:

$$\ln K_o = -58.0931 + 90.5069 \left[\frac{100}{T_{°K}}\right] + 22.294 \ln \left[\frac{T_{°K}}{100}\right] + S°/_{°°}\left\{.027766 - .025888 \left[\frac{T_{°K}}{100}\right] + .0050578 \left[\frac{T_{°K}}{100}\right]\right.$$

2 The experimental work of Lyman [1957] as represented by Edumnd and Gieskes [1970], is given by:

$$pK_1 = 3404.71/T_{°K} + .032786\ T_{°K} - 14.7122 - .19178\ \sqrt[3]{Cl°/_{°°}}$$

3 The experimental work of Lyman [1957] as represented by Edmund and Gieskes [1970], is given by:

$$pK_B = 2291.90/T_{°K} + .01756\ T_{°K} - 3.3850 - .32051\ \sqrt[3]{Cl°/_{°°}}$$

Table 5. Values of Constants and Other Parameters (contd.)

(Notes contd.)

4 Obtained by linear interpolation from the table of Harvey [1955] (p. 160). Variation with salinity was neglected.

5 From the $\mathrm{B}/\mathrm{Cl}^\circ/_{\circ\circ}$ ratio of .00002126 moles/ℓ/(g/kg) from unpublished data of Greenhalgh and Riley as quoted in Riley and Chester [1971] (p. 81). The original dimensionless ratio of .00023 was converted (Keeling [1973], p. 297) using an atomic weight of 10.81 and disregarding difference between 1 kg and 1 liter for seawater.

6 For comparison purposes, the following constants, as interpreted by Edmund and Gieskes [1970] are given by:

Buch $pK_1 = 3523.46/T_{\circ K} - 15.65 + .034153T - .074709\sqrt{\mathrm{Cl}^\circ/_{\circ\circ}} - .0023483\ \mathrm{Cl}^\circ/_{\circ\circ}$

Buch $pK_2 = 2902.39/T_{\circ K} - 6.498 + .02379T_{\circ K} - .45322\sqrt{\mathrm{Cl}^\circ/_{\circ\circ}} + .035226\ \mathrm{Cl}^\circ/_{\circ\circ}$

Lyman $pK_2 = 2902.39/T_{\circ K} + .02379T_{\circ K} - 6.4710 - .4693\sqrt[3]{\mathrm{Cl}^\circ/_{\circ\circ}}$

<u>Table 6. Calculation of Φ and A</u>

Point No.	Equilibration Nos.	P_{CO_2} (μ atm)	T_{CO_2} (m mol/liter)		Calculated Φ for Various Alkalinities						
				A =	2.3830	2.3832	2.3833	2.3834	2.3835	2.3840	m mol/liter
1	3.7, 3.8, 3.9	3512.4	2.4527		47.181	46.878	46.728	46.579	46.431	45.704	
2	3.10	1810.0	2.3570		47.110	46.940	46.855	46.771	46.687	46.271	
3	3.11, 3.12, 3.13	1021.6	2.2763		46.910	46.802	46.748	46.694	46.641	46.374	
4	3.14, 3.15	651.70	2.2045		46.908	46.828	46.788	46.749	46.709	46.512	
5	3.16, 3.17	463.18	2.1420		46.768	46.702	46.670	46.638	46.605	46.444	
				Φav	46.975	46.830	46.758	46.686	46.615	46.261	
				σ	.167	.089	.069	.079	.110	.324	
				% σ	.36	.19	.15	.17	.24	.70	

Table 7. Calculation of Buffer Factor

Point No.	T_{CO_2} (m mol/liter)	P_{CO_2} (Calc.) (μ atm)	Revelle Factor
1	2.4527	3512.0	15.68
	(a) 2.4282	2999.6	
2	2.3570	1811.4	17.07
	(a) 2.3334	1524.8	
3	2.2763	1021.5	14.84
	(a) 2.2535	879.5	
4	2.2045	651.95	12.47
	(a) 2.1825	575.20	
5	2.1420	462.63	10.87
	(a) 2.1206	414.75	

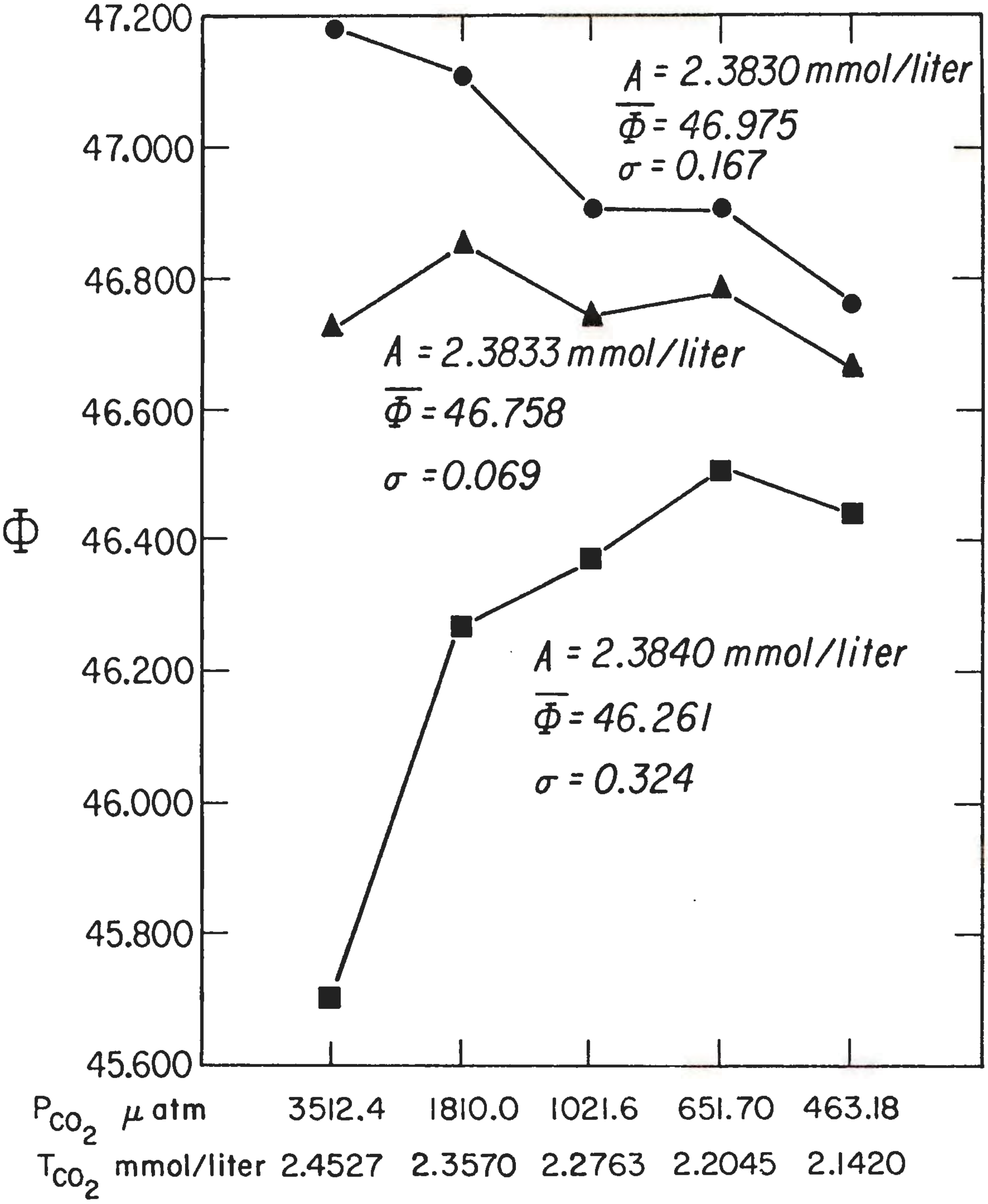


Figure 1. Variation of Φ with A - No. 1

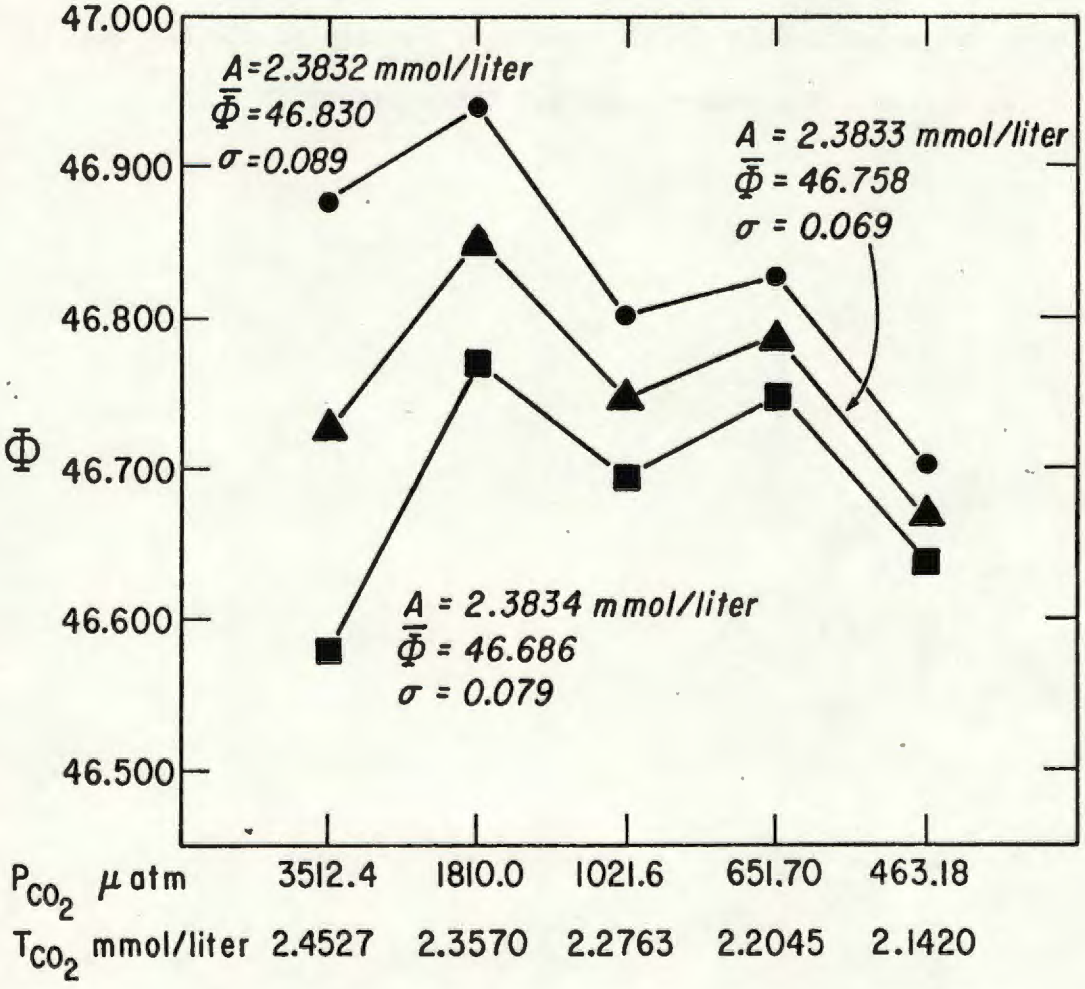


Figure 2. Variation of Φ with A - No. 2

ACKNOWLEDGEMENTS

I wish to thank C. D. Keeling for the conception of this work and for critical comments. I am grateful to Robert Bacastow for help with the calculations and for the computer programming. This work was supported by the Oceanography Section of the National Science Foundation under Grant No. DES74-21496.

REFERENCES

Buch, K., Harvey, H.W., Wattenberg, H. and Gripenberg, S. 1932. Über das Kohlensäuresystem im Meerwasser. *Rapports et Procès-Verbaux des Réunions, Conseil permanent international pour l'exploration de la mer, 79,* 1-70.

Buch, K. 1938. New determinations of the second dissociation constant of carbonic acid in sea water. *Acta Acad. Aboensis, Math Phys 11,* 1-18.

Buch, K. 1951. Das Kohlensäure Gleichgewichtssystem im Meerwasser: Kritische Durchsicht und Neuberechnungen der Konstituenten, *Hausforskningsinstitutets Skrift, No. 151,* 1-18.

Cady, H.P., Elsey, H.M. and Berger, E.V. 1922. The solubility of Helium in water. *J. Am. Chem. Soc., 44,* 1456-1461.

Edmund, J.M. and Gieskes, J.M.T.M. 1970. On the calculation of the degree of saturation of sea water with respect to calcium carbonate under *in situ* conditions. *Geochim. Cosmochim. Acta, 34,* 1261-1291.

Fine, R.A., Wang, Dong-Ping and Millero, F.J. 1974. The equation of state of seawater. *J. Mar. Res., 1974,* 433-456.

Guenther, P.R. 1976. *Manometer Report IV.* (Report of Carbon Dioxide Project, S.I.O.)

Guenther, P.R. and Keeling, C.D. 1976. *Manometer Report III.* (Report of Carbon Dioxide Project, S.I.O.)

Harvey, H.W. 1955. *The Chemistry and Fertility of Sea Waters.* University Press, Cambridge, 224 pp.

Keeling, C.D. 1973. The carbon dioxide cycle: reservoir models to depict the exchange of atmospheric carbon dioxide with the oceans and land plants. In *Chemistry of the Lower Atmosphere.* S.I. Rasool, ed. Plenum, New York, pp. 251-329.

Keeling, C.D. and Guenther, P.R. 1977. The thermodynamic ionization constants of carbonic acid: determination of ratio of K_1 to K_2 from measurements in very dilute aqueous solutions. *S.I.O. Reference Series, No. 77-29.* Scripps Institution of Oceanography, La Jolla, 67 pp.

Lyman, J. 1957. *Buffer Mechanisms of Sea Water.* Ph.D. Thesis, U.C.L.A., 196 pp.

Lyman, J. and Fleming, R.H. 1940. Composition of seawater. *J. Mar. Res.*, *3*, 134-146.

MacInnes, D.A. and Belcher, D. 1933. The thermodynamic ionization constants of carbonic acid. *J. Am. Chem. Soc.*, *55*, 2630-2646.

Murray, C.N. and Riley, J.P. 1971. The solubility of gases in distilled water and seawater IV. Carbon Dioxide. *Deep Sea Res.* *18*, 533-541.

Riley, J.P. and Chester, R. 1971. *Introduction to Marine Chemistry.* Academic Press, New York, 465 pp.

Sengers, J.M.H. Levelt, Klein, M. and Gallagher, J.S. 1971. *Pressure - Volume - Temperature Relationships of Gases - Virial Coefficients.* U.S. N.B.S. Rept., U.S. Air Force Tech. Publ., AEDC-TR-71-39, 47 pp.

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

Wilson, T.R.S. 1975. Salinity and the major elements of seawater. In *Chemical Oceanography*, Vol I, 2nd edition. J.P. Riley and G. Skirrow, ed. Academic Press, New York, pp. 365-413.

Wong, C.S. 1970. Quantitative analysis of total carbon dioxide in seawater: a new extraction method. *Deep-Sea Res.* *17*, 9-17.

Appendix: Computer Analysis of Data

The computer analysis (by PROGRAM SEAPHI written by Bob Bacastow) differs slightly from the more manual analysis in treatment of the data. A sigma based on the experimental precision is ascribed to each P_{CO_2} data point. This sigma is determined first by calculating the average relative sigma in P_{CO_2} for Equil. Nos. 3.7 to 3.17 using equation (6). The average relative sigma, .00068 or one part in 1469, is then multiplied by the average P_{CO_2} for each set of repetitive equilibrations and divided by the square root of the number of runs made to obtain the experimental sigma for each average P_{CO_2}. The program determines X to a part in 10^7 in the iteration and then minimizes the chi square to find the best Φ and A to fit the data. The buffer or Revelle factors are found by numerical integration between points .000001 mole/liter higher and lower than each of the experimental total CO_2 points.

Appendix Table 1 is the computer printout for the base run on the computer using Lyman's K_1 and K_B (as interpreted by Edmund and Gieskes [1976]) Weiss's [1974] interpretation of K_o, Harvey's [1955] K_W and the borate concentration as obtained by Keeling [1973]. There are slight differences in K_W and borate from the values listed in Table 5 due to recalculating by Bob Bacastow. Also, the manual calculations used a slightly different value of K_o, 3.322×10^{-2}, obtained from the table in Weiss [1974] rather than from his equation.

Appendix Table 2 presents the effects of changing each of the five parameters, one at a time, on the results. Each of the parameters was lowered by 2% in order to compare similar changes: this change was chosen because lowering the K_1 by 2% gives almost exactly the K_1 determined by Buch (Buch et al. [1932], Buch [1938] and Buch [1951]). It is seen that K_o has by far the largest effects on A and BUF and a similar effect as K_1, K_B or B on Phi. An interesting result is the effect of the variation in K_o on the Chisquare, increasing it tremendously. An obvious possibility is to fit the data also to K_o. There are five data points fit to two parameters, Φ and A, leaving three degrees of freedom. The borate concentration B has the next largest effect on the calculation overall. K_1 and K_B have similar effects, although in the opposite direction, on Φ, implying, as discussed in this report, a greater effect by K_1 on the determination of K_2.

A 2% change in K_w has essentially no effect on the calculation results, as expected. However, the K_w of seawater, defined as the ion product

$$K_w = [H+]\ [OH-] = \frac{a_w K^\circ_w}{f_H f_{OH}} \tag{37}$$

where

a_w is the activity of water

K°_w is the thermodynamic ionization constant of water

f_H is the activity coefficient of hydrogen ion

f_{OH} is the activity coefficient of hydroxide ion

H+, OH- include all forms including ion pairs is not known very well. Recent estimates, based upon potentionmetric titration data by Culberson and Pytkowicz [1973] and Dyrssen and Hansson [1972] are considerally lower in pK_w than the value used in the calculations reported here. Therefore, in Appendix Table 2, K_w is also varied by lowering the pK_w a full unit, which amounts to raising the K_w by 900%. This value of K_w is not inconsistent with the recent estimates. It is seen that this change has a profound effect on the calculated quantity Φ and some effect on BUF and A (although not nearly as much). One can say that the determination of K_2 to high accuracy must await a better knowledge of K_w in seawater.

Appendix Table 3 is the computer printout detailing the results of fitting the data to Φ, A <u>and</u> K_o simultaneously. It can be seen in comparison with Appendix Table 1, that the chi square per degree of freedom is not increased very much and that in fact the errors on the PFIT are improved considerally for the high-P_{CO_2} data points where the K_o is most important. The error on K_o, $.80 \times 10^{-4}$ moles/ℓ. atm., is comparable to the error, cited by Weiss [1974], in the Murray and Riley [1971] data, 1.4×10^{-4} moles/ℓ. atm. The value found for K_o differs from the literature value by about the error on K_o, indicating that this one experiment has determined K_o about as well as it had been known. Better results should be obtained by equilibrations with much higher P_{CO_2}, up to 30,000 ppm or more.

The fit to the three parameters results in sizeable changes in the determined Φ, about one part in a thousand lower, and in the determined BUF's, about a part per thousand for the highest-P_{CO_2} experiment, again not surprising because of the importance of K_o in describing that particular system.

A copy of the listing of the Fortran program SEAPHI is included in the Appendix.

Appendix: Computer Analysis of Data (Continued)

PROGRAM SEAPHI was run including the high-P_{CO_2} data point obtained by averaging the replicate Equil. Nos. 3.1, 3.2 and 3.3, which agree well with each other, having a sigma of 1.2 parts per thousand. This point, however, does not fit with the other five data points and the program iterations do not converge. Further investigation reveals that a fit can nearly be obtained if Φ is made very large and the alkalinity negative. Using a reasonable Φ and A (46.377 and 2.38×10^{-3} respectively), the P_{CO_2} calculated by the program comes out much higher, 15030 ppm, than the measured P_{CO_2}, 14400 ppm. This result can be explained by the phenomenon of supersaturation. It turns out that the very first equilibration, Equil. No. 3.0, yields a result much closer to the predicted value.

A modification of SEAPHI was made with the assistance of the Antioch student Nancy Phillips. This program, named BUFFACTOR, calculates P_{CO_2} and the buffer factor for any T_{CO_2}, using the values of Φ and A, 47.3609 and 2.3833 respectively, found by SEAPHI and the same K_o, K_1, B, K_B, and K_W used in the computer analysis. The program output was arranged to print out tables of these quantities between specified end points and with specified steps in T_{CO_2}. Appendix Table 4 is the listing of the output of BUFFACTOR for T_{CO_2} between 1.0 and 4.0 m mol/liter with a step of .01 m mol/liter. Other runs were made with fine steps of .0001 m mol/liter around the regions of minimum and maximum buffer factor and the assumed pre-industrial P_{CO_2} level, 290 ppm, in order to define those regions more precisely.

Appendix Figure 1 is a plot made from the values in Appendix Table 4. The $P(P_{CO_2})$ and $\Sigma C(T_{CO_2})$ are ratioed to the preindustrial values, 290 ppm and 2.0454 m mol/liter respectively, obtained from BUFFACTOR. The experimental data points are located on the curve by circles. The pairs of lines adjacent to the data points represent fifty times the experimental standard deviations.

Appendix Figure 2 plots the buffer factor versus T_{CO_2} for the range of T_{CO_2} covered in Appendix Table 4. Since the buffer factor is a form of slope, Figure 2 shows a different kind of detail than Figure 1. The experimental data points are again represented by circles. Figure 2 represents the predicted behavior of the studied seawater system if a "CO_2 gas titation" were carried out over a very extended range. The region where the buffer factor minimizes is nominally where all the dissolved carbon has been converted into the form of carbonate. If the system contained only carbon this minimum would be expected to occur at one-half the alkalinity or at a T_{CO_2} of 1.19 m mol/liter. See section III E of this report. This point is offset, however, by the hydrolysis contribution, and in real seawater by the borate contribution, both of which are highest in the alkaline region. The broadness of the buffer factor minimum reflects the chemistry of the three systems in the alkaline region. The buffer factor maximum is when the dissolved carbon in the system is all in the form of bicarbonate. Since this region is much more acid, where W(X), the borate and hydrolysis contributions, is much smaller, it is not surprising that T_{CO_2} at the maximum is very close to the alkalinity in value and that the peak is quite sharp. Moving to higher T_{CO_2} values the bicarbonate is converted to dissolved CO_2 gas, and the buffer factor decreases, asymptotically approaching 1.0 at the theoretical extreme. Appendix Table 4 also lists WX so that its changing contribution can be followed.

A listing of the computer PROGRAM BUFFACTOR is included also in the Appendix.

Additional References for Appendix

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

Dyrssen, D. and Hansson, I. 1972. Ionic medium effects in sea water - a comparison of acidity constants of carbonic acid and boric acid in sodium chloride and synthetic sea water. *Mar. Chem.*, *1*, 137-149.

Appendix Table 1. Base Run - Fit to Φ and A (PROGRAM SEAPHI Printout)

```
  CONSTANTS AND INITIAL VALUES
             K0             K1             K2             KW             KB         BORATE
.332057E-01   .100443E-05   .719164E-09   .659298E-14   .190561E-08   .422059E-03

CHISQUARE/(DEGREES FREEDOM)          STEPS         FLAMDA
                      1.365              3     0.00000100

        PHI            ALK             K0             K1
   47.36092      2.3833405
     +/-            +/-            +/-            +/-
    0.04516      0.0000806


   TOTAL CO2          PCO2          SIGMA           PFIT          ERROR              X             WX             PH            BUF

      2.4527     3512.4000         1.3800      3511.8034         0.5966       0.523200       0.015331       6.456143      15.245308
      2.3570     1810.0000         1.2320      1811.0526        -1.0526       0.985597       0.026060       6.731175      17.250417
      2.2763     1021.6000         0.4020      1021.4164         0.1836       1.676219       0.045661       6.961806      15.256350
      2.2045      651.7000         0.3140       652.1349        -0.4349       2.503211       0.064606       7.135973      12.808118
      2.1420      463.1800         0.2230       462.9448         0.2352       3.363518       0.082801       7.264269      11.107758
```

Appendix Table 2. Effects of Parameters on Φ, A and BUF

Parameter	Value	Change from Base Run	Chi Square per degree of freedom	Phi $\left[\frac{K_1 K_o}{K_2}\right]$	Phi % Change	Alkalinity	A % Change	BUF at Points 1 and 5	BUF % Change
	BASE RUN		1.386	47.3609		2.3833405		15.245308 11.107758	
(Parameters Below Changed one at a time)									
	↓ = down	↑ = up							
K_o	3.25417×10^{-2}	2% ↓	20.272	46.8676	1.04 ↓	2.3861	.12 ↑	15.398 11.059	1.00 ↑ .44 ↓
K_1	9.84336×10^{-7}	2% ↓	1.441	47.8143	.96 ↑	2.3833539	.00056 ↑	15.244865 11.108977	.0029 ↓ .011 ↑
K_B	1.86751×10^{-9}	2% ↓	1.342	46.9256	.92 ↓	2.3833303	.00043 ↓	15.245740 11.106658	.0028 ↑ .010 ↓
B	4.13659×10^{-4}	2% ↓	1.901	46.8154	1.15 ↓	2.3834144	.003 ↑	15.242 11.117	.02 ↓ .08 ↑
K_w	6.55908×10^{-15}	2% ↓	1.394	47.3551	.01 ↓	2.3833420	.00006 ↑	15.245251 11.107988	.0004 ↓ .002 ↑
K_w	6.6988×10^{-14}	1 pK unit or 900% ↑	10.842	50.1112	5.81 ↑	2.3827	.03 ↓	15.274 11.011	.19 ↑ .87 ↓

Appendix Table 3. Fit to Φ, A and K_o (PROGRAM SEAPHI Printout)

```
  CONSTANTS AND INITIAL VALUES
        KO            K1            K2            KW            KB         BORATE
 .332057E-01   .100443E-05   .719164E-09   .669298E-14   .190561E-08   .422059E-03

CHISQUARE/(DEGREES FREEDOM)      STEPS        FLAMDA
                     1.785           4   10.00000000

       PHI           ALK            KO            K1
  47.31543     2.3835922  .33145062E-01
      +/-           +/-           +/-           +/-
   0.00200     0.0000036  .11733603E-05


   TOTAL CO2         PCO2         SIGMA          PFIT         ERROR             X            WX            PH           BUF

      2.4527    3512.4000        1.3800     3512.3321        0.0679      0.523888      0.015357      6.457111     15.259153
      2.3570    1810.0000        1.2320     1810.6208       -0.6208      0.987230      0.026115      6.732290     17.253512
      2.2763    1021.6000        0.4020     1021.2512        0.3488      1.678800      0.045741      6.962871     15.250781
      2.2045     651.7000        0.3140      652.1550       -0.4550      2.506531      0.064903      7.136945     12.802332
      2.1420     463.1800        0.2230      463.0274        0.1526      3.367446      0.082906      7.265173     11.103301
```

Appendix Table 4. Variation of BUF with CO_2 Content

Total CO_2	P_{CO_2}	BUF	PH	WX
1.0600	0.7490	17.040490	9.012613	.440371E-03
1.0700	0.8765	16.448341	8.977476	.434415E-03
1.0800	1.0187	15.866512	8.943751	.428816E-03
1.0900	1.1760	15.303819	8.911391	.423526E-03
1.1000	1.3490	14.765844	8.880335	.418503E-03
1.1100	1.5383	14.255771	8.850513	.413710E-03
1.1200	1.7443	13.774984	8.821854	.409117E-03
1.1300	1.9676	13.323718	8.794284	.404697E-03
1.1400	2.2085	12.901347	8.767732	.400427E-03
1.1500	2.4676	12.506707	8.742130	.396288E-03
1.1600	2.7454	12.138445	8.717413	.392265E-03
1.1700	3.0423	11.794969	8.693520	.388342E-03
1.1800	3.3589	11.474664	8.670395	.384507E-03
1.1900	3.6958	11.175902	8.647986	.380750E-03
1.2000	4.0533	10.897161	8.626243	.377063E-03
1.2100	4.4321	10.636950	8.605123	.373437E-03
1.2200	4.8327	10.393889	8.584594	.369865E-03
1.2300	5.2558	10.166726	8.564587	.366342E-03
1.2400	5.7018	9.954228	8.545098	.362862E-03
1.2500	6.1714	9.755341	8.526083	.359422E-03
1.2600	6.6652	9.569055	8.507513	.356016E-03
1.2700	7.1840	9.394458	8.489361	.352642E-03
1.2800	7.7283	9.230704	8.471600	.349296E-03
1.2900	8.2989	9.077034	8.454206	.345975E-03
1.3000	8.8964	8.932764	8.437158	.342678E-03
1.3100	9.5217	8.797234	8.420435	.339402E-03
1.3200	10.1756	8.669890	8.404017	.336145E-03
1.3300	10.8587	8.550182	8.387887	.332905E-03
1.3400	11.5720	8.437624	8.372028	.329680E-03
1.3500	12.3163	8.331783	8.356425	.326470E-03
1.3600	13.0925	8.232249	8.341062	.323273E-03
1.3700	13.9016	8.138654	8.325927	.320087E-03
1.3800	14.7446	8.050654	8.311006	.316913E-03
1.3900	15.6223	7.967939	8.296287	.313748E-03
1.4000	16.5360	7.890225	8.281758	.310592E-03
1.4100	17.4866	7.817245	8.267410	.307444E-03
1.4200	18.4753	7.748762	8.253231	.304303E-03
1.4300	19.5033	7.684557	8.239211	.301170E-03
1.4400	20.5719	7.624421	8.225343	.298042E-03
1.4500	21.6822	7.568175	8.211616	.294920E-03
1.4600	22.8357	7.515643	8.198023	.291803E-03
1.4700	24.0337	7.466668	8.184555	.288691E-03
1.4800	25.2777	7.421107	8.171205	.285582E-03
1.4900	26.5692	7.378833	8.157965	.282478E-03
1.5000	27.9098	7.339713	8.144830	.279377E-03
1.5100	29.3011	7.303645	8.131791	.276279E-03
1.5200	30.7448	7.270526	8.118842	.273184E-03
1.5300	32.2429	7.240261	8.105978	.270091E-03
1.5400	33.7971	7.212771	8.093192	.267001E-03
1.5500	35.4094	7.187971	8.080478	.263912E-03
1.5600	37.0819	7.165801	8.067830	.260826E-03
1.5700	38.8168	7.146194	8.055244	.257741E-03
1.5800	40.6163	7.129094	8.042713	.254657E-03
1.5900	42.4829	7.114452	8.030233	.251574E-03
1.6000	44.4190	7.102227	8.017798	.248493E-03
1.6100	46.4272	7.092381	8.005404	.245413E-03
1.6200	48.5103	7.084877	7.993045	.242333E-03
1.6300	50.6713	7.079695	7.980716	.239254E-03

Appendix Table 4 (contd.)

Total CO_2	P_{CO_2}	BUF	PH	WX
1.6400	52.9131	7.076807	7.968414	.236175E-03
1.6500	55.2389	7.076201	7.956132	.233097E-03
1.6600	57.6522	7.077861	7.943868	.230019E-03
1.6700	60.1564	7.081782	7.931615	.226942E-03
1.6800	62.7554	7.087961	7.919369	.223865E-03
1.6900	65.4531	7.096400	7.907126	.220789E-03
1.7000	68.2536	7.107106	7.894881	.217711E-03
1.7100	71.1615	7.120089	7.882630	.214634E-03
1.7200	74.1813	7.135368	7.870368	.211557E-03
1.7300	77.3179	7.152961	7.858091	.208480E-03
1.7400	80.5767	7.172896	7.845793	.205403E-03
1.7500	83.9631	7.195202	7.833471	.202326E-03
1.7600	87.4831	7.219915	7.821119	.199249E-03
1.7700	91.1427	7.247075	7.808734	.196172E-03
1.7800	94.9488	7.276729	7.796309	.193095E-03
1.7900	98.9082	7.308928	7.783840	.190018E-03
1.8000	103.0286	7.343729	7.771323	.186941E-03
1.8100	107.3178	7.381195	7.758752	.183864E-03
1.8200	111.7843	7.421396	7.746122	.180788E-03
1.8300	116.4373	7.464406	7.733427	.177711E-03
1.8400	121.2864	7.510309	7.720663	.174634E-03
1.8500	126.3419	7.559194	7.707823	.171558E-03
1.8600	131.6149	7.611158	7.694902	.168482E-03
1.8700	137.1174	7.666306	7.681894	.165407E-03
1.8800	142.8619	7.724752	7.668794	.162332E-03
1.8900	148.8622	7.786616	7.655593	.159258E-03
1.9000	155.1329	7.852034	7.642287	.156185E-03
1.9100	161.6898	7.921143	7.628868	.153113E-03
1.9200	168.5499	7.994098	7.615330	.150041E-03
1.9300	175.7315	8.071062	7.601664	.146971E-03
1.9400	183.2545	8.152211	7.587864	.143903E-03
1.9500	191.1402	8.237731	7.573921	.140836E-03
1.9600	199.4118	8.327827	7.559827	.137771E-03
1.9700	208.0944	8.422712	7.545574	.134709E-03
1.9800	217.2153	8.522619	7.531152	.131648E-03
1.9900	226.8040	8.627794	7.516553	.128591E-03
2.0000	236.8929	8.738500	7.501765	.125537E-03
2.0100	247.5170	8.855020	7.486779	.122486E-03
2.0200	258.7147	8.977653	7.471583	.119438E-03
2.0300	270.5280	9.106717	7.456167	.116396E-03
2.0400	283.0027	9.242552	7.440518	.113358E-03
2.0500	296.1892	9.385516	7.424624	.110325E-03
2.0600	310.1427	9.535986	7.408470	.107298E-03
2.0700	324.9240	9.694363	7.392044	.104278E-03
2.0800	340.6000	9.861062	7.375330	.101265E-03
2.0900	357.2445	10.036519	7.358313	.982595E-04
2.1000	374.9392	10.221183	7.340976	.952634E-04
2.1100	393.7741	10.415515	7.323302	.922772E-04
2.1200	413.8493	10.619982	7.305274	.893020E-04
2.1300	435.2756	10.835049	7.286872	.863389E-04
2.1400	458.1759	11.061169	7.268077	.833893E-04
2.1500	482.6873	11.298771	7.248869	.804547E-04
2.1600	508.9616	11.548242	7.229226	.775367E-04
2.1700	537.1685	11.809901	7.209127	.746372E-04
2.1800	567.4965	12.083977	7.188550	.717582E-04
2.1900	600.1555	12.370564	7.167472	.689020E-04
2.2000	635.3792	12.669579	7.145870	.660710E-04
2.2100	673.4274	12.980707	7.123724	.632682E-04
2.2200	714.5884	13.303327	7.101011	.604966E-04
2.2300	759.1813	13.636439	7.077712	.577598E-04

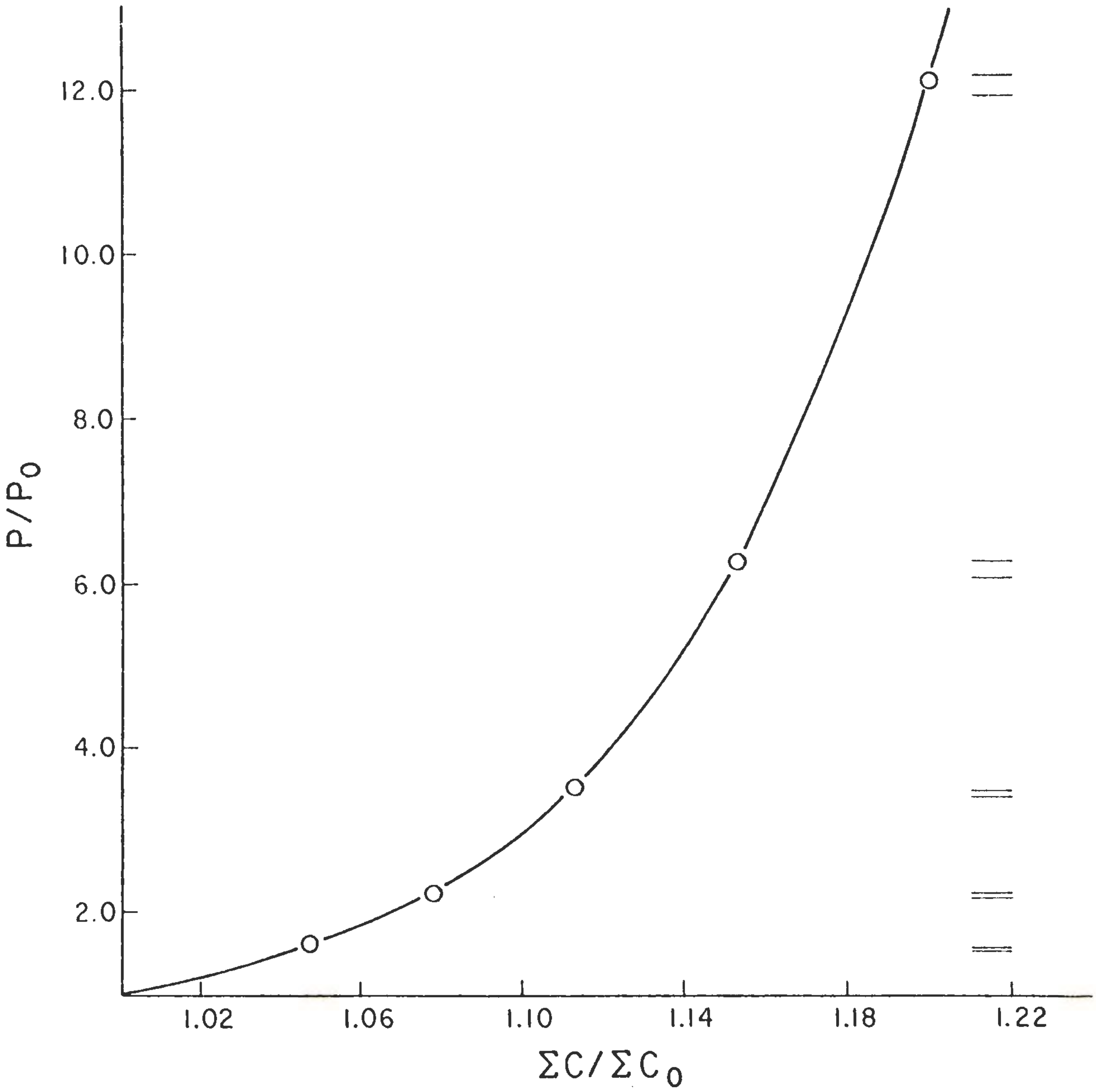
Appendix Table 4 (contd.)

Total CO_2	P_{CO_2}	BUF	PH	WX
2.2400	807.5580	13.978564	7.053810	.550615E-04
2.2500	860.1047	14.327648	7.029291	.524060E-04
2.2600	917.2431	14.680948	7.004145	.497978E-04
2.2700	979.4289	15.034937	6.978368	.472419E-04
2.2800	1047.1506	15.385209	6.951964	.447436E-04
2.2900	1120.9246	15.726432	6.924946	.423086E-04
2.3000	1201.2880	16.052352	6.897335	.399427E-04
2.3100	1288.7884	16.355885	6.869168	.376519E-04
2.3200	1383.9700	16.629316	6.840493	.354422E-04
2.3300	1487.3566	16.864625	6.811373	.333193E-04
2.3400	1599.4316	17.053927	6.781885	.312885E-04
2.3500	1720.6167	17.190033	6.752120	.293545E-04
2.3600	1851.2509	17.267022	6.722182	.275210E-04
2.3700	1991.5716	17.280789	6.692182	.257908E-04
2.3800	2141.7009	17.229471	6.662238	.241654E-04
2.3900	2301.6379	17.113650	6.632468	.226447E-04
2.4000	2471.2589	16.936320	6.602987	.212276E-04
2.4100	2650.3248	16.702605	6.573902	.199116E-04
2.4200	2838.4954	16.419287	6.545308	.186932E-04
2.4300	3035.3479	16.094224	6.517288	.175679E-04
2.4400	3240.3982	15.735755	6.489909	.165306E-04
2.4500	3453.1221	15.352160	6.463224	.155756E-04
2.4600	3672.9752	14.951237	6.437270	.146972E-04
2.4700	3899.4100	14.540008	6.412070	.138895E-04
2.4800	4131.8896	14.124552	6.387637	.131468E-04
2.4900	4369.8979	13.709947	6.363972	.124635E-04
2.5000	4612.9471	13.300292	6.341070	.118345E-04
2.5100	4860.5816	12.898784	6.318916	.112548E-04
2.5200	5112.3805	12.507821	6.297493	.107199E-04
2.5300	5367.9580	12.129120	6.276779	.102257E-04
2.5400	5626.9626	11.763831	6.256751	.976839E-05
2.5500	5889.0757	11.412650	6.237381	.934455E-05
2.5600	6154.0094	11.075911	6.218644	.895109E-05
2.5700	6421.5044	10.753667	6.200513	.858522E-05
2.5800	6691.3273	10.445763	6.182960	.824443E-05
2.5900	6963.2685	10.151887	6.165960	.792647E-05
2.6000	7237.1396	9.871618	6.149487	.762930E-05
2.6100	7512.7716	9.604459	6.133516	.735111E-05
2.6200	7790.0125	9.349866	6.118024	.709026E-05
2.6300	8068.7256	9.107271	6.102988	.684528E-05
2.6400	8348.7882	8.876092	6.088386	.661485E-05
2.6500	8630.0896	8.655752	6.074197	.639778E-05
2.6600	8912.5300	8.445682	6.060404	.619299E-05
2.6700	9196.0192	8.245328	6.046986	.599951E-05
2.6800	9480.4759	8.054159	6.033926	.581646E-05
2.6900	9765.8264	7.871665	6.021209	.564305E-05
2.7000	10052.0037	7.697361	6.008819	.547856E-05
2.7100	10338.9473	7.530787	5.996740	.532234E-05
2.7200	10626.6019	7.371507	5.984960	.517378E-05
2.7300	10914.9173	7.219112	5.973465	.503235E-05
2.7400	11203.8476	7.073215	5.962243	.489756E-05
2.7500	11493.3510	6.933454	5.951282	.476895E-05
2.7600	11783.3891	6.799488	5.940572	.464611E-05
2.7700	12073.9269	6.670997	5.930102	.452866E-05
2.7800	12364.9322	6.547681	5.919862	.441625E-05
2.7900	12656.3753	6.429260	5.909843	.430857E-05
2.8000	12948.2291	6.315470	5.900037	.420532E-05
2.8100	13240.4685	6.206066	5.890435	.410623E-05
2.8200	13533.0703	6.100815	5.881029	.401105E-05
2.8300	13826.0132	5.999501	5.871811	.391955E-05

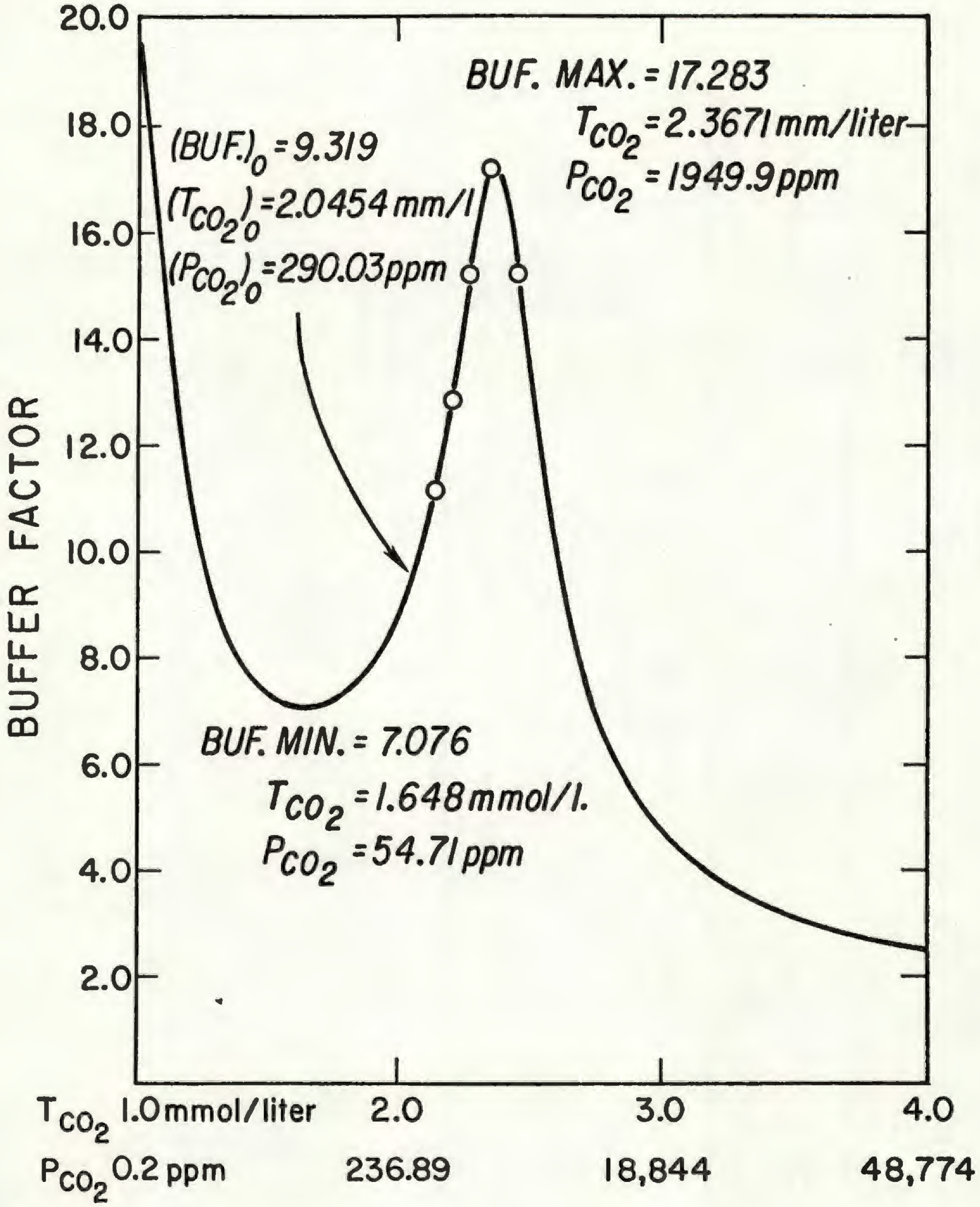
Total CO_2	P_{CO_2}	BUF	PH	WX
2.8400	14119.2773	5.901922	5.862776	.383157E-05
2.8500	14412.8445	5.807886	5.853916	.374677E-05
2.8600	14706.6976	5.717215	5.845224	.366509E-05
2.8700	15000.8209	5.629742	5.836696	.358634E-05
2.8800	15295.1998	5.545308	5.828324	.351034E-05
2.8900	15589.8207	5.463766	5.820105	.343695E-05
2.9000	15884.6708	5.384977	5.812031	.336604E-05
2.9100	16179.7383	5.308810	5.804100	.329747E-05
2.9200	16475.0120	5.235143	5.796305	.323113E-05
2.9300	16770.4818	5.163858	5.788643	.316691E-05
2.9400	17066.1379	5.094847	5.781109	.310470E-05
2.9500	17361.9712	5.028008	5.773699	.304440E-05
2.9600	17657.9733	4.963242	5.766409	.298592E-05
2.9700	17954.1362	4.900459	5.759235	.292918E-05
2.9800	18250.4524	4.839571	5.752175	.287410E-05
2.9900	18546.9149	4.780498	5.745224	.282059E-05
3.0000	18843.5171	4.723161	5.738380	.276859E-05
3.0100	19140.2527	4.667489	5.731639	.271804E-05
3.0200	19437.1160	4.613410	5.724998	.266886E-05
3.0300	19734.1013	4.560861	5.718454	.262100E-05
3.0400	20031.2034	4.509779	5.712006	.257440E-05
3.0500	20328.4174	4.460104	5.705649	.252900E-05
3.0600	20625.7387	4.411782	5.699381	.248477E-05
3.0700	20923.1628	4.364758	5.693201	.244165E-05
3.0800	21220.6856	4.318984	5.687105	.239959E-05
3.0900	21518.3030	4.274409	5.681092	.235855E-05
3.1000	21816.0115	4.230991	5.675159	.231850E-05
3.1100	22113.8073	4.188684	5.669305	.227939E-05
3.1200	22411.6872	4.147447	5.663527	.224119E-05
3.1300	22709.6479	4.107242	5.657823	.220386E-05
3.1400	23007.6864	4.068031	5.652192	.216737E-05
3.1500	23305.7998	4.029779	5.646631	.213169E-05
3.1600	23603.9853	3.992450	5.641139	.209679E-05
3.1700	23902.2403	3.956014	5.635715	.206264E-05
3.1800	24200.5624	3.920438	5.630357	.202921E-05
3.1900	24498.9490	3.885694	5.625062	.199648E-05
3.2000	24797.3981	3.851752	5.619831	.196442E-05
3.2100	25095.9073	3.818587	5.614660	.193302E-05
3.2200	25394.4747	3.786172	5.609550	.190224E-05
3.2300	25693.0982	3.754482	5.604498	.187207E-05
3.2400	25991.7761	3.723493	5.599503	.184248E-05
3.2500	26290.5063	3.693184	5.594564	.181347E-05
3.2600	26589.2873	3.663532	5.589680	.178500E-05
3.2700	26888.1174	3.634516	5.584849	.175706E-05
3.2800	27186.9951	3.606117	5.580071	.172963E-05
3.2900	27485.9187	3.578315	5.575344	.170270E-05
3.3000	27784.8868	3.551092	5.570666	.167625E-05
3.3100	28083.8981	3.524430	5.566040	.165026E-05
3.3200	28382.9512	3.498313	5.561461	.162473E-05
3.3300	28682.0449	3.472723	5.556929	.159964E-05
3.3400	28981.1779	3.447646	5.552443	.157497E-05
3.3500	29280.3490	3.423066	5.548002	.155071E-05
3.3600	29579.5571	3.398969	5.543606	.152685E-05
3.3700	29878.8011	3.375342	5.539254	.150338E-05
3.3800	30178.0799	3.352169	5.534944	.148029E-05
3.3900	30477.3927	3.329440	5.530676	.145756E-05
3.4000	30776.7383	3.307140	5.526449	.143519E-05
3.4100	31076.1158	3.285259	5.522262	.141316E-05
3.4200	31375.5244	3.263785	5.518115	.139147E-05
3.4300	31674.9632	3.242706	5.514007	.137011E-05

Appendix Table 4 (contd.)

Total CO_2	P_{CO_2}	BUF	PH	WX
3.4400	31974.4314	3.222012	5.509937	.134906E-05
3.4500	32273.9281	3.201693	5.505904	.132832E-05
3.4600	32573.4526	3.181738	5.501908	.130788E-05
3.4700	32873.0041	3.162138	5.497948	.128773E-05
3.4800	33172.5820	3.142884	5.494024	.126786E-05
3.4900	33472.1855	3.123967	5.490135	.124828E-05
3.5000	33771.8139	3.105378	5.486279	.122896E-05
3.5100	34071.4666	3.087108	5.482458	.120990E-05
3.5200	34371.1430	3.069150	5.478669	.119110E-05
3.5300	34670.8425	3.051495	5.474913	.117255E-05
3.5400	34970.5644	3.034137	5.471188	.115425E-05
3.5500	35270.3083	3.017068	5.467496	.113618E-05
3.5600	35570.0736	3.000280	5.463834	.111834E-05
3.5700	35869.8597	2.983767	5.460202	.110072E-05
3.5800	36169.6662	2.967522	5.456601	.108333E-05
3.5900	36469.4925	2.951540	5.453028	.106615E-05
3.6000	36769.3382	2.935812	5.449485	.104918E-05
3.6100	37069.2028	2.920335	5.445970	.103241E-05
3.6200	37369.0858	2.905100	5.442483	.101584E-05
3.6300	37668.9869	2.890104	5.439024	.999471E-06
3.6400	37968.9055	2.875341	5.435592	.983288E-06
3.6500	38268.8414	2.860805	5.432187	.967292E-06
3.6600	38568.7940	2.846490	5.428808	.951477E-06
3.6700	38868.7631	2.832393	5.425454	.935839E-06
3.6800	39168.7482	2.818508	5.422127	.920374E-06
3.6900	39468.7490	2.804830	5.418824	.905079E-06
3.7000	39768.7651	2.791355	5.415547	.889949E-06
3.7100	40068.7962	2.778079	5.412293	.874982E-06
3.7200	40368.8420	2.764997	5.409064	.860172E-06
3.7300	40668.9021	2.752104	5.405858	.845518E-06
3.7400	40968.9762	2.739398	5.402676	.831015E-06
3.7500	41269.0641	2.726873	5.399517	.816661E-06
3.7600	41569.1654	2.714526	5.396381	.802451E-06
3.7700	41869.2798	2.702353	5.393266	.788384E-06
3.7800	42169.4071	2.690351	5.390174	.774456E-06
3.7900	42469.5471	2.678516	5.387104	.760664E-06
3.8000	42769.6993	2.666845	5.384055	.747005E-06
3.8100	43069.8636	2.655334	5.381027	.733476E-06
3.8200	43370.0398	2.643980	5.378020	.720076E-06
3.8300	43670.2276	2.632780	5.375034	.706801E-06
3.8400	43970.4267	2.621731	5.372068	.693648E-06
3.8500	44270.6370	2.610829	5.369122	.680616E-06
3.8600	44570.8581	2.600072	5.366196	.667702E-06
3.8700	44871.0900	2.589457	5.363289	.654903E-06
3.8800	45171.3323	2.578982	5.360401	.642217E-06
3.8900	45471.5849	2.568642	5.357533	.629643E-06
3.9000	45771.8476	2.558437	5.354683	.617177E-06
3.9100	46072.1202	2.548363	5.351852	.604818E-06
3.9200	46372.4024	2.538418	5.349039	.592564E-06
3.9300	46672.6942	2.528599	5.346244	.580412E-06
3.9400	46972.9953	2.518903	5.343466	.568361E-06
3.9500	47273.3055	2.509330	5.340707	.556409E-06
3.9600	47573.6247	2.499876	5.337964	.544554E-06
3.9700	47873.9528	2.490539	5.335239	.532795E-06
3.9800	48174.2894	2.481317	5.332531	.521128E-06
3.9900	48474.6346	2.472208	5.329839	.509554E-06
4.0000	48774.9881	2.463210	5.327164	.498069E-06



Appendix Figure 1. CO_2 partial pressure vs. total inorganic carbon for seawater equilibration. Each is divided by its assumed pre-industrial value, 290 ppm and 2.0454 mmol/liter, respectively. Circles represent experimental data points. The curve is best fit thermodynamic function (see text). Separations of lines adjacent to data points represents fifty times the experimental standard deviations.



Appendix Figure 2. Buffer Factor as function of CO_2 content for seawater equilibration. Circles indicate experimental data points.

```
      B6700/B7700   F O R T R A N   C O M P I L A T I O N   M A R K   2.8.060  THURSDAY, 02/02/78     04:45 PM

C                       PROGRAM SEAPHI                                                  C  000:0000:5
                                                                                         START OF SEGMENT 002
      CLLKO(T,S)=-58.0931+90.5069*(100./T)+22.2940*ALOG(T/100.)+                        C  002:0000:0
     X  S*(.027766-.025888*(T/100.)+.0050578*(T/100.)**2)                               C  002:0008:5
      CALK1(T,C)= 3404.71/T+.032786*T-14.7122-.19178*C**(1./3.)                         C  002:0012:0
      CALK2(T,C)=2902.39/T+.02379*T-6.4710-.4693*C**(1./3.)                             C  002:001C:3
      CALKB(T,C)=2291.90/T+.01756*T-3.3850-.32051*C**(1./3.)                            C  002:0027:3
      CALKW(T)=-4.671527+4265.365/T+.01465488*T                                         C  002:0032:3
      COMMON         AK2,AKB,AKW,G(3),BORATE,X,WX                                       C  002:0039:5
      DIMENSION TOTCO2(10),PCO2(10),SIGP(10),PFIT(10),                                  C  002:0039:5
     X  DELALP(10),SIGALP(10),ALP(10)                                                   C  002:0039:5
 1000 FORMAT(6PF10.2,3PF10.2,6PF10.2)                                                   C  002:0039:5
 1001 FORMAT('0  CHISQUARE/(DEGREES FREEDOM)             STEPS              FLAMDA      C  002:0039:5
     X ')                                                                               C  002:0039:5
 1002 FORMAT(1H ,14X,F14.3,I14,F14.8)                                                   C  002:0039:5
 1003 FORMAT('0                 PHI              ALK               K0              K1   C  002:0039:5
     X  ')                                                                              C  002:0039:5
 1004 FORMAT(1H ,F14.5,3PF14.7,0PE14.8,E14.8)                                           C  002:0039:5
 1005 FORMAT('          +/-              +/-              +/-              +/-')        C  002:0039:5
 1006 FORMAT(////)                                                                      C  002:0039:5
 1007 FORMAT('          TOTAL CO2              PCO2              SIGMA              PFIT  C  002:0039:5
     X          ERROR              X              WX              PH                  C  002:0039:5
     XBUF',/)                                                                           C  002:0039:5
 1009 FORMAT('0  FIT FAILED TO CONVERGE')                                               C  002:0039:5
 1011 FORMAT(1H ,3PF14.4,4(6PF14.4),0PF14.6,3PF14.6,0PF14.6,F14.6)                      C  002:0039:5
 1012 FORMAT('                 K0              K1              K2              KW         C  002:0039:5
     X          KB          BORATE')                                                    C  002:0039:5
 1013 FORMAT(1H ,9E14.6)                                                                C  002:0039:5
 1014 FORMAT('        CONSTANTS AND INITIAL VALUES')                                    C  002:0039:5
 1020 FORMAT(8E10.4)                                                                    C  002:0039:5
 1021 FORMAT(8F10.2)                                                                    C  002:0039:5
      TEMP=20.                                                                          C  002:0039:5
      TEMK=TEMP+273.16                                                                  C  002:003A:4
      CL=19.375                                                                         C  002:003C:4
      SAL=1.80655*CL                                                                    C  002:003E:3
C         DENSITY OF SEA WATER (20 DEG. C) = 1.02478 KGM/LITER                          C  002:0041:0
      READ(5,1020)DKO,DK1,DKB,DB,DKW                                                    C  002:0041:0
                                                                                             FIB IS 0006 LONG
      BORATE=.000230*1.02478/10.82*CL                                                   C  002:0050:2
      BORATE=BORATE+DB                                                                  C  002:0057:5
      AKO=EXP( CLLKO(TEMK,SAL))                                                         C  002:0059:4
      AKO=AKO+DKO                                                                       C  002:005C:1
      AK1=10.**(-CALK1(TEMK,CL))                                                        C  002:005D:1
      AK1=AK1+DK1                                                                       C  002:0060:3
      AK2=10.**(-CALK2(TEMK,CL))                                                        C  002:0061:3
      AKB=10.**(-CALKB(TEMK,CL))                                                        C  002:0065:1
      AKB=AKB+DKB                                                                       C  002:0068:5
      AKW=10.**(-CALKW(TEMK))                                                           C  002:006A:3
      AKW=AKW+DKW                                                                       C  002:006E:0
      G(3)=AK1*SQRT(AKO)                                                                C  002:006F:5
      G(2)=AKW/G(3)                                                                     C  002:0072:2
      G(1)=G(3)/AKB                                                                     C  002:0074:5
      WRITE(6,1014)                                                                     C  002:0077:1
                                                                                             FIB IS 0006 LONG
      WRITE(6,1012)                                                                     C  002:0078:2
      WRITE(6,1013)AKO,AK1,AK2,AKW,AKB,BORATE                                           C  002:007F:2
      READ(5,1021)TERMS,FLAMDA                                                          C  002:008E:2
      NTERMS=TERMS                                                                      C  002:0097:2
```

```
      NPTS=0                                                            C  002:0098:2
   10 NPTS=NPTS+1                                                       C  002:0099:0
      READ(5,1000,END=20)PCO2(NPTS),TOTCO2(NPTS),SIGP(NPTS)             C  002:009A:2
      GO TO 10                                                          C  002:00A9:0
   20 NPTS=NPTS-1                                                       C  002:00A9:3
C         INITIAL TRIAL VALUES                                          C  002:00AA:5
      ALP(1)=AK1*AK0/AK2                                                C  002:00AA:5
      DELALP(1)=.001                                                    C  002:00AD:1
      ALP(2)=.00238                                                     C  002:00AF:1
      DELALP(2)=.0000001                                                C  002:00B1:1
      ALP(3)=AK0                                                        C  002:00B3:1
      DELALP(3)=.00001                                                  C  002:00B4:3
      ALP(4)=AK1                                                        C  002:00B7:1
      DELALP(4)=.0001E-05                                               C  002:00B8:3
      MODE=1                                                            C  002:00BB:1
      CHISQ1=0.                                                         C  002:00BB:5
      DO 100 J=1,100                                                    C  002:00BC:3
      CALL CURFIT(TOTCO2,PCO2,SIGP,NPTS,NTERMS,MODE,ALP,DELALP,         C  002:00BE:0
     X  SIGALP,FLAMDA,PFIT,CHISQR)                                      C  002:00C3:2
      IF(ABS(CHISQ1-CHISQR)-   .0001)200,200,100                        C  002:00C5:5
  100 CHISQ1=CHISQR                                                     C  002:00C9:4
      WRITE(5,1009)                                                     C  002:00CC:4
  200 CONTINUE                                                          C  002:00D0:2
      WRITE(6,1001)                                                     C  002:00D0:2
      WRITE(6,1002)CHISQR,J,FLAMDA                                      C  002:00D4:2
      WRITE(6,1003)                                                     C  002:00DE:2
      WRITE(6,1004)(ALP(I),I=1,NTERMS)                                  C  002:00E2:2
      WRITE(6,1005)                                                     C  002:00EE:2
      WRITE(6,1004)(SIGALP(I),I=1,NTERMS)                               C  002:00F2:2
      WRITE(6,1006)                                                     C  002:00FE:2
      WRITE(6,1007)                                                     C  002:0102:2
      DEL=.000001                                                       C  002:0106:2
      DO 250 I=1,NPTS                                                   C  002:0108:3
      ERR=PCO2(I)-PFIT(I)                                               C  002:010A:0
      TOTCO2(I)=TOTCO2(I)+DEL                                           C  002:010C:4
      BUF= FUNCTN(TOTCO2,I,ALP)                                         C  002:010E:5
      TOTCO2(I)=TOTCO2(I)-2.*DEL                                        C  002:0111:5
      BUF=(BUF-FUNCTN(TOTCO2,I,ALP))/(2.*DEL)                           C  002:0114:3
      TOTCO2(I)=TOTCO2(I)+DEL                                           C  002:0119:0
      BUF=BUF*TOTCO2(I)/PFIT(I)                                         C  002:011B:1
      P=FUNCTN(TOTCO2,I,ALP)                                            C  002:011E:2
      PH=-ALOG10(G(3)/X)                                                C  002:0121:2
  250 WRITE(6,1011)TOTCO2(I),PCO2(I),SIGP(I),PFIT(I),ERR,X,WX,PH,BUF    C  002:0124:1
      END                                                               C  002:013C:3
      002:0140:3  IS THE LOCATION FOR EXCEPTIONAL ACTION ON THE I/O STATEMENT AT 002:009A
                                                                      SEGMENT 002 IS 016E LONG
```

```
                                                                        START OF SEGMENT 00A
      FUNCTION FUNCTN(CTOT,IND,ALP)                                    C  00A:0000:0
C        CALC. PCO2 OF SEA WATER FOR TOTAL CO2 CTOT                    C  00A:0000:0
C        ALP(1)=PHI=K1*K0/K2                                           C  00A:0000:0
C        ALP(2)=ALKALINITY                                             C  00A:0000:0
C        ALP(3)=K0                                                     C  00A:0000:0
C        ALP(4)=K1                                                     C  00A:0000:0
      DIMENSION CTOT(1),ALP(1)                                         C  00A:0000:0
      COMMON          AK2,AKB,AKW,G(3),BORATE,X,WX                     C  00A:0000:0
      PHI=ALP(1)                                                       C  00A:0000:0
      ALK=ALP(2)                                                       C  00A:0001:1
      AK0=ALP(3)                                                       C  00A:0002:4
      AK1=ALP(4)                                                       C  00A:0004:2
      G(3)=AK1*SQRT(AK0)                                               C  00A:0006:0
      G(2)=AKW/G(3)                                                    C  00A:0008:3
      G(1)=G(3)/AKB                                                    C  00A:000B:0
      CT=CTOT(IND)                                                     C  00A:000D:2
      A=AK0*(PHI-4.*AK0)                                               C  00A:000F:2
      X=1.                                                             C  00A:0011:4
      DO 100 I=1,100                                                   C  00A:0012:5
      X1=X2P                                                           C  00A:0014:0
      X2=X3                                                            C  00A:0014:5
      X2P=XX                                                           C  00A:0015:4
      X3=X                                                             C  00A:0016:3
      IF(I-3)10,10,20                                                  C  00A:0017:4
   10 XX=X                                                             C  00A:0019:0
      GO TO 30                                                         C  00A:001A:1
   20 XX=X2P+(X3-X2P)*(X1-X2P)/(X1-X2-X2P+X3)                          C  00A:001A:4
   30 CONTINUE                                                         C  00A:001F:3
      Z=SQRT(PHI)*XX                                                   C  00A:001F:3
      WX=BORATE/(1.+G(1)/Z)+G(2)*Z-G(3)/Z                              C  00A:0021:3
      ALKP=ALK-WX                                                      C  00A:0027:3
      B=PHI*(ALKP-CT)+4.*AK0*(2.*CT-ALKP)                              C  00A:0029:1
      C=-(2.*CT-ALKP)**2                                               C  00A:002D:3
      P=(-B+SQRT(B**2-4.*A*C))/(2.*A)                                  C  00A:002F:5
      X=     SQRT((ALKP-CT)/(AK0*P)+1.)                                C  00A:0034:5
      IF(ABS(X-XX)/X-.00000001)200,200,100                             C  00A:0038:4
  100 CONTINUE                                                         C  00A:003C:4
      WRITE(6,1001)                                                    C  00A:003E:5
      WRITE(6,1002)                                                    C  00A:0043:2
      WRITE(6,1003)CT,PHI,ALK,AK0,AK1,ALKP,WX,X,P                      C  00A:0047:2
  200 FUNCTN=P                                                         C  00A:005A:2
      RETURN                                                           C  00A:005B:1
 1001 FORMAT('0  CONVERGENCE OF POCEAN HAS FAILED, X=',E14.6)          C  00A:005B:4
 1002 FORMAT('0            CT            PHI           ALK           K0 C  00A:005B:4
     X            K1            ALKP          WX            X          C  00A:005B:4
     Y  P')                                                            C  00A:005B:4
 1003 FORMAT(1H ,9E14.6)                                               C  00A:005B:4
      END                                                              C  00A:005B:4
                                                                  SEGMENT 00A IS 0066 LONG
```

```
                                                                         START OF SEGMENT 008
      FUNCTION FCHISQ (Y, SIGMAY, NPTS, NFREE, MODE, YFIT)                 1   008:0000:0
C                                                                          1   008:0000:0
C     PURPOSE                                                              1   008:0000:0
C       EVALUATE REDUCED CHI SQUARE FOR FIT TO DATA                        1   008:0000:0
C          FCHISQ = SUM ((Y-YFIT)**2/SIGMA**2) / NFREE                     1   008:0000:0
C                                                                          1   008:0000:0
C     USAGE                                                                1   008:0000:0
C       RESULT = FCHISQ (Y, SIGMAY, NPTS, NFREE, MODE, YFIT)               1   008:0000:0
C                                                                          1   008:0000:0
C     DESCRIPTION OF PARAMETERS                                            1   008:0000:0
C       Y      - ARRAY OF DATA POINTS                                      1   008:0000:0
C       SIGMAY - ARRAY OF STANDARD DEVIATIONS FOR DATA POINTS              1   008:0000:0
C       NPTS   - NUMBER OF DATA POINTS                                     1   008:0000:0
C       NFREE  - NUMBER OF DEGREES OF FREEDOM                              1   008:0000:0
C       MODE   - DETERMINES METHOD OF WEIGHTING LEAST-SQUARES FIT          1   008:0000:0
C                +1 (INSTRUMENTAL) WEIGHT(I) =1./SIGMAY(I)**2              1   008:0000:0
C                 0 (NO WEIGHTING) WEIGHT(I) =1.                           1   008:0000:0
C                -1 (STATISTICAL) WEIGHT(I) =1./Y(I)                       1   008:0000:0
C       YFIT   - ARRAY OF CALCULATED VALUES OF Y                           1   008:0000:0
C                                                                          1   008:0000:0
      DOUBLE PRECISION CHISQ, WEIGHT                                       1   008:0000:0
      DIMENSION Y(1), SIGMAY(1), YFIT(1)                                   1   008:0000:0
   11 CHISQ=0.                                                             1   008:0000:0
   12 IF (NFREE) 13, 13, 20                                                1   008:0000:5
   13 FCHISQ=0.                                                            1   008:0002:0
      GO TO 40                                                             1   008:0002:4
C                                                                          1   008:0003:1
C        ACCUMULATE CHI SQUARE                                             1   008:0003:1
C                                                                          1   008:0003:1
   20 DO 30 I=1, NPTS                                                      1   008:0003:1
   21 IF (MODE) 22, 27, 29                                                 1   008:0004:0
   22 IF (Y(I)) 25, 27, 23                                                 1   008:0006:2
   23 WEIGHT=1./Y(I)                                                       1   008:000A:2
      GO TO 30                                                             1   008:000C:5
   25 WEIGHT=1./(-Y(I))                                                    1   008:000D:2
      GO TO 30                                                             1   008:0010:0
   27 WEIGHT=1.                                                            1   008:0010:3
      GO TO 30                                                             1   008:0011:2
   29 WEIGHT=1./SIGMAY(I)**2                                               1   008:0011:5
   30 CHISQ=CHISQ + WEIGHT*(Y(I)-YFIT(I))**2                               1   008:0014:4
C                                                                          1   008:0018:5
C        DIVIDE BY NUMBER OF DEGREES OF FREEDOM                            1   008:0018:5
C                                                                          1   008:0018:5
   31 FREE=NFREE                                                           1   008:0018:5
   32 FCHISQ=CHISQ/FREE                                                    1   008:001C:4
   40 RETURN                                                               1   008:001E:1
      END                                                                  1   008:001E:4
                                                                       SEGMENT 008 IS 0028 LONG
```

```
                                                                       START OF SEGMENT 00C
      SUBROUTINE CURFIT (X,Y,SIGMAY,NPTS,NTERMS,MODE,A,DELTAA,          1  00C:0000:0
     1 SIGMAA,FLAMDA,YFIT,CHISQR)                                       1  00C:0000:0
C                                                                       1  00C:0000:0
C         FROM BEVINGTON BUT MODIFIED BY BACASTOW                       1  00C:0000:0
C     PURPOSE                                                           1  00C:0000:0
C       MAKE A LEAST-SQUARES FIT TO A NON-LINEAR FUNCTION               1  00C:0000:0
C          WITH A LINEARIZATION OF THE FITTING FUNCTION                 1  00C:0000:0
C                                                                       1  00C:0000:0
C     USAGE                                                             1  00C:0000:0
C       CALL CURFIT (X, Y, SIGMAY, NPTS, NTERMS, MODE, A, DELTAA,       1  00C:0000:0
C          SIGMAA, FLAMDA, YFIT, CHISQR)                                1  00C:0000:0
C                                                                       1  00C:0000:0
C     DESCRIPTION OF PARAMETERS                                         1  00C:0000:0
C       X      - ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE          1  00C:0000:0
C       Y      - ARRAY OF DATA POINTS FOR DEPENDENT VARIABLE            1  00C:0000:0
C       SIGMAY - ARRAY OF STANDARD DEVIATIONS FOR Y DATA POINTS         1  00C:0000:0
C       NPTS   - NUMBER OF PAIRS OF DATA POINTS                         1  00C:0000:0
C       NTERMS - NUMBER OF PARAMETERS                                   1  00C:0000:0
C       MODE   - DETERMINES METHOD OF WEIGHTING LEAST-SQUARES FIT       1  00C:0000:0
C                +1 (INSTRUMENTAL) WEIGHT(I) = 1./SIGMAY(I)**2          1  00C:0000:0
C                 0 (NO WEIGHTING) WEIGHT(I) = 1.                       1  00C:0000:0
C                -1 (STATISTICAL) WEIGHT(I) = 1./Y(I)                   1  00C:0000:0
C       A      - ARRAY OF PARAMETERS                                    1  00C:0000:0
C       DELTAA - ARRAY OF INCREMENTS FOR PARAMETERS A                   1  00C:0000:0
C       SIGMAA - ARRAY OF STANDARD DEVIATIONS FOR PARAMETERS A          1  00C:0000:0
C       FLAMDA - PROPORTION OF GRADIENT SEARCH INCLUDED                 1  00C:0000:0
C       YFIT   - ARRAY OF CALCULATED VALUES OF Y                        1  00C:0000:0
C       CHISQR - REDUCED CHI SQUARE FOR FIT                             1  00C:0000:0
C                                                                       1  00C:0000:0
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                     1  00C:0000:0
C       FUNCTN (X, I, A)                                                1  00C:0000:0
C          EVALUATES THE FITTING FUNCTION FOR THE ITH TERM              1  00C:0000:0
C       FCHISQ (Y, SIGMAY, NPTS, NFREE, MODE, YFIT)                     1  00C:0000:0
C          EVALUATES REDUCED CHI SQUARE FOR FIT TO DATA                 1  00C:0000:0
C       FDERIV (X, I, A, DELTAA, NTERMS, DERIV)                         1  00C:0000:0
C          EVALUATES THE DERIVATIVES OF THE FITTING FUNCTION            1  00C:0000:0
C          FOR THE ITH TERM WITH RESPECT TO EACH PARAMETER              1  00C:0000:0
C       MATINV (ARRAY, NTERMS, DET)                                     1  00C:0000:0
C          INVERTS A SYMMETRIC TWO-DIMENSIONAL MATRIX OF DEGREE NTERMS  1  00C:0000:0
C          AND CALCULATES ITS DETERMINANT                               1  00C:0000:0
C                                                                       1  00C:0000:0
C     COMMENTS                                                          1  00C:0000:0
C       DIMENSION STATEMENT VALID FOR NTERMS UP TO 10                   1  00C:0000:0
C       SET FLAMDA = 0.001 AT BEGINNING OF SEARCH                       1  00C:0000:0
C                                                                       1  00C:0000:0
      DOUBLE PRECISION ARRAY                                            1  00C:0000:0
      DIMENSION X(1), Y(1), SIGMAY(1), A(1), DELTAA(1), SIGMAA(1),      1  00C:0000:0
     1 YFIT(1)                                                          1  00C:0000:0
      DIMENSION WEIGHT(100), ALPHA(10,10), BETA(10), DERIV(10),         1  00C:0000:0
     1 ARRAY(10,10), B(10)                                              1  00C:0000:0
   11 NFREE=NPTS-NTERMS                                                 1  00C:0000:0
      IF (NFREE) 13,13,20                                               1  00C:0001:3
   13 CHISQR=0.                                                         1  00C:0002:2
      GO TO 110                                                         1  00C:0003:0
C                                                                       1  00C:0003:3
C        EVALUATE WEIGHTS                                               1  00C:0003:3
C                                                                       1  00C:0003:3
   20 DO 30 I=1, NPTS                                                   1  00C:0003:3
   21 IF (MODE) 22,27,29                                                1  00C:0005:0
```

```
   22 IF (Y(I)) 25,27,23                                                     1   00C:0007:2
   23 WEIGHT(I)=1./Y(I)                                                      1   00C:0005:2
      GO TO 30                                                               1   00C:000E:3
   25 WEIGHT(I)=1./(-Y(I))                                                   1   00C:000F:0
      GO TO 30                                                               1   00C:0012:2
   27 WEIGHT(I)=1.                                                           1   00C:0012:5
      GO TO 30                                                               1   00C:0014:2
   29 WEIGHT(I)=1./SIGMAY(I)**2                                              1   00C:0014:5
   30 CONTINUE                                                               1   00C:0018:2
C                                                                            1   00C:001A:3
C          EVALUATE ALPHA AND BETA MATRICES                                  1   00C:001A:3
C                                                                            1   00C:001A:3
   31 DO 34 J=1, NTERMS                                                      1   00C:001A:3
      BETA(J)=0.                                                             1   00C:001C:0
      DO 34 K=1, J                                                           1   00C:001D:3
   34 ALPHA(J,K)=0.                                                          1   00C:001F:0
   41 DO 50 I=1, NPTS                                                        1   00C:0026:0
      YFIT(I)=FUNCTN(X,I,A)                                                  1   00C:0027:0
      CALL FDERIV (X,I,A,DELTAA,NTERMS,DERIV)                                1   00C:0028:4
      DO 46 J=1, NTERMS                                                      1   00C:0030:3
      BETA(J)=BETA(J)+WEIGHT(I)*(Y(I)-YFIT(I)        )*DERIV(J)              1   00C:0032:0
      DO 46 K=1, J                                                           1   00C:0039:2
   46 ALPHA(J,K)=ALPHA(J,K)+WEIGHT(I)*DERIV(J)*DERIV(K)                      1   00C:003A:0
   50 CONTINUE                                                               1   00C:0044:4
   51 DO 53 J=1, NTERMS                                                      1   00C:0046:5
      DO 53 K=1, J                                                           1   00C:0048:0
   53 ALPHA(K,J)=ALPHA(J,K)                                                  1   00C:0049:0
C                                                                            1   00C:0052:0
C          EVALUATE CHI SQUARE AT STARTING POINT                             1   00C:0052:0
C                                                                            1   00C:0052:0
   63 CHISQ1=FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)                           1   00C:0052:0
C                                                                            1   00C:0057:1
C          INVERT MODIFIED CURVATURE MATRIX TO FIND NEW PARAMETERS           1   00C:0057:1
C                                                                            1   00C:0057:1
   71 DO 74 J=1, NTERMS                                                      1   00C:0057:1
      DO 73 K=1, NTERMS                                                      1   00C:0058:0
   73 ARRAY(J,K)=ALPHA(J,K)/SQRT(ALPHA(J,J)*ALPHA(K,K))                      1   00C:0059:0
   74 ARRAY(J,J)=1.+FLAMDA                                                   1   00C:0065:2
   80 CALL MATINV (ARRAY,NTERMS,DET)                                         1   00C:006A:5
C                                                                            1   00C:006D:1
C          INSERTED TO PERMIT USE OF PARAMETERS ABOVE NTERMS                 1   00C:006D:1
      DO 85 J=1,10                                                           1   00C:006D:1
   85 B(J)=A(J)                                                              1   00C:006E:0
C                                                                            1   00C:0073:0
   81 DO 84 J=1, NTERMS                                                      1   00C:0073:0
      B(J)=A(J)                                                              1   00C:0074:0
      DO 84 K=1, NTERMS                                                      1   00C:0076:5
   84 B(J)=B(J)+BETA(K)*ARRAY(J,K)/SQRT(ALPHA(J,J)*ALPHA(K,K))               1   00C:0078:0
C                                                                            1   00C:0087:0
C          IF CHI SQUARE INCREASED, INCREASE FLAMDA AND TRY AGAIN            1   00C:0087:0
C                                                                            1   00C:0087:0
   91 DO 92 I=1, NPTS                                                        1   00C:0087:0
   92 YFIT(I)=FUNCTN(X,I,B)                                                  1   00C:0088:0
   93 CHISQR=FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)                           1   00C:008E:4
      IF (CHISQ1-CHISQR) 95,101,101                                          1   00C:0093:5
   95 FLAMDA=10.*FLAMDA                                                      1   00C:0095:1
      GO TO 71                                                               1   00C:0096:3
C                                                                            1   00C:0097:0
C          EVALUATE PARAMETERS AND UNCERTAINTIES                             1   00C:0097:0
C                                                                            1   00C:0097:0
```

```
101 DO 103 J=1, NTERMS                                              1  00C:0097:0
    A(J)=B(J)                                                       1  00C:0098:0
103 SIGMAA(J)=DSQRT(ARRAY(J,J)/ALPHA(J,J))                          1  00C:009A:5
    FLAMDA=FLAMDA/10.                                               1  00C:00A4:1
110 RETURN                                                          1  00C:00A5:3
    END                                                             1  00C:00A6:0
                                                                 SEGMENT 00C IS 00C1 LONG
```

```
                                                              START OF SEGMENT 00E
      SUBROUTINE MATINV (ARRAY, NORDER, DET)                  1  00E:0000:0
C                                                             1  00E:0000:0
C     PURPOSE                                                 1  00E:0000:0
C       INVERT A SYMMETRIC MATRIX AND CALCULATE ITS DETERMINANT   1  00E:0000:0
C                                                             1  00E:0000:0
C     USAGE                                                   1  00E:0000:0
C       CALL MATINV (ARRAY, NORDER, DET)                      1  00E:0000:0
C                                                             1  00E:0000:0
C     DESCRIPTION OF PARAMETERS                               1  00E:0000:0
C       ARRAY  - INPUT MATRIX WHICH IS REPLACED BY ITS INVERSE   1  00E:0000:0
C       NORDER - DEGREE OF MATRIX (ORDER OF DETERMINANT)      1  00E:0000:0
C       DET    - DETERMINANT OF INPUT MATRIX                  1  00E:0000:0
C                                                             1  00E:0000:0
C     COMMENTS                                                1  00E:0000:0
C       DIMENSION STATEMENT VALID FOR NORDER UP TO 10         1  00E:0000:0
C                                                             1  00E:0000:0
      DOUBLE PRECISION ARRAY, AMAX, SAVE                      1  00E:0000:0
      DIMENSION ARRAY(10,10), IK(10), JK(10)                  1  00E:0000:0
   10 DET=1.                                                  1  00E:0000:0
   11 DO 100 K=1, NORDER                                      1  00E:0000:4
C                                                             1  00E:0002:0
C        FIND LARGEST ELEMENT ARRAY(I,J) IN REST OF MATRIX    1  00E:0002:0
C                                                             1  00E:0002:0
      AMAX=0.                                                 1  00E:0002:0
   21 DO 30 I=K, NORDER                                       1  00E:0002:5
      DO 30 J=K, NORDER                                       1  00E:0004:0
   23 IF (DABS(AMAX)-DABS(ARRAY(I,J))) 24, 24, 30             1  00E:0005:0
   24 AMAX=ARRAY(I,J)                                         1  00E:0009:2
      IK(K)=I                                                 1  00E:000C:3
      JK(K)=J                                                 1  00E:000E:1
   30 CONTINUE                                                1  00E:000F:5
C                                                             1  00E:0014:1
C        INTERCHANGE ROWS AND COLUMNS TO PUT AMAX IN ARRAY(K,K)   1  00E:0014:1
C                                                             1  00E:0014:1
   31 IF (AMAX) 41, 32, 41                                    1  00E:0014:1
   32 DET=0.                                                  1  00E:0015:2
      GO TO 140                                               1  00E:0016:0
   41 I=IK(K)                                                 1  00E:0016:3
      IF (I-K) 21, 51, 43                                     1  00E:0018:0
   43 DO 50 J=1, NORDER                                       1  00E:001B:0
      SAVE=ARRAY(K,J)                                         1  00E:001C:0
      ARRAY(K,J)=ARRAY(I,J)                                   1  00E:001F:1
   50 ARRAY(I,J)=-SAVE                                        1  00E:0024:5
   51 J=JK(K)                                                 1  00E:002A:3
      IF (J-K) 21, 61, 53                                     1  00E:002C:0
   53 DO 60 I=1, NORDER                                       1  00E:002F:0
      SAVE=ARRAY(I,K)                                         1  00E:0030:0
      ARRAY(I,K)=ARRAY(I,J)                                   1  00E:0033:1
   60 ARRAY(I,J)=-SAVE                                        1  00E:0038:5
C                                                             1  00E:003E:3
C        ACCUMULATE ELEMENTS OF INVERSE MATRIX                1  00E:003E:3
C                                                             1  00E:003E:3
   61 DO 70 I=1, NORDER                                       1  00E:003E:3
      IF (I-K) 63, 70, 63                                     1  00E:0040:0
   63 ARRAY(I,K)=-ARRAY(I,K)/AMAX                             1  00E:0041:2
   70 CONTINUE                                                1  00E:0045:2
   71 DO 80 I=1, NORDER                                       1  00E:0047:3
      DO 80 J=1, NORDER                                       1  00E:0049:0
      IF (I-K) 74, 80, 74                                     1  00E:004A:0
```

```
   74 IF (J-K) 75, 80, 75                                                    1   00E:0048:2
   75 ARRAY(I,J)=ARRAY(I,J)+ARRAY(I,K)*ARRAY(K,J)                            1   00E:004C:4
   80 CONTINUE                                                               1   00E:0055:4
   81 DO 90 J=1, NORDER                                                      1   00E:005A:0
      IF (J-K) 83, 90, 83                                                    1   00E:005B:0
   83 ARRAY(K,J)=ARRAY(K,J)/AMAX                                             1   00E:005C:2
   90 CONTINUE                                                               1   00E:0060:1
      ARRAY(K,K)=1./AMAX                                                     1   00E:0062:2
  100 DET=DET*AMAX                                                           1   00E:0066:0
C                                                                            1   00E:0069:4
C        RESTORE ORDERING OF MATRIX                                          1   00E:0069:4
C                                                                            1   00E:0069:4
  101 DO 130 L=1, NORDER                                                     1   00E:0069:4
      K=NORDER-L+1                                                           1   00E:006B:0
      J=IK(K)                                                                1   00E:006C:5
      IF (J-K) 111, 111, 105                                                 1   00E:006E:0
  105 DO 110 I=1, NORDER                                                     1   00E:006F:0
      SAVE=ARRAY(I,K)                                                        1   00E:0070:0
      ARRAY(I,K)=-ARRAY(I,J)                                                 1   00E:0073:1
  110 ARRAY(I,J)=SAVE                                                        1   00E:0079:0
  111 I=JK(K)                                                                1   00E:007E:3
      IF (I-K) 130, 130, 113                                                 1   00E:0080:0
  113 DO 120 J=1, NORDER                                                     1   00E:0081:0
      SAVE=ARRAY(K,J)                                                        1   00E:0082:0
      ARRAY(K,J)=-ARRAY(I,J)                                                 1   00E:0085:1
  120 ARRAY(I,J)=SAVE                                                        1   00E:0088:0
  130 CONTINUE                                                               1   00E:0090:3
  140 RETURN                                                                 1   00E:0092:4
      END                                                                    1   00E:0093:1
                                                                       SEGMENT 00E IS 00A0 LONG
```

```
                                                                   START OF SEGMENT 00F
      SUBROUTINE FDERIV (X,I,A,DELTAA,NTERMS,DERIV)                1  00F:0000:0
C                                                                  1  00F:0000:0
C     PURPOSE                                                      1  00F:0000:0
C       EVALUATE DERIVATIVES OF FUNCTION FOR LEAST-SQUARES SEARCH  1  00F:0000:0
C           FOR ARBITRARY FUNCTION GIVEN BY FUNCTN                 1  00F:0000:0
C                                                                  1  00F:0000:0
C     USAGE                                                        1  00F:0000:0
C       CALL FDERIV (X, I, A, DELTAA, NTERMS, DERIV)               1  00F:0000:0
C                                                                  1  00F:0000:0
C     DESCRIPTION OF PARAMETERS                                    1  00F:0000:0
C       X      - ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE     1  00F:0000:0
C       I      - INDEX OF DATA POINTS                              1  00F:0000:0
C       A      - ARRAY OF PARAMETERS                               1  00F:0000:0
C       DELTAA - ARRAY OF PARAMETER INCREMENTS                     1  00F:0000:0
C       NTERMS - NUMBER OF PARAMETERS                              1  00F:0000:0
C       DERIV  - DERIVATIVES OF FUNCTION                           1  00F:0000:0
C                                                                  1  00F:0000:0
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                1  00F:0000:0
C       FUNCTN (X, I, A)                                           1  00F:0000:0
C           EVALUATES THE FITTING FUNCTION FOR THE ITH TERM        1  00F:0000:0
C                                                                  1  00F:0000:0
      DIMENSION X(1), A(1), DELTAA(1), DERIV(1)                    1  00F:0000:0
   11 DO 18 J=1, NTERMS                                            1  00F:0000:0
      AJ=A(J)                                                      1  00F:0001:0
      DELTA=DELTAA(J)                                              1  00F:0003:0
      A(J)=AJ + DELTA                                              1  00F:0005:0
      YFIT=FUNCTN(X,I,A)                                           1  00F:0007:4
      A(J)=AJ - DELTA                                              1  00F:0008:0
      DERIV(J)=(YFIT-FUNCTN(X,I,A))/(2.*DELTA)                     1  00F:000D:4
   18 A(J)=AJ                                                      1  00F:0013:5
      RETURN                                                       1  00F:0018:1
      END                                                          1  00F:0018:4
                                                               SEGMENT 00F IS 0020 LONG
```

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      B6700/B7700   F O R T R A N   C O M P I L A T I O N   M A R K   2.8.060  THURSDAY, 02/02/78     05:18 PM

  C                  PROGRAM BUFFACTOR                                                   C  000:0000:5
                                                                                          START OF SEGMENT 002
        CLLKO(T,S)=-58.0931+90.5069*(100./T)+22.2940*ALOG(T/100.)+                        C  002:0000:0
      X  S*(.027766-.025885*(T/100.)+.0050578*(T/100.)**2)                                C  002:0006:5
        CALK1(T,C)= 3404.71/T+.032786*T-14.7122-.19178*C**(1./3.)                         C  002:0012:0
        CALK2(T,C)=2902.39/T+.02379*T-6.4710-.4693*C**(1./3.)                             C  002:001C:3
        CALKB(T,C)=2291.90/T+.01756*T-3.3850-.32051*C**(1./3.)                            C  002:0027:3
        CALKW(T)=-4.671527+4265.385/T+.01465488*T                                         C  002:0032:3
        COMMON AK2,AKB,AKW,G(3),BORATE,X,HX                                               C  002:0039:5
        DIMENSION ALP(10)                                                                 C  002:0039:5
   1000 FORMAT(3PF10.2, 3PF10.2, 3PF10.2)                                                 C  002:0039:5
   1006 FORMAT(////)                                                                      C  002:0039:5
   1007 FORMAT('      TOTAL CO2              PCO2              BUF              PH        C  002:0039:5
      X           HX',/)                                                                  C  002:0039:5
   1009 FORMAT('0  FIT FAILED TO CONVERGE')                                               C  002:0039:5
   1011 FORMAT(1H , 3PF14.4, 6PF14.4, 0PF14.6, 0PF14.6, E14.6)                            C  002:0039:5
   1012 FORMAT('               KO              K1              K2              KW         C  002:0039:5
      X           KB             BORATE')                                                 C  002:0039:5
   1013 FORMAT(1H ,9E14.6)                                                                C  002:0039:5
   1014 FORMAT('      CONSTANTS AND INITIAL VALUES',/)                                    C  002:0039:5
   1015 FORMAT (F10.2, 3PF10.2)                                                           C  002:0039:5
        TEMP=20.                                                                          C  002:0039:5
        TEMK=TEMP+273.16                                                                  C  002:003A:4
        CL=19.375                                                                         C  002:003C:4
        SAL=1.80655*CL                                                                    C  002:003E:3
  C          DENSITY OF SEA WATER (20 DEG. C) = 1.02478 KGM/LITER                         C  002:0041:0
        BORATE=.000230*1.02478/10.82*CL                                                   C  002:0041:0
        AKO=EXP( CLLKO(TEMK,SAL))                                                         C  002:0047:5
        AK1=10.**(-CALK1(TEMK,CL))                                                        C  002:004A:2
        AK2=10.**(-CALK2(TEMK,CL))                                                        C  002:004D:4
        AKB=10.**(-CALKB(TEMK,CL))                                                        C  002:0051:2
        AKW=10.**(-CALKW(TEMK))                                                           C  002:0055:0
        G(3)=AK1*SQRT(AKO)                                                                C  002:0058:3
        G(2)=AKW/G(3)                                                                     C  002:005B:0
        G(1)=G(3)/AKB                                                                     C  002:005D:3
        WRITE(6,1014)                                                                     C  002:005F:5
                                                                                            FIB IS 0006 LONG
        WRITE(6,1012)                                                                     C  002:0064:2
        WRITE(6,1013)AKO,AK1,AK2,AKW,AKB,BORATE                                           C  002:0068:2
        READ(5,1015) PHI, ALK                                                             C  002:0077:2
                                                                                            FIB IS 0006 LONG
        ALP(1)=PHI                                                                        C  002:0080:2
        ALP(2)=ALK                                                                        C  002:0081:3
        ALP(3)=AKO                                                                        C  002:0082:4
        ALP(4)=AK1                                                                        C  002:0084:0
        WRITE(6,1006)                                                                     C  002:0085:2
        WRITE(6,1007)                                                                     C  002:0089:2
        READ(5,1000) STAVAL, ENDVAL, ADDVAL                                               C  002:008D:2
        DEL=.000001                                                                       C  002:0098:2
        TOTCO2=STAVAL-ADDVAL                                                              C  002:009A:3
     10 TOTCO2=TOTCO2+ADDVAL                                                              C  002:009B:5
        TOTCO2=TOTCO2+DEL                                                                 C  002:009D:1
        BUF=POCEAN(TOTCO2,ALP)                                                            C  002:009E:1
        TOTCO2=TOTCO2-2.*DEL                                                              C  002:00A0:3
        BUF=(BUF-POCEAN(TOTCO2,ALP))/(2.*DEL)                                             C  002:00A2:2
        TOTCO2=TOTCO2+DEL                                                                 C  002:00A6:1
        P=POCEAN(TOTCO2,ALP)                                                              C  002:00A7:3
        BUF=BUF*TOTCO2/P                                                                  C  002:00A9:5
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      PH=-ALOG10(G(3)/X)                                               C  002:00AB:4
      WRITE(6,1011) TOTCO2, P, BUF, PH, WX                             C  002:00AE:3
      IF(TOTCO2-ENDVAL)10,10,20                                        C  002:00BB:2
   20 CONTINUE                                                         C  002:00BC:4
      END                                                              C  002:00BC:4
                                                                 SEGMENT 002 IS 00D7 LONG
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                                                                      START OF SEGMENT 00A
      FUNCTION POCEAN(CT, ALP)                                         C  00A:0000:0
C        CALC. PCO2 OF SEA WATER FOR TOTAL CO2 CTOT                    C  00A:0000:0
C        ALP(1)=PHI=K1*K0/K2                                           C  00A:0000:0
C        ALP(2)=ALKALINITY                                             C  00A:0000:0
C        ALP(3)=K0                                                     C  00A:0000:0
C        ALP(4)=K1                                                     C  00A:0000:0
      DIMENSION ALP(1)                                                 C  00A:0000:0
      COMMON AK2,AKB,AKW,G(3),BORATE,X,WX                              C  00A:0000:0
      PHI=ALP(1)                                                       C  00A:0000:0
      ALK=ALP(2)                                                       C  00A:0001:1
      AK0=ALP(3)                                                       C  00A:0002:4
      AK1=ALP(4)                                                       C  00A:0004:2
      G(3)=AK1*SQRT(AK0)                                               C  00A:0006:0
      G(2)=AKW/G(3)                                                    C  00A:0008:3
      G(1)=G(3)/AKB                                                    C  00A:000B:0
      A=AK0*(PHI-4.*AK0)                                               C  00A:000D:2
      X=1.                                                             C  00A:000F:4
      DO 100 I=1,100                                                   C  00A:0010:5
      X1=X2P                                                           C  00A:0012:0
      X2=X3                                                            C  00A:0012:5
      X2P=XX                                                           C  00A:0013:4
      X3=X                                                             C  00A:0014:3
      IF(I-3)10,10,20                                                  C  00A:0015:4
   10 XX=X                                                             C  00A:0017:0
      GO TO 30                                                         C  00A:0018:1
   20 XX=X2P+(X3-X2P)*(X1-X2P)/(X1-X2-X2P+X3)                          C  00A:0018:4
   30 CONTINUE                                                         C  00A:001D:3
      Z=SQRT(PHI)*XX                                                   C  00A:001D:3
      WX=BORATE/(1.+G(1)/Z)+G(2)*Z-G(3)/Z                              C  00A:001F:3
      ALKP=ALK-WX                                                      C  00A:0025:3
      B=PHI*(ALKP-CT)+4.*AK0*(2.*CT-ALKP)                              C  00A:0027:1
      C=-(2.*CT-ALKP)**2                                               C  00A:0028:3
      P=(-B+SQRT(B**2-4.*A*C))/(2.*A)                                  C  00A:002D:5
      X=      SQRT((ALKP-CT)/(AK0*P)+1.)                               C  00A:0032:5
      IF(ABS(X-XX)/X-.00000001)200,200,100                             C  00A:0035:4
  100 CONTINUE                                                         C  00A:003A:4
      WRITE(6,1001) X                                                  C  00A:003C:5
      WRITE(6,1002)                                                    C  00A:0044:2
      WRITE(6,1003)CT,PHI,ALK,AK0,AK1,ALKP,WX,X,P                      C  00A:0048:2
  200 POCEAN=P                                                         C  00A:005B:2
      RETURN                                                           C  00A:005C:1
 1001 FORMAT('0  CONVERGENCE OF POCEAN HAS FAILED, X=',E14.6)          C  00A:005C:4
 1002 FORMAT('0              CT              PHI             ALK              K0  C  00A:005C:4
     X              K1              ALKP            WX              X      C  00A:005C:4
     Y  P')                                                            C  00A:005C:4
 1003 FORMAT(1H ,9E14.6)                                               C  00A:005C:4
      END                                                              C  00A:005C:4
                                                                  SEGMENT 00A IS 0069 LONG
```