

AN ABSTRACT OF THE THESIS OF

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Title PRESSURE DEPENDENCE OF THE APPARENT
DISSOCIATION CONSTANTS OF CARBONIC AND BORIC
ACIDS IN SEAWATER

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The pressure coefficients of the first and second apparent dissociation constants of carbonic acid (K_1' and K_2') and of the first apparent dissociation constant of boric acid (K_B') were determined from pH measurements at high pressure with a pressure compensated glass electrode. The effect of pressure on the apparent constants was determined at 2°C, 11.6°C, and 22°C in artificial seawater of 34.8‰ salinity, and at 13.5°C in artificial seawater of 38.5‰ salinity.

The effect of pressure on the pH of seawater of 34.8‰ salinity was calculated from the pressure dependence of the apparent constants. At 1000 atmospheres, the calculated values of the change in pH with pressure agreed to within 4%, with values measured in natural seawater.

The effect of pressure on the apparent constants and on the pH was used to calculate the vertical distributions of the carbon dioxide constituents at in situ temperatures and pressures for a hydrographic station in the North Pacific Ocean.

Pressure Dependence of the Apparent Dissociation Constants
of Carbonic and Boric Acids in Seawater

by

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LIST OF SYMBOLS

A	$T(\text{CO}_2)/\text{CA}$
a_A	Activity of A.
CA	Carbonate alkalinity.
c	Designates molar concentrations.
E_p	The potential of the high pressure pH cell at pressure p.
$(E_{\text{asym}})_p$	The asymmetry potential of the high pressure pH cell at pressure p.
i	Subscript designating the solution inside the glass electrode of the high pressure pH cell.
K	A thermodynamic dissociation constant.
K'	An apparent dissociation constant.
$(K')_p$	An apparent dissociation constant at pressure p.
$(K')_p/(K')_1$	The pressure coefficient of K' .
K'_1	The first apparent dissociation constant of carbonic acid.
K'_2	The second apparent dissociation constant of carbonic acid.
K'_B	The first apparent dissociation constant of boric acid.
m	Designates molal concentrations.
o	Subscript designating the solution outside the glass electrode of the high pressure pH cell.
$\text{p}K'$	$-\log(K')$
S	The slope of the glass electrode response.
T	Subscript designating total concentrations.
TA	Titration alkalinity.

\bar{V}_i	The partial molal volume of species i.
(A)	The molal concentration of A. Moles of A per kilogram of solvent.
$\gamma_{\pm i}$	The mean ionic activity coefficient of species i.
γ_i	The individual ionic activity coefficient of species i.
$\Delta pK'$	$\log [(K')_p / (K')_1]$
$^{\circ}/_{\infty}$	Parts per thousand, grams of salt per kilogram of solution.
mM	Millimole per liter of solution.
mM/kg-H ₂ O	Millimole per kilogram of solvent.

PRESSURE DEPENDENCE OF THE APPARENT
DISSOCIATION CONSTANTS OF CARBONIC
AND BORIC ACIDS IN SEAWATER

I. INTRODUCTION

The first and second apparent dissociation constants of carbonic acid (K_1' and K_2') and the first apparent dissociation constant of boric acid (K_B') must be known as functions of the temperature, salinity, and pressure to calculate and interpret the pH and the distributions of CO_2 , HCO_3^- , and CO_3^{--} in the ocean. At atmospheric pressure the effects of temperature and salinity on the apparent constants have been studied by Buch et al. (1932), Buch (1951), and Lyman (1956). The effect of pressure on the apparent constants is less well known, and the purpose of this thesis is to determine the pressure dependence of K_1' , K_2' , and K_B' as a function of the temperature and salinity.

Lyman defined the apparent constants, which are used in this work, as

$$K_1' = \frac{a_{\text{H}(\text{HCO}_3^-)}_{\text{T}}}{(\text{CO}_2 + \text{H}_2\text{CO}_3)_{\text{T}}} \quad (1)$$

$$K_2' = \frac{a_{\text{H}(\text{CO}_3^{--})}_{\text{T}}}{(\text{HCO}_3^-)_{\text{T}}} \quad (2)$$

$$K_B' = \frac{a_{\text{H}(\text{H}_2\text{BO}_3^-)}_{\text{T}}}{(\text{H}_3\text{BO}_3)_{\text{T}}} \quad (3)$$

The parentheses represent molal concentrations. The subscript T signifies that concentrations in equations (1), (2), and (3) are total concentrations, that is, the concentration of each species is the sum of its free and its complexed forms.

In this thesis apparent constants are represented by K' and thermodynamic constants by K . Apparent constants are functions of the salinity, while thermodynamic constants are independent of salinity. However, concentrations rather than activities are usually measured in seawater, and the use of thermodynamic constants requires a knowledge of activity coefficients as a function of salinity. Activity coefficients are poorly known in seawater and the use of apparent constants in conjunction with concentrations is more direct than the use of thermodynamic constants.

Early studies of the conductivity of electrolytic solutions showed that pressure increased the conductance of weak electrolytes more than that of strong electrolytes. This indicated that the dissociation of weak electrolytes increased with pressure. From conductivity measurements in dilute solutions, Brander (1932) calculated the pressure dependence of the dissociation constant of acetic acid and of the first dissociation constant of carbonic acid.

Buch and Gripenberg (1932) applied Brander's results to the carbon dioxide system in seawater. They assumed that the pressure coefficients, $(K'_1)_p / (K'_1)_1$ and $(K'_2)_p / (K'_2)_1$, of the first and second

apparent dissociation constants of carbonic acid were equal to Brander's pressure coefficients for carbonic and acetic acids respectively. From their calculations they concluded that, for a seawater sample, the pH will decrease with increasing pressure, the concentrations of CO_2 and $\text{CO}_3^{=}$ will decrease, and the concentration of HCO_3^- will increase slightly. The importance of Buch and Gripenberg's work is that they were the first to show that pressure has significant effects on the carbon dioxide system in seawater.

Pytkowicz (1963) suggested the need to verify the pressure coefficients used by Buch and Gripenberg since these coefficients depend on the extent of ion-pair formation and on partial molal volumes, and since these quantities vary with the temperature, pressure, and composition of the solution. The assumptions made by Buch and Gripenberg are examined in the following paragraphs.

Buch and Gripenberg assumed that Brander's pressure coefficients, measured at 20°C , could be applied to seawater at temperatures between 0°C and 5°C . Recently, Ellis (1959) measured the effect of pressure on the first dissociation constant of carbonic acid in pure water at temperatures between 25°C and 65°C . His results show that the pressure coefficient of K_1 increases with decreasing temperature. This suggests that the pressure coefficient of K_1' may also be temperature dependent. The effect of temperature on the pressure dependence of either K_2 or K_2' had not been studied

before the present work.

A second assumption made by Buch and Gripenberg was that the pressure coefficients were independent of salinity (ionic strength), and that Brander's values, measured in dilute solutions, could be used in seawater. This assumption had to be checked because the pressure dependence of the apparent constants depends on ion-pair formation and on partial molal volumes which are functions of the salinity.

In their calculations Buch and Gripenberg replaced the pressure coefficient of K_2' by the pressure coefficient of acetic acid. Owen and Brinkley (1941) calculated the effect of pressure on K_2 from partial molal volumes which were obtained from density data. Their results indicate that, by using the pressure coefficient of acetic acid, Buch and Gripenberg underestimated the pressure dependence of K_2' .

The presence of relatively large amounts of boric acid in seawater was first shown by Goldschmidt and Peters in 1932 (Buch, 1933). Buch and Gripenberg were unaware that boric acid occurred in seawater and thus they did not consider its effect on the pressure dependence of the pH.

Disteche (1959) made the first measurement of the effect of pressure on the pH of seawater. He used a pressure protected glass electrode and measured the change in pH with pressure for a seawater

of 36 ‰ salinity at 22° C. He found that the pH change with pressure was -0.30 pH/1000 atm., and that it was unaffected by the pH at atmospheric pressure for pH's between 7.4 and 7.9. For surface pH's of 7.4 and 7.9, Buch and Gripenberg predicted pH shifts of -0.38 and -0.23 pH/1000 atm. respectively.

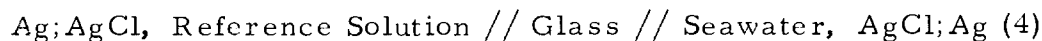
In a later paper, Disteché and Disteché (1967) determined K_1' , K_2' , and K_B' at 1000 bars. Their experiments were made at 22° C in seawater of 36.1 ‰ salinity and need to be extended to other pressures, temperatures, and salinities. Their data show that boric acid has a relatively large effect on the pressure dependence of the pH.

Some preliminary results of the values of K_1' , K_2' , and K_B' for pressures up to 654 atmospheres in seawater of 34.8 ‰ salinity and 22° C, were reported by Culberson, Kester, and Pytkowicz (1967).

II. THEORY

Pressure Dependence of the Emf

The pressure dependence of the apparent constants was determined from pH measurements at high pressures. The following cell was used to measure the pH:



The reference solution contained 0.01m HCl plus enough NaCl to make the ionic strength equal to that of the seawater being tested.

At any pressure the potential of this cell is,

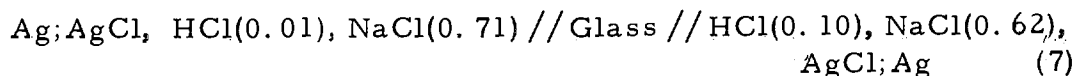
$$E = S \cdot \log (a_{\text{H}} a_{\text{Cl}})_i - S \cdot \log (a_{\text{H}} a_{\text{Cl}})_o + E_{\text{asym}} \quad (5)$$

The subscripts i and o designate the solutions inside and outside the glass electrode. The reference solution is always placed in the internal compartment. The external solution may be either seawater or reference solution depending on the experiment. S is the slope of the glass electrode response which is theoretically equal to $2.3RT/F$. E_{asym} is the asymmetry potential of cell (4), that is, the potential developed when identical solutions are placed on the two sides of the glass membrane.

The change in potential of cell (4) with pressure is,

$$E_1 - E_p = S \cdot \log \left[\frac{a_{\text{H}}}{a_{\text{H}_1}} \right]_o \left[\frac{a_{\text{H}_1}}{a_{\text{H}_p}} \right]_i + S \cdot \log \left[\frac{a_{\text{Cl}}}{a_{\text{Cl}_1}} \right]_o \left[\frac{a_{\text{Cl}_1}}{a_{\text{Cl}_p}} \right]_i + \Delta E_{\text{asym}} \quad (6)$$

where $\Delta E_{\text{asym}} = (E_{\text{asym}})_1 - (E_{\text{asym}})_p$. In the derivation of equation (6) the slope of the glass electrode, S , was assumed to be independent of pressure. To verify this assumption, the effect of pressure on the cell



was measured. The results of this experiment are shown in Table I.

Table I. Effect of pressure on glass electrode slope at 22° C.

Pressure (atm)	E_p (mv) ^a	$E_1 - E_p$	E_{asym} (mv) ^b	ΔE_{asym}
1	-59.32	0.00	-0.18	0.00
340	-59.34	+0.02	-0.20	+0.02
680	-59.36	+0.04	-0.22	+0.04
1020	-59.37	+0.05	-0.25	+0.07

^a Outside solution: 0.62m NaCl + 0.10m HCl,
Inside solution: 0.71m NaCl + 0.01m HCl.

^b Asymmetry potentials measured with 0.71m NaCl + 0.01m HCl on both sides.

The potential of cell (7) is given by equation (5). Expanding this equation gives,

$$E = S \cdot \log \frac{[(\text{H})(\text{Cl})]_i}{[(\text{H})(\text{Cl})]_o} + 2 \cdot S \cdot \log \frac{(\gamma_{\pm})_i}{(\gamma_{\pm})_o} + E_{\text{asym}} \quad (8)$$

where γ_{\pm} is the mean ionic activity coefficient of HCl. In cell (7),

$$[(H)(Cl)]_i = (0.01)(0.72)$$

$$[(H)(Cl)]_o = (0.10)(0.72)$$

Substituting these values into equation (8) yields,

$$E = S \left[-1 + 2 \cdot \log \frac{(\gamma_{\pm})_i}{(\gamma_{\pm})_o} \right] + E_{\text{asym}} \quad (9)$$

Because the two solutions are similar in composition,

$\log \left[\frac{(\gamma_{\pm})_i}{(\gamma_{\pm})_o} \right]$ should change very little with pressure, and the term

$$\left[-1 + 2 \log \frac{(\gamma_{\pm})_i}{(\gamma_{\pm})_o} \right]$$

in equation (9) should be nearly independent of pressure. Therefore, the effect of pressure on the potential of cell (7) depends on the pressure dependence of S and of E_{asym} . If S is a function of pressure, the potential of cell (7) will change with pressure; if S is independent of pressure the only change in potential will be that due to a change in the asymmetry potential. The data in Table I show that S is unaffected by pressure. Disteché (1959) and Hamann (1963) also show that S is independent of pressure.

Before equation (6) can be used to calculate the pH at pressure, several simplifying approximations must be made. The term

$$S \cdot \log \left[\frac{a_{Cl_p}}{a_{Cl_i}} \right] \left[\frac{a_{Cl_i}}{a_{Cl_p}} \right]_o \quad (10)$$

can be expanded to

$$S \cdot \log \left[\frac{C_{1P}}{C_{1l}} \right]_i \left[\frac{C_{1l}}{C_{1P}} \right]_o + S \cdot \log \left[\frac{\gamma_{ClP}}{\gamma_{Cl_l}} \right]_i \left[\frac{\gamma_{Cl_l}}{\gamma_{ClP}} \right]_o$$

The molal concentration of chloride is independent of pressure. Thus,

$$\left[\frac{C_{1P}}{C_{1l}} \right]_i = \left[\frac{C_{1P}}{C_{1l}} \right]_o = 1$$

and (10) reduces to,

$$S \cdot \log \left[\frac{\gamma_{ClP}}{\gamma_{Cl_l}} \right]_i \left[\frac{\gamma_{Cl_l}}{\gamma_{ClP}} \right]_o \quad (11)$$

If the effect of pressure on the activity coefficients of chloride is similar inside and outside the glass electrode, then,

$$\left[\frac{\gamma_{ClP}}{\gamma_{Cl_l}} \right]_i \approx \left[\frac{\gamma_{ClP}}{\gamma_{Cl_l}} \right]_o \quad (12)$$

and (11) becomes,

$$S \cdot \log \left[\frac{\gamma_{ClP}}{\gamma_{Cl_l}} \right]_i \left[\frac{\gamma_{Cl_l}}{\gamma_{ClP}} \right]_o \approx 0$$

This approximation will be evaluated later.

With this approximation equation (6) becomes,

$$E_1 - E_p \approx S \cdot \log \left[\frac{a_{H_p}}{a_{H_l}} \right]_o \left[\frac{a_{H_l}}{a_{H_p}} \right]_i + \Delta E_{\text{asym}}$$

This equation can be expanded to

$$E_1 - E_p \approx S \cdot \log \left[\frac{a_{H_p}}{a_{H_1}} \right]_o + S \cdot \log \left[\frac{H_1}{H_p} \right]_i \left[\frac{\gamma_{H_1}}{\gamma_{H_p}} \right]_i + \Delta E_{\text{asym}} \quad (13)$$

The molal concentration of hydrogen ion in the reference solution is independent of pressure and equation (13) can be simplified to,

$$E_1 - E_p \approx S \cdot \log \left[\frac{a_{H_p}}{a_{H_1}} \right]_o + S \cdot \log \left[\frac{\gamma_{H_1}}{\gamma_{H_p}} \right]_i + \Delta E_{\text{asym}}$$

In terms of the pH of the solution outside the glass electrode this becomes,

$$\left[\frac{E_1 - E_p - \Delta E_{\text{asym}}}{S} \right] \approx \text{pH}_1 - \text{pH}_p + \log \left[\frac{\gamma_{H_1}}{\gamma_{H_p}} \right]_i \quad (14)$$

It will be shown later that $\log \left[\frac{(\gamma_{H_1})}{(\gamma_{H_p})} \right]_i \approx 0$. Using this approximation equation (14) may be written,

$$\left[\frac{E_1 - E_p - \Delta E_{\text{asym}}}{S} \right] \approx \text{pH}_1 - \text{pH}_p \quad (15)$$

This equation will be used to calculate the effect of pressure on pH.

Two approximations were made in the derivation of equation (15). It was assumed that

$$\left[\frac{\gamma_{Cl_p}}{\gamma_{Cl_1}} \right]_i \approx \left[\frac{\gamma_{Cl_p}}{\gamma_{Cl_1}} \right]_o \quad (12)$$

and that

$$\left[\gamma_{H_1} / \gamma_{H_p} \right] \approx 1 \quad (16)$$

These approximations are not exact and the values of $pH_1 - pH_p$ calculated from equation (15) differ slightly from the thermodynamic values of $pH_1 - pH_p$. Pytkowicz, Kester, and Burgener (1966) showed that, because of liquid junction and asymmetry potentials, pH measurements in seawater with a glass-calomel electrode pair do not yield values of the thermodynamic hydrogen ion activity. However, differences between the pH scale in seawater and the operational scale defined in dilute buffers cancel within the reproducibility of liquid junction and asymmetry potentials, if the same techniques are used in the measurement and in the application of apparent dissociation constants (Kester and Pytkowicz, 1967).

This same argument is true for pH measurements at high pressures. The apparent constants at pressure are determined from pH values calculated from equation (15). Any difference between the calculated values of pH_p and the thermodynamic values will cancel when the apparent constants are used to calculate the concentrations of the various carbonate species. Therefore, the difference between the calculated values of pH_p and the thermodynamic values of pH_p does not affect the accuracy of the calculated values of $(CO_2 + H_2CO_3)_T$, $(HCO_3^-)_T$, and $(CO_3^{2-})_T$.

The validity of equations (12) and (16) will now be considered. It must be remembered, however, that the validity of these two equations does not affect the accuracy of the calculated concentrations of the carbonate species. The effect of pressure on individual ionic activity coefficients is given by

$$\left[\frac{\partial \ln \gamma_i}{\partial P} \right]_{T, m} = \frac{\bar{V}_i - \bar{V}_i^0}{RT} \quad (17)$$

\bar{V}_i and \bar{V}_i^0 are the partial molal volumes of the ion in the solution and in pure water respectively. Equation (17) shows that (12) will be a good approximation if \bar{V}_{Cl} in seawater is nearly the same as \bar{V}_{Cl} in the reference solution.

Wirth (1937, 1940) studied the partial molal volumes of NaCl, KCl, KBr, and K_2SO_4 in NaCl solutions. He found that the partial molal volumes of KCl and KBr (and of K_2SO_4 to a close approximation) depend only on the ionic strength. Owen and Brinkley (1941) studied the effect of pressure on ionic equilibria in NaCl solutions of the same ionic strength as seawater. They assumed that, as a first approximation, the partial molal volumes of salts in 0.725m NaCl are a function of ionic strength only.

Wirth (1940) studied the partial molal volume of NaCl in HCl solutions, and his results show that \bar{V}_{NaCl} in 0.71m NaCl + 0.01m HCl is nearly identical to \bar{V}_{NaCl} in 0.72m NaCl. Therefore, the partial molal volume of chloride ion in 0.71m NaCl + 0.01m HCl

(the reference solution) should be nearly equal to its value in 0.72m NaCl.

Duedall and Weyl (1967) determined the partial equivalent volumes of several salts in seawater. In Table II their results for \bar{V}_{NaCl} and \bar{V}_{KCl} are compared with data obtained by Wirth (1937) in single salt solutions of the same ionic strength as seawater.

Table II. Comparison of partial molal volumes in seawater and in single salt solutions of the same ionic strength.

	<u>Seawater</u> ^a	<u>Single salt solution</u>
\bar{V}_{NaCl}	18.88	19.00 ^b
\bar{V}_{KCl}	29.18	29.34 ^c

^a Calculated from Duedall and Weyl (1967) at 25° C and 34.7‰.

^b Interpolated from Wirth (1940) for (NaCl) = 0.72m.

^c Interpolated from Wirth (1937) for (KCl) = 0.72m.

The agreement between the partial molal volumes measured in the various solutions is good. Therefore, as a first approximation it is reasonable to assume that \bar{V}_{Cl} in seawater is the same as \bar{V}_{Cl} in a NaCl solution of the same ionic strength, even though it is not possible to prove this experimentally for a single ion.

The arguments given above suggest that \bar{V}_{Cl} in seawater is nearly equal to \bar{V}_{Cl} in the reference solution (0.71m NaCl + 0.01m HCl). In this case equation (17) shows that the pressure dependence

of γ_{Cl} in the two solutions is approximately the same, and that equation (12) is a good approximation.

In equation (16) it is assumed that pressure has no effect on γ_H in the reference solution. This is only an approximation because pressure tends to increase activity coefficients. In terms of hydrogen ion equation (17) may be written,

$$\left[\frac{\partial \ln \gamma_H}{\partial P} \right]_{T, m} = \frac{\bar{V}_H - \bar{V}_H^{\circ}}{RT} \quad (18)$$

This equation could be used to calculate $(\gamma_H)_p / (\gamma_H)_1$ if $(\bar{V}_H - \bar{V}_H^{\circ})$ was known as a function of the ionic strength and of pressure.

Unfortunately, $(\bar{V}_i - \bar{V}_i^{\circ})$ is not known for individual ions, and for this reason $[(\gamma_H)_p / (\gamma_H)_1]_i$ cannot be calculated accurately.

Harned and Owen (1958, p. 507) calculated the effect of pressure on the mean ionic activity coefficients of HCl, NaCl, KCl, and NaOH. Their equations were used to calculate the effect of pressure on these salts at $m = 0.72$, and the results are given in Table III.

Table III. Effect of pressure on γ_{\pm} in single salt solutions at 25° C.

Salt	$(\gamma_{\pm})_{1000} / (\gamma_{\pm})_1$
HCl	1.018
KCl	1.045
NaCl	1.042
NaOH	1.084

^a Calculated from Harned and Owen (1958, p. 507) at $m=0.72$

The data in Table III show that at 1000 atmospheres the increase in γ_{\pm} ranges from about 2% for HCl to about 8% for NaOH. The values of $(\gamma_{\pm})_p / (\gamma_{\pm})_1$ in Table III give some idea of the magnitude of the effect of pressure on γ_H . They suggest that $(\gamma_H)_{1000} / (\gamma_H)_1$ is less than 1.10. However, the pressure dependence of γ_{\pm} depends on the pressure dependence of γ_+ and γ_- , and no rigorous calculation of $(\gamma_H)_p / (\gamma_H)_1$ is possible.

Pressure Dependence of K'_1 and K'_2

The pressure dependence of K'_1 , K'_2 , and K'_B was determined in two steps. First, the effect of pressure on K'_1 and K'_2 was determined in artificial seawater free of boric acid. Then, the pressure dependence of K'_B was determined in artificial seawater containing both boric and carbonic acids, using the previously obtained values of K'_1 and K'_2 .

The effect of pressure on K'_1 and K'_2 was calculated from equation (19) which was first derived by Buch and Gripenberg.

$$(a_H)_p^2 - (A - 1) (K'_1)_p (a_H)_p - (2A - 1) (K'_1)_p (K'_2)_p = 0 \quad (19)$$

A is the ratio of total carbon dioxide, $T(\text{CO}_2)$, to the carbonate alkalinity, CA. $T(\text{CO}_2)$ is defined as,

$$T(\text{CO}_2) = (\text{CO}_2)_T + (\text{H}_2\text{CO}_3)_T + (\text{HCO}_3^-)_T + (\text{CO}_3^{--})_T \quad (20)$$

The carbonate alkalinity is defined by equation (25).

Equation (19) will now be derived. From the definitions of K_1' and K_2' equation (20) may be written as

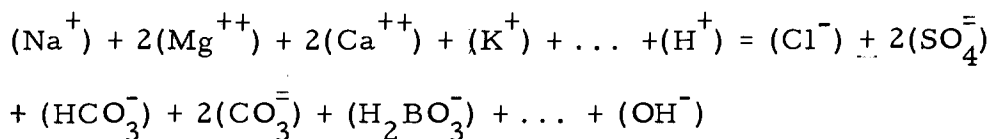
$$T(\text{CO}_2) = (\text{HCO}_3^-) \left[1 + \frac{(a_{\text{H}^+})_p}{(K_1')_p} + \frac{(K_2')_p}{(a_{\text{H}^+})_p} \right] \quad (21)$$

$T(\text{CO}_2)$ is independent of temperature and pressure if molal concentrations are used.

On a molal scale the alkalinity is also independent of pressure.

Electrical neutrality requires that the equivalents of positive ions

in seawater must equal the equivalents of negative ions, that is,



Rearranging this equation and placing the ions which react with

hydrogen ions on the right yields

$$(\text{Na}^+) + \dots + (\text{K}^+) + \dots - (\text{Cl}^-) + \dots = \\ (\text{HCO}_3^-) + 2(\text{CO}_3^{--}) + (\text{H}_2\text{BO}_3^-) + (\text{OH}^-) - (\text{H}^+) \quad (22)$$

The quantity $(\text{HCO}_3^-) + \dots + (\text{OH}^-) - (\text{H}^+)$ is the alkalinity, and since

the left side of equation (22) is independent of temperature and

pressure, the alkalinity must also be independent of temperature

and pressure.

If boric acid is absent, the definition of alkalinity becomes,

$$\text{TA} = (\text{HCO}_3^-) + 2(\text{CO}_3^{--}) + (\text{OH}^-) - (\text{H}^+) \quad (23)$$

In seawater $(\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) \approx 10^{-3}$, and $(\text{OH}^-) - (\text{H}^+) \approx 10^{-6}$.

Therefore, $(\text{OH}^-) - (\text{H}^+)$ can be neglected in comparison to $(\text{HCO}_3^-) + 2(\text{CO}_3^{2-})$, and equation (23) becomes,

$$\text{TA} \approx (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) \quad (24)$$

The quantity $(\text{HCO}_3^-) + 2(\text{CO}_3^{2-})$ is the carbonate alkalinity,

$$\text{CA} \equiv (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) \quad (25)$$

In the absence of boric acid the carbonate alkalinity is independent of temperature and pressure.

Using the definitions of K_1' and K_2' , CA may be written,

$$\text{CA} = (\text{HCO}_3^-) \left[1 + \frac{2(K_2')_p}{(a_{\text{H}^+})_p} \right] \quad (26)$$

Dividing equation (21) by equation (26) yields the ratio $\text{T}(\text{CO}_2)/\text{CA}$,

$$\frac{\text{T}(\text{CO}_2)}{\text{CA}} = \frac{\left[(a_{\text{H}^+})_p^2 + (a_{\text{H}^+})_p (K_1')_p + (K_1')_p (K_2')_p \right]}{\left[(a_{\text{H}^+})_p (K_1')_p + 2(K_1')_p (K_2')_p \right]} \equiv A \quad (27)$$

Rearranging equation (27) yields equation (19),

$$(a_{\text{H}^+})_p^2 - (A-1)(K_1')_p (a_{\text{H}^+})_p - (2A-1)(K_1')_p (K_2')_p = 0 \quad (19)$$

Since both $\text{T}(\text{CO}_2)$ and CA are independent of pressure on a molal concentration scale, their ratio A is also independent of pressure.

Equation (19) was used to calculate the pressure dependence of K_1' and K_2' from the measured values of $(a_{\text{H}^+})_p$. In the calculations A was obtained from equation (27) at atmospheric pressure. For each

seawater sample pH_1 , the pH at 1 atmosphere, was measured; $(K'_1)_1$ and $(K'_2)_1$ were known from Lyman's work; and A could be calculated from (27).

To determine $(K'_1)_p$ and $(K'_2)_p$ the pH at pressure was measured in pairs of seawater samples that had different carbonate alkalinities and, therefore, different values of $(a_{\text{H}})_1$ and A. When substituted into equation (19) the two sets of values of $(a_{\text{H}})_p$ and A provided two simultaneous equations which could be solved for the two unknowns, $(K'_1)_p$ and $(K'_2)_p$. If the two seawater samples are designated by the subscripts 1 and 2, the two simultaneous equations are,

$$(a_{\text{H}_1})_p^2 - (A_1 - 1)(a_{\text{H}_1})_p (K'_1)_p - (2A_1 - 1)(K'_1)_p (K'_2)_p = 0 \quad (28)$$

$$(a_{\text{H}_2})_p^2 - (A_2 - 1)(a_{\text{H}_2})_p (K'_1)_p - (2A_2 - 1)(K'_1)_p (K'_2)_p = 0 \quad (29)$$

Solving these two equations for $(K'_1)_p$ and $(K'_2)_p$ yields,

$$(K'_2)_p = \frac{(A_2 - 1)(a_{\text{H}_2})_p (a_{\text{H}_1})_p^2 - (A_1 - 1)(a_{\text{H}_1})_p (a_{\text{H}_2})_p^2}{(2A_1 - 1)(a_{\text{H}_2})_p^2 - (2A_2 - 1)(a_{\text{H}_1})_p^2} \quad (30)$$

$$(K'_1)_p = \frac{(a_{\text{H}_1})_p^2}{(A_1 - 1)(a_{\text{H}_1})_p + (2A_1 - 1)(K'_2)_p} \quad (31)$$

Pressure Dependence of K'_B

The effect of pressure on K'_B was determined in artificial seawater containing both boric and carbonic acids. The equations

are similar to those used to determine $(K'_1)_p$ and $(K'_2)_p$, except that the contribution of boric acid to the alkalinity is considered.

Equation (27) may be rearranged to give,

$$T(\text{CO}_2) = \text{CA} \left[\frac{(a_{\text{H}^+})^2 + (a_{\text{H}^+}) (K'_1)_p + (K'_1)_p (K'_2)_p}{(a_{\text{H}^+}) (K'_1)_p + 2(K'_1)_p (K'_2)_p} \right] \quad (32)$$

In the presence of boric acid the alkalinity is given by,

$$\text{TA} = \text{CA} + (\text{H}_2\text{BO}_3^-) + (\text{OH}^-) - (\text{H}^+) \quad (33)$$

In seawater,

$$\text{CA} + (\text{H}_2\text{BO}_3^-) \gg (\text{OH}^-) - (\text{H}^+)$$

and equation (33) reduces to,

$$\text{TA} = \text{CA} + (\text{H}_2\text{BO}_3^-) \quad (34)$$

The concentration of total boric acid is,

$$T(\text{B}) = (\text{H}_3\text{BO}_3) + (\text{H}_2\text{BO}_3^-) \quad (35)$$

Using the definition of K'_B shown in equation (3), equation (35)

becomes,

$$T(\text{B}) = (\text{H}_2\text{BO}_3^-) \left[1 + \frac{(a_{\text{H}^+})_p}{(K'_B)_p} \right] \quad (36)$$

or,

$$(\text{H}_2\text{BO}_3^-) = \frac{T(\text{B}) \cdot (K'_B)_p}{(a_{\text{H}^+})_p + (K'_B)_p} \quad (37)$$

Substituting equation (37) into equation (34) and rearranging yields,

$$CA = TA - \left[\frac{T(B) \cdot (K'_{Bp})}{(a_{Hp}) + (K'_{Bp})} \right] \quad (38)$$

Introducing this expression for CA into equation (32) and dividing by T(B) yields,

$$\frac{T(CO_2)}{T(B)} = \left[\frac{TA}{T(B)} - \frac{(K'_{Bp})}{(a_{Hp}) + (K'_{Bp})} \right] \left[\frac{(a_{Hp})^2 + (a_{Hp})(K'_{1p}) + (K'_{1p})(K'_{2p})}{(a_{Hp})(K'_{1p}) + 2(K'_{1p})(K'_{2p})} \right] \quad (39)$$

To calculate (K'_{Bp}) let

$$\frac{TA}{T(B)} - \left[\frac{[T(CO_2)/T(B)]}{\frac{(a_{Hp})^2 + (a_{Hp})(K'_{1p}) + (K'_{1p})(K'_{2p})}{(a_{Hp})(K'_{1p}) + 2(K'_{1p})(K'_{2p})}} \right] = F \quad (40)$$

Since $T(CO_2)$, $T(B)$, and TA are independent of temperature and pressure on a molal concentration scale, their ratios $T(CO_2)/T(B)$ and $TA/T(B)$ are also independent of temperature and pressure. In terms of F equation (39) may be rearranged to

$$(K'_{Bp}) = \left[\frac{(a_{Hp}) \cdot F}{1 - F} \right] \quad (41)$$

(K'_{Bp}) was calculated from equation (41) by the following procedure. Artificial seawater was prepared with known concentrations of $T(B)$ and TA , and the ratio $TA/T(B)$ was calculated. At atmospheric pressure the ratio $T(CO_2)/T(B)$ was calculated from equation (39), using Lyman's values of the apparent constants, the ratio $TA/T(B)$, and a measured value of $(a_{H^+})_1$. The pH of the sample was measured as a function of pressure. Values of F at each pressure

were then calculated from equation (40), using the previously determined values of $(K'_1)_p$ and $(K'_2)_p$, and the ratios $T_A/T(B)$ and $T(\text{CO}_2)/T(B)$ which were calculated at atmospheric pressure. Finally, $(K'_B)_p$ was calculated from equation (41) for each pressure at which F was known.

III. EXPERIMENTAL METHODS

Construction of the High Pressure pH Cell

The high pressure pH cell is shown in Figure 1. The cell was designed so that it could be quickly assembled and disassembled, so that it could be completely assembled outside the pressure bomb, and so that once assembled there could be no carbon dioxide exchange between the solution being tested and the surroundings.

The silver-silver chloride electrodes were made electrolytically. Pure silver wire (1.6 mm in diameter) was used, and the electrodes were chloridized in 0.1 N HCl for 30 minutes with a current density of 0.5 ma/cm^2 . Old electrodes were rejuvenated by the following procedure:

1. The electrode assembly was taken apart, and the old silver-silver chloride electrodes were removed from their receptacles.
2. The silver-silver chloride electrodes were placed in concentrated ammonium hydroxide for 5 minutes, to remove most of the silver chloride coating.
3. The electrodes were then rubbed with steel wool to remove any remaining silver chloride, and replaced in the concentrated ammonium hydroxide for about 2 hours.
4. Next the silver wires were soaked in acetone for 30

The High Pressure pH Cell

The Internal Reference Electrode Assembly

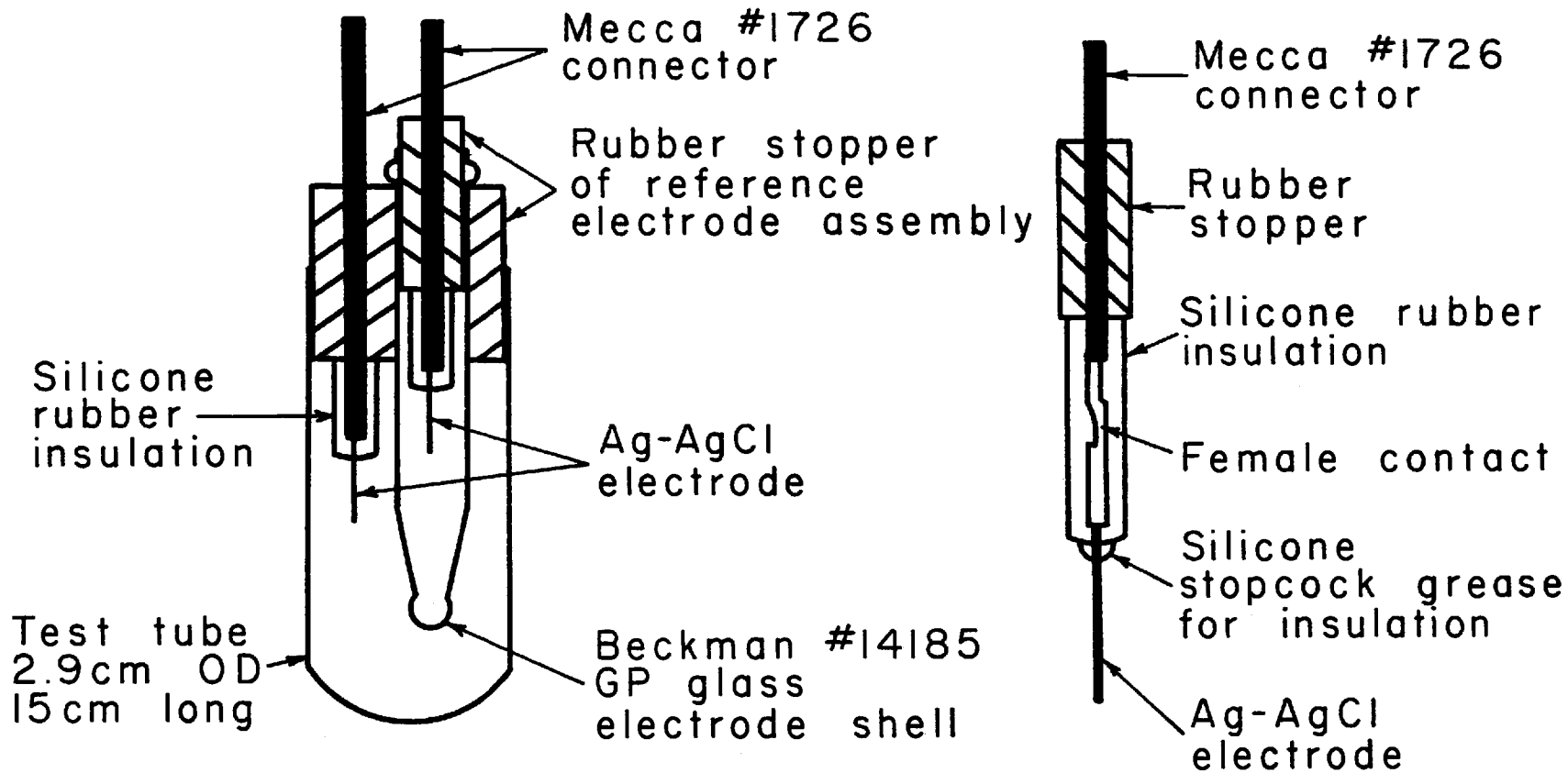


Figure 1. Construction of the high pressure pH cell.

minutes to remove any traces of silicone grease.

5. Finally, the silver wires were soaked in distilled water for 2 hours.

6. The clean silver wires were then inserted into their receptacles in the pressure cell, and the joint between the wire and silicone rubber was insulated with a little silicone stopcock grease.

7. Each silver wire and part of its silicone rubber insulation was then immersed in a beaker of 0.1 N HCl. The two silver wires were chloridized in series, using a 1.5 volt dry cell.

8. Usually, the finished silver-silver chloride electrodes were soaked in distilled water for several hours before use.

Once the silver-silver chloride electrodes had been prepared the pH cell could be assembled. The procedure is given below.

1. The glass electrode shell was rinsed, and then filled with reference solution.

2. The rubber stopper of the internal reference electrode assembly was coated with silicone stopcock grease, the internal reference electrode assembly rinsed with reference solution, and the assembly inserted into the glass electrode. The silicone grease was used to lubricate the rubber stopper so that it could be easily inserted into the glass electrode shell.

3. A short length of wire was inserted into the glass electrode shell before insertion of the reference electrode. This allowed

excess reference solution to escape between the glass and the rubber stopper. Once the reference electrode was inserted the wire was pulled out.

4. The glass electrode was then inserted into the external reference electrode assembly.

5. The rubber stopper of the external reference electrode assembly was coated with silicone stopcock grease, the entire assembly was rinsed with the solution to be tested, and the assembly was inserted into a test tube containing the solution being tested. Excess solution escaped through a small hole in the external rubber stopper. Once the assembly was in place, the hole was stoppered with a short glass rod. The electrode was now ready to be placed in the pressure bomb.

Behavior of the High Pressure pH Cell

The ability to make precise measurements with the high pressure pH cell depends on several factors; the reproducibility of the asymmetry potential, the stability of the pH cell, and the electrical noise and drift of the circuitry.

The asymmetry potential of the pH cell is due to the asymmetry potential of the glass electrode and to differences in potential between the two silver-silver chloride electrodes. The asymmetry potential was measured with reference solution in the two electrode

compartments. It is possible that the ions in seawater affect the response of the glass electrode (Pytkowicz, Kester, and Burgener, 1966). In this case the asymmetry potentials measured with reference solution on both sides of the glass membrane may only approximate the asymmetry potential that exists when there is reference solution on one side and seawater on the other. With freshly prepared silver-silver chloride electrodes, the asymmetry potential at atmospheric pressure was usually less than 0.5 mv, and it became more negative as the pressure increased. The change in asymmetry potential with pressure, $(E_{\text{asym}})_1 - (E_{\text{asym}})_p$, was approximately linear, and usually amounted to about +0.5 mv at 1000 atmospheres. Occasionally the change in asymmetry potential with pressure was as small as +0.1 mv at 1000 atmospheres.

One set of silver-silver chloride electrodes could be pressurized from 10 to 15 times before having to be replaced. After each pressurization the asymmetry potential tended to become more negative, and its change with pressure tended to increase. The silver-silver chloride electrodes were usually replaced when either the asymmetry potential or its change with pressure between 1 and 1000 atmospheres exceeded 1 mv.

After each pressurization the potential of the high pressure pH cell reached a steady state value in about 2 hours. Once a steady state value had been reached the potential was very stable at all

temperatures and pressures. It was assumed that equilibrium had been reached when the rate of change of potential became less than 0.1 mv/hour. This corresponds to a drift of less than 0.002 pH/hour.

Electrical noise becomes a problem when conventional glass electrodes are used at low temperatures. With a regular glass-saturated calomel electrode pair, noise was negligible at room temperature, but increased to about ± 0.1 mv at 2° C. However, because of the excellent shielding furnished by the steel pressure bomb, noise was negligible at all temperatures and pressures when the high pressure pH cell was used in the pressure bomb.

Pressure System

Figure 2 is a diagram of the pressure system. The temperature of the bomb was controlled to $\pm 0.05^{\circ}$ C with water circulated by an Aminco¹ constant temperature water bath (No. 4-8605). The Heise² pressure gauge was calibrated to ± 1.5 atm. at the beginning of the experiments.

¹ American Instrument Co., Inc., 8030 Georgia Avenue, Silver Spring, Maryland.

² Heise Bourdon Tube Company, Inc., Newtown, Connecticut.

① 4 electrical terminals
Mecca #10216
Mecca Division, Teledyne Inc.
P. O. Box 36393
Houston, Texas

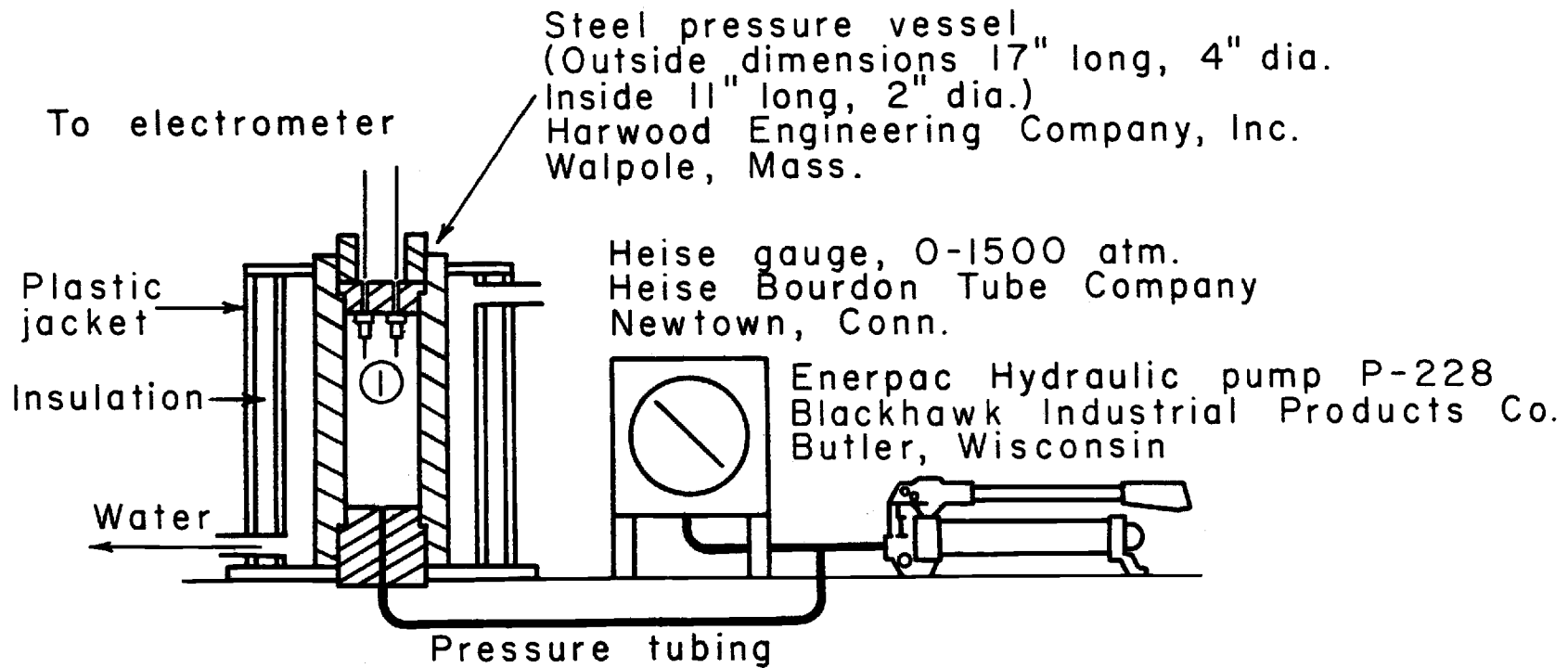


Figure 2. Pressure system. The figure is not drawn to scale.

Electronics

Potentials were measured with the circuit shown in Figure 3. The electrode output was amplified by a Cary³ Model 31V vibrating reed electrometer (VRE), and a Leeds and Northrup⁴ Type K-3 potentiometer was used as a voltage source to supply a bucking potential. The null balance between the bucking potential and the electrode potential was measured on the VRE output meter, and recorded with a Varian⁵ Model G-11A strip chart recorder with a sensitivity of 3 mv full scale. On the 3 mv scale the resolution obtainable with the above equipment was about ± 0.03 mv.

Preparation of Artificial Seawater

Artificial seawater used in the experiments was prepared by the procedure of Kester, Duedall, Connors, and Pytkowicz (1967) with the following alterations. KCl was substituted for KBr, boric acid was omitted in the determination of $(K'_1)_p$ and $(K'_2)_p$, while in the $(K'_B)_p$ experiments the concentration of boric acid was increased to 3 mM. The artificial seawater was prepared from reagent grade

³ Applied Physics Corporation, 2724 South Peck Road, Monrovia, California.

⁴ Leeds and Northrup Company, 4901 Stenton Avenue, Philadelphia, Pennsylvania.

⁵ Varian Associates, Instrument Division, Palo Alto, California.

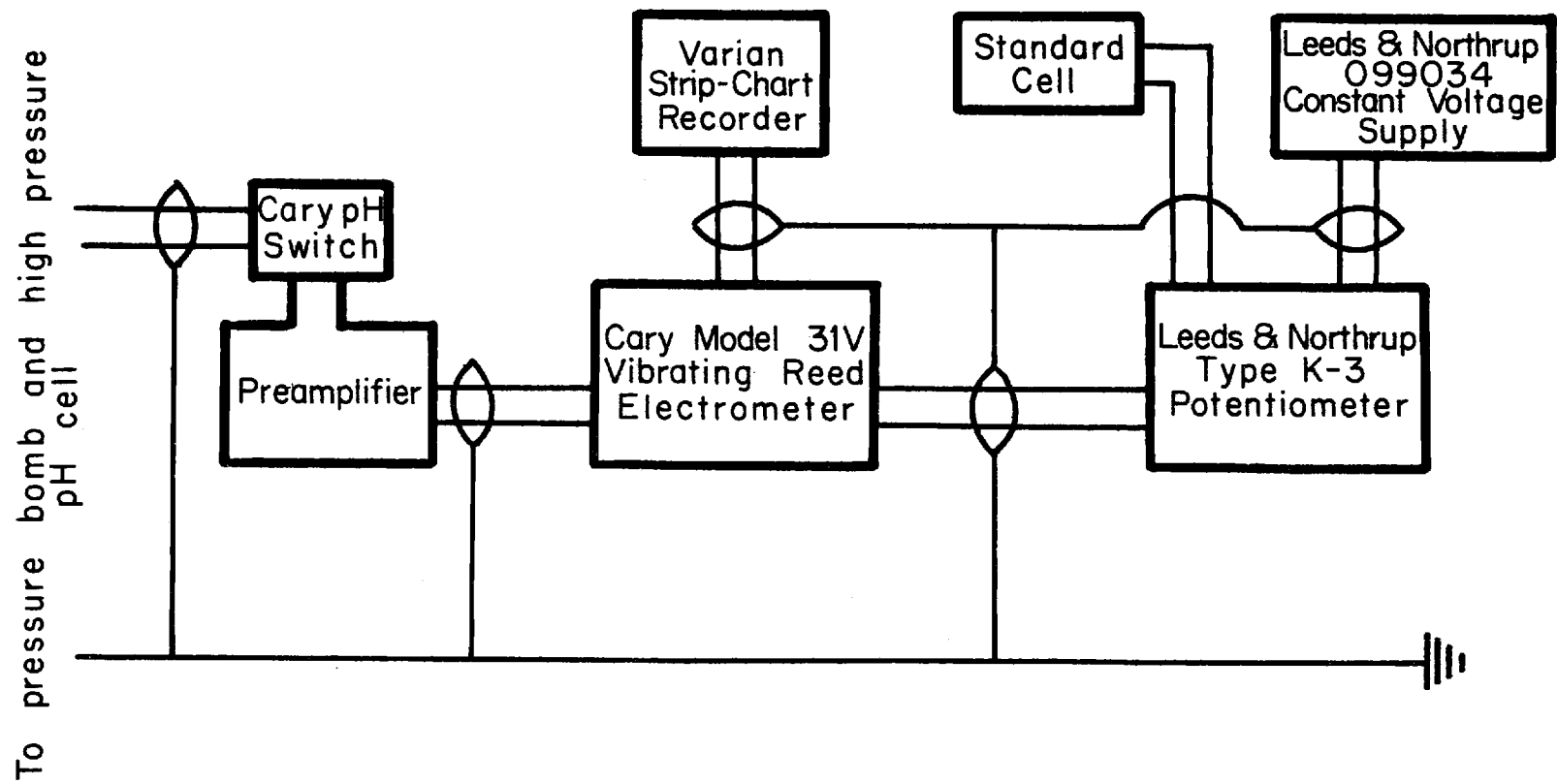


Figure 3. Instrumentation for potentiometric pH measurements.

chemicals, which were not further purified. KCl was substituted for KBr because bromide affects the potential of silver-silver chloride electrodes (Pinching and Bates, 1946).

Two artificial seawaters were prepared to determine the pressure dependence of K_1' and K_2' . One seawater had a pH near 6.7 and the other a pH of about 8.1. NaHCO_3 was omitted in the initial preparation of the seawater. The pH was then adjusted by adding NaHCO_3 and by partially equilibrating the seawater with atmospheric carbon dioxide.

The artificial seawater used to determine (K_B') contained known amounts of boric acid and Na_2CO_3 . The titration alkalinity, TA, of this seawater was equal to the amount of Na_2CO_3 that was added. To prevent precipitation of CaCO_3 , Na_2CO_3 was added in small amounts with vigorous stirring. The seawater was partially equilibrated with atmospheric carbon dioxide after the addition of boric acid and Na_2CO_3 .

Artificial seawater was used to determine the effect of pressure on the apparent constants for two reasons. First, natural seawater contains both carbonic and boric acids. If natural seawater were used, the effect of pressure on K_1' , K_2' , and K_B' would have to be evaluated simultaneously, and it was felt that this would decrease the accuracy of the calculations. Second, natural seawater contains relatively large amounts of silicic acid plus unknown amounts of

organic acids. The pressure dependence of the apparent constants is calculated from measured values of pH_p . If natural seawater were used the effect of pressure on the dissociation of any additional weak acids and bases would have to be considered, because their dissociation might affect the pressure dependence of the pH. The effect of pressure on the pH of natural seawater will be examined later.

Determination of the pH

The potential of the high pressure pH cell was calibrated in terms of pH before each pressure run. Two aliquots of each seawater sample were taken; one for the determination of the pH at atmospheric pressure, and the other for the pressure run.

The pH at atmospheric pressure was determined with a conventional glass-saturated calomel electrode pair (Figure 4) using the equation (Bates, 1964),

$$pH_{SW} = pH_{S1} + (E_{SW} - E_{S1}) \left[\frac{pH_{S2} - pH_{S1}}{E_{S2} - E_{S1}} \right] \quad (42)$$

The subscript SW denotes seawater, while the subscripts S1 and S2 refer to the buffers used to standardize the glass-saturated calomel electrode pair. E is the potential of the glass-calomel pair in the designated solution.

National Bureau of Standards buffers 186-I-b and 186-II-b (pH = 7.413 at 25° C), and 185-d (pH = 4.008 at 25° C) were used to standardize the glass electrodes. The 7.413 buffer was prepared from boiled distilled water to reduce the concentration of dissolved carbon dioxide.

The pH at pressure was calculated from equation (43),

$$\text{pH}_p = \text{pH}_{SW} - (E_1 - E_p - \Delta E_{\text{asym}})/S \quad (43)$$

Here pH_{SW} is the pH at atmospheric pressure obtained from equation (42). The slope, S , of the high pressure glass electrode was determined from potential measurements in the two standard buffers, using a saturated calomel electrode as the reference electrode. The method shown in Figure 4 was used, and S was calculated from equation (44),

$$S = (E_{S2} - E_{S1})/(\text{pH}_{S2} - \text{pH}_{S1}) \quad (44)$$

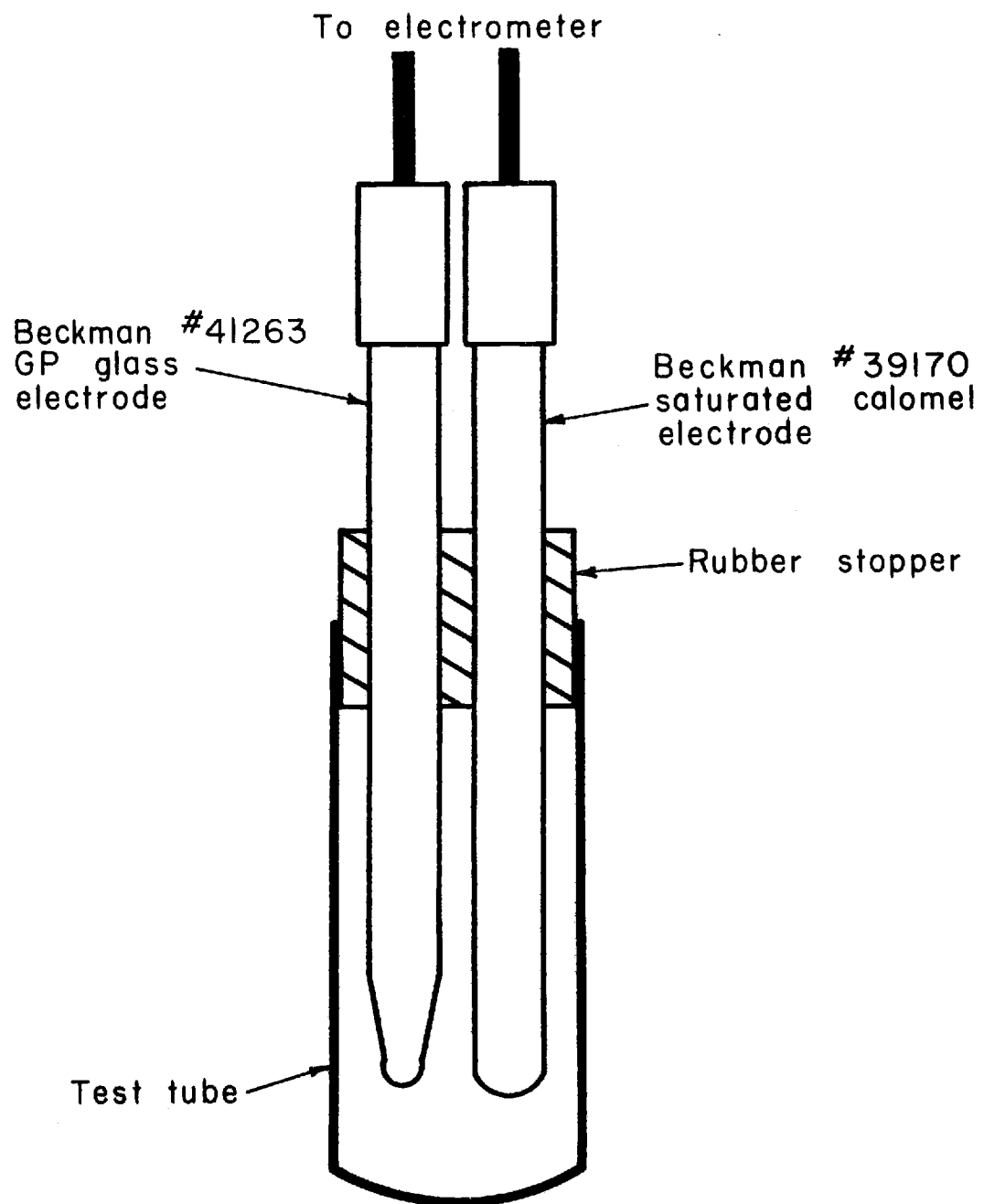


Figure 4. Method of pH measurement at atmospheric pressure.

IV. RESULTS

Values of the Apparent Dissociation Constants

The effect of pressure on K'_1 , K'_2 , and K'_B was determined at 2° C, 11.6° C, and 22° C in seawater of 34.8 ‰ salinity, and at 13.5° C in seawater of 38.5 ‰. Measurements at 2° C were made at 330, 660, and 1000 atmospheres. At the other temperatures measurements were made at 500 and 1000 atmospheres. The temperatures, salinities, and pressures studied were chosen to duplicate the conditions occurring in the open ocean below 1000 meters, where temperatures range from about -2° C to $+10^\circ$ C, and salinities range from about 34.2 ‰ to 35.2 ‰. The experiments at 13.5° C and 38.5 ‰ were made to study the pressure dependence of the apparent constants at temperatures and salinities characteristic of the Mediterranean Sea, and also to study the effect of salinity on the pressure coefficients.

The calculated values of the apparent dissociation constants, based on Lyman's constants at atmospheric pressure, are given in Table IV. Each value is the average of two determinations and is given with the average deviation from the mean. The experimental data used in the calculations are presented in Appendix I, and a sample calculation is shown in Appendix II.

The effect of pressure on the apparent constants can also be

expressed in terms of $\Delta pK'$, which is defined by,

$$\Delta pK' = \log \left[\frac{(K')_p}{(K')_1} \right]$$

$(K')_p/(K')_1$ is the pressure coefficient of the apparent dissociation constant. Values of $\Delta pK'$ for 34.8 ‰ salinity were fitted by the method of least squares to the following equations, where the temperature is in °K and the pressure is in atmospheres.

Table IV. Pressure dependence of the apparent dissociation constants.

Pressure (atm)	$K'_1 \times 10^6$			
	^a 2	Temperature °C 11.6 ^a	^a 22	^b 13.5
1 ^c	0.74	0.86	0.98	0.92
330	1.06±0.01	-----	-----	-----
500	-----	1.43±0.01	1.55±0.01	1.53±0.01
660	1.50±0.01	-----	-----	-----
1000	2.12±0.02	2.30±0.02	2.44±0.02	2.44±0.01
$K'_2 \times 10^9$				
1 ^c	0.43	0.55	0.73	0.63
330	0.544±0.001	-----	-----	-----
500	-----	0.775±0.001	1.01±0.01	0.867±0.001
660	0.688±0.003	-----	-----	-----
1000	0.885±0.007	1.09±0.01	1.37±0.01	1.20±0.01
$K'_B \times 10^9$				
1 ^c	1.17	1.48	1.86	1.66
500	2.20±0.00	2.65±0.01	3.20±0.02	2.90±0.01
1000	3.99±0.01	4.60±0.01	5.39±0.01	4.99±0.04

^a 34.8 ‰ salinity.

^b 38.5 ‰ salinity.

^c Values at 1 atmosphere from Lyman (1956).

$$\Delta pK'_1 = 0.013 + 1.319 \times 10^{-3} P - 3.061 \times 10^{-6} PT - 0.161 \times 10^{-6} T^2 - 0.020 \times 10^{-6} P^2 \quad (45)$$

$$\Delta pK'_2 = -0.015 + 0.839 \times 10^{-3} P - 1.908 \times 10^{-6} PT + 0.182 \times 10^{-6} T^2 \quad (46)$$

$$\Delta pK'_B = 1.809 \times 10^{-3} P - 4.515 \times 10^{-6} PT - 0.169 \times 10^{-6} P^2 + 1.759 \times 10^{-12} P^2 T^2 \quad (47)$$

Equations (45), (46), and (47) reproduce the experimental values of $\Delta pK'$ to within $\pm 0.004 \Delta pK'$ units.

To calculate the effect of pressure on the carbon dioxide system in seawater, the pressure coefficients of the apparent constants must be known as functions of the temperature, salinity, and pressure. The pressure coefficients, $(K')_p / (K')_1$, at several temperatures and pressures were calculated from equations (45), (46), and (47), and the results are given in Table V. The pressure coefficients in Table V are for a salinity of 34.8 ‰. However, in the next section it will be shown that the effect of salinity on the pressure coefficients is small and that the pressure coefficients in Table V can be used for salinities between 34.2 ‰ and 35.2 ‰.

Effects of Temperature and Salinity on the Pressure Dependence of the Apparent Constants

The pressure coefficients in Table V show that the apparent dissociation constants increase with increasing pressure, and that the increase with pressure becomes larger as the temperature

Table V. Pressure coefficients of the apparent dissociation constants for 34.8‰ salinity.

Pressure (atm)	$(K'_1)_p / (K'_1)_1$		
	Temperature °C		
	0	5	10
100	1.12	1.11	1.11
200	1.25	1.24	1.23
300	1.39	1.38	1.36
400	1.55	1.53	1.50
500	1.73	1.69	1.66
600	1.92	1.88	1.84
700	2.13	2.08	2.03
800	2.37	2.30	2.23
900	2.62	2.54	2.46
1000	2.91	2.80	2.70

Pressure (atm)	$(K'_2)_p / (K'_2)_1$		
	Temperature °C		
	0	5	10
100	1.07	1.07	1.07
200	1.15	1.15	1.15
300	1.24	1.23	1.23
400	1.34	1.33	1.32
500	1.44	1.42	1.41
600	1.55	1.53	1.51
700	1.66	1.64	1.62
800	1.79	1.76	1.73
900	1.97	1.89	1.86
1000	2.07	2.03	1.99

Pressure (atm)	$(K'_B)_p / (K'_B)_1$		
	Temperature °C		
	0	5	10
100	1.14	1.13	1.13
200	1.30	1.28	1.27
300	1.47	1.45	1.43
400	1.67	1.64	1.61
500	1.90	1.85	1.81
600	2.14	2.09	2.03
700	2.42	2.35	2.28
800	2.73	2.64	2.55
900	3.07	2.96	2.85
1000	3.45	3.31	3.18

decreases.

The effect of salinity on the pressure dependence of the apparent constants at 13.5° C is shown in Table VI. In the open ocean below 1000 meters the salinity generally lies between 34.2 ‰ and 35.2 ‰. The data in Table VI show that at 1000 atmospheres the effect of salinity on the pressure dependence of the apparent constants is less than 0.004 $\Delta pK'$ units for a 1 ‰ change in salinity. This is a small effect and it shows that the pressure coefficients measured at 34.8 ‰ salinity can be applied to any salinity between 34.2 ‰ and 35.2 ‰ without causing a significant error in the calculations.

Table VI. Salinity effects on the pressure dependence of the apparent constants at 13.5° C.

Pressure (atm)	Salinity (‰)	$\Delta pK'_1$	$\Delta pK'_2$	$\Delta pK'_B$
500	34.8 ^a	0.215	0.146	0.251
500	38.5	0.223	0.139	0.242
1000	34.8 ^a	0.421	0.292	0.490
1000	38.5	0.423	0.281	0.478

^a Calculated from equations (45), (46), and (47).

The Change of pH with Pressure

The pH of seawater samples taken at depth is usually measured aboard ship, at atmospheric pressure. For this reason, the change in pH with pressure must be known in order to correct pH values

measured at the surface to the in situ conditions.

Equation (39) can be used to calculate a_{H^+} , and thus the pH_i , as a function of pressure once $(K_1')_p$, $(K_2')_p$, and $(K_B')_p$ are known. In Table VII calculated values of $(\text{pH}_1 - \text{pH}_p)$ at $34.8^\circ/\text{oo}$ salinity are given for several temperatures and pressures. The calculations were made with $\text{TA} = 2.50 \text{ meq/kg-H}_2\text{O}$ and $\text{T(B)} = 0.436 \text{ mM/kg-H}_2\text{O}$. The quantity $(\text{pH}_1 - \text{pH}_p)$ does not vary significantly with the small changes of salinity, TA, and T(B) that occur below 1000 meters in the open ocean. For example, at 2°C and $\text{pH}_1 = 8.00$, changing TA from 2.60 to 2.40 meq/kg-H₂O causes $(\text{pH}_1 - \text{pH}_{1000})$ to change from 0.399 to 0.403.

Table VII. pH shifts $(\text{pH}_1 - \text{pH}_p)$ as a function of temperature and pressure at $34.8^\circ/\text{oo}$ salinity.

Temperature ($^\circ\text{C}$)	Pressure (atm)	<u>pH at Atmospheric Pressure</u>				
		7.6	7.8	8.0	8.2	8.4
0	250	0.112	0.107	0.103	0.100	0.098
	500	0.222	0.213	0.205	0.200	0.196
	750	0.330	0.318	0.308	0.300	0.294
	1000	0.437	0.422	0.409	0.399	0.391
5	250	0.107	0.102	0.098	0.096	0.094
	500	0.212	0.203	0.197	0.192	0.189
	750	0.316	0.304	0.294	0.288	0.283
	1000	0.417	0.402	0.391	0.383	0.376
10	250	0.102	0.098	0.094	0.092	0.091
	500	0.203	0.195	0.189	0.185	0.182
	750	0.302	0.291	0.283	0.277	0.272
	1000	0.401	0.387	0.376	0.369	0.362

V. DISCUSSION

Comparison of Results with Previous Estimates

The pressure coefficients determined in this thesis are compared in Table VIII with those reported by Buch and Gripenberg, and by Disteché and Disteché.

Table VIII. Comparison of results for $\Delta pK'$ at 1000 atmospheres.

	This Work			B & G (1932) ^{a, c}	D&D (1967) ^b
	2°C	11.6°C	22°C	0°C to 5°C	22°C
$\Delta pK'_1$	0.457	0.427	0.396	0.467	0.383
$\Delta pK'_2$	0.314	0.297	0.275	0.174	0.246
$\Delta pK'_B$	0.533	0.492	0.462	-----	0.459

^a Converted to molal concentrations, and to pressure in atmospheres.

^b Corrected for differences in reference solution and in salinity.

^c Measured at 20°C but assumed by Buch and Gripenberg to be valid at 0-5°C.

Buch and Gripenberg assumed that temperature and salinity effects on the pressure coefficients were negligible and applied coefficients measured in dilute solutions at 20°C to seawater at temperatures between 0°C and 5°C. They did not consider the effect of boric acid on the pressure dependence of the pH, and they assumed that the pressure coefficient of K'_2 was equal to that of acetic acid

and that $\Delta pK'_1 = \Delta pK_1$.

The data in Table VIII shows that Buch and Gripenberg's estimate of $\Delta pK'_1$ agrees well with my measured value at 2° C. However, the agreement is fortuitous since $\Delta pK'_1$ is temperature dependent. At 20° C equation (45) gives $\Delta pK'_1 = 0.402$, while Brander found $\Delta pK_1 = 0.467$ at this temperature. Table VII also shows that the pressure dependence of pK'_2 is much greater than Buch and Gripenberg estimated, and that their assumption that $\Delta pK'_2$ equals the ΔpK for acetic acid was not correct.

In Table IX Buch and Gripenberg's predicted pH shifts are compared with mine. Our values differ for several reasons: they underestimated the pressure dependence of K'_2 , they did not consider the effect of boric acid on the pH shifts, and they did not consider the effect of temperature on the pressure coefficients. For these reasons the actual pH shifts are less dependent on the pH at atmospheric pressure than was thought by Buch and Gripenberg.

Table IX. Comparison of pH shifts at 1000 atmospheres.

	Temperature (°C)	pH at atmospheric pressure		
		7.8	8.0	8.2
This Work	2	0.413	0.399	0.390
	22	0.349	0.341	0.335
B & G (1932)	0-5 ^a	0.24	0.20	0.18

^a Converted from molar to molal concentrations.

Disteche and Disteche measured $\Delta pK'_1$, $\Delta pK'_2$, $\Delta pK'_B$ in seawater of 36.1 ‰ salinity at 22° C. Their results are not directly comparable to mine because we used different reference solutions in our measurements. Because of this difference our measured values of $(E_1 - E_p - \Delta E_{\text{asym}})$ and of $\Delta pK'$ differ by a constant amount at each pressure.

My reference solution contained 0.71m NaCl + 0.01m HCl. Disteche and Disteche's reference solution contained 0.49c NaCl + 0.026c MgCl₂ + 0.030c MgSO₄ + 0.010c CaCl₂ + 0.010c HCl. Because sulfate ion is a weak base, a considerable amount of HSO₄⁻ will form in the reference solution used by Disteche and Disteche. The dissociation of HSO₄⁻ under pressure (Horne, Courant, and Fysinger, 1964) will cause the hydrogen ion concentration of their reference to change with pressure. This effect will now be examined.

Equation (6) shows that the measured values of $(E_1 - E_p - \Delta E_{\text{asym}})$ depend on the term,

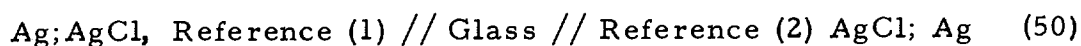
$$S \cdot \log \left[\frac{a_{H_1} \cdot a_{Cl_1}}{a_{H_p} \cdot a_{Cl_p}} \right]_i \quad (48)$$

The molal concentration of chloride ion in the reference solution is independent of pressure and (48) becomes,

$$S \cdot \log \left[\frac{a_{H_1} \cdot \gamma_{Cl_1}}{a_{H_p} \cdot \gamma_{Cl_p}} \right]_i \quad (49)$$

Disteche and Disteche's values of $(E_1 - E_p - \Delta E_{\text{asym}})$ differ from mine because term (49) has different values in our two reference solutions. The molal concentration of H^+ is constant with pressure in my reference solution and the value of (49) depends on the pressure dependence of γ_H and γ_{Cl} . In Disteche and Disteche's reference the molal concentration of H^+ increases with pressure due to the dissociation of HSO_4^- , and the value of (49) depends on the pressure dependence of (H^+) , γ_H and γ_{Cl} .

The difference in our measured values of $(E_1 - E_p - \Delta E_{\text{asym}})$ can be found by subtracting the value of (49) in Disteche and Disteche's reference solution from the value of (49) in my reference. Making this subtraction is equivalent to measuring the effect of pressure on the potential of the following cell,



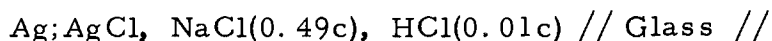
Reference (1) is the reference solution used in this work and reference (2) is that used by Disteche and Disteche. In view of equation (6) the potential of cell (50) can be written,

$$(E_1 - E_p - \Delta E_{\text{asym}}) = S \cdot \log \left[\frac{\gamma_{H_1} \cdot \gamma_{Cl_1}}{\gamma_{H_p} \cdot \gamma_{Cl_p}} \right]_{\text{ref (1)}} - S \cdot \log \left[\frac{a_{H_1} \cdot \gamma_{Cl_1}}{a_{H_p} \cdot \gamma_{Cl_p}} \right]_{\text{ref (2)}} \quad (51)$$

The right side of equation (51) is the difference in the values of term (49) in the two reference solutions.

The effect of pressure on cell (50) has not been measured, but

Disteche and Disteche did measure $(E_1 - E_p - \Delta E_{\text{asym}})$ for cell (52),



Disteche and Disteche's reference solution, AgCl;Ag (52)

For cell (52) Disteche and Disteche found that $(E_1 - E_{1000} - \Delta E_{\text{asym}})$ was 3.4 mv. $(E_1 - E_p - \Delta E_{\text{asym}})$ for cell (52) should be approximately equal to $(E_1 - E_p - \Delta E_{\text{asym}})$ for cell (50), since as a first approximation the effect of pressure on $\gamma_{\text{-HCl}}^+$ in (0.49c NaCl + 0.01c HCl) and in (0.71m NaCl + 0.01m HCl) should be the same. Therefore, 3.4 mv is approximately the difference between our measured values of $(E_1 - E_{1000} - \Delta E_{\text{asym}})$ in seawater. 3.4 mv corresponds to 0.058 $\Delta pK'$ units, and this quantity must be added to Disteche and Disteche's values of $\Delta pK'$ to compare them with mine.

Our results are still not strictly comparable even when corrected for the different reference solutions, because our measurements were made at different salinities. Disteche and Disteche's measurements were made at 36.1^o/oo salinity, and mine at 34.8^o/oo salinity. Disteche and Disteche investigated the effects of ionic strength on the pressure coefficients at 22^o C. Their results show that decreasing the salinity from 36.1^o/oo to 34.8^o/oo will increase $\Delta pK'_1$, $\Delta pK'_2$, and $\Delta pK'_B$ by 0.001, 0.004, and 0.001 $\Delta pK'$ units respectively.

The results of Disteche and Disteche, corrected for the differences in reference solution and salinity, are compared with mine

in Table VIII. There is good agreement for $\Delta pK'_1$ and $\Delta pK'_B$. Their value of $\Delta pK'_2$ is about 10% smaller than mine. This corresponds to a difference of about 6% in the pressure coefficient of K'_2 . The reason for this difference is not known. Disteche and Disteche give two values of $\Delta pK'_2$; 0.246 valid in natural seawater, and 0.251 valid in artificial seawater. If their value of $\Delta pK'_2$ in artificial seawater is compared with mine our difference is 0.024 $\Delta pK'$ units.

In Figure 5 the values of $\Delta pK'$ determined in this thesis at 22° C are compared with those reported earlier by Culberson, Kester, and Pytkowicz. The agreement for $\Delta pK'_1$ and $\Delta pK'_2$ is satisfactory, but at 654 atmospheres the difference between the values of $\Delta pK'_B$ is about 0.01 $\Delta pK'$ units. This is a difference of about 4% in the pressure coefficient of K'_B . Since my present value for $\Delta pK'_B$ agrees well with that reported by Disteche and Disteche, the value of $\Delta pK'_B$ reported by Culberson, Kester, and Pytkowicz is probably too small.

Results in Natural Seawater

The change in pH with pressure was measured for two natural seawater samples to check the values of $(pH_1 - pH_p)$ which had been calculated with the pressure coefficients measured in artificial seawater. The seawater samples were collected off the Oregon coast at depths below 2000 meters. Their pH was adjusted in the laboratory

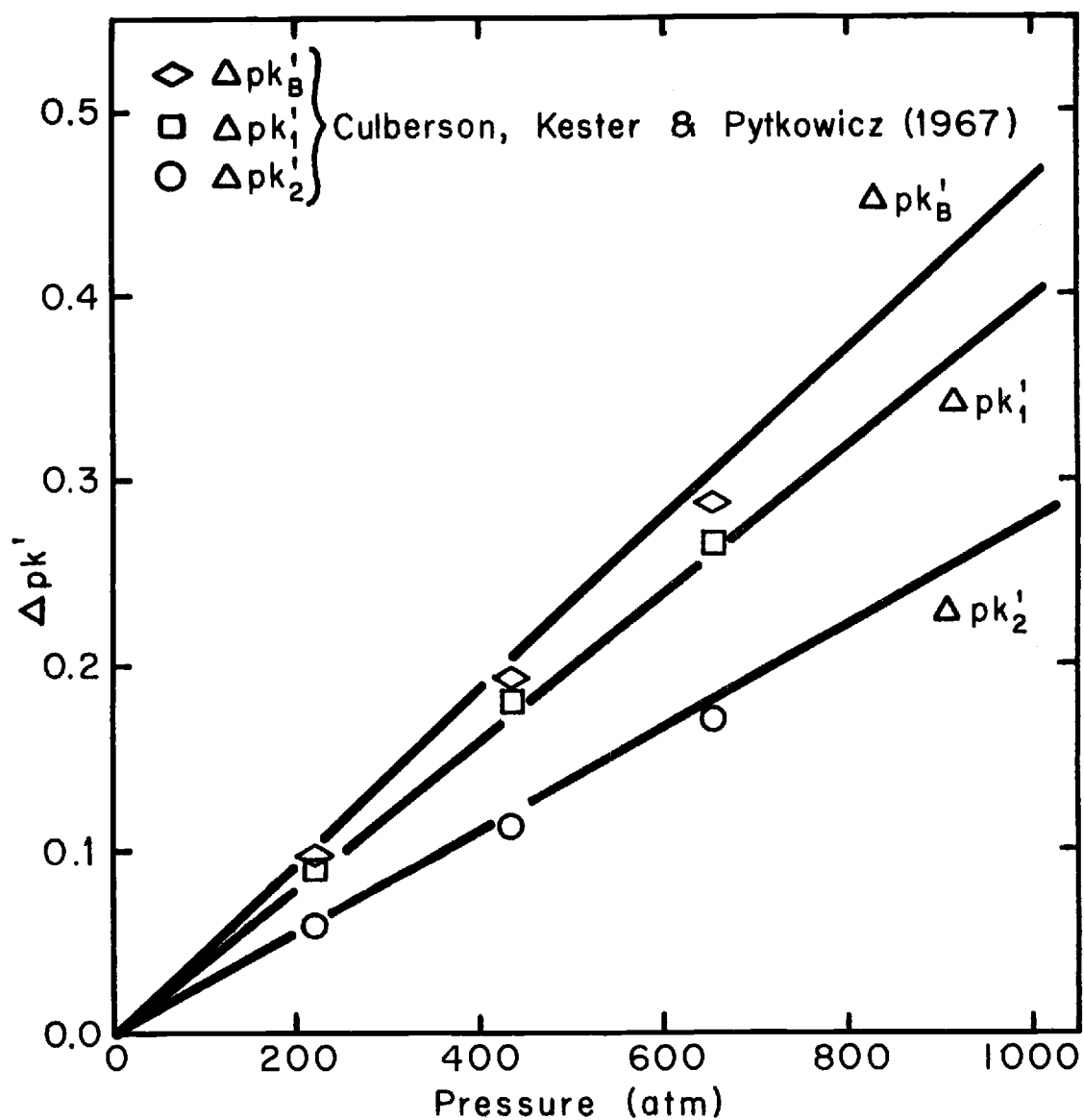


Figure 5. Comparison of pK' values from this work with those reported by Culberson, Kester, and Pytkowicz (1967). The solid lines are based on this work.

with a few drops of 1 N HCl, or by adding small amounts of Na_2CO_3 .

The results of the measurements with natural seawater are given in Table X. The pH shifts in natural seawater, at 1000 atmospheres and 2°C , are about 0.017 pH units greater than the pH shifts calculated from equation (39) with the pressure coefficients measured in artificial seawater. This is a difference of about 4% in the hydrogen ion activity. At 22°C the measured and calculated pH shifts agree well, but since only one measurement was made the agreement may be fortuitous.

Table X. pH shifts in natural seawater.

Temperature ($^\circ\text{C}$)	pH_1	Pressure (atm)	$\text{pH}_1 - \text{pH}_p$		
			Observed	Calculated	Difference
2	7.791 ^a	500	0.216	0.209	+0.007
		1000	0.428	0.415	+0.013
2	8.285 ^a	500	0.210	0.194	+0.016
		1000	0.412	0.387	+0.025
2	8.404 ^b	1000	0.397	0.383	+0.014
22	8.333 ^b	1000	0.330	0.331	-0.001

^a Natural seawater with $S^\circ/\text{oo} = 34.7$, $(\text{SiO}_2) = 0.196$ mM.

^b Natural seawater with $S^\circ/\text{oo} = 34.6$, $(\text{SiO}_2) = 0.188$ mM.

Since the natural seawater samples contained about 0.2 mM of dissolved silicate, I thought that the larger pH shifts in natural seawater might be due to the presence of silicic acid. Two artificial

seawaters were prepared to check the effect of silicate. Each contained the correct amount of boric acid. However, one was made silicate free, while 0.204 mM of solid silicic acid were added to the other. The effect of pressure on the pH of these two artificial seawaters is shown in Table XI.

Table XI. Effect of silicic acid on pH shifts.

Temperature (° C)	pH ₁	Pressure (atm)	pH ₁ - pH _p		
			Observed	Calculated	Difference
2	8.303 ^a	500	0.191	0.184	+0.007
		1000	0.378	0.368	+0.010
	8.365 ^b	500	0.202	0.194	+0.008
		1000	0.399	0.387	+0.012

^a Artificial seawater with S^o/oo = 34.8, TA = 4.08, (SiO₂) = 0.204mM

^b Artificial seawater with S^o/oo = 34.8, TA = 2.43, (SiO₂) = 0.0.

The pH shifts measured in artificial seawater are larger than the calculated pH shifts. However, the difference between the measured and calculated values is the same for the two seawater samples, and no effect of silicate on the pH can be seen. Therefore, the larger pH shifts in natural seawater are not explained by the presence of silicic acid. In Table XI the pH shifts measured in artificial seawater are consistently larger than the calculated values. The difference is about 0.011 pH units at 1000 atmospheres, and is probably due to errors in the calculated pH shifts. Such errors

explain part of the difference between the pH shifts measured in natural seawater and the calculated pH shifts. The difference between the observed and calculated pH shifts will be considered in more detail in the Discussion of Errors.

Another possible cause for the difference in pH shifts is the effect of the bromide present in natural seawater on the potential of the external silver-silver chloride electrode. Pinching and Bates report that small amounts of bromide cause changes as large as 3 mv in the potential of silver-silver chloride electrodes. For this reason KCl was substituted for KBr in the artificial seawaters used in this thesis. The only bromide in the artificial seawaters or in the reference solutions was that due to impurities in the reagents.

Figure 6 shows that the potential of the high pressure pH cell at 2° C decreased by about 8.6 mv when artificial seawater was replaced by natural seawater of the same pH₁. At 22° C the decrease, based on only one measurement, was about 5.0 mv.

The following experiment was performed to determine if the decrease in potential was due to bromide. Enough KBr (0.88 mM/kg-H₂O) was added to a sample of reference solution (0.71m NaCl + 0.01m HCl) to make the bromide concentration in the reference solution approximately equal to that in seawater of 34.8‰ salinity. The high pressure pH cell was inserted into a portion of the bromide enriched reference solution, and the potential was measured as a

function of pressure. Table XII presents the results of this experiment. The first and fourth experiments were made with bromide free reference solution in both compartments, and the second and third experiments with bromide enriched reference solution in the external compartment. At 1 atmosphere, bromide in the external reference solution depressed the potential about 8.0 mv. This accounts for most of the difference in potential between natural and artificial seawater that was shown in Figure 6. Also, the presence of bromide in the reference solution increased the asymmetry potential by about 0.7 mv at 1000 atmospheres. An increase of 0.7 mv in the asymmetry potential corresponds to an apparent increase of 0.013 in the pH, and would account for part of the difference between the pH shifts measured in natural seawater and the calculated values, which was about 0.017 pH units.

Figure 6 and the experiments with the bromide enriched reference solution show that bromide ion affects the potential and the asymmetry potential of the high pressure pH cell. This is due to the effect of bromide on the potential of the external silver-silver chloride electrode. It is not due to an effect of bromide on the pressure dependence of the pH and pH shifts determined from measurements in artificial seawater free of bromide can be applied to natural seawater.

Table XII. Effect of bromide on the potential of the high pressure pH cell at 2° C.

Experiment number	Pressure (atm)	E_p (mv)	$E_1 - E_p$ (mv)
1 ^c	1	-0.03 ^a	0.00
	500	-0.32	+0.29
	991	-0.43	+0.40
2	1	-7.75 ^b	0.00
	503	-8.58	+0.63
	1000	-9.01	+1.06
3	1	-8.10 ^b	0.00
	500	-8.65	+0.55
	1000	-9.14	+1.04
4	1	-1.85 ^a	0.00
	500	-2.03	+0.18
	1000	-2.15	+0.30

^a Bromide free reference solution.

^b Bromide enriched reference solution in the external compartment, $(Br^-) = 0.88 \text{ mM/kg-H}_2\text{O}$.

^c All experiments were performed with the same set of silver-silver chloride electrodes, and in the order given.

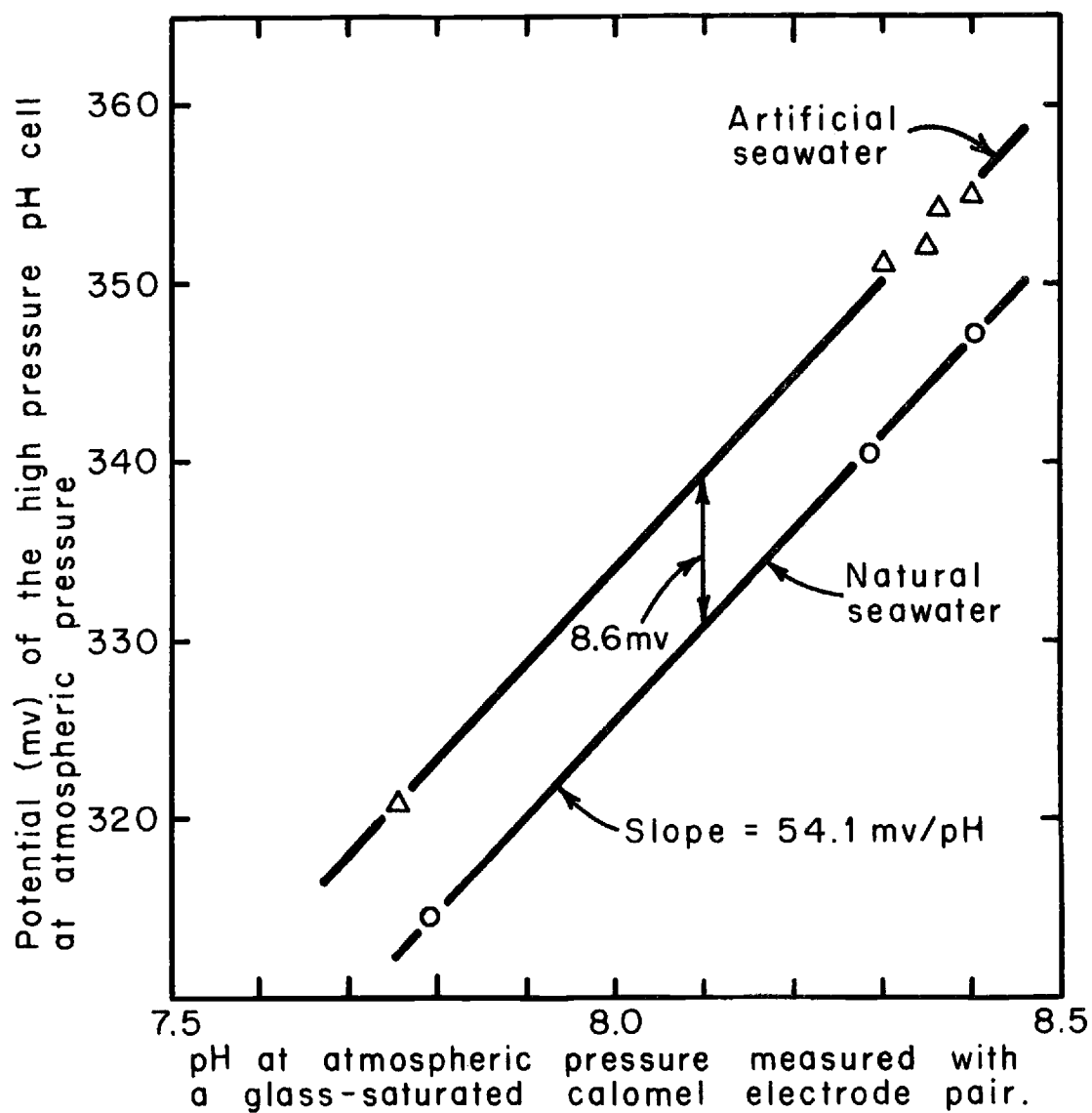


Figure 6. Effect of bromide on the potential of the high pressure pH cell at 2°C. The outside solution is either artificial or natural seawater. The inside solution is always the reference solution.

The Relationship of Apparent and Thermodynamic
Dissociation Constants

In the Introduction it was mentioned that the effect of pressure on apparent and on thermodynamic constants differs because of ion-pair formation and because of the effects of temperature and salinity on partial molal volumes. The relationship between apparent and thermodynamic constants will now be considered.

Garrels and Thompson (1962) studied ion-pair formation in seawater. They found that approximately 30% of the bicarbonate and 90% of the carbonate are complexed with cations and that, as a first approximation, only complexes with Na^+ , Mg^{++} , and Ca^{++} are important. If complexes with cations other than Na^+ , Mg^{++} , and Ca^{++} are shown to be important the following arguments can easily be expanded to include them. Ion-pair formation of borate in seawater has not been studied.

The following derivations are similar to those made by Weyl (1961) and by Kester and Pytkowicz (1967). Consider the apparent constant K_{HA}^1 for the reaction $\text{HA} = \text{H} + \text{A}$,

$$K_{\text{HA}}^1 = a_{\text{H}}(A)_{\text{T}}/(\text{HA})_{\text{T}} \quad (53)$$

where,

$$(A)_{\text{T}} = (A)_{\text{U}} + (A)_{\text{C}} \quad (54)$$

and

$$(\text{HA})_{\text{T}} = (\text{HA})_{\text{U}} + (\text{HA})_{\text{C}} \quad (55)$$

The subscript T represents the total concentration, and the subscripts C and U denote the complexed and uncomplexed forms of each species. Suppose that HA and A form complexes with Na^+ , Mg^{++} , and Ca^{++} , and that these complexes have thermodynamic dissociation constants given by,

$$K_{\text{MHA}} = \frac{a_{\text{M}} \cdot a_{\text{HA}}}{a_{\text{MHA}}} = \frac{\left[\frac{\text{M}_{\text{U}} \cdot \text{HA}_{\text{U}}}{\text{MHA}} \right] \left[\frac{\gamma_{\text{M}} \cdot \gamma_{\text{HA}}}{\gamma_{\text{MHA}}} \right]}{\quad} \quad (56)$$

$$K_{\text{MA}} = \frac{a_{\text{M}} \cdot a_{\text{A}}}{a_{\text{MA}}} = \frac{\left[\frac{\text{M}_{\text{U}} \cdot \text{A}_{\text{U}}}{\text{MA}} \right] \left[\frac{\gamma_{\text{M}} \cdot \gamma_{\text{A}}}{\gamma_{\text{MA}}} \right]}{\quad} \quad (57)$$

where M represents Na^+ , Mg^{++} , or Ca^{++} . If equations (56) and (57) are written for each of the three cations, and if these equations are substituted into equations (54) and (55) the result is,

$$(\text{A})_{\text{T}} = (\text{A})_{\text{U}} \left[1 + \frac{\text{Na}_{\text{U}}}{K_{\text{NaA}}} \frac{\gamma_{\text{Na}} \cdot \gamma_{\text{A}}}{\gamma_{\text{NaA}}} + \dots \right] \quad (58)$$

$$(\text{HA})_{\text{T}} = (\text{HA})_{\text{U}} \left[1 + \frac{\text{Na}_{\text{U}}}{K_{\text{NaHA}}} \frac{\gamma_{\text{Na}} \cdot \gamma_{\text{HA}}}{\gamma_{\text{NaHA}}} + \dots \right] \quad (59)$$

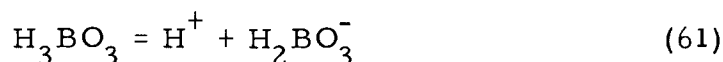
Equations (58) and (59) can now be substituted into equation (53). In terms of the thermodynamic constant K_{HA} , and equations (58) and (59), equation (53) may be written,

$$K'_{\text{HA}} = \frac{\gamma_{\text{HA}}}{\gamma_{\text{A}}} K_{\text{HA}} \frac{\left[1 + \frac{\text{Na}_{\text{U}}}{K_{\text{NaA}}} \frac{\gamma_{\text{Na}} \cdot \gamma_{\text{A}}}{\gamma_{\text{NaA}}} + \dots \right]}{\left[1 + \frac{\text{Na}_{\text{U}}}{K_{\text{NaHA}}} \frac{\gamma_{\text{Na}} \cdot \gamma_{\text{HA}}}{\gamma_{\text{NaHA}}} + \dots \right]} \quad (60)$$

Equation (60) shows that K'_{HA} is a complicated function of K_{HA} , of complex formation, and of activity coefficients. Each of these factors will influence the pressure dependence of K'_{HA} and no simple relation exists between the effect of pressure on K'_{HA} and the pressure dependence of K_{HA} . Equation (60) does show however, that the difference between the pressure dependence of apparent and thermodynamic constants is due to the effect of pressure on the extent of ion-pair formation and on activity coefficients. Although the effect of pressure on the extent of ion-pair formation of the various species cannot be rigorously determined at present, Disteché and Disteché (1967) and Pytkowicz, Disteché, and Disteché (1967) have shown that the dissociation of carbonate ion-pairs increases with increasing pressure.

The Ionization of Boric Acid

Lyman (1956) and Buch (1933) represent the ionization of boric acid as,

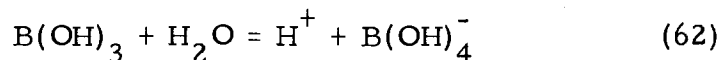


They define K'_B in terms of this reaction.

$$K'_B = \frac{a_H(H_2BO_3^-)_T}{(H_3BO_3)_T} \quad (3)$$

However, Edwards et al. (1955) show that the borate anion in

aqueous solution is B(OH)_4^- , and this suggests that the reaction which actually occurs is (Ingri *et al.*, 1957),



The apparent dissociation constant for this reaction can be defined as,

$$K_B^* = \frac{a_{\text{H}^+} a_{\text{B(OH)}_4^-}}{a_{\text{B(OH)}_3}} \quad (63)$$

It should be noted that K_B' and K_B^* have the same value, and that they differ only in the way in which boric acid and the borate anion are represented. The purpose of this section is to show that the pressure dependence of K_B also suggests that (62) is the correct reaction.

The effect of pressure on thermodynamic dissociation constants is given by

$$\left[\frac{\partial \ln K}{\partial P} \right]_T = - \frac{\Delta \bar{V}^{\circ}}{RT} \quad (64)$$

where $\Delta \bar{V}^{\circ}$ is the difference in partial molal volumes of the products and reactants at infinite dilution. Values of $\Delta \bar{V}^{\circ}$ for several weak acids and bases are compared in Table XIII.

Table XIII. Partial molal volume changes upon ionization.

Reaction	$\Delta\bar{V}^{\circ}$ (cm ³ /mole)	Source
$\text{H}_3\text{PO}_4 = \text{H}^+ + \text{H}_2\text{PO}_4^-$	-15.5	Ellis and Anderson (1961a)
$\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$	-15.0	Ellis and Anderson (1961b)
$\text{NH}_3 + \text{H}_2\text{O} = \text{NH}_4^+ + \text{OH}^-$	-28.9	Hamann (1957)
$\text{CO}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$	-26.5	Ellis (1959)
$\text{B}(\text{OH})_3 = ?$	-32.1	Disteche and Disteche (1967)

It is easily seen that $\Delta\bar{V}^{\circ}$ values for weak electrolytes which undergo hydration are much more negative than those of weak electrolytes which do not undergo hydration. From data similar to that in Table XIII, Ellis and Anderson (1961b) show that values of $\Delta\bar{V}^{\circ}$ for simple weak acids which do not undergo hydration lie in the range -7 to -16 cm³/mole. They conclude that for simple weak acids "large negative $\Delta\bar{V}^{\circ}$ values arise only where hydration equilibria are involved in the ionization process."

$\Delta\bar{V}^{\circ}$ for boric acid is -32.1 cm³/mole (Disteche and Disteche, 1967), and Ellis and Anderson's argument suggests that hydration is involved in the ionization process. Since equation (61) does not involve hydration, their argument suggests that (62) is the correct reaction.

Discussion of Errors

The errors involved in the determination of the pressure dependence of the apparent constants can be divided into two classes; experimental errors associated with the measurement of the pH, and systematic errors due to the approximations that were made in the derivation of equations (30), (31), and (41).

Errors in the measurement of pH can occur at atmospheric pressure and at high pressures. Errors in pH measurements at atmospheric pressure, with the glass-saturated calomel electrode pair, are not as serious as those occurring at high pressures with the high pressure pH cell. This is shown by the following argument.

The two artificial seawaters used to determine $(K'_1)_p$ and $(K'_2)_p$ had pH's of about 6.7 and 8.1. Distech and Distech show that at pH's less than 7,

$$\Delta pK'_1 \cong (pH_1 - pH_p) \quad (65)$$

and that at pH's greater than 8 in the absence of boric acid,

$$\Delta pK'_2 \cong (pH_1 - pH_p) \quad (66)$$

A similar approximation, valid in the artificial seawater used to determine $(K'_B)_p$, can be written for $\Delta pK'_B$,

$$\Delta pK'_B \cong (pH_1 - pH_p) \quad (67)$$

At pH's less than 7 and greater than 8, $(\text{pH}_1 - \text{pH}_p)$ is nearly independent of the value of pH_1 . For this reason the calculated values of the pressure coefficients are insensitive to errors in the value of pH_1 determined with the glass-calomel electrode pair. However, equations (65), (66), and (67) show that the pressure coefficients are very sensitive to errors in the value of $(\text{pH}_1 - \text{pH}_p)$ calculated from equation (15).

The experimental data in Appendix I show that duplicate measurements on aliquots of the same sample gave values of $(\text{pH}_1 - \text{pH}_{1000})$ and agreed to within ± 0.004 pH units. This reproducibility is reflected in the values of the apparent constants given in Table IV. The average deviation from the mean of the apparent constants in Table IV is always less than $\pm 1\%$, or less than ± 0.004 in $\Delta\text{pK}'$ at 1000 atmospheres.

It is important to distinguish between the precision and the accuracy of the calculated values of the apparent constants. The accuracy of $\Delta\text{pK}'$ and $(\text{pH}_1 - \text{pH}_p)$ relative to values based on the thermodynamic pH scale cannot be estimated because of the approximations which were made in the derivation of equation (15). However, it was shown earlier that precision and not accuracy is the important consideration, since systematic differences between the calculated values of $(\text{pH}_1 - \text{pH}_p)$ and the thermodynamic values will cancel between the determination and application of $(\text{pH}_1 - \text{pH}_p)$.

The calculated values of $(K')_p$ depend on the values of the apparent constants at atmospheric pressure, and any error in $(K')_1$ will be included in $(K')_p$. At present there are two sets of apparent constants in general use. One set is based on the work of Buch et al. (1932) and Buch (1951), and the other on the work of Lyman. Buch's and Lyman's values of $(K'_1)_1$ and $(K'_B)_1$ show good agreement, but their values of $(K'_2)_1$ differ by as much as 30% (Lyman, 1956). Equations (65), (66), and (67) show that the calculated values of the pressure coefficients depend mainly on $(\text{pH}_1 - \text{pH}_p)$, and that they are not very sensitive to the values of $(K'_1)_1$, $(K'_2)_1$ and $(K'_B)_1$ used in equations (27) and (39). For this reason, the pressure coefficients determined in this thesis can be used with either Lyman's or Buch's values of the apparent constants at atmospheric pressure.

In Tables X and XI the pH shifts calculated from equation (39) are compared with pH shifts observed in natural and in artificial seawater. The values of $(\text{pH}_1 - \text{pH}_{1000})$ measured in natural seawater at 2°C averaged about 0.017 pH units higher than the calculated values, and it was shown that part of this difference was due to the effect of bromide on the potential of the external silver-silver chloride electrode. The pH of seawater samples that are brought to the surface is usually measured with a glass-saturated calomel electrode pair, and the liquid junction of the calomel reference electrode protects it from bromide. Therefore, the effect of

bromide is not needed when the in situ pH is calculated and the true agreement between the measured and calculated values of $(\text{pH}_1 - \text{pH}_{1000})$ is better than 0.017 pH units. This means that in natural seawater the calculated values of $(a_{\text{H}})_{1000}$ should be valid to within 4%.

In Table XI the pH shifts measured in artificial seawater are larger than those calculated from equation (39) using pressure coefficients determined in artificial seawater. The difference between the measured and calculated values of $(a_{\text{H}})_{1000}$ is about 2.5%. This difference is probably due to errors in the calculated pH shifts. These errors could be due to errors in the pressure coefficients, or to errors in the values of Lyman's constants at atmospheric pressure. The pressure coefficients were reproducible to $\pm 1\%$. At 1000 atmospheres a 1% error in each of the pressure coefficients would cause errors of 0.005 pH units in the calculated pH shifts. Errors of 5% in each of Lyman's constants would also cause errors of 0.005 pH units in the calculated pH shifts at 1000 atmospheres.

Systematic errors in the pressure coefficients will now be considered. In the derivation of equations (30), (31), and (41) it was assumed that,

$$\text{CA} \gg (\text{OH}^-) - (\text{H}^+) \quad (68)$$

The alkalinities of the artificial seawaters used to determine $(K'_1)_p$,

$(K'_2)_p$, and $(K'_B)_p$ are given in Appendix I. Except for the 34.8^o/oo seawater, with pH 6.7, the carbonate alkalinities of the artificial seawaters are sufficiently high for (68) to be a good approximation. The carbonate alkalinity of the pH 6.7 seawater is low enough to introduce small errors into the calculated values of $(K'_1)_p$ at 34.8^o/oo salinity. This can be shown in the following way.

$(K'_1)_p$ was calculated from equation (31) and in the calculation it was assumed that A was independent of pressure. This assumption is only true if CA is independent of pressure and, at the alkalinity of the pH 6.7 artificial seawater, changes in (H^+) with pressure begin to affect the value of CA. An estimate of the error in $(K'_1)_p$ caused by assuming that CA was independent of pressure can be made by calculating the change in the quantity $(OH^-) - (H^+)$ that occurs as the pressure is increased. This calculation will be made for the pH 6.7 seawater at 22^o C.

Equation (23) can be rearranged to

$$CA = TA + (H^+)_p - (K_w)_p / (H^+)_p \quad (23a)$$

where K_w is the ion product of water. It will be assumed that $a_H = (H^+)$ and that $K_w = 10^{-14}$. These assumptions are valid because only one significant figure is needed in the calculated values of $(OH^-) - (H^+)$. For the pH 6.7 seawater, $TA = 0.13 \times 10^{-3}$ eq/kg-H₂O and is independent of pressure. At atmospheric pressure $pH_1 = 6.64$

and,

$$CA_1 = 0.1302 \times 10^{-3}$$

At 1000 atmospheres $pH_{1000} = 6.24$ and,

$$CA_{1000} = 0.1305 \times 10^{-3}$$

$(K_w)_{1000}$ was calculated from the pressure coefficient of K_w measured by Hamann (1963) at 25° C.

Equation (31) can be used to calculate $(K'_1)_p$, even though CA varies with pressure, if the correct value of A is used in the calculation. From the definition of A, $A_{1000} = A_1(CA_1/CA_{1000})$. A_{1000} was estimated by multiplying A_1 by the ratio CA_1/CA_{1000} . This value of A_{1000} was then used to calculate a "corrected" value of $(K'_1)_{1000}$ at $34.8^\circ/00$ salinity. The "corrected" value is about 1.2% larger than the value of $(K'_1)_{1000}$ calculated assuming that CA is independent of pressure. The correction is also about 1% at 11.6° C and at 2° C.

VI. DETERMINATION OF THE IN SITU CONCENTRATIONS OF THE CARBON DIOXIDE CONSTITUENTS

At atmospheric pressure the quantities CA , $T(\text{CO}_2)$, CO_2 , HCO_3^- , and $\text{CO}_3^{=}$ can be calculated from the following equations (Skirrow, 1965),

$$CA = TA - \left[\frac{K'_B \cdot T(B)}{a_H + K'_B} \right] \quad (69)$$

$$T(\text{CO}_2) = CA \left[\frac{a_H^2 + a_H K'_1 + K'_1 K'_2}{a_H K'_1 + 2K'_1 K'_2} \right] \quad (70)$$

$$(\text{CO}_2 + \text{H}_2\text{CO}_3)_T = CA \left[\frac{a_H^2}{a_H K'_1 + 2K'_1 K'_2} \right] \quad (71)$$

$$(\text{HCO}_3^-)_T = CA \left[\frac{a_H}{a_H + 2K'_2} \right] \quad (72)$$

$$(\text{CO}_3^{=})_T = CA \left[\frac{K'_2}{a_H + 2K'_2} \right] \quad (73)$$

These same equations can be used at any pressure if the values of a_H , K'_1 , K'_2 , and K'_B at that pressure are used in the calculations.

The apparent dissociation constants determined in this thesis are based on molal concentrations. Therefore, concentrations calculated from equations (69) through (73) are molalities, and the concentrations of TA and $T(B)$ used in equation (69) must be molal. Molal concentrations make $T(\text{CO}_2)$, $T(B)$, and TA independent of pressure and temperature. Molalities can be calculated from molarities by the equation

$$m = \frac{c}{d \cdot (1 - (S^{\circ}/\infty)/1000)} \quad (74)$$

where d is the density of seawater.

The calculation of the carbon di oxide constituents at depth involves the following steps:

1. The pH and TA of the seawater sample are measured at 1 atmosphere and at some known temperature.
2. The pH of the sample at the in situ temperature is calculated. Harvey (1963) gives temperature corrections for pH.
3. The pressure in atmospheres is calculated by dividing the depth in meters by 10. Pressures calculated in this way will be accurate to $\pm 2\%$.
4. To obtain the pH at the in situ temperature and pressure, the change of pH with pressure is read from Table VII and subtracted from the temperature corrected pH. $(a_{H^+})_p$ is then calculated from the in situ pH.
5. The pressure coefficients for K_1' , K_2' , and K_B' at the in situ temperature and pressure are calculated from equations (45), (46), and (47), or interpolated from Table V. The apparent dissociation constants at 1 atmosphere and the in situ temperature are multiplied by the pressure coefficient to give the apparent constants at the in situ temperature and pressure.
6. The molality of total boric acid is calculated from the

boron to chlorinity ratio (Culkin, 1965).

7. The carbonate alkalinity in situ is calculated from equation (69), using the measured TA and the calculated values of $T(B)$, $(K'_B)_p$, and $(a_H)_p$.

8. $T(CO_2)$, CO_2 , HCO_3^- , and $CO_3^{=}$ are calculated from equations (70) through (73) using the calculated values of CA, $(K'_1)_p$, $(K'_2)_p$, and $(a_H)_p$.

The calculations outlined above were performed for a hydrographic station in the North Pacific Ocean to illustrate the calculation of the carbon dioxide constituents at depth.

The original field data is given in Table XIV, and the calculated quantities are given in Tables XV and XVI. A sample calculation of the carbon dioxide constituents is shown in Table XVII. The vertical distributions of the carbon dioxide constituents are shown in Figure 7. This figure also shows the concentrations of the various species at the in situ temperature, but at atmospheric pressure. The difference between the two curves is the effect of pressure on the concentration of each constituent at the in situ temperature.

Figure 7 shows that increasing pressure decreases the pH and the concentrations of $CO_3^{=}$ and $CO_2 + H_2CO_3$. The concentration of HCO_3^- increases very slightly with increasing pressure. Buch and Gripenberg predicted that pressure would have these general effects on the concentrations of the carbon dioxide constituents.

At 7210 meters (721 atmospheres) the effect of pressure is to decrease the concentrations of $\text{CO}_3^{=}$ and $\text{CO}_2 + \text{H}_2\text{CO}_3$ by about 15%, and to increase the concentration of HCO_3^- by about 0.6%. Pressure has a large effect on the pH and at 7210 meters the pH at the in situ temperature and pressure is 0.29 pH units less than the pH at the in situ temperature and 1 atmosphere pressure.

The results of this work will be of use in the determination and interpretation of the distributions of the carbon dioxide constituents in the deep sea. Such studies are needed for a greater understanding of the chemical, geological, and biological processes occurring at depth which affect the carbon dioxide system. The effect of pressure on the pH will also be useful in the study of other pH dependent systems such as phosphoric acid.

Table XIV. Original field data for sample calculation of carbon dioxide constituents.

Station: HAH-56

Location: $50^{\circ} 27.5' N$, $176^{\circ} 13.8' W$

Date: 22 June 1966

Depth (meters)	T ^o C	Salinity (^o / _{oo})	TA x 10 ³ (eq/kg-H ₂ O)	pH(25 ^o C)	Oxygen (mg-at/l)
0	6.63	32.79	2.37	7.97	0.656
190	3.82	33.94	2.47	7.41	0.079
468	3.47	34.22	2.53	7.42	0.037
753	2.97	34.38	2.56	7.43	0.037
1425	2.15	34.55	2.58	7.53	0.084
2262	1.74	34.63	2.58	7.62	0.194
3256	1.49	34.67	2.59	7.71	0.266
4499	1.49	34.69	2.58	7.74	0.317
7210	1.86	34.69	2.60	7.78	0.330

Table XV. Calculated values of the carbon dioxide constituents at in situ temperatures and pressures for Station HAH-56.

Depth (meters)	pH	Molal concentrations $\times 10^3$				
		CA	T(CO ₂)	(HCO ₃ ⁻) _T	(CO ₃ ⁼) _T	(CO ₂ + H ₂ CO ₃) _T
0	8.16	2.31	2.19	2.03	0.138	0.018
190	7.58	2.45	2.49	2.37	0.040	0.081
468	7.58	2.51	2.55	2.43	0.042	0.081
753	7.58	2.54	2.58	2.46	0.042	0.080
1425	7.67	2.55	2.56	2.44	0.055	0.060
2262	7.75	2.54	2.52	2.41	0.066	0.045
3256	7.82	2.54	2.50	2.38	0.083	0.035
4499	7.80	2.53	2.47	2.36	0.087	0.031
7210	7.73	2.54	2.48	2.36	0.091	0.027

Table XVI. Calculated values of the carbon dioxide constituents at in situ temperature and 1 atm. pressure for Station HAH-56.

Depth (meters)	pH	Molal concentrations $\times 10^3$				
		CA	T(CO ₂)	(HCO ₃ ⁻) _T	(CO ₃ ⁼) _T	(CO ₂ + H ₂ CO ₃) _T
0	8.16	2.31	2.19	2.03	0.138	0.018
190	7.59	2.45	2.49	2.37	0.041	0.081
468	7.60	2.51	2.55	2.43	0.043	0.081
753	7.61	2.54	2.58	2.45	0.043	0.080
1425	7.73	2.55	2.56	2.44	0.056	0.061
2262	7.84	2.55	2.52	2.41	0.070	0.047
3256	7.95	2.55	2.50	2.37	0.089	0.036
4499	7.98	2.54	2.48	2.35	0.094	0.034
7210	8.02	2.55	2.48	2.34	0.105	0.030

Table XVII. Sample calculation of the carbon dioxide constituents at 7210 meters.

Step 1. The pH measured at 25°C is 7.78. The measured value of TA is 2.60×10^{-3} eq/kg-H₂O.

Step 2. The in situ temperature is 1.86°C. The pH at 1.86°C can be calculated from the equation (Harvey, 1963),

$$\text{pH}_{t_2} = \text{pH}_{t_1} + x(t_1 - t_2)$$

Using values of x given in Harvey,

$$\text{pH}_{1.86} = \text{pH}_{25} - 0.0097(20 - 25) - 0.0105(1.86 - 20) = 8.02$$

Step 3. Pressure = (7210 meters)/(10 meters/atm) = 721 atm.

Step 4. The change in pH with pressure at 1.86°C and 34.69‰ salinity is interpolated from Table VII.

$$\text{pH}_1 - \text{pH}_{721} = 0.29$$

The pH at 7210 meters is,

$$\text{pH}_{721} = 8.02 - 0.29 = 7.73$$

The value of a_{H} at 7210 meters is,

$$a_{\text{H}} = 1.86 \times 10^{-8}$$

Step 5. The pressure coefficients of the apparent constants interpolated from Table V are,

$$\begin{aligned} (K'_1)_{721} / (K'_1)_1 &= 2.16 & (K'_2)_{721} / (K'_2)_1 &= 1.68 & (K'_B)_{721} / (K'_B)_1 \\ &= 2.45 \end{aligned}$$

Lyman's values of the apparent constants at 1 atmosphere, 1.86°C, and 34.69‰ salinity are,

$$(K'_1)_1 = 0.74 \times 10^{-6} \quad (K'_2)_1 = 0.43 \times 10^{-9} \quad (K'_B)_1 = 1.17 \times 10^{-9}$$

Table XVII. Continued.

Multiplying the values at 1 atmosphere by the pressure coefficients gives the values of the apparent constants at the in situ temperature and pressure,

$$(K'_1)_{721} = 1.60 \times 10^{-6} \quad (K'_2)_{721} = 0.72 \times 10^{-9} \quad (K'_B)_{721} = 2.87 \times 10^{-9}$$

Step 6. The boron to chlorinity ratio (Culkin, 1965) is,

$$(\text{mg of boron/kg of seawater}) / (\text{Cl}^{\circ}/\text{oo}) = 0.237$$

The molecular weight of boron is 10.82, and a salinity of 34.69^o/oo corresponds to a chlorinity of 19.20^o/oo.

The total concentration of boric acid is,

$$T(\text{B}) = \frac{(0.237 \text{ mg-B/kg seawater}) / (\text{Cl}^{\circ}/\text{oo}) \times (19.20^{\circ}/\text{oo})}{(10.82 \text{ mg-B/mM}) \times (1 - \text{salinity}/1000)}$$

$$T(\text{B}) = 0.436 \times 10^{-3} \text{ moles/kg-H}_2\text{O}$$

Step 7. The carbonate alkalinity is calculated from equation (69),

$$\text{CA} = 2.54 \times 10^{-3} \text{ eq/kg-H}_2\text{O}$$

Step 8. The concentrations of the carbon dioxide constituents are calculated from equations (70), (71), (72), and (73).

$$T(\text{CO}_2) = 2.48 \times 10^{-3} \text{ moles/kg-H}_2\text{O}$$

$$(\text{HCO}_3^-)_T = 2.36 \times 10^{-3} \text{ moles/kg-H}_2\text{O}$$

$$(\text{CO}_3^{=})_T = 0.091 \times 10^{-3} \text{ moles/kg-H}_2\text{O}$$

$$(\text{CO}_2 + \text{H}_2\text{CO}_3)_T = 0.027 \times 10^{-3} \text{ moles/kg-H}_2\text{O}$$

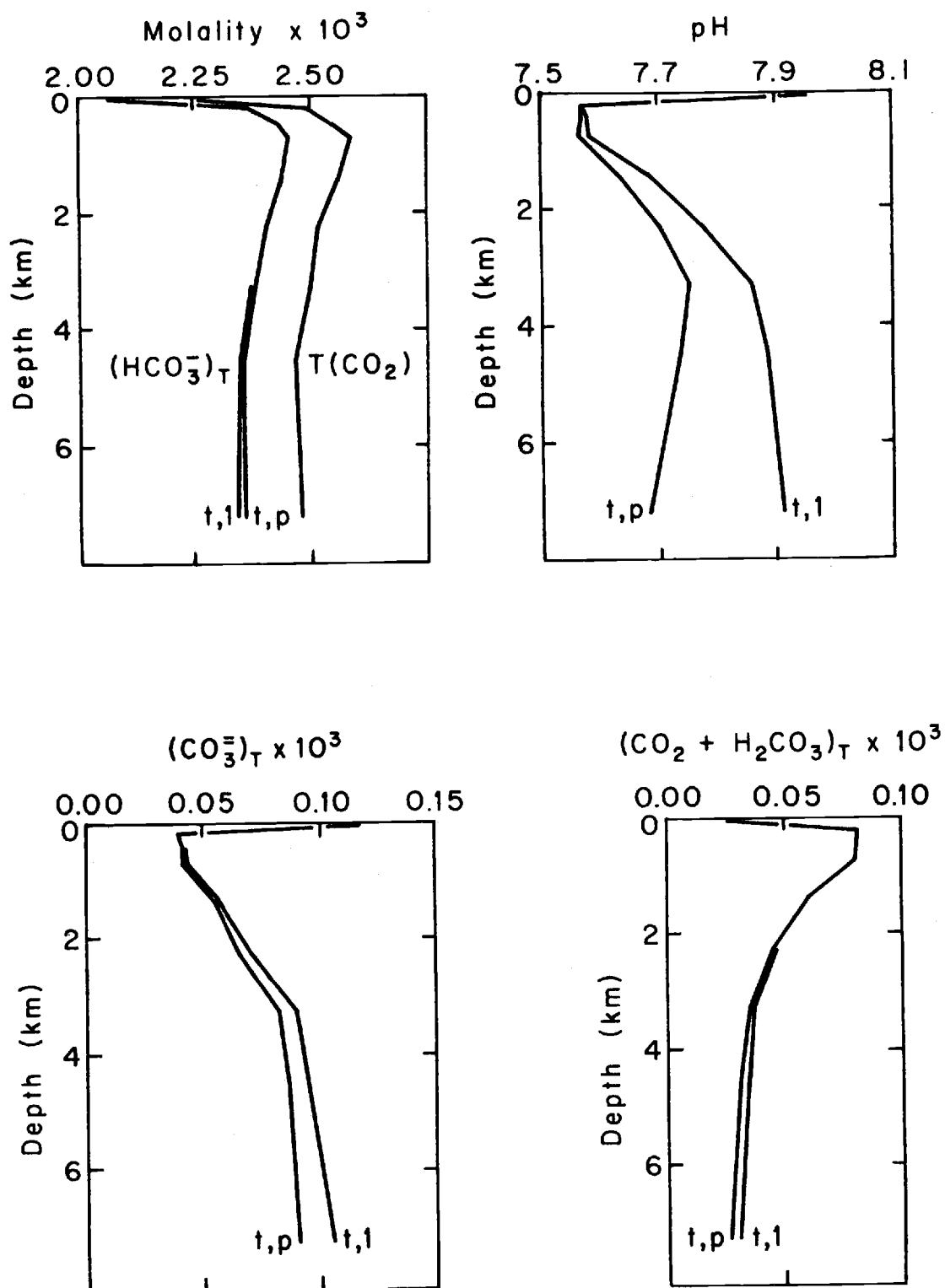


Figure 7. Vertical distributions of the carbon dioxide constituents. The curves labeled t, p are corrected for temperature and pressure. The curves labeled t, l are corrected for temperature only.

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APPENDICES

APPENDIX I

Experimental Data

Data for the calculation of $(K'_1)_p$ and $(K'_2)_p$:

Date: 5/30/67 Temp: 22^o C Salinity: 34.76 pH₁: 8.085 TA: 3.16x10⁻³

Time	Pressure (atm)	E _p (mv)	ΔE _{asym} (mv)	ΔpH
1025	1	+361.56	+0.00	+0.000 (Slope =
1200	500	353.03	0.27	0.143 57.76
1400	1000	344.71	0.35	0.286 mv/pH)

Date: 5/31/67 Temp: 22^o C Salinity: 34.76 pH₁: 6.648 TA: 0.13x10⁻³

1040	1	+277.86	+0.00	+0.000 (Slope =
1400	500	266.01	0.27	0.200 57.76
2100	1030	253.96	0.35	0.408 mv/pH)

Date: 6/1/67 Temp: 22^o C Salinity: 34.76 pH₁: 8.065 TA: 3.16x10⁻³

1315	1	+359.08	+0.00	+0.000 (Slope =
1610	515	349.90	0.27	0.154 57.76
1935	999	342.19	0.35	0.286 mv/pH)

Date: 6/1-2/67 Temp: 22^o C Salinity: 34.76 pH₁: 6.637 TA: 0.13x10⁻³

2135	1	+279.36	+0.00	+0.000 (slope =
0110	500	267.81	0.27	0.195 57.76
0430	1000	256.41	0.35	0.391 mv/pH)

Date: 6/4-5 Temp: 11.6^o C Salinity: 34.76 pH₁: 8.217 TA: 3.16x10⁻³

2250	1	+356.59	+0.00	+0.000 (Slope =
0310	499	347.91	0.04	0.154 56.19
0520	1000	339.32	0.08	0.306 mv/pH)

Date: 6/5/67 Temp: 11.6^o C Salinity: 34.76 pH₁: 6.737 TA: 0.13x10⁻³

1510	1	+274.34	+0.00	+0.000 (Slope =
2040	500	262.09	0.04	0.217 56.19
2330	999	250.67	0.08	0.420 mv/pH)

Date: 6/6/67 Temp: 11.6°C Salinity: 34.76 pH₁: 8.214 TA: 3.16x10⁻³

1450	1	+356.53	+0.00	+0.000 (Slope =
1700	500	347.78	0.04	0.155 56.19
1950	1000	339.12	0.08	0.308 mv/pH)

Date: 6/6-7 Temp: 11.6°C Salinity: 34.76 pH₁: 6.689 TA: 0.13x10⁻³

2145	1	+273.62	+0.00	+0.000 (Slope =
2345	500	261.06	0.15	0.221 56.19
0105	1001	249.23	0.28	0.429 mv/pH)

Date: 6/21/67 Temp: 2°C Salinity: 34.76 pH₁: 8.349 TA: 3.16x10⁻³

1745	1	+352.09	+0.00	+0.000 (Slope =
1930	500	342.99	0.45	0.160 54.12
2045	1000	333.84	0.66	0.325 mv/pH)
	330	(Interpolated)		0.106
	660	(Interpolated)		0.212

Date: 6/24/67 Temp: 2°C Salinity: 34.76 pH₁: 6.761 TA: 0.13x10⁻³

1450	1	+266.87	+0.00	0.000 (Slope =
1610	330	258.22	0.33	0.154 54.12
2150	660	249.94	0.55	0.303 mv/pH)
0010	1001	241.82	0.66	0.451

Date: 6/20-21 Temp: 2°C Salinity: 34.76 pH₁: 8.350 TA: 3.16x10⁻³

0300	1	+352.05	+0.00	+0.000 (Slope =
0520	500	343.16	0.32	0.158 54.12
0730	997	334.19	0.65	0.318 mv/pH)
	330	(Interpolated)		0.105
	660	(Interpolated)		0.209

Date: 6/23/67 Temp: 2°C Salinity: 34.76 pH₁: 6.827 TA: 0.13x10⁻³

1745	1	+266.85	+0.00	+0.000 (Slope =
2105	330	258.09	0.34	0.156 54.12
2210	660	249.65	0.54	0.308 mv/pH)
2310	1000	241.43	0.66	0.458

Date: 6/28/67 Temp: 13.5°C Salinity: 38.50 pH₁: 8.331 TA: 1.83x10⁻³

2030	1	+364.82	+0.00	+0.000 (Slope =
0020	500	356.74	0.04	0.142 56.59
0145	1000	348.55	0.10	0.286 mv/pH)

Date: 8/20/67 Temp: 13.5^oC Salinity: 38.58 pH₁: 7.186 TA: 0.37x10⁻³
 1745 1 302.36 +0.00 +0.000 (Slope =
 2010 500 290.16 0.29 0.210 56.59
 2230 1000 278.82 0.52 0.407 mv/pH)

Date: 6/29/67 Temp: 13.5^oC Salinity: 38.50 pH₁: 8.331 TA: 1.83x10⁻³
 1330 1 +366.33 +0.00 0.000 (Slope =
 1525 500 357.99 0.23 0.143 56.59
 1740 1000 349.68 0.38 0.288 mv/pH)

Date: 7/2-3 Temp: 13.5^oC Salinity: 38.50 pH₁: 7.434 TA: not measured
 1525 1 +310.58 +0.00 +0.000 (Slope =
 1810 500 299.25 0.08 0.199 56.59
 2100 1000 288.65 0.36 0.381 mv/pH)

Data for the calculation of (K'_{Bp}):

Date: 7/12/67 Temp: 22^oC Salinity: 34.84 pH₁: 8.200

TA/T(B): 0.524086 T(B): 3.13x10⁻³ TA: 1.64x10⁻³

Time	Pressure (atm)	E _p (mv)	ΔE _{asym} (mv)	ΔpH
1525	1	+368.38	+0.00	+0.000 (Slope =
1735	500	355.27	0.07	0.226 57.76
1920	1000	342.69	0.16	0.442 mv/pH)

Date: 7/12-13/67 Temp: 22^oC Salinity: 34.84 pH₁: 8.190

TA/T(B): 0.524086 T(B): 3.13x10⁻³ TA: 1.64x10⁻³

2155	1	+368.24	+0.00	+0.00 (Slope =
0010	500	355.37	0.03	0.222 57.76
0140	1000	342.73	0.05	0.441 mv/pH)

Date: 7/15-16/67 Temp: 11.6^oC Salinity: 34.84 pH₁: 8.301

TA/T(B): 0.524086 T(B): 3.13x10⁻³ TA: 1.64x10⁻³

2130	1	+361.04	+0.00	+0.000 (Slope =
2335	500	347.44	0.11	0.240 56.19
0155	1000	334.44	0.14	0.471 mv/pH)

Date: 7/16/67 Temp: 11.6°C Salinity: 34.84 pH₁: 8.296

TA/T(B): 0.524086 T(B): 3.13x10⁻³ TA: 1.64x10⁻³

1345	1	+361.29	+0.00	0.000 (Slope =
1530	500	347.61	0.13	0.241 56.19
1730	1000	334.57	0.20	0.472 mv/pH)

Date: 7/17/67 Temp: 2°C Salinity: 34.84 pH₁: 8.401

TA/T(B): 0.524086 T(B): 3.13x10⁻³ TA: 1.64x10⁻³

1830	1	+355.03	+0.00	+0.000 (Slope =
2050	500	340.85	0.05	0.261 54.12
2345	1000	327.32	0.03	0.511 mv/pH)

Date 7/18/67 Temp: 2°C Salinity: 34.84 pH₁: 8.398

TA/T(B): 0.524086 T(B): 3.13x10⁻³ TA: 1.64x10⁻³

0315	1	+355.04	+0.00	+0.000 (Slope =
0530	500	340.81	0.03	0.262 54.12
0730	1000	327.33	0.16	0.509 mv/pH)

Date: 7/7/67 Temp: 13.5°C Salinity: 38.50 pH₁: 8.473

TA/T(B): 0.775927 T(B): 3.05x10⁻³ TA: 2.36x10⁻³

1320	1	+373.19	+0.00	+0.000 (Slope =
1540	500	360.22	0.33	0.223 56.59
1720	1001	347.80	0.40	0.442 mv/pH)

Date: 7/8/67 Temp: 13.5°C Salinity: 38.50 pH₁: 8.462

TA/T(B): 0.775927 T(B): 3.05x10⁻³ TA: 2.36x10⁻³

----	1	+373.12	0.00	0.000 (Slope =
----	500	360.12	0.24	0.225 56.59
2300	1000	347.57	0.28	0.477 mv/pH)

APPENDIX II

Sample Calculation of $(K'_1)_p$, $(K'_2)_p$, and $(K'_B)_p$ Sample Calculation of $(K'_1)_p$ and $(K'_2)_p$:

The values of K'_1 and K'_2 at 22° C, 34.8 ‰ salinity, and 1000 atmospheres will be calculated from the experimental data taken on May 30 and 31, 1967 (see Appendix I).

Seawater Sample	pH_1	$(a_{\text{H}})_1$	$\text{pH}_1 - \text{pH}_{1000}$	$(a_{\text{H}})_{1000}$
1	6.648	2.249×10^{-7}	0.396	5.598×10^{-7}
2	8.085	0.8222×10^{-8}	0.286	1.589×10^{-8}

First the value of $A (= T(\text{CO}_2) / \text{CA})$ for each seawater sample is calculated at 1 atmosphere. Lyman's values of the apparent constants at 22° C and 34.8 ‰ salinity are

$$(K'_1)_1 = 0.98 \times 10^{-6} \quad (K'_2)_1 = 0.73 \times 10^{-9}$$

Using these values and the measured value of $(a_{\text{H}})_1$, the value of A for each seawater sample is calculated from equation (27).

$$A_1 = 1.2248 \quad A_2 = 0.93173$$

The value of $(K'_2)_{1000}$ is now calculated from equation (30) using the calculated values of A_1 and A_2 , and the measured values of $(a_{\text{H}1})_{1000}$ and $(a_{\text{H}2})_{1000}$. The result is

$$(K'_2)_{1000} = 1.38 \times 10^{-9}$$

The calculated value of $(K'_2)_{1000}$ is now used in equation (31) to calculate $(K'_1)_{1000}$. The result is $(K'_1)_{1000} = 2.45 \times 10^{-6}$.

Sample Calculation of (K'_{B_p}) :

The value of K'_B at 22°C , $34.8^\circ/\text{oo}$ salinity, and 1000 atmospheres will be calculated from the experimental data taken on July 12, 1967 (see Appendix I).

pH_1	$(a_{\text{H}^+})_1$	$\text{pH}_1 - \text{pH}_{1000}$	$(a_{\text{H}^+})_{1000}$
8.200	0.631×10^{-8}	0.442	1.746×10^{-8}

Lyman's values of the apparent constants at 22°C and $34.8^\circ/\text{oo}$ salinity are

$$(K'_1)_1 = 0.98 \times 10^{-6} \quad (K'_2)_1 = 0.73 \times 10^{-9} \quad (K'_B)_1 = 1.86 \times 10^{-9}$$

First, $T(\text{CO}_2)/T(\text{B})$ is calculated from equation (39) using the value of $\text{TA}/T(\text{B})$, Lyman's constants, and the measured value of $(a_{\text{H}^+})_1$.

The ratio $\text{TA}/T(\text{B})$ is 0.524086, and

$$T(\text{CO}_2)/T(\text{B}) = 0.270125$$

Next, the value of F at 1000 atmospheres is calculated from equation (40), using the measured value of $(a_{\text{H}^+})_{1000}$. The values of $(K'_1)_{1000}$ and $(K'_2)_{1000}$ used in the calculation are the average values given in Table IV.

$$(K'_1)_{1000} = 2.44 \times 10^{-6} \quad (K'_2)_{1000} = 1.37 \times 10^{-9}$$

The calculated value of F is,

$$F_{1000} = 0.236154$$

Finally $(K'_B)_{1000}$ is calculated from equation (41),

$$(K'_B)_{1000} = 5.40 \times 10^{-9}.$$