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Title DETERMINATION OF THE APPARENT DISSOCIATION CONSTANTS OF PHOSPHORIC ACID IN SEAWATER

Abstract approved Redacted for Privacy
(Major Professor)

The three apparent dissociation constants of phosphoric acid, K'_1, K'_2, and K'_3, relate the hydrogen ion activity to the molar concentrations of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. These apparent dissociation constants must be known in seawater before the chemistry of inorganic phosphate in the ocean can be studied in detail.

A method, based on potentiometric pH measurements, was developed for the determination of the apparent dissociation constants of a tribasic acid in complex ionic solutions. The values of K'_1, K'_2, and K'_3 of H_3PO_4 were determined in artificial seawater between 30‰ and 36‰ salinity over the temperature range 5 to 25° C at atmospheric pressure. Measurements were also made in an NaCl solution of ionic strength 0.68. From these values the effect of complex formation between PO_4^{3-} and the major divalent cations in seawater was evaluated.

DETERMINATION OF THE APPARENT DISSOCIATION CONSTANTS OF PHOSPHORIC ACID IN SEAWATER

by

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a_A = activity of A.

$[A]$ = concentration of A in moles/liter.

CA = carbonate alkalinity.

$F(x)$ = an expression which depends only on x; defined by equation (25) p. 10.

K = thermodynamic dissociation constant.

K' = an apparent dissociation constant.

K'' = an apparent dissociation constant which depends only on non-specific interactions.

K'_1 = the first apparent dissociation constant of H_3PO_4.

K'_2 = the second apparent dissociation constant of H_3PO_4.

K'_3 = the third apparent dissociation constant of H_3PO_4.

M = concentration, moles/liter.

N = concentration, equivalents/liter.

$N(x)$ = the sum concentration of all ions which interact with H^+ except for the weak acid of interest.

$pK'_i = -\log K'_i$

P_o = the sum initial concentration of all ions which do not interact with H^+.

x = defined by $-\log x = pH$.

y = moles/liter of weak acid titrant.

z = equivalents/liter of strong acid or base titrant.

$\alpha = K'_1 K'_2$.

$\beta = K'_2 K'_3$.

γ = activity coefficient on the molarity scale.

γ (NaCl) = activity coefficient in an NaCl solution of $\mu = 0.68$.

γ (SW) = activity coefficient in artificial seawater of $\mu = 0.68$.

μ = ionic strength.

‰ = units for salinity, parts per thousand, g of salt/kg of solution.

DETERMINATION OF THE APPARENT DISSOCIATION CONSTANTS OF PHOSPHORIC ACID IN SEAWATER

I. INTRODUCTION

Apparent dissociation constants are quasi-stoichiometric constants which relate the hydrogen ion activity to the concentrations of the other species involved in the dissociation reaction. These constants were first used in seawater by Buch *et al*. (1932) for carbonic acid.

A knowledge of the apparent dissociation constants of H_3PO_4 in seawater is needed for studies of the formation of apatites and phosphorites (Dietz, Emery, and Shepard, 1942; Roberson, 1965) and for studies of the uptake of phosphate in the photosynthesis of organic matter (Kuhl, 1962). In physicochemical studies these constants provide information on the ionic interactions and complex formation of phosphate ions in seawater.

Several attempts have been made to estimate the values of the apparent dissociation constants of H_3PO_4 in seawater. The first estimates were made by Dietz, Emery, and Shepard (1942). These were based on extrapolations of the expressions of Sendroy and Hastings (1927) for the apparent dissociation constants of H_3PO_4 as a function of ionic strength, μ[1]. Several assumptions are made in

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[1] $\mu = 1/2 \sum c_i z_i^2$, where c_i is the molal concentration and z_i is the valence of the ith species (Lewis and Randall, 1921).

applying the data of Sendroy and Hastings to seawater. For the first apparent dissociation constant of H_3PO_4 (K'_1), Sendroy and Hastings assumed that the activity coefficient of H_3PO_4 was unity and then used the limiting equation from the Debye-Hückel theory to express K'_1 as a function of μ. Their relationship was consistent with experimental values of K'_1 at 18° C for H_3PO_4 solutions with ionic strengths between 0.002 and 0.10. Sendroy and Hastings measured the second and third apparent dissociation constants of H_3PO_4 (K'_2 and K'_3) in NaCl solutions of various ionic strengths at 38° C. They noted that the activity coefficient of HPO_4^{2-} was dependent on the medium in which it was determined due to specific ion effects. Dietz, Emery, and Shepard, who extrapolated the data of Sendroy and Hastings to the ionic strength of seawater, recognized that their estimates of K'_1, K'_2, and K'_3 were subject to errors. These errors are due to deviations from the Debye-Hückel limiting law at high ionic strengths and due to the effect of temperature on the apparent dissociation constants. The specific ion effects noted by Sendroy and Hastings could also alter the magnitude of the apparent dissociation constants in seawater, making extrapolations based on ionic strength alone invalid.

Cooper (1948) estimated the concentrations of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} in seawater by assuming that all activity coefficients were unity and then using thermodynamic dissociation constants. This work was recently cited by Armstrong (1965) as the basis for concluding that $H_2PO_4^-$, and HPO_4^{2-} are the major species of inorganic phosphate in seawater.

In the absence of the necessary apparent dissociation constants and apparent solubility products, Kramer (1964) used the Debye-Hückel limiting law to calculate activity coefficients in seawater. Using thermodynamic constants he concluded that seawater was supersaturated with respect to hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$.

Richards et al. (1965) required the apparent dissociation constants of H_3PO_4 to estimate the ion product of $Ca_3(PO_4)_2$. They used the data of Sendroy and Hastings to obtain the values of K_1', K_2', and K_3' at $\mu = 0.64$. They applied temperature corrections to obtain estimates at 10° C. The validity of their temperature corrections may be questioned on two accounts: they assumed that the temperature dependence of the apparent dissociation constants was independent of ionic strength, and they replaced the constant term in the expressions of Sendroy and Hastings with thermodynamic dissociation constants at 10° C given by Bates (1951), Bates and Acree (1943), and Farr (1950). The constant term of Sendroy and Hastings was based on measurements in relatively concentrated solutions ($0.08 < \mu < 0.2$, for K_3'), and thus may not correspond to a thermodynamic dissociation constant.

The only previous attempt to measure an apparent dissociation constant of H_3PO_4 in seawater was made by Roberson (1965). He assumed that K_1' was greater than 10^{-2} and that K_3' was less than 10^{-10} and concluded that the phosphate equilibria for pH values near 8.0 could be characterized by the value of K_2' only. He measured a value, $K_2' = 0.8 \pm 0.3 \times 10^{-6}$, in artificial seawater with $\mu = 0.71$. Roberson's value of K_2' was based on a titration curve in carbonate and borate-free artificial seawater. His value requires verification, because it is subject to error due to the presence of other weak acids (e. g. CO_2).

The purpose of this work was to measure the apparent dissociation constants of H_3PO_4 in seawaters of several salinities over a range of temperatures.

II. THEORY AND METHODS

Definition of Apparent Dissociation Constants

The dissociation of an acid may be represented by the following equilibrium reaction:

$$HA \rightleftharpoons H^{+} + A^{-}$$

The thermodynamic dissociation constant for the acid, HA, is defined as:

$$K = \frac{a_{H^+} a_{A^-}}{a_{HA}} \qquad (1)$$

where a indicates the activity of the various species involved. The value of K depends on temperature and pressure, but is independent of the ionic composition of the solution. For seawater equation (1) is of little value, because at the present time the activities of most dissolved species are not accessible to direct measurement. Therefore, apparent dissociation constants have been defined, in terms of measurable quantities, as:

$$K' = \frac{a_{H^+}[A^-]}{[HA]} \qquad (2)$$

The brackets indicate the concentrations of the various species in moles/liter. K' depends on the ionic strength and the composition of the solution as well as on temperature and pressure.

At the present time the principal method for determining a_{H^+} in seawater is from pH measurements using the glass electrode.

pH measurements in seawater do not yield the thermodynamic hydrogen ion activity, a_{H^+}, and may depart from standard buffer scales, because of the effects of liquid junction and asymmetry potentials (Bates, 1964; Barnes, 1959; Smith and Hood, 1964; Pytkowicz, Kester, and Burgener, in press). It is better to consider pH measurements in seawater as yielding an empirical quantity x, defined by:

$$-\log x = \text{pH} \qquad (3)$$

In the absence of liquid junction and asymmetry potentials, x and a_{H^+} are identical. The advantage of this distinction is that attention is focused on the reproducibility of x rather than on the accuracy with which pH measurements in seawater approximate a_{H^+}. If equilibrium constants are determined and also applied using similar electrodes and techniques, departures from a thermodynamic or a buffer scale are cancelled within the reproducibility of the measurements. Accordingly, the apparent dissociation constants in this work are defined as:

$$K' = \frac{x\,[A^-]}{[HA]} \qquad (4)$$

Theoretical Considerations in the Determination of Apparent Dissociation Constants

Buch *et al.* (1932) developed the necessary equations for the evaluation of the apparent dissociation constants of carbonic acid in seawater. Lyman (1956) modified the derivation to obtain a more accurate procedure. Weyl (1961) rederived the necessary equations in a more convenient form. He defined a function, F(x), which is related to the ratio of carbonate alkalinity (CA) to total carbon dioxide (ΣCO_2) used by Buch et al. (1932) by:

$$F(x) = \frac{CA}{\sum CO_2} - 1 \tag{5}$$

The following derivations are extensions and modifications for tribasic acids of the equations of Weyl (1961) for dibasic acids. These were developed by Dr. R. M. Pytkowicz (Personal communication).

A tribasic acid may undergo the following dissociations:

$$H_3A \rightleftharpoons H^+ + H_2A^-$$
$$H_2A^- \rightleftharpoons H^+ + HA^{2-}$$
$$HA^{2-} \rightleftharpoons H^+ + A^{3-}$$

from which the three apparent dissociation constants may be defined by:

$$K'_1 = \frac{x\,[H_2A^-]}{[H_3A]} \tag{6}$$

$$K'_2 = \frac{x\,[HA^{2-}]}{[H_2A^-]} \tag{7}$$

$$K'_3 = \frac{x\,[A^{3-}]}{[HA^{2-}]} \tag{8}$$

Rearrangement of equations (6), (7), and (8) yields:

$$[H_3A] = \frac{x}{K_1'} [H_2A^-] \qquad (9)$$

$$[HA^{2-}] = \frac{K_2'}{x} [H_2A^-] \qquad (10)$$

$$[A^{3-}] = \frac{K_3'}{x} [HA^{2-}] \qquad (11)$$

Substituting equation (10) into (11) gives:

$$[A^{3-}] = \frac{K_2' K_3'}{x^2} [H_2A^-] \qquad (12)$$

Next we consider a solution that contains initially y_o moles/liter of A, regardless of species form. During a titration we add y moles/liter of A. The conservation of mass will be given by:

$$y + y_o = [H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}] . \qquad (13)$$

Introducing (9), (10), and (12) into (13) gives:

$$y + y_o = [H_2A^-] \left\{ \frac{x}{K_1'} + 1 + \frac{K_2'}{x} + \frac{K_2' K_3'}{x^2} \right\} \qquad (14)$$

Let A be in a solution with other ions (e. g. seawater); the condition for electroneutrality may be written as:

$$[H_2A^-] + 2\,[HA^{2-}] + 3\,[A^{3-}] + N(x) = P_o \qquad (15)$$

Those ions which do not interact with H^+ have been placed on the right hand side of the equation and grouped together as P_o. Thus, $P_o = [Na^+] + [K^+] + 2[Mg^{2+}] - 2[SO_4^{2-}] - [Cl^-] + \ldots .$ Those ions which interact with H^+ have been placed on the left hand side of equation (15) with those related to A given explicitly and all others grouped together as N(x). $N(x) = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] + \ldots$ is a function of x.

Consider the condition of electroneutrality when a solution, initially characterized by equation (15), is titrated with several different titrants. y is the number of moles/liter of A^{3-}, HA^{2-}, H_2A^-, or H_3A added when one of these species is the titrant, and z is the number of equivalents/liter of a strong acid or base added as the titrant. Then the condition of electroneutrality becomes:

Titrant	Condition of Electroneutrality	
A^{3-}	$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + N(x) = P_o + 3y$	(16)
HA^{2-}	$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + N(x) = P_o + 2y$	(17)
H_2A^-	$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + N(x) = P_o + y$	(18)
H_3A	$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + N(x) = P_o$	(19)
Strong acid	$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + N(x) = P_o - z$	(20)
Strong base	$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] + N(x) = P_o - z$	(21)

From equations (10), (11), and (13) the first three terms of (15) may be written as:

$$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] = [H_2A^-] \left\{ 1 + \frac{2K'_2}{x} + \frac{3K'_2\,K'_3}{x^2} \right\} \quad (22)$$

Solving (14) and (22) for H_2A^- and equating gives:

$$[H_2A^-] = \frac{y + y_o}{\frac{x}{K'_1} + 1 + \frac{K'_2}{x} + \frac{K'_2\,K'_3}{x^2}} = \frac{[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}]}{1 + \frac{2K'_2}{x} + \frac{3K'_2\,K'_3}{x^2}} \qquad (23)$$

or

$$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] = (y+y_o)\,\frac{1 + \frac{2K'_2}{x} + \frac{3K'_2\,K'_3}{x^2}}{\frac{x}{K'_1} + 1 + \frac{K'_2}{x} + \frac{K'_2\,K'_3}{x^2}} \qquad (24)$$

If we define F(x), a function of x only, by:

$$F(x) = \frac{K'_1\,K'_2\,x + 2K'_1\,K'_2\,K'_3 - x^3}{K'_1\,x^2 + x^3 + K'_1\,K'_2\,x + K'_1\,K'_2\,K'_3} \qquad (25)$$

then equation (24) may be simplified to:

$$[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}] = (y+y_o)\,\{1 + F(x)\} \qquad (26)$$

In a similar manner equations (17) through (21) may be transformed to yield equations (28) through (32).

Titrant	Condition of Electroneutrality	
A^{3-}	$y_o\,\{1 + F(x)\} + N(x) = P_o + y\,\{2 - F(x)\}$	(27)
HA^{2-}	$y_o\,\{1 + F(x)\} + N(x) = P_o + y\,\{1 - F(x)\}$	(28)
H_2A^-	$y_o\,\{1 + F(x)\} + N(x) = P_o - y\,F(x)$	(29)
H_3A	$y_o\,\{1 + F(x)\} + N(x) = P_o - y\,\{1 + F(x)\}$	(30)
Strong acid	$y_o\,\{1 + F(x)\} + N(x) = P_o - z$	(31)
Strong base	$y_o\,\{1 + F(x)\} + N(x) = P_o + z$	(32)

Equations (27) through (32) are the basis for the method of determining the apparent dissociation constants of a tribasic acid in a complex ionic solution. The effects of weak acids other than H_3A are eliminated by the use of pairs of titrations.

A typical procedure is as follows. First, y moles/liter of H_2A^- are added to an aliquot of the solution changing the initial pH which corresponds to x_o to a final pH corresponding to x_1. A second titration is performed on an identical aliquot over the same pH interval with z equivalents/liter of a strong acid if $x_1 > x_o$, or a strong base if $x_1 < x_o$. For the purpose of discussion, we assume that $x_1 > x_o$ so that the second titration is done with a strong acid. From equation (29) the condition of electroneutrality after the first titration will be given by:

$$y_o \{1 + F(x_1)\} + N(x_1) = P_o - y F(x_1) \tag{33}$$

and from (31) after the second titration it will be given by:

$$y_o \{1 + F(x_1)\} + N(x_1) = P_o - z \tag{34}$$

Subtracting (34) from (33) gives:

$$z - y F(x_1) = 0 \quad \text{or} \quad F(x_1) = \frac{z}{y} \tag{35}$$

Hence, $F(x_1)$ may be evaluated from y and z. Other titrants and combinations of equations (27) through (32) could also be used to obtain F(x) from y and z.

If F(x) were determined for three different values of x, a system of three equations, in the form of equation (25), could be generated and the three unknowns K'_1, K'_2, and K'_3, could be calculated.

F(x) was introduced to simplify the equations in the preceding development. Its physical significance is seen from equation (26) which may be written as:

$$F(x) = \frac{[H_2A^-] + 2[HA^{2-}] + 3[A^{3-}]}{y + y_o} - 1$$

The numerator of the first term on the right is the alkalinity associated with A (the phosphate alkalinity). The denominator is the total amount of A in solution (total inorganic phosphate). Buch (1951) expressed his values for the apparent dissociation constants of carbonic acid by the ratio of total inorganic carbon to carbonate alkalinity, which is closely related to the function F(x), as shown by equation (5).

The preceding derivations have been general and required no restrictions on the relative magnitudes of K'_1, K'_2, K'_3, and x. The presence of other weak acids or bases were accounted for by the term N(x). The price of this generality is a lack of precision in the solution of the final system of three simultaneous cubic equations.

Practical Considerations

The precision of the determination of the apparent dissociation constants may be improved by placing a few restrictions on the relative magnitudes of K'_1, K'_2, K'_3 and x. From the definition of F(x), equation (25), it is apparent that if some of the terms in the numerator or denominator are orders of magnitude smaller than the others, they can be neglected thereby simplifying the expression for F(x). For example, if $2K'_1 K'_2 K'_3 << K'_1 K'_2 x$ and if $2K'_1 K'_2 K'_3 << x^3$, equation (25) becomes:

$$F(x) = \frac{K'_1 K'_2 x - x^3}{K'_1 x^2 + x^3 + K'_1 K'_2 x} \qquad (36)$$

This condition can be obtained in practice at low pH values.

If H_2A^- is added to a solution, the pH will tend toward some equilibrium value at which it will be unchanged by further addition of H_2A^-. At this pH the reactions (37) and (38) occur to the same extent, consuming and liberating equal amounts of H^+:

$$H_2A^- + H^+ \rightarrow H_3A \qquad (37)$$

$$H_2A^- \rightarrow H^+ + HA^{2-} \qquad (38)$$

A similar equilibrium pH may be found at which the addition of HA^{2-} will not change the pH due to a balance of reactions (39) and (40):

$$HA^{2-} + H^+ \rightarrow H_2A^- \qquad (39)$$

$$HA^{2-} \rightarrow H^+ + A^{3-} \qquad (40)$$

To interpret the significance of the equilibrium pH for the addition of H_2A^-, we consider equation (29):

Before adding H_2A^-, $y_o \{1 + F(x_o)\} + N(x_o) = P_o$ (29a)

After adding H_2A^-, $y_o \{1 + F(x_1)\} + N(x_1) = P_o - y F(x_1)$ (29b)

For the equilibrium pH, $x_1 = x_o$ and (29a) minus (29b) gives:

$$y F(x_1) = 0$$

and since $y \neq 0$ this requires that

$$F(x_1) = 0 \tag{41}$$

From preliminary experiments with phosphoric acid, the equilibrium pH was $x_o^3 = x_1^3 \approx 10^{-12}$ and $K_1' K_2' x \approx 10^{-12}$, while $K_1' K_2' K_3' < 10^{-16}$. Therefore, equation (36) can be used, and set equal to zero, because of (41) giving:

$$F(x) = \frac{K_1' K_2' x - x^3}{K_1' x^2 + x^3 + K_1' K_2' x} = \frac{K_1' K_2' - x^2}{K_1' x + x^2 + K_1' K_2'} = 0$$

or

$$x^2 = K_1' K_2'$$

Thus, the equilibrium pH corresponds to $1/2(pK_1' + pK_2')$.

In determining the significance of the equilibrium pH for addition of HA^{2-} we consider equation (25) when x^3 is several orders of magnitude smaller than the other terms. In this case the expression for F(x) is reduced to:

$$F(x) = \frac{K_1' K_2' x + 2K_1' K_2' K_3'}{K_1' x^2 + K_1' K_2' x + K_1' K_2' K_3'} \tag{42}$$

Equation (28), before addition of HA^{2-}, is

$$y_o \{1 + F(x_o)\} + N(x_o) = P_o \tag{28a}$$

and after adding HA^{2-}, (28) becomes:

$$y_o \{1 + F(x_1) + N(x_1) = P_o + y \{1 - F(x_1)\} \tag{28b}$$

Subtracting (28a) from (28b), with $x_o = x_1$,

$$y \{1 - F(x_1)\} = 0$$

or

$$F(x_1) = 1 \tag{43}$$

From (42) the value of <u>x</u> satisfying (43) is

$$x^2 = K_2' K_3'$$

Thus, the equilibrium pH for HA^{2-} is $1/2(pK_2' + pK_3')$. In the case of H_3PO_4, for $x = \sqrt{K_2' K_3'}$, $x^3 < 3x10^{-20}$, whereas $2K_1' K_2' K_3' > 10^{-17}$ and $K_1' K_2' x > 10^{-16}$. The requirements for the validity of equation (42) are satisfied.

<u>Method for Determining the Apparent Dissociation Constants of Phosphoric Acid in Seawater</u>

The apparent dissociation constants of H_3PO_4 in seawater were determined from measurements of the equilibrium pH values for additions of KH_2PO_4 and of K_2HPO_4 and from values of F(x) obtained from titrations yielding y and z. The products $\alpha = K_1' K_2'$ and $\beta = K_2' K_3'$ were calculated from $1/2(pK_1' + pK_2')$ and $1/2(pK_2' + pK_3')$, the

the equilibrium pH values for the additions of KH_2PO_4 and K_2HPO_4 respectively. Substituting α and β into equation (25):

$$F(x) = \frac{\alpha x + 2K_1' \beta - x^3}{K_1' x^2 + x^3 + \alpha x + K_1'\beta} \tag{44}$$

Solving (44) for K_1':

$$K_1' = \frac{\alpha x\{1 - F(x)\} - x^3 \{1 + F(x)\}}{x^2 F(x) + \beta F(x) - 2\beta} \tag{45}$$

After calculating K_1', K_2' was obtained from:

$$K_2' = \frac{\alpha}{K_1'} \tag{46}$$

and K_3' from:

$$K_3' = \frac{\beta}{K_2'} \tag{47}$$

III. EXPERIMENTAL PROCEDURE

Determination of the pH

The pH was determined electrometrically using a pH-sensitive glass electrode (Beckman[2] #40498) and a fiber junction calomel reference electrode (Beckman #39170). Following the recommendation of Bates (1964), the pH was calculated from equation (48):

$$pH(X) = pH(S_1) + \{E(X) - E(S_1)\} \frac{pH(S_2) - pH(S_1)}{E(S_2) - E(S_1)} \tag{48}$$

pH(X) is the pH of the test solution; $pH(S_1)$ and $pH(S_2)$ are the pH values of two standard buffer solutions S_1 and S_2. E(X) is the emf of the pH-sensitive cell in the test solution, and $E(S_1)$ and $E(S_2)$ are the emf values of the electrode cell in buffers S_1 and S_2.

The glass and calomel electrodes were mounted in No. 2 rubber stoppers which were fitted into a large rubber stopper in a thermostated beaker (Figure 1). The emf of the glass-calomel pair was fed into a Cary[3] Model 31V vibrating reed electrometer (VRE) for amplification; a Leeds and Northrup[4] Type K-3 potentiometer was used to supply a bucking emf. The null balance was read on the VRE output

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[2] Beckman Instruments, Inc., Scientific and Process Instruments Division, Fullerton, California.

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

[4] Leeds and Northrup Company, 4901 Stenton Avenue, Philadelphia 44, Pennsylvania.

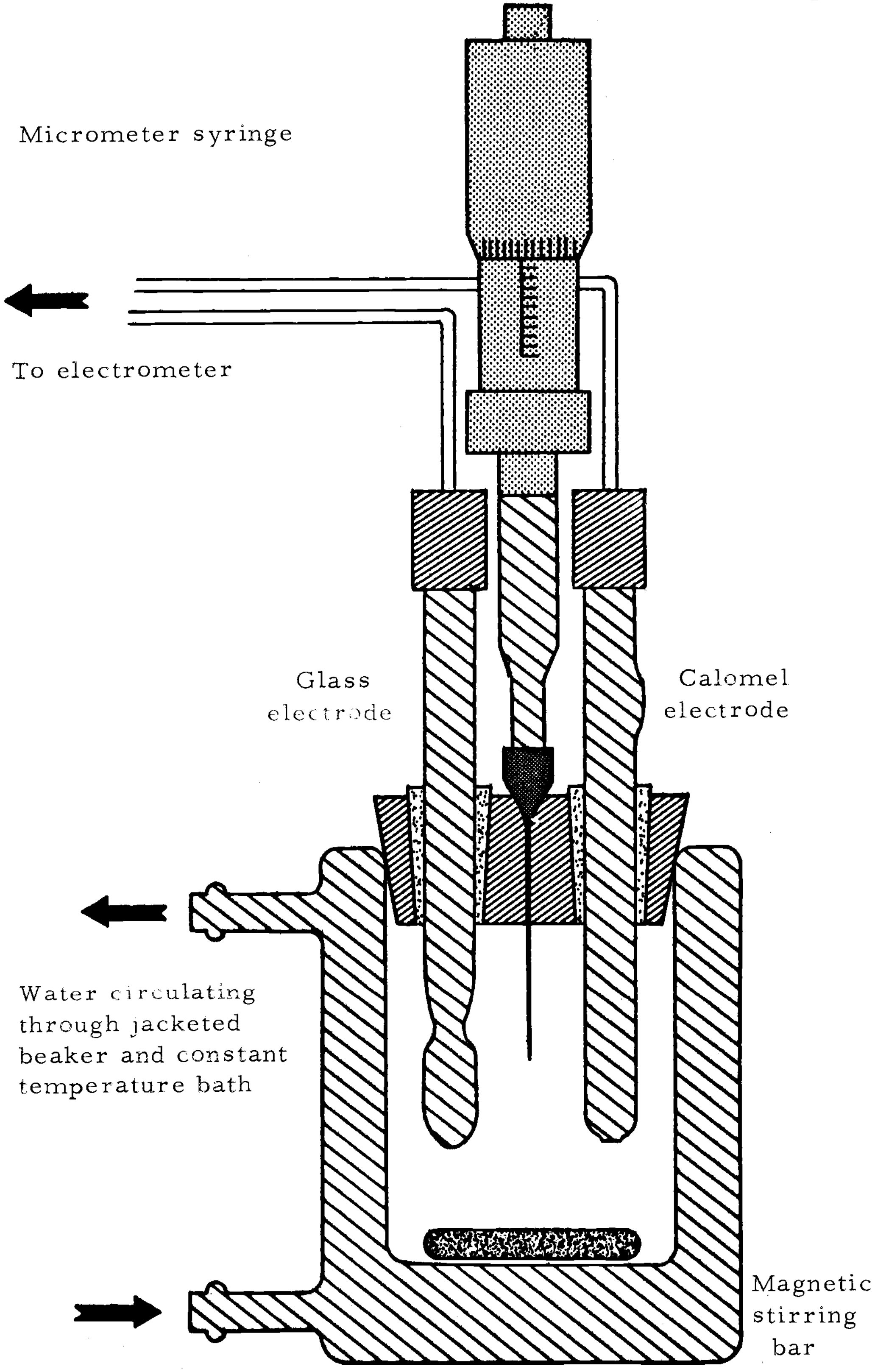

Figure 1. Thermostated beaker with pH electrodes.

meter and recorded with a Varian[5] Model G-11A strip-chart recorder with a sensitivity of 1 millivolt full-scale. The temperature was controlled to ± 0.02° C with an Aminco[6] constant temperature bath (No. 4-8605). Solutions were stirred, prior to all pH measurements, with a magnetic stirrer to assure thermal equilibrium and homogeneity, but the stirring was discontinued during pH measurements in order to reduce the electrical noise. Pick-up was reduced by shielding the thermostated beaker and pH electrodes with a copper screened box. Figure 2 illustrates the instrumentation used.

The electronic circuit is capable of resolving pH measurements to ± 0.0005 pH units (Lebowitz and Laskowski, 1962). However, the observations of Pytkowicz, Kester, and Burgener (in press) indicate that such precision is not presently attainable with glass electrodes in seawater due to the lack of reproducibility of the asymmetry potential. The reproducibility of a glass electrode in seawater is about ± 0.003 pH units, whereas pH measurements with several different glass electrodes are reproducible to only ± 0.006 pH units.

Determination of $1/2(pK'_1 + pK'_2)$

While at a pH of about 5, artificial seawater was equilibrated with CO_2 by stirring in a thermostated beaker open to the atmosphere.

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

[6] American Instrument Co., Inc., 8030 Georgia Avenue, Silver Spring, Maryland.

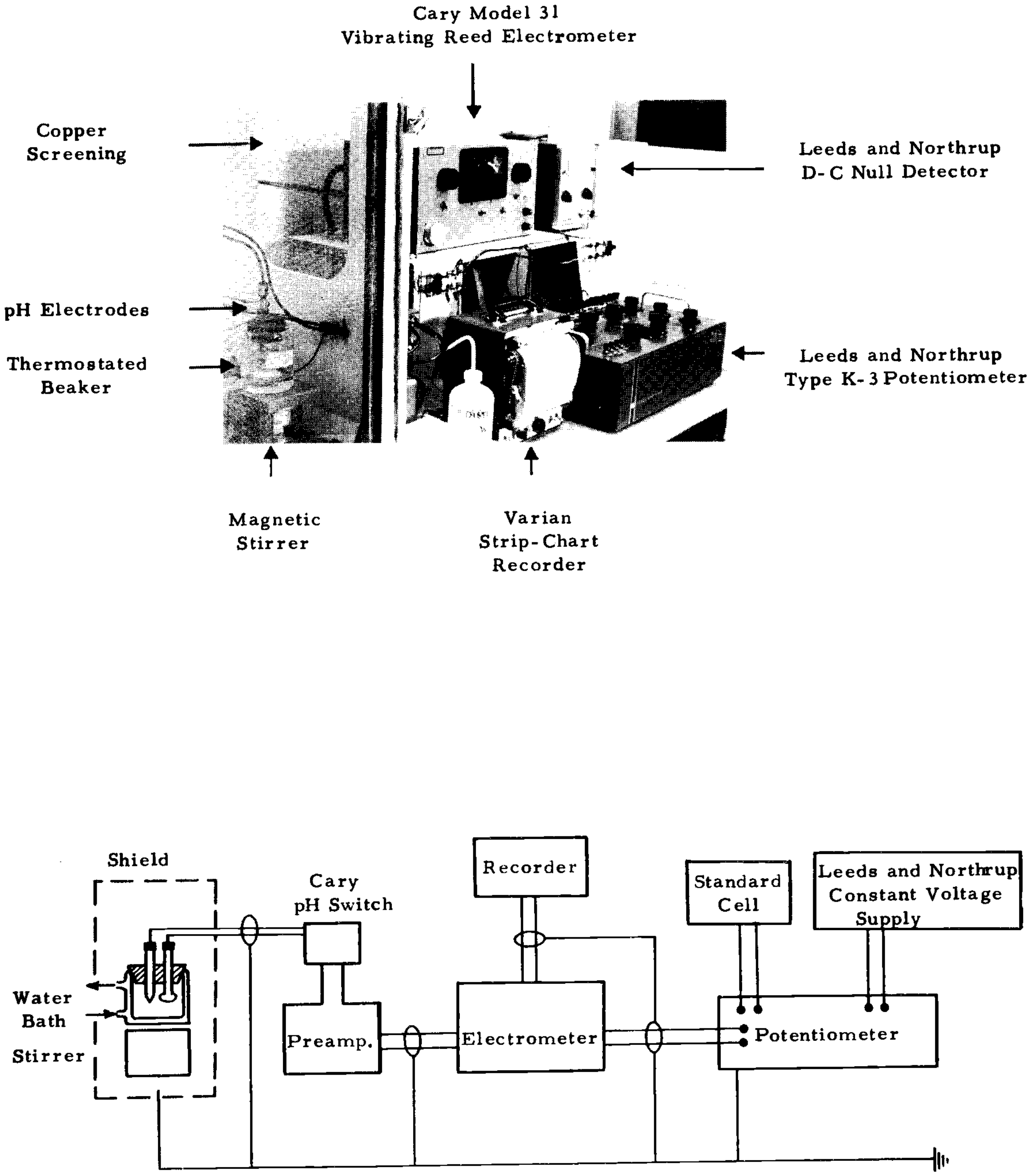


Figure 2. Instrumentation for potentiometric pH measurements.

A 100 ml aliquot was placed in the thermostated beaker with the pH electrodes; its pH was adjusted to the desired value by adding a small amount (0. 1-0. 2 ml) of 0. 10 N HCl. Approximately 0. 07 g of KH_2PO_4 ($5x10^{-3}$ moles/liter) were added to the seawater, and the pH change was measured. Repeated measurements of this type were made until the pH of the seawater was not changed by the addition of KH_2PO_4. This pH was equal to $1/2(pK_1' + pK_2')$.

In practice it was possible to measure this pH value to ± 0. 001 pH units. This is illustrated by the results obtained in five repeated measurements for 36‰ salinity at 20° C (Figure 3). The pH of the artificial seawater was plotted as a function of time, with t denoting the time at which the KH_2PO_4 was added. By properly adjusting the initial pH for successive measurements, it was possible to converge rapidly to the equilibrium pH.

Determination of $1/2(pK_2' + pK_3')$

The determination of $1/2(pK_2' + pK_3')$ was similar to that of $1/2(pK_1' + pK_2')$, but CO_2 transfer was more critical. After equilibrating the artificial seawater with the atmosphere, an aliquot was transferred to the thermostated beaker. The beaker was filled completely and stoppered tightly to eliminate CO_2 exchange. The pH was adjusted to the desired value with CO_2-free NaOH solution, and 0. 07 g of K_2HPO_4 were added to the 200 ml sample (approximately $2x10^{-3}$

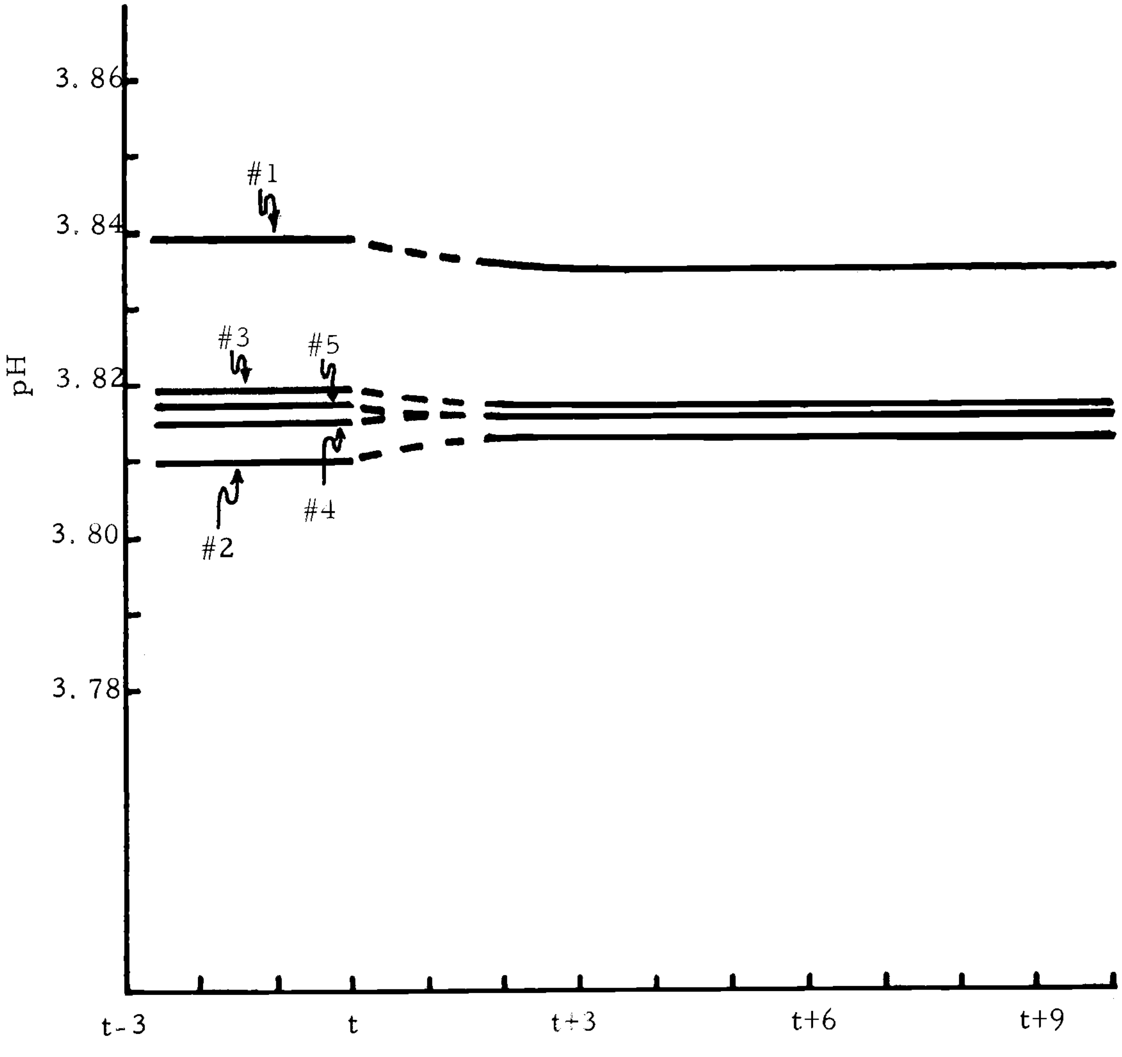


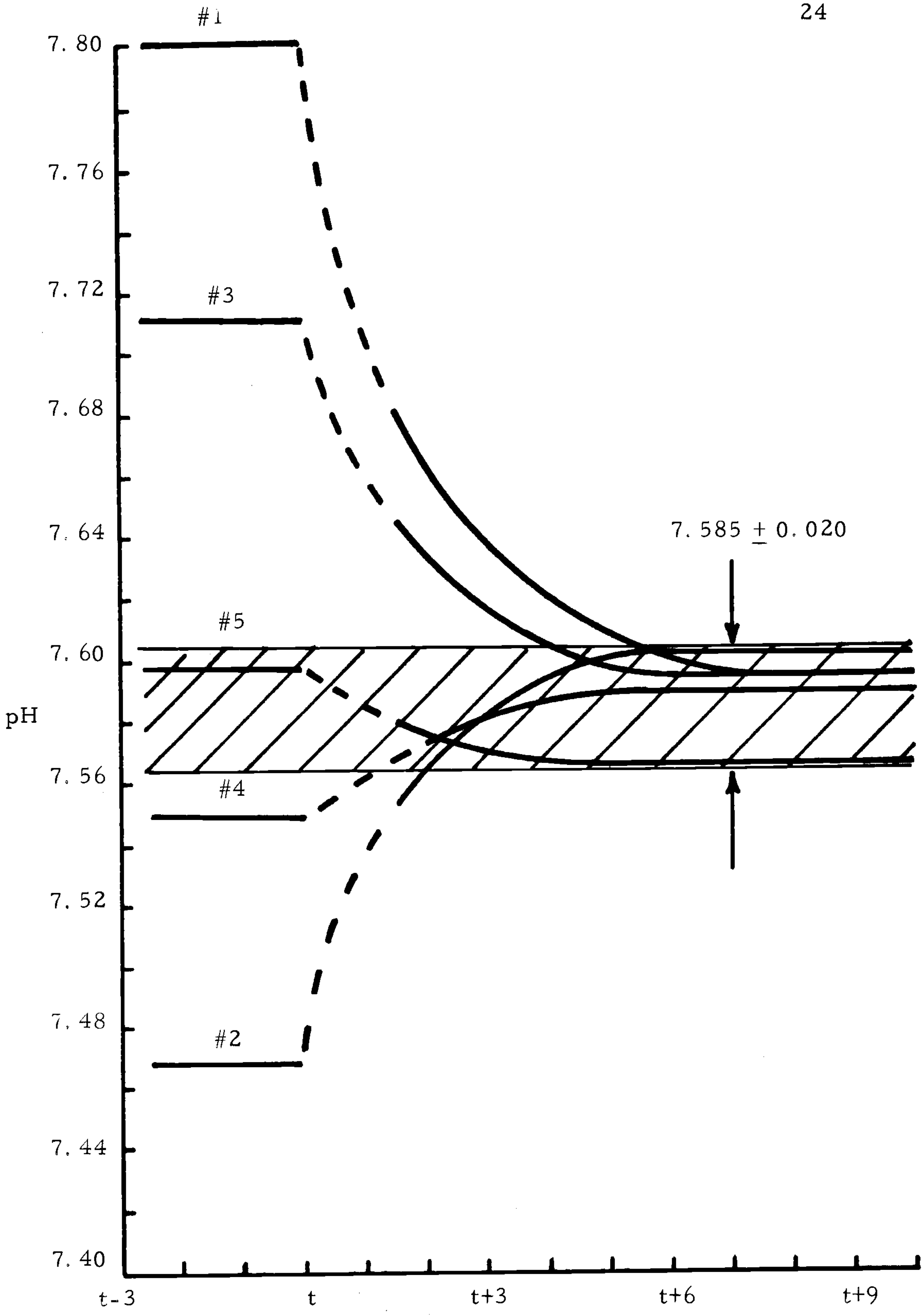
Figure 3. Measurement of $1/2(pK'_1 + pK'_2)$ for 36‰ at 20° C.

moles of K_2HPO_4 per liter of solution). The pH change was measured.

The convergence to the equilibrium pH for K_2HPO_4 was not as precise as for KH_2PO_4. The pH values tended to fall within a band of 0.02 to 0.04 pH units. For example, the pH values of the samples used in determining $1/2(pK'_2 + pK'_3)$ for 33‰ at 15° C were plotted as a function of time (Figure 4). After the addition of K_2HPO_4 the pH values were within the pH band 7.585 ± 0.020, but they did not define a unique value. The tendency for the values to cross over each other indicates that the pH was affected by something other than the phosphate buffer mechanism. At these pH values the pH of the weakly buffered solutions was very sensitive to CO_2 transfer. Even though precautions were taken to minimize CO_2 exchange, there may have been some transfer during or after the addition of K_2HPO_4. To account for the uncertainty in $1/2(pK'_2 + pK'_3)$ the two extreme values of the band 7.585 ± 0.020 were used in the calculation of K'_3. For $1/2(pK'_2 + pK'_3)$ at other temperatures and salinities the uncertainty varied between ± 0.010 and ± 0.020 pH units.

Determination of F(x)

The quantity F(x) was determined by two titrations over the same pH interval. For these measurements 0.1361 g of KH_2PO_4 were added to make 1000 ml of artificial seawater 1.00×10^{-3} M in KH_2PO_4. The pH was adjusted to about 5.6 by adding CO_2-free NaOH solution.



Time in minutes relative to t, the time of addition of K_2HPO_4

Figure 4. Measurement of $1/2(pK'_2 + pK'_3)$ for 33‰ at 15° C.

This seawater solution was stirred in a thermostated beaker, open to the atmosphere, to equilibrate it with atmospheric CO_2.

An aliquot of this solution was carefully transferred to a thermostated beaker for titration; the beaker was filled completely and sealed tightly. The initial pH was measured, and then the sample was titrated over a pH range of about 0.3 pH units with 0.100 N HCl. Another aliquot was titrated over the same pH interval with 0.085 M KH_2PO_4. After each titration the amount of artificial seawater was determined by weighing, and the volume was calculated from Knudsen's Hydrographic Tables (1901) for seawater. From these titrations $F(x) = \frac{z}{y}$, where z was the number of equivalents of HCl to titrate 1000 ml of the artificial seawater over the observed pH interval, and y was the number of moles of KH_2PO_4 to titrate 1000 ml of artificial seawater over the same pH interval.

The titration curve consisted of two segments which were defined by four data points each (Figure 5). Since y and z are determined by the initial and final values of x, the intermediate portions of the titration curve (represented by the broken line in Figure 5) were not required. The individual points were fitted with a smooth curve. In nearly all cases a linear fit was adequate due to the close spacing of the data points. The initial pH values of the two aliquots were the same within ± 0.002 pH units (Table I). The final pH was selected to minimize the amount of interpolation between the data points of the

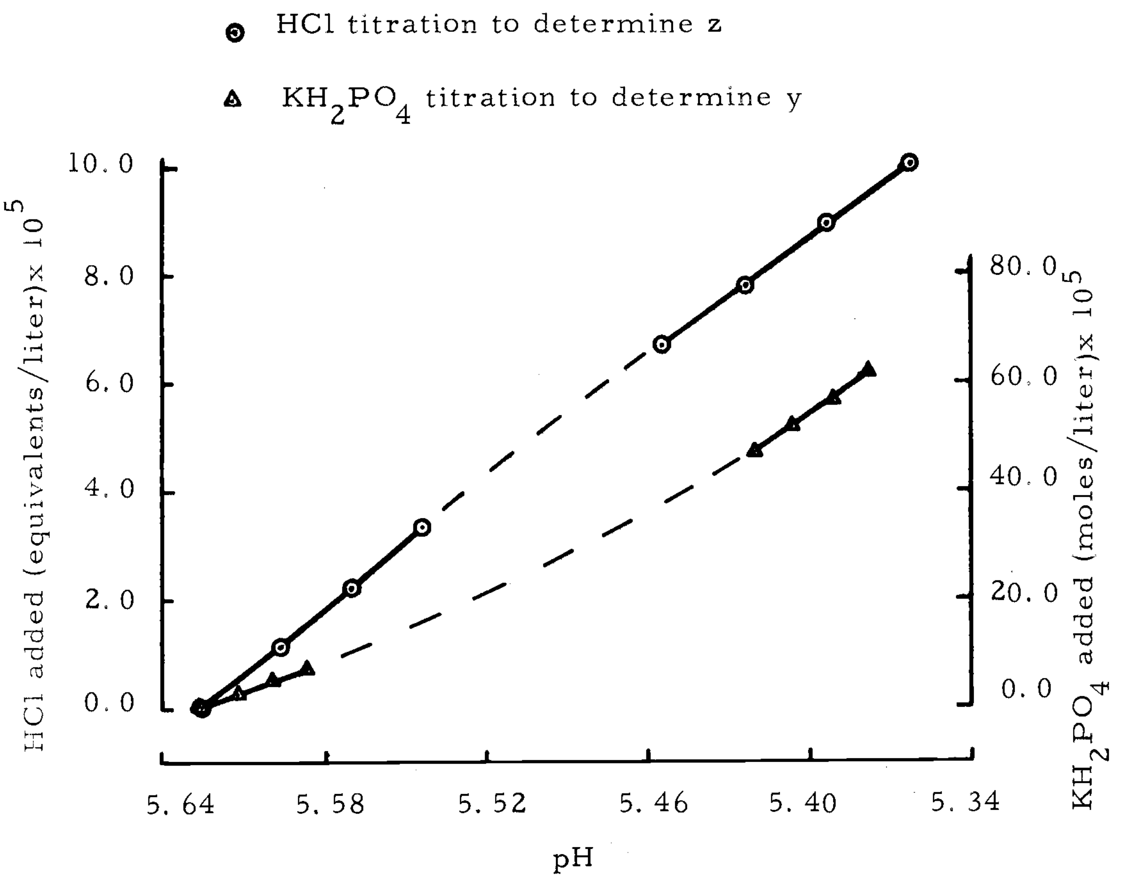


Figure 5. Titration curves for the determination of y and z for 36‰ at 15° C.

Table I. pH of Artificial Seawater Samples Before y-z Titrations.

1	2	3	4	5	6	7	8
T °C	S ‰	$(pH)_{y_1}$	$(pH)_{z_1}$	ΔpH_1	$(pH)_{y_2}$	$(pH)_{z_2}$	ΔpH_2
25	36	5.570	5.567	0.003	5.570	5.572	0.002
25	33	5.717	5.617	0.000	5.618	5.617	0.001
25	30	5.691	5.691	0.000	5.688	5.690	0.002
20	36	5.632	5.633	0.001	5.631	5.633	0.002
20	33	5.496	5.495	0.001	5.496	5.492	0.004
20	30	5.545	5.548	0.003	5.544	5.542	0.002
15	36	5.625	5.624	0.001	5.625	5.625	0.000
15	33	5.588	5.587	0.001	5.586	5.587	0.001
15	30	5.748	5.748	0.000	5.747	5.745	0.002
10	36	5.945	5.949	0.004	5.872	5.874	0.002
10	33	5.695	5.694	0.001	5.693	5.694	0.001
5	36	5.958	5.960	0.002	5.958	5.959	0.001
5	33	6.034	6.032	0.002	6.033	6.032	0.001

Columns 1 and 2: Temperature and salinity of artificial seawater.
Column 3: Initial pH of aliquot for the first y-titration.
Column 4: Initial pH of aliquot for the first z-titration.
Column 5: Absolute difference of columns 3 and 4.
Column 6: Initial pH of aliquot for the second y-titration.
Column 7: Initial pH of aliquot for the second z-titration.
Column 8: Absolute difference of columns 6 and 7.

y and z titrations. A linear interpolation between the points was adequate. The values of K'_1, K'_2, and K'_3 were independent of the value selected for the final pH.

Preparation of Solutions

Reagent Solutions

1. Standard HCl for the determination of z: 0.100 N HCl was prepared from Hellige[7] Certified Reagent Concentrate (No. R-1193 C) by dilution of the concentrate to 1000 ml at 20° C.

2. Standard phosphate solution for the determination of y: Reagent grade Baker and Adamson[8] KH_2PO_4 was dried at 120° C for two hours and cooled in a desiccator before weighing. 11.5678 g of KH_2PO_4 were dissolved in distilled water to make 1000 ml of 0.08500 M KH_2PO_4.

3. KH_2PO_4 for the determination of $1/2(pK'_1 + pK'_2)$: Reagent grade Baker and Adamson KH_2PO_4 was used in the determination of $1/2(pK'_1 + pK'_2)$.

4. K_2HPO_4 for the determination of $1/2(pK'_2 + pK'_3)$: Reagent grade Matheson, Coleman, and Bell[9] K_2HPO_4 was used in the determination of $1/2(pK'_2 + pK'_3)$.

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[7] Hellige, Inc., Garden City, New York.

[8] Allied Chemical, General Chemical Division, Morristown, New Jersey.

[9] Division of Matheson Company, Inc., Norwood, Ohio.

5. pH buffers for the standardization of electrodes: Beckman #14044 (pH 4.01), Beckman #14268 (pH 6.86) and Beckman #97361 (pH 7.413) buffers were used to standardize the pH electrodes. These buffers were standardized, using a glass-calomel electrode pair, against the National Bureau of Standards buffers 186-I-b, 186-II-b (pH 7.413) and 185-d (pH 4.008). The precision of these buffers is ± 0.002 pH units at 25° C (Bates, personal communication).

6. CO_2-free NaOH: CO_2-free NaOH was prepared by bubbling CO_2-free N_2 gas through distilled water for 40 minutes and then adding 0.20 g of reagent grade NaOH to prepare 20 ml of 0.25 M NaOH.

Artificial Seawater

1. The artificial seawater used in this study was based on the formula given by Lyman and Fleming (1940). It was modified by omitting the $NaHCO_3$ and H_3BO_3 in order to maximize the dependence of pH on the phosphate equilibria. The amounts of the various salts added to give 1000 g of solution with a chlorinity of 19‰ are shown below:

Salt	Weight (g/kg)
NaCl	23.477
$MgCl_2$	4.981
Na_2SO_4	3.917
$CaCl_2$	1.102
KCl	0.664
KBr	0.096
$SrCl_2$	0.024
NaF	0.003
Water to 1000.000 g	

2. The following salts were dried and weighed in anhydrous form: NaCl, Na_2SO_4, KCl, KBr, and NaF. The $MgCl_2$, $CaCl_2$, and $SrCl_2$ could not be weighed directly with sufficient accuracy due to their waters of hydration. Concentrated solutions (1-2 M) of these three salts were prepared and standardized by determining the chloride concentration using the Mohr method (Blaedel and Meloche, 1957). The necessary amounts of these solutions to produce the required amounts of $MgCl_2$, $CaCl_2$, and $SrCl_2$ were added volumetrically to the artificial seawater. The densities of these solutions were determined with a Westphal balance to account for the amount of water added to the artificial seawater.

3. The chlorinity of the artificial seawater was verified by determination of Cl^- and Br^- using the Mohr method.

IV. RESULTS

Values of the Apparent Dissociation Constants of Phosphoric Acid

Values of K'_1, K'_2, and K'_3 were determined in artificial seawater of 30‰ salinity at 15, 20, and 25° C. At 33‰ and 36‰ salinity determinations were made at 5, 10, 15, 20, and 25° C. Measurements were also made in 0.680 M NaCl at 20° C to compare the results obtained in a single-salt solution with those obtained in seawater of the same ionic strength.

The calculations are illustrated with the data at 36‰ salinity at 15° C. The values of $1/2(pK'_1 + pK'_2)$, $1/2(pK'_2 + pK'_3)$, and $F(x)$ were obtained as described in the previous chapter. $1/2(pK'_1 + pK'_2) = 3.819 \pm 0.001$ and $1/2(pK'_2 + pK'_3) = 7.652 \pm 0.010$. The maximum and minimum values of $1/2(pK'_1 + pK'_2)$ and $1/2(pK'_2 + pK'_3)$ were used to calculate α and β:

$1/2(pK'_1 + pK'_2) = 3.818$ $\qquad \alpha_1 = 2.312 \times 10^{-8}$

$1/2(pK'_1 + pK'_2) = 3.820$ $\qquad \alpha_2 = 2.291 \times 10^{-8}$

$1/2(pK'_2 + pK'_3) = 7.642$ $\qquad \beta_1 = 5.200 \times 10^{-16}$

$1/2(pK'_2 + pK'_3) = 7.662$ $\qquad \beta_2 = 4.742 \times 10^{-16}$

The initial pH for the determination of y and z was 5.625, and the final pH was taken as 5.390, for which $x = 4.074 \times 10^{-6}$. From the titration with 0.085 M KH_2PO_4, $y_1 = 57.300 \times 10^{-5}$ moles/liter, and from the titration with 0.100 N HCl, $z_1 = 8.864 \times 10^{-5}$ equivalents/liter.

Therefore, $F(x)_1 = \frac{y_1}{z_1} = 0.155$. The determination of F(x) was repeated with another set of titrations over the same pH interval, and a value $F(x)_2 = 0.157$ was obtained.

K'_1 was calculated using a modification of equation (45). Since $\beta F(x)$ and 2β were negligible compared to $x^2 F(x)$ equation (45) may be written as:

$$K'_1 = \frac{\alpha x \{1 - F(x)\} - x^3 \{1 + F(x)\}}{x^2 F(x)} \qquad (49)$$

One value of K'_1 was calculated using α_1, the larger value of α, and $F(x)_1$, the smaller value of F(x). A second value of K'_1 was calculated using α_2 and $F(x)_2$. These two values were $K'_1 = 3.08 \times 10^{-2}$ and $K'_1 = 3.02 \times 10^{-2}$.

Two values of K'_2 were calculated using the larger value of α with the smaller value of K'_1 and the smaller value of α with the larger value K'_1. In the same manner two extreme values of K'_3 were calculated from β and K'_2.

$$K'_2 = \frac{\alpha_1}{3.02 \times 10^{-2}} = 0.76 \times 10^{-6} \text{ and } K'_2 = \frac{\alpha_2}{3.08 \times 10^{-2}} = 0.74 \times 10^{-6}$$

$$K'_3 = \frac{\beta_1}{0.74 \times 10^{-6}} = 0.70 \times 10^{-9} \text{ and } K'_3 = \frac{\beta_2}{0.76 \times 10^{-6}} = 0.62 \times 10^{-9}$$

The same procedure was used for the calculation of K'_1, K'_2, and K'_3 at the other temperatures and salinities. The data used in these calculations are summarized in Tables II and III. Two extreme

Table II. First Set of Data for the Calculation of K_1', K_2', and K_3'.

T $^\circ$C	S ‰	x_1 $\times 10^6$	y_1 $\times 10^5$	z_1 $\times 10^5$	$F(x)_1$	α_1 $\times 10^8$	β_1 $\times 10^{16}$
25.0	36.0	4.677	58.899	9.706	0.1648	2.219	26.791
25.0	33.0	3.908	47.978	8.008	0.1669	2.005	20.323
25.0	30.0	3.420	51.800	9.023	0.1742	1.748	13.489
20.0	36.0	3.532	41.031	9.150	0.2230	2.343	12.882
20.0	33.0	5.129	52.371	7.264	0.1387	2.080	12.590
20.0	30.0	4.677	54.167	6.890	0.1272	1.847	9.333
15.0	36.0	4.074	57.300	8.864	0.1547	2.312	5.200
15.0	33.0	4.677	67.839	8.942	0.1318	2.033	7.413
15.0	30.0	3.020	51.339	9.185	0.1791	1.805	3.631
10.0	36.0	1.910	28.736	7.835	0.2727	1.960	4.446
10.0	33.0	3.373	52.384	8.960	0.1710	1.716	4.426
5.0	36.0	1.660	32.888	9.388	0.2855	1.838	2.793
5.0	33.0	1.355	28.645	8.895	0.3105	1.662	3.006

Table III. Second Set of Data for the Calculation of K'_1, K'_2, and K'_3.

T °C	S ‰	x_2 $x10^6$	y_2 $x10^5$	z_2 $x10^5$	$F(x)_2$	$\hat{\alpha}_2$ $x10^8$	β_2 $x10^{16}$
25.0	36.0	4.677	57.725	9.673	0.1676	2.198	25.591
25.0	33.0	3.908	48.188	8.180	0.1698	1.984	19.410
25.0	30.0	3.420	50.382	9.099	0.1806	1.727	12.878
20.0	36.0	3.532	40.211	9.231	0.2296	2.322	11.751
20.0	33.0	5.129	53.042	8.198	0.1546	2.060	11.480
20.0	30.0	4.677	53.819	7.373	0.1370	1.827	8.511
15.0	36.0	4.074	57.401	9.053	0.1577	2.291	4.742
15.0	33.0	4.677	66.948	8.922	0.1333	2.013	6.166
15.0	30.0	3.020	51.865	9.294	0.1792	1.785	3.311
10.0	36.0	1.799	37.061	10.861	0.2931	1.940	4.055
10.0	33.0	1.585	34.585	10.205	0.2951	1.696	3.855
5.0	36.0	1.660	33.322	9.553	0.2867	1.818	2.547
5.0	33.0	1.355	28.891	9.102	0.3150	1.642	2.742

values for each apparent dissociation constant were calculated. The average of the two values was obtained, and the deviation of the values from the average was taken as the reproducibility of the determination of the apparent dissociation constant. The results are given in Tables IV, V, and VI.

Temperature and Salinity Dependence of the Apparent Dissociation Constants

An examination of Tables IV, V, and VI reveals the variation of the apparent dissociation constants with temperature and salinity. At 5, 10, and 15° C K_1' appears to increase slightly with increasing salinity. K_1' decreases slightly with increasing salinity at 20° C; at 25° C it passes through a maximum between 30‰ and 36‰ salinity. The significance of these trends may be questioned, because in many cases the variations are only slightly greater than the reproducibility of the values. The data for K_1' does not show a consistent trend with temperature. K_2' shows a slight increase with increasing temperature and increasing salinity. K_3' appears to go through a maximum between 30‰ and 36‰ salinity. K_3' increases appreciably as temperature increases.

Table IV. Values of $K_1' \times 10^2$.

Salinity	30.0‰	33.0‰	36.0‰
T °C			
25.0	2.36 ± 0.05	2.52 ± 0.03	2.37 ± 0.03
20.0	2.58 ± 0.11	2.35 ± 0.15	2.26 ± 0.04
15.0	2.72 ± 0.01	2.83 ± 0.02	3.05 ± 0.03
10.0		2.51 ± 0.06	2.67 ± 0.05
5.0		2.68 ± 0.04	2.75 ± 0.01

Table V. Values of $K_2' \times 10^6$.

Salinity	30.0‰	33.0‰	36.0‰
T °C			
25.0	0.74 ± 0.02	0.79 ± 0.01	0.93 ± 0.01
20.0	0.71 ± 0.03	0.88 ± 0.06	1.03 ± 0.02
15.0	0.66 ± 0.01	0.72 ± 0.01	0.75 ± 0.01
10.0		0.68 ± 0.02	0.73 ± 0.02
5.0		0.62 ± 0.01	0.67 ± 0.01

Table VI. Values of $K'_3 \times 10^9$.

Salinity T °C	30.0‰	33.0‰	36.0‰
25.0	1.79 ± 0.08	2.50 ± 0.07	2.80 ± 0.10
20.0	1.26 ± 0.12	1.37 ± 0.15	1.20 ± 0.08
15.0	0.52 ± 0.03	0.95 ± 0.09	0.66 ± 0.04
10.0		0.61 ± 0.06	0.58 ± 0.04
5.0		0.46 ± 0.03	0.40 ± 0.02

V. DISCUSSION OF THE RESULTS

Comparison of the Results With Previous Estimates

Previous estimates, based on several assumptions, of the apparent dissociation constants of H_3PO_4 were discussed in Chapter I. A comparison may be made between these estimates and the results obtained in this study, to evaluate the validity of the assumptions made by earlier workers.

The values of K'_1, K'_2, and K'_3 at 10° C and 33‰ salinity were selected for comparison (Table VII). This temperature and salinity corresponds to the conditions at a few hundred meters depth off southern California (California University, Scripps Institution of Oceanography, 1965) studied by Dietz, Emery, and Shepard (1942) and by Roberson (1965). The values of K'_2 determined in this work and that obtained by Roberson agree within the stated uncertainties. In comparing the results of this work with those of Dietz, Emery, and Shepard, and Richards, _et al._, the agreement between K'_1 and K'_2 indicates that the errors in their extrapolations were not severe. However, K'_3 obtained by extrapolation was 30 times too small. This is probably due to the fact that the linear extrapolation could at best account for ionic strength effects, but did not account for complex formation between PO_4^{3-} and the cations in seawater. This is substantiated by the reasonable agreement between the extrapolated

Table VII. A Comparison of Various Values of the Apparent Dissociation Constants of H_3PO_4.

T °C	S ‰	K'_1 $x10^2$	K'_2 $x10^6$	K'_3 $x10^9$	Source
10	33.0	2.51 ± 0.06	0.68 ± 0.02	0.62 ± 0.10	This work
N. S.[a]	34.4	----	0.8 ± 0.3	----	Roberson (1965)
38	34.4	2.04[b]	0.79	0.017	Dietz *et al.* (1942)[c]
10	$\mu = 0.64$	2.09	0.60	0.015	Richards *et al.* (1965)[d]
20	0.68 M NaCl	2.83 ± 0.08	0.41 ± 0.04	0.010 ± 0.001	This work

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[a] Not specified.

[b] Data of Sendroy and Hastings (1927) for K'_1 was obtained at 18° C.

[c] Obtained by linear extrapolation of data of Sendroy and Hastings (1927) to $\mu = 0.71$

[d] Obtained by linear extrapolation of data of Sendroy and Hastings to $\mu = 0.64$ and corrected to 10° C.

value of K'_3 and our value measured in 0.680 M NaCl.

Effect of Ionic Composition on the Apparent Dissociation Constants

The interactions of an ion in solution may be attributed to nonspecific interactions, which depend only on ionic strength, and to specific interactions, which depend also on the composition of the solution. The results of the previous chapter were used to obtain estimates of the specific interactions for some of the phosphate species in seawater.

From the relationship between activity (a), activity coefficient (γ), and concentration $[A] = \frac{a_A}{\gamma_A}$, the apparent dissociation constants may be written as:

$$K'_1 = \frac{a_{H^+}\, a_{H_2PO_4^-}}{a_{H_3PO_4}} \; \frac{\gamma_{H_3PO_4}}{\gamma_{H_2PO_4^-}} = K_1 \frac{\gamma_{H_3PO_4}}{\gamma_{H_2PO_4^-}} \qquad (50)$$

$$K'_2 = \frac{a_{H^+}\, a_{HPO_4^{2-}}}{a_{H_2PO_4^-}} \; \frac{\gamma_{H_2PO_4^-}}{\gamma_{HPO_4^{2-}}} = K_2 \frac{\gamma_{H_2PO_4^-}}{\gamma_{HPO_4^{2-}}} \qquad (51)$$

$$K'_3 = \frac{a_{H^+}\, a_{PO_4^{3-}}}{a_{HPO_4^{2-}}} \; \frac{\gamma_{HPO_4^{2-}}}{\gamma_{PO_4^{3-}}} = K_3 \frac{\gamma_{HPO_4^{2-}}}{\gamma_{PO_4^{3-}}} \qquad (52)$$

K_1, K_2, and K_3 are the thermodynamic dissociation constants which are independent of the ionic strength and the composition of the solution. Denoting the apparent dissociation constants determined in seawater by $K'_i(SW)$ and those determined in NaCl of the same ionic strength by K_i' (NaCl), and using equations (50), (51), and (52), the following expressions may be obtained:

$$\frac{K_1'(\mathrm{SW})}{K_1'(\mathrm{NaCl})} = \frac{\gamma_{H_3PO_4}(\mathrm{SW})}{\gamma_{H_2PO_4^-}(\mathrm{SW})} \; \frac{\gamma_{H_2PO_4^-}(\mathrm{NaCl})}{\gamma_{H_3PO_4}(\mathrm{NaCl})} \qquad (53)$$

$$\frac{K_2'(\mathrm{SW})}{K_2'(\mathrm{NaCl})} = \frac{\gamma_{H_2PO_4^-}(\mathrm{SW})}{\gamma_{HPO_4^{2-}}(\mathrm{SW})} \; \frac{\gamma_{HPO_4^{2-}}(\mathrm{NaCl})}{\gamma_{H_2PO_4^-}(\mathrm{NaCl})} \qquad (54)$$

$$\frac{K_3'(\mathrm{SW})}{K_3'(\mathrm{NaCl})} = \frac{\gamma_{HPO_4^{2-}}(\mathrm{SW})}{\gamma_{PO_4^{3-}}(\mathrm{SW})} \; \frac{\gamma_{PO_4^{3-}}(\mathrm{NaCl})}{\gamma_{HPO_4^{2-}}(\mathrm{NaCl})} \qquad (55)$$

Since H_3PO_4 is uncharged and should not form ion pairs, it may be assumed that $\frac{\gamma_{H_3PO_4}(\mathrm{SW})}{\gamma_{H_3PO_4}(\mathrm{NaCl})} = 1$. The following ratios were calculated from the data obtained at 20° C in 0.680 M NaCl and in artificial seawater of 33‰ salinity:

$$\frac{\gamma_{H_2PO_4^-}(\mathrm{NaCl})}{\gamma_{H_2PO_4^-}(\mathrm{SW})} = 0.83$$

$$\frac{\gamma_{HPO_4^{2-}}(\mathrm{NaCl})}{\gamma_{HPO_4^{2-}}(\mathrm{SW})} = 1.78$$

$$\frac{\gamma_{PO_4^{3-}}(\mathrm{NaCl})}{\gamma_{PO_4^{3-}}(\mathrm{SW})} = 250$$

$\gamma_{H_2PO_4^-}$ was less in NaCl than in seawater of the same ionic strength. This is similar to the results of Platford (1965) regarding γ_{NaCl} in seawater and NaCl solutions of the same ionic strength. These observations are contrary to what would be expected on the basis of specific and non-specific interactions and may be explained by the following argument. The interactions of a univalent ion in solution are primarily non-specific and therefore mainly dependent on ionic strength rather than on ionic composition. The ionic strength of seawater was calculated from the formula of Lyman and Fleming (1940) which is based on the total concentration of ionic species in seawater. Garrels and Thompson (1962) have estimated that appreciable amounts of divalent ions in seawater exist as complexes. This would reduce the effective ionic strength of seawater, and thereby account for the larger values of $\gamma_{H_2PO_4^-}$ and γ_{NaCl} in seawater than in NaCl solution of the same calculated ionic strength. It may not be valid to compare the ionic strength of seawater calculated from the formula of Lyman and Fleming with the ionic strength of single-salt solutions.

$\gamma_{PO_4^{3-}}$ (NaCl) is 250 times larger than $\gamma_{PO_4^{3-}}$(SW). As a first approximation, one may assume that $\gamma_{PO_4^{3-}}$(NaCl) represents the effect of non-specific interactions and complex formation with Na^+ on the activity of PO_4^{3-} in seawater, while $\gamma_{PO_4^{3-}}$ (SW) represents, in addition, complex formation with Mg^{2+}, Ca^{2+}, Sr^{2+}, and K^+. This means that $\gamma_{PO_4^{3-}}$ is reduced to 0.004 of its value in an NaCl solution by the interaction of PO_4^{3-} with Mg^{2+}, Ca^{2+}, Sr^{2+}, and K^+. Thus, only 0.4% of the available PO_4^{3-} ions are free, while 99.6% are complexed. Similarly, the ratio of $\gamma_{HPO_4^{2-}}$ (NaCl) to $\gamma_{HPO_4^{2-}}$(SW) suggests that 44% of the available HPO_4^{2-} is complexed with these four cations in seawater. The term "available" in the preceding statements refers to that portion of the PO_4^{3-} or HPO_4^{2-} ions in seawater which is not tied up by either non-specific interactions or by complex formation with Na^+.

The preceding treatment was based on the model of seawater presented by Garrels and Thompson (1962). They used the concept of ion-pair formation as the result of specific interactions. This model is a helpful idealization, and it permits an approximate interpretation of the properties of seawater. However, specific and non-specific interactions result primarily from the coulombic forces between charged particles; they may differ only by a matter of degree. These two types of interaction may not be additive and separable. A more realistic analysis of interactions in seawater will require a theory that describes complex concentrated solutions.

Sources of Error

Lyman (1956) has pointed out three sources of errors in determining apparent dissociation constants. One is the effect of using various seawater samples for the determination of a single constant, the second is the effect of titrants on the composition of the sample, and the third is the concurrent use of several techniques that cannot be intercalibrated. The latter problem occurred in the work of Buch et al. (1932) in which the pH was measured using the quinhydrone electrode, the partial pressure of CO_2 was determined gasometrically, and the carbonate alkalinity was measured by titration. The method used in this work was self-consistent, because all measurements were made potentiometrically and with the same pH electrodes. The other two sources of errors cited by Lyman will be examined in detail.

The titrations in this work were performed with a small volume of titrant so that the composition of the seawater was not significantly altered. The titration for determining z was done by adding 0.18 ml of 0.100 N HCl to a 175 ml sample of artificial seawater. During this titration the volume was increased by 0.1% and 1×10^{-4} moles of HCl were added per liter of sample. These changes produced a negligible change in the ionic composition of the seawater. y was determined by adding 1 ml of 0.085 M KH_2PO_4 to 175 ml of artificial seawater. This resulted in a 0.6% increase in volume and the addition of 5×10^{-4} moles of KH_2PO_4 per liter of sample. The KH_2PO_4 increased the ionic strength by about 0.1%, and the increase in volume decreased the ionic strength by about 0.6%. Thus, the ionic strength of the sample decreased by about 0.5% during the determination of y. This decrease in ionic strength corresponds to a 0.16‰ decrease in salinity. From the observed salinity dependence, this would have changed the apparent dissociation constants by less than 1%.

A difference in the composition of the two aliquots used in determining F(x) could introduce errors. The concentrations of major constituents in the artificial seawater were maintained constant by avoiding evaporation and contamination. The chlorinity was measured periodically throughout the experiments and did not vary. The most likely source of error due to the use of separate aliquots would be differences in the CO_2 content of the samples. The theoretical considerations (Chapter II) have shown that the method is not affected by the presence of CO_2, if the concentration of CO_2 remains constant during the determinations of y and z.

Initially, attempts were made to perform the titrations in CO_2-free solutions, but these were unsuccessful--the pH drifted rapidly. The best procedure found was to equilibrate the artificial seawater with atmospheric CO_2, and then draw aliquots for the titrations. The pH of the aliquots prior to titration was taken as an indication of the similarity in CO_2 content of successive samples. The precision of the measurements was about ± 0.002 pH units. Therefore, as long as the difference in the initial pH of the two aliquots used in the determination of F(x) was less than 0.005 pH units, the two aliquots were considered to be identical. This has been shown by Table I (p. 27).

In this work analytical errors may be associated with measurements of the pH, the salinity of the artificial seawater, the concentration of the titrant solutions, and the volume of the titrants added. pH measurements constitute one of the major sources of errors. The primary standards for the pH measurements were National Bureau of Standards buffers. Successive solutions of these buffers are reproducible to ± 0.002 pH units (Bates, personal communication). Beckman buffers were used as secondary standards and were standardized to ± 0.002 pH units relative to the NBS standards. The pH of the test solution was measured relative to the secondary standards with a precision of ± 0.002 pH units. Combining these estimates of probable errors gives $\sqrt{(0.002)^2 + (0.002)^2 + (0.002)^2} = 0.0035$ pH units as the precision of pH measurements in this work. If these pH measurements were compared with those obtained with a different glass electrode, it would be necessary to consider the error of ± 0.006 pH units due to different glass electrodes (Pytkowicz, *et al.* in press).

The chlorinity of the artificial seawater was determined with a precision of ± 0.04 g/kg; therefore the salinity was precise to within ± 0.07‰. All weighings and volumetric measurements in preparing solutions were performed to limit the error in the calculation of the solution concentration to 0.1%. The titrations were performed with a Cole-Parmer[10] (7844) syringe with a 2 ml delivery and a

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[10] Cole-Parmer Instrument and Equipment Co., 7330 North Clark Street, Chicago, Illinois.

micrometer scale graduated in 0.002 ml divisions (Figure 1). The syringe was calibrated with distilled water and was accurate to ± 0.001 ml which assured that errors due to titrant volume measurement did not exceed 0.5%.

The propagation of these errors through the experimental procedure cannot be meaningfully calculated. The calculated values of the apparent dissociation constants depend on two pH measurements for α and β, a pH measurement for x at the end of each titration, and pH measurements for the interval over which y and z are determined. To calculate the propagation of random errors, the errors must be independent; this is not the case for x, y, and z. The uncertainty of each of these measurements may be estimated, but the best indication of the precision of the final results was obtained from the reproducibility of repeated evaluations of the apparent dissociation constants.

Validity of the Experimentally Obtained Results for Seawater

Some assumptions are implied in applying to natural seawater, values of the apparent dissociation constants which were measured in artificial seawater. The validity of the results depends on the degree to which the experimental system approximates the natural system. There are several advantages in using artificial seawater for physicochemical studies; biological activity is minimized, and the solutions are of known composition and may be prepared reproducibly.

The physicochemical properties of inorganic phosphate in artificial and natural seawaters should be very nearly the same. The specific and non-specific interactions of phosphate with the major constituents of seawater are accounted for by measurements in artificial seawater. It is possible that additional specific interactions are important in some aspects of the chemistry of phosphate in seawater. For example, the adsorption of inorganic phosphate on organic matter (Armstrong, 1965) may be important at the air-sea interface. The presence of minor constituents such as iron (Cooper, 1948) may also introduce additional specific interactions. The apparent dissociation constants determined in this work are valid for environments in which phosphate is primarily affected by the major constituents of seawater. They may not be valid for environments where the composition of the seawater may be significantly modified, such as in the interstitial water of sediments.

The total phosphate concentration of the experimental solutions was 10^{-3} M, whereas natural seawater is 10^{-6} M in phosphate. It will be shown that the high phosphate concentration did not significantly alter the specific and the non-specific interactions of phosphate in seawater.

The addition of 1×10^{-3} M KH_2PO_4 increased the ionic strength by 0.4%, but the absence of $NaHCO_3$ and H_3BO_3 reduced the ionic strength by 0.3%. Thus, non-specific interactions were not significantly altered by the enrichment of the solution with phosphate.

Comparison of the apparent dissociation constants in NaCl and artificial seawater of the same ionic strength revealed that complexing was most significant for K'_3; therefore, the effect of high phosphate concentrations on specific interactions will be examined for K'_3. Similar analyses can be used for K'_1 and K'_2. The following considerations are based on an extension of the analysis made by Weyl (1961) for carbonate complexes.

The total orthophosphate ion concentration ($[PO_4^{3-}]_T$) may be expressed as the sum of the uncomplexed ($[PO_4^{3-}]_U$) and the complexed ($[PO_4^{3-}]_C$) orthophosphate ions.

$$[PO_4^{3-}]_T = [PO_4^{3-}]_U + [PO_4^{3-}]_C \qquad (56)$$

Since Mg^{2+} and Ca^{2+} are the most abundant divalent cations and hence, most significant in complexing:

$$[PO_4^{3-}]_C = [MgPO_4^-] + [CaPO_4^-] \qquad (57)$$

The Mg^{2+} and Ca^{2+} complexes with PO_4^{3-} may be characterized by the equilibrium constants:

$$K_{MgPO_4^-} = \frac{[Mg^{2+}]\ [PO_4^{3-}]_U}{[MgPO_4^-]} \qquad (58)$$

$$K_{CaPO_4^-} = \frac{[Ca^{2+}]\ [PO_4^{3-}]_U}{[CaPO_4^-]} \qquad (59)$$

which depend only on non-specific interactions, since they are defined in terms of the uncomplexed PO_4^{3-} concentration. In this notation $K_3' = \frac{x[PO_4^{3-}]_T}{[HPO_4^{2-}]_T}$. Another apparent dissociation constant which depends only on non-specific interactions may be defined as

$$K_3'' = \frac{x[PO_4^{3-}]_U}{[HPO_4^{2-}]_U}.$$

Taking the ratio K_3'/K_3'' and introducing equation (56):

$$\frac{K_3'}{K_3''} = \frac{[PO_4^{3-}]_T}{[HPO_4^{2-}]_T}\ \frac{[HPO_4^{2-}]_U}{[PO_4^{3-}]_U} = \left\{1 + \frac{[PO_4^{3-}]_C}{[PO_4^{3-}]_U}\right\} \frac{1}{1 + \frac{[HPO_4^{2-}]_C}{[HPO_4^{2-}]_U}} \qquad (60)$$

Substituting (57) into (60) and using similar expressions for the HPO_4^{2-} species:

$$\frac{K_3'}{K_3''} = \left\{1 + \frac{[MgPO_4^-]}{[PO_4^{3-}]_U} + \frac{[CaPO_4^-]}{[PO_4^{3-}]_U}\right\} \frac{1}{1 + \frac{[MgHPO_4]}{[PO_4^{3-}]_U} + \frac{[CaHPO_4]}{[PO_4^{3-}]_U}} \qquad (61)$$

Substituting equations (58) and (59) into (61):

$$\frac{K_3'}{K_3''} = \left\{1 + \frac{[Mg^{2+}]}{K_{MgPO_4^-}} + \frac{[Ca^{2+}]}{K_{CaPO_4^-}}\right\} \frac{1}{1 + \frac{[Mg^{2+}]}{K_{MgHPO_4}} + \frac{[Ca^{2+}]}{K_{CaHPO_4}}} \qquad (62)$$

Therefore, the ratio K_3'/K_3'' will remain constant as long as $[Mg^{2+}]$ and $[Ca^{2+}]$ are not significantly reduced by the complexing with

PO_4^{3-}. The total phosphate was $1x10^{-3}$ M and approximately 5% or at pH 8 $5x10^{-5}$ M was available as PO_4^{3-}. This is very small compared to $[Mg^{2+}] = 5x10^{-2}$ M and $[Ca^{2+}] = 1x10^{-2}$ M. Thus, increasing the total phosphate from 10^{-6} M to 10^{-3} M did not significantly alter K'_3.

These apparent dissociation constants were determined at atmospheric pressure, so they are of limited use in describing the phosphate equilibria at high pressures. Techniques presently being developed by Dr. R. M. Pytkowicz for the effect of pressure on equilibrium constants might eventually be applied to the apparent dissociation constants of phosphoric acid in seawater.

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