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The Determination of the Apparent Dissociation Constants for Arsenic Acid in Seawater

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THE DETERMINATION OF THE APPARENT DISSOCIATION
CONSTANTS FOR ARSENIC ACID IN SEAWATER

BY

DOUGLAS H. LOWENTHAL

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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1976

THESIS ABSTRACT

The object of this study was the determination of the first, second and third apparent dissociation constants for arsenic acid in seawater, based on a free molal hydrogen scale. This was accomplished through potentiometric monitoring of acid-base titrations of arsenate in artificial seawater and data analysis using a computerized curve fitting technique. Experiments were carried out at atmospheric pressure over a range of salinities and temperatures. Constants determined in artificial seawater and sodium chloride solutions at equal effective ionic strengths were compared in order to evaluate the effects of specific ion interactions on the dissociation of arsenic acid in seawater. The results suggest that about 25% of the reactive arsenate in seawater is ion paired with cations other than sodium. A comparison of arsenic acid with its analogue, phosphoric acid, revealed the latter as the more dissociated under typical seawater conditions. A series of conversion factors was determined so that these constants could also be applied in conjunction with pH measurements in seawater based on the NBS activity scale.

This thesis is dedicated to Dr. Thomas R. P. Gibb
of the Department of Chemistry at Tufts University.

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PREFACE

This thesis has been written following the manuscript plan. The manuscript is intended for publication; it is written in the style of the Journal of Marine Research.

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INTRODUCTION

A number of studies have been made on the concentration and distribution of arsenate and arsenite in the marine environment (Johnson and Pilson 1972; Ishibashi et al. 1960; Gohda 1974). However, no measurements have yet been made of the dissociation constants of arsenic acid in seawater.

Arsenic acid, H_3AsO_4 , is a weak acid whose chemical behavior in seawater most likely parallels that of phosphoric acid. Sillen (1963) suggested that HAsO_4^{2-} may be the major species in seawater. Although thermodynamic dissociation constants for arsenic acid have been determined by Flis et al. (1959), application of these to seawater is not practical since the appropriate activity coefficients are unknown and can be only poorly estimated for use with multi-electrolyte solutions of high ionic strength.

Apparent constants have been used to describe acid-base equilibria in seawater for carbonic (Lyman 1956; Hansson 1973) and phosphoric acids (Kester and Pytkowicz 1967). The determination of the apparent dissociation constants for arsenic acid in seawater will serve as a basis for studying arsenate ion pairing and solubility, important for evaluating the effects of arsenic waste disposal. An understanding

of the significance and action of arsenate in the biosphere is desirable since it acts as a competitive inhibitor of phosphate uptake in some organisms (Blum 1966) and is also concentrated in the marine food chain (Leatherland and Burton 1974).

The object of this study was the determination of the first, second and third apparent dissociation constants of arsenic acid in artificial seawater systems at various salinities and temperatures, based on a free molal hydrogen scale. Constants were also determined in a simple salt medium to make possible an evaluation of ion pairing between arsenate species and the major cations in seawater.

THEORY

Derivation

Definitions and abbreviations are given in Table 1.

The apparent dissociation constants for arsenic acid are defined as follows for the accompanying reactions.



A free molal hydrogen scale is used to describe the hydrogen ion concentration in these equilibria. This has the advantage over the NBS scale of being thermodynamically better defined for potentiometric measurements of pH in seawater (Bates and Macaskill 1975).

The concentrations of the protonated species, H_1A , can be derived from (1), (2) and (3).

$$(HA) = \frac{[H] (A)}{K_3'} \quad (4)$$

Table 1.--Definitions, abbreviations and symbols.

-
1. $(A) = (AsO_4^{3-}) = [A] (1 + K_{MgA}^* [Mg^{2+}] + K_{CaA}^* [Ca^{2+}] + \dots)$
 2. $(HA) = (HASO_4^{2-}) = [HA] (1 + K_{MgHA}^* [Mg^{2+}] + K_{CaHA}^* [Ca^{2+}] + K_{NaHA}^* [Na^+] + \dots)$
 3. $(H_2A) = (H_2AsO_4^-) = [H_2A] (1 + K_{NaH_2A}^* [Na^+] + K_{MgH_2A}^* [Mg^{2+}] + \dots)$
 4. $(H_3A) = (H_3AsO_4)$
 5. $A_1 = H_2O$
 6. $A_2 = K_w (1 + K_{MOH}^* [M^{2+}])$
 7. $A_3 = 1 + K'_{HSO_4^-} (SO_4^{2-}) + K'_{HF} (F^-)$
 8. ASW = artificial seawater
 9. $ASW_{(As)}$ = artificial seawater to which KH_2AsO_4 has been added
 10. A_t = total arsenate or KH_2AsO_4 added, moles/kg (water)
 11. B = an algebraic variation on K' (see equations 7, 8 and 9)
 12. C = concentration of NaOH or HCl solution, (N)
 13. c = micrometer correction
 14. DDW = doubly deionized water

Table 1.--(Continued)

-
15. E_s = potential in standard HCl or phthalate buffer
 16. E_x = potential in test solution
 17. $F = (HA) + 2(H_2A) + 3(H_3A)$, the total hydrogen associated with arsenate
 18. g = a free activity coefficient, dependent on T , P and ionic strength, but independent of medium composition
 19. $[H_2O]$ = water formed by combination of H^+ and OH^- when NaOH is added to test solution
 20. H_o = total initial hydrogen concentration, as defined by equation 17
 21. $[H]$ = free hydrogen ion, H^+ , concentration (including such forms as H^+ , H_3O^+ , $H_9O_4^+$, etc.)
 22. $[H]_o$ = initial free hydrogen ion concentration
 23. $[H]_s$ = free hydrogen ion concentration in standard HCl solution
 24. K = a thermodynamic dissociation constant = $f(T,P)$ only
 25. K^* = a "free" concentration dissociation constant = $f(T,P,\mu)$ defined for a complex of cation M and anion N such that $K^*_{MN} = [MN]/[M][N]$ and $[MN] = K^*_{MN}[M][N]$
 26. K' = an apparent dissociation constant = $f(T,P,S \text{ } ^\circ/\text{oo})$
 27. m = concentration, moles/kg (water)
 28. $[MOH]$ = sum of $[MgOH^+]$, $[CaOH^+]$ and $[SrOH^+]$

Table 1.--(Continued)

-
29. mv_0 = potential in ASW before addition of KH_2AsO_4 or titrant
30. N = concentration, equivalents/liter
31. $[OH]$ = free hydroxide ion, OH^- , concentration
32. $OH_{(AS)}$ = amount of NaOH titrant added to $ASW_{(AS)}$, (m)
33. $OH_{(n)}$ = amount of NaOH titrant added to ASW without arsenate (m)
34. pH = a general term for $-\log$ (hydrogen concentration)
35. $p[H]$ = $-\log[H]$
36. P = pressure
37. T = temperature
38. V_A = ml acid added
39. V_B = ml base added
40. wt_0 = initial water content by weight (g)
41. X = an empirical quantity related to hydrogen activity when pH measurements are made in concentrated electrolytes
42. $Y = f(B_1, B_2, B_3, [H])$, see eq. 24
43. Z = moles KH_2AsO_4 added
44. γ = a total activity coefficient
45. μ = effective ionic strength
46. $()$ = molal concentration equal to free plus ion paired species
47. $[]$ = molal "free" concentration
-

$$(H_2A) = \frac{[H]^2 (A)}{K_2' K_3'} \quad (5)$$

$$(H_3A) = \frac{[H]^3 (A)}{K_1' K_2' K_3'} \quad (6)$$

For simplification, let:

$$B_1 = (K_3')^{-1} \quad (7)$$

$$B_2 = (K_2' K_3')^{-1} \quad (8)$$

$$B_3 = (K_1' K_2' K_3')^{-1}. \quad (9)$$

Then, from (7) - (9), (4) - (6) become

$$(HA) = B_1 (A) [H] \quad (10)$$

$$(H_2A) = B_2 (A) [H]^2 \quad (11)$$

$$(H_3A) = B_3 (A) [H]^3. \quad (12)$$

The total arsenate, A_T , is

$$A_T = (A) + (HA) + (H_2A) + (H_3A) \quad (13)$$

and from (10) - (12),

$$A_T = (A) (1 + B_1 [H] + B_2 [H]^2 + B_3 [H]^3). \quad (14)$$

By definition (Table 1),

$$F = (HA) + 2(H_2A) + 3(H_3A). \quad (15)$$

Substituting (10) - (12) in (15), factoring out (A) and combining with (14),

$$F = A_T \left(\frac{B_1 [H] + 2B_2 [H]^2 + 3B_3 [H]^3}{1 + B_1 [H] + B_2 [H]^2 + B_3 [H]^3} \right). \quad (16)$$

A batch of ASW, carbonate and borate free, is adjusted with concentrated HCl to a $p[H]_0 \approx 3$. At this $p[H]$, $[OH]$ and $[MOH]$ are quantitatively insignificant. An aliquot is withdrawn with the following total hydrogen concentration:

$$H_O = [H] + (HSO_4^-) + (HF). \quad (17)$$

Enough KH_2AsO_4 is added to bring the solution to about 1×10^{-3} m in arsenate. From (16) and (17), the total hydrogen in this sample, now denoted $ASW_{(As)}$, is

$$H_O + 2A_T = [H] + (HSO_4^-) + (HF) + F. \quad (18)$$

As titration with 1N NaOH proceeds, total hydrogen decreases due to the combination of H^+ and OH^- to form water. The amount of hydroxide added through the i^{th} addition can be accounted for as follows:

$$OH_{(As)i} = [OH]_i + [MOH]_i + [H_2O]_i \quad (19)$$

rearranging (19),

$$[H_2O]_i = OH_{(As)i} - [OH]_i - [MOH]_i. \quad (20)$$

From (18) and (20), the total hydrogen after the i^{th} addition is equal to

$$\begin{aligned} H_O + 2A_T - OH_{(As)i} + [OH]_i + [MOH]_i = \\ [H]_i + (HSO_4^-)_i + (HF)_i + F_i. \end{aligned} \quad (21)$$

To a second aliquot from the batch ASW, $OH_{(n)i}$ is added to bring the free hydrogen ion concentration to the value of $[H]_i$ in (21). The total hydrogen in this second system is now

$$H_O - OH_{(n)i} + [OH]_i + [MOH]_i = [H]_i + (HSO_4^-)_i + (HF)_i. \quad (22)$$

Subtracting (22) from (21),

$$2A_T - OH_{(As)i} + OH_{(n)i} = F_i, \quad (23)$$

since, as both systems are at the same pH, $[H]$, (HSO_4^-) , (HF) , $[MOH]$ and $[OH]$ in each will be the same.

With both systems at the same pH, a dimensionless function $Y = f(B_1, B_2, B_3, [H])$ can be defined by combining (16) and (23) such that:

$$Y = \frac{2A_T - OH_{(As)} + OH_{(n)}}{A_T} = \frac{(B_1[H] + 2B_2[H]^2 + 3B_3[H]^3)}{(1 + B_1[H] + B_2[H]^2 + B_3[H]^3)} \quad (24)$$

The ASW_(As) system is titrated to about $p[H] = 9$ and values are obtained through about 30 additions in total, for $OH_{(As)}$ and $[H]_{(As)}$. To calculate the empirical value for Y at each point, it is necessary to titrate the ASW system without arsenate over the same range but not necessarily to the same $p[H]$ values. The relationship between $OH_{(n)}$ and $[H]_n$ is adequately described by the equation,

$$OH_{(n)} = A_1 + A_2/[H]_n - A_3[H]_n \quad (25)$$

(where A_1 , A_2 and A_3 are defined in Table 1).

The regression constants, A_1 , A_2 and A_3 were obtained and $OH_{(n)}$ calculated for each $[H]_{As}$.

The ASW_(As) titration was done on two aliquots and $OH_{(n)}$ values from one titration applied to each replicate.

A Fortran computer program entitled, "Least Squares Estimation of Non-Linear Parameters," or, NLIN-2,

(Marquardt 1963) was used to solve (25) and (24) for the requisite parameters. The program is a revision of Share Distribution No. 1428 by T. Baumeister, III, Donald W. Marquardt, J. Ann Sheldon and Ruby M. Stanley. Through iterative modification of initial estimates for A_1 , A_2 , A_3 , and B_1 , B_2 and B_3 , NLIN-2 calculated the least-squares best fit to the non-linear equations (25) and (24) using data sets $OH_{(n)i}$, $[H]_{ni}$ and y_i , $[H]_{(As)i}$ respectively. The resultant values for B_1 , B_2 and B_3 were converted to K'_1 , K'_2 and K'_3 by rearrangement and substitution in (7) - (9).

The Free Molal Hydrogen Scale

Use of a free molal hydrogen scale allows for the direct measurement of $p[H]$ in artificial seawater (ionic strength = μ), provided that the glass electrode is calibrated in a solution of equal ionic strength and known $p[H]$, and is based on the assumptions that the free activity coefficient of hydrogen is independent of ionic composition and is invariant as a function of $p[H]$ in an electrolyte solution at an ionic strength similar to that of seawater. A strict interpretation requires that the liquid junction potential of the calomel reference electrode is stabilized in a solution at high ionic strength and that the residual liquid junction potential between a NaCl solution and ASW of the same ionic strength is negligible or zero. These assumptions are discussed in Bates and Macaskill (1975) and

are probably valid for experimental determinations of $p[H]$.

The standard state on this scale should be defined for any temperature and pressure as hydrogen ion at unit activity and molality in pure water.

MATERIALS AND METHODS

The pH was measured with a Corning glass pH electrode (cat. #476022) - calomel reference electrode with ceramic junction (cat. #475109) pair, by converting the potential measured with a Corning 112 digital pH meter with 0.1 mv resolution capacity, using the formula,

$$p[H]_x = p[H]_s + \frac{E_x - E_s}{S} \quad (26)$$

where S is the Nernstian slope of the glass electrode.

The electrodes were standardized before each experiment by preparing a standard of known HCl concentration in a CO₂ free NaCl solution of equal effective ionic strength (Kester 1974) to that of the ASW to be titrated. p[H]_s was calculated from the formula,

$$p[H]_s = -\log \left[\frac{V_A \times C_{HCl}}{wt_O + [V_A \times 0.95 \times c]} \right] \quad (27)$$

The factor 0.95 is used because this was the approximate fraction of water by weight in the HCl standard: E_s was also measured in 0.05 m phthalate buffer for calibration on the NBS scale.

The temperature was maintained to better than 0.05°C with a Beckman Thermocirculator (model 1818, cat. #181800)

with cooling accessory and 250 ml capacity thermostated beakers.

All solutions were pre-acidified and bubbled with nitrogen for 1/2 hour to remove CO_2 . Nitrogen was passed over solutions during experiments to prevent solution of atmospheric CO_2 . Stirring with a magnetic stirrer was maintained for the duration of an experiment.

Artificial seawater was prepared according to the formula used by Kester (1966). The salinity was checked against Copenhagen water using an inductive salinometer. The initial salinity of an ASW stock solution was 40.016 ± 0.001 ‰. Dilutions of this stock solution to salinities of 35, 30 and 20 ‰ were made gravimetrically with DDW. All salts were reagent grade and were weighed to 0.0001 g.

Standard HCl was prepared by diluting concentrated HCl with DDW to about 1 N and standardizing potentiometrically against standard grade Na_2CO_3 . The NaOH titrant was prepared from Baker CO_2 -free 1 N "Dilute-It" and calibrated potentiometrically against standard grade potassium acid phthalate. The titrant was stored in a specially constructed polyethylene container, under nitrogen, protected by ascarite and surrounded by about an inch of paraffin wax, to maintain the solution as CO_2 -free as possible.

Titrations and standardization were done using 2 ml and 0.2 ml capacity micrometer syringes (Gilmont) fitted

with small bore Teflon tubing. The HCl and NaOH solutions were calibrated using the syringes with which each would later be used; all syringes were also calibrated gravimetrically with DDW so that volume and weight corrections could be made.

EXPERIMENTAL PROCEDURE

Three titrations, two with arsenate and one without, were done to generate K_1' , K_2' and K_3' for each test salinity and temperature. Aliquots of about 140 g were drawn from a pre-acidified batch of ASW (to insure the same $[H]_0$ for each) purged with nitrogen and weighed into a thermostated beaker. About 1×10^{-3} g KH_2AsO_4 was carefully added to each of the two aliquots, and titrations to about $p[H] = 9$ were carried out with about 30 evenly spaced additions of base. The ASW without arsenate was titrated with about 20 additions over the same $p[H]$ range. The function, Y , was calculated through each $ASW_{(As)}$ titration point (i), using a Monroe 1860 programmable calculator, from the formula:

$$Y_i = \left(\frac{2000Z - V_{Bi} C_{NaOH}}{wt_0 + [V_{Bi} \times c \times 0.98]} + OH_{[n]i} \right) \left(\frac{wt_0 + [V_{Bi} \times c \times 0.98]}{1000 Z} \right) \quad (28)$$

The factor 0.98 is used because this was the approximate fraction of water by weight in the NaOH titrant. Using NLIN-2, values of B_1 , B_2 and B_3 were calculated for the replicate $ASW_{(As)}$ titrations, and from these, using (7) - (9), K_1' , K_2' and K_3' were calculated and averaged. The precision was taken as one-half the difference between replicate values.

RESULTS AND DISCUSSION

Salinity and Temperature Dependence

Values for K_1' , K_2' and K_3' were determined in ASW at 25°C and 30°C at salinities of 40, 35, 30 and 20 ‰, at 15° at salinities of 35, 30, and 20 ‰, at 5°C at salinities of 35 and 20 ‰ and at 30° in 0.6733 m NaCl. Values for K_1' , K_2' and K_3' appear in Tables 2 through 4.

Temperature and salinity effects on the dissociation of arsenic acid were significant but not entirely consistent. K_1' decreased with increasing temperature at salinities of 20, 30 and 35 ‰, but at 40 ‰ the trend was reversed. K_2' showed no clear temperature dependence. K_3' appeared to increase with increasing temperature at all experimental salinities.

At 4°C the value of K_1' was less at 35 ‰ than at 20 ‰, but at 15°C the difference was reversed. K_2' went through a maximum value at 30 ‰ at 25°C and appeared to increase with increasing salinity at 30°C. K_3' appeared to increase from 20 ‰ to 35 ‰ at all temperatures but due to the uncertainty in K_3' , it is not clear whether or not it actually decreased between 35 and 40 ‰ salinity.

There is some overlap in the equilibria of a tribasic

Table 2.--The first apparent dissociation constant for arsenic acid ($K_1' \times 10^3$).

T°C	Salinity (‰)			
	40	35*	30	20
5		11.70±0.03		12.04±0.04
15		11.40±0.33	10.67±0.02	10.29±0.05
25	9.32±0.07	10.08±0.26	10.42±0.02	9.73±0.13
30	9.93±0.10	8.95±0.06	8.90±0.17	8.66±0.02

*The value at 30°C in 0.6733 m NaCl (equivalent in ionic strength to 35 ‰ salinity) was 9.58±0.08.

Table 3.--The second apparent dissociation constant for arsenic acid ($K_2' \times 10^7$).

T°C	Salinity (‰)			
	40	35*	30	20
5		6.47±0.05		5.18±0.11
15		7.01±0.26	6.38±0.02	5.63±0.08
25	7.43±0.02	7.34±0.22	7.36±0.17	5.40±0.004
30	8.05±0.24	7.28±0.04	6.92±0.17	5.84±0.03

*The value at 30°C in 0.6733 m NaCl (equivalent in ionic strength to 35 ‰ salinity) was 4.94±0.03.

Table 4.--The third apparent dissociation constant for arsenic acid ($K_3' \times 10^{10}$).

T°C	Salinity (‰)			
	40	35*	30	20
5		0.85±0.01		0.58±0.07
15		1.05±0.13	0.83±0.08	0.82±0.11
25	1.57±0.02	1.61±0.20	1.38±0.20	0.74±0.03
30	1.91±0.36	2.02±0.15	1.75±0.001	1.30±0.06

*The value at 30°C in 0.6733 m NaCl (equivalent in ionic strength to 35 ‰ salinity) was 0.17±0.004.

acid as well as complicated, and at this point poorly understood, interactions between arsenic acid and other seawater constituents. Data are presented for experimental temperatures and salinities only. No attempt was made to smooth or curve fit the experimental results, because there was little basis for choosing the shape of the curve.

Specific Ion Effects on the Apparent Constants

The following analysis is the same as that used by Kester and Pytkowicz (1967). One can observe ion pairing effects on the dissociation of arsenic acid in artificial seawater by comparing values for K'_1 , K'_2 and K'_3 determined in ASW with those determined in an NaCl solution of the same effective ionic strength. Differences should be attributable to ion pairing of arsenate species with K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} and perhaps other ions, not present in the simple salt solution. The relationship between thermodynamic and apparent constants is such that

$$\begin{aligned}
 K_1 &= K'_1(\text{NaCl}) g_{H^+}(\text{NaCl}) \frac{\gamma_{H_2A}(\text{NaCl})}{\gamma_{H_3A}(\text{NaCl})} \\
 &= K'_1(\text{ASW}) g_{H^+}(\text{ASW}) \frac{\gamma_{H_2A}(\text{ASW})}{\gamma_{H_3A}(\text{ASW})} . \quad (29)
 \end{aligned}$$

Since $\mu_{\text{NaCl}} = \mu_{\text{ASW}}$, $g_{H^+}(\text{NaCl}) = g_{H^+}(\text{ASW})$, and as H_3A is neutrally charged and not expected to form ion pairs, $\gamma_{H_3A}(\text{NaCl}) = \gamma_{H_3A}(\text{ASW})$. Therefore (29) may be rearranged

to give

$$\frac{\gamma_{\text{H}_2\text{A}}(\text{NaCl})}{\gamma_{\text{H}_2\text{A}}(\text{ASW})} = \frac{K'_1(\text{ASW})}{K'_1(\text{NaCl})} \quad (30)$$

This analysis can be continued for HA and A resulting in the following equalities:

$$\frac{\gamma_{\text{HA}}(\text{NaCl})}{\gamma_{\text{HA}}(\text{ASW})} = \frac{K'_2(\text{ASW})}{K'_2(\text{NaCl})} \times \frac{\gamma_{\text{H}_2\text{A}}(\text{NaCl})}{\gamma_{\text{H}_2\text{A}}(\text{ASW})} \quad (31)$$

$$\frac{\gamma_{\text{A}}(\text{NaCl})}{\gamma_{\text{A}}(\text{ASW})} = \frac{K'_3(\text{ASW})}{K'_3(\text{NaCl})} \times \frac{\gamma_{\text{HA}}(\text{NaCl})}{\gamma_{\text{HA}}(\text{ASW})} \quad (32)$$

K'_1 , K'_2 and K'_3 were determined at 30°C in 0.6733 m NaCl and ASW of 35 ‰. The ratios expressed on the left hand side of equations (30) - (32) should be indicative of differences in the degrees of ion pairing of arsenate species in the simple salt and ASW solutions. Values for the ratios of γ in NaCl to γ in ASW and the percentage of each species ion paired in ASW relative to that ion paired in the simple salt solution are given in Table 5.

The value for $\gamma_{\text{H}_2\text{A}}$ was smaller in the simple salt solution than in ASW. This cannot be attributed to differences in non-specific interactions since both solutions were at the same effective ionic strength. One must conclude that there was more H_2A associated with sodium in 0.6733 m NaCl than with sodium plus the other cations in 35 ‰ salinity ASW. This is possible because although Mg^{2+} and Ca^{2+} would be expected to associate somewhat more

Table 5.--Ratio of γ values of H_2A , HA and A in NaCl and ASW, and percent of each form ion-paired in ASW relative to NaCl solution.

	H_2A	HA	A
Ratio: $\frac{\gamma_{in} (NaCl)}{\gamma_{in} (ASW)}$	0.934	1.375	16.132
% ion-paired in ASW relative to NaCl	(-6.6)*	27.3	93.8

*This apparent negative % is discussed in the text.

strongly with H_2A than would Na^+ , the $[Na^+]$ was considerably higher (almost 50%) in the simple salt solution than in the ASW. The results of phosphate ion pairing studies (Atlas 1975) suggest that $MgHA$ was the dominant ion pair in the ASW and that $Na^+ - HA$ ion pairing may have been significant. Since the $[Na^+]$ was considerably higher in the NaCl solution, there may have been more $Na^+ - HA$ association in this medium than in the ASW. The difference between $\gamma_{HA}(NaCl)$ and $\gamma_{HA}(ASW)$ was probably due largely but not entirely to HA ion pairing with ions other than sodium in the ASW. It follows that somewhat more than 27% (Table 5) of the HA in the ASW was ion paired with ions such as Mg^{2+} and Ca^{2+} . Atlas' values for the association constants of $MgPO_4^-$ and $CaPO_4^-$ at $\mu = 0.68$ are three and four orders of magnitude higher respectively than the association constant for $NaPO_4^{2-}$. By analogy, it is probable that the difference in $\gamma_A(ASW)$ and $\gamma_A(NaCl)$ was due almost entirely to the formation of $MgAsO_4^-$ and $CaAsO_4^-$ in the ASW and that most of the AsO_4^{3-} in seawater is complexed with Mg^{2+} and Ca^{2+} .

Conversion to NBS System

Since the pH electrodes were also calibrated in the phthlate buffer, K'_1 , K'_2 and K'_3 on the free hydrogen scale can be converted for use when pH measurements are made on the NBS scale. The following treatment applies also for K'_2 and K'_3 . (The subscripts ([H]) and (NBS) designate the

pH scale on which the constants apply.)

$$K'_1(\text{NBS}) = \frac{X(\text{H}_2\text{A})}{(\text{H}_3\text{A})} \quad (33)$$

$$K'_1[\text{H}] = \frac{[\text{H}](\text{H}_2\text{A})}{(\text{H}_3\text{A})} \quad (34)$$

Dividing (33) by (34),

$$\frac{K'_1(\text{NBS})}{K'_1[\text{H}]} = \frac{X}{[\text{H}]} \quad (35)$$

Rearranging (35)

$$K'_1(\text{NBS}) = \frac{XK'_1[\text{H}]}{[\text{H}]} \quad (36)$$

Then, let $r = \frac{X}{[\text{H}]}$.

A value for r can be obtained for any set of K'_1 , K'_2 and K'_3 by calculating a value for X and $[\text{H}]$ for any potential, E , based on electrode calibrations on the NBS and free hydrogen scales done for three experiments at a given salinity and temperature. Conversion factors (r) for each experimental salinity and temperature appear in Table 6.

Comparison with Phosphoric Acid

Values for the apparent dissociation constants of phosphoric acid (Kester and Pytkowicz 1967) and arsenic acid at 35 ‰ salinity and 25°C accompanied by the calculated percentages of each of the dissociation products present at $p[\text{H}] = 8.00$ are presented in Table 7. Phosphoric

Table 6.--Conversion factors (r), where $K'_{(NBS)} = rK'_{[H]}$.

T°C	Salinity (‰)			
	40	35*	30	20
5		1.007		0.883
15		0.993	0.933	0.885
25	0.986	0.948	0.918	0.861
30	1.040	0.921	0.904	0.865

*The value for r at 30°C in 0.6733 m NaCl (equivalent in ionic strength to seawater of salinity 35 ‰) was 1.007.

Table 7.--Comparison of arsenic acid with phosphoric acid,
35 ‰ salinity, 25°C, p[H] = 8.00.

	H_3AsO_4	H_3PO_4^*
$K'_1 (\times 10^2)$	1.007	2.45
$K'_2 (\times 10^7)$	7.328	8.7
$K'_3 (\times 10^9)$	0.160	2.73
% H_3A	1.32×10^{-6}	3.25×10^{-7}
% H_2A	1.33	0.84
% HA	97.13	76.99
% A	1.55	22.17

*Phosphoric acid K' -values from Kester and Pytkowicz (1967). Calculated percent values were adjusted to the free hydrogen scale. H_3A , H_2A , HA and A symbolize the species of phosphoric and arsenic acids.

acid appears to be more completely dissociated, especially in the final dissociation, as K'_3 for phosphoric acid is 17 times larger than K'_3 for arsenic acid. This may reflect a higher degree of ion pairing of Mg^{2+} and Ca^{2+} with PO_4^{3-} than with AsO_4^{3-} .

Sources of Error

Pre-acidification and addition of titrant to an aliquot of ASW (35 ‰) increased the salinity by about 0.4 ‰. The effect of this increase on K'_1 , K'_2 and K'_3 (from Tables 2-4) would be changes of 0.6%, 0.1% and 0.2% respectively. The micrometer was calibrated to $\pm 0.07\%$ for a 1 ml delivery. Errors between additions in a titration would be somewhat higher. These would be random, however, and would tend to be averaged out in the fitting process. The procedure used to calibrate the glass electrode was reproducible to ± 0.001 p[H] units on the average. Errors of pH measurements in seawater are expected to be about ± 0.003 pH units, (Pytkowicz, Kester and Burgener 1966) but these should be random in a buffered system. The poorest precision was in the determination of K'_3 ($\pm 8.5\%$). This may have been caused by introduction of CO_3^{2-} , reaction of AsO_4^{3-} with Mg^{2+} or $Mg(OH)_2$, or a departure from a Nernstian or linear response of the glass electrode. However, no evidence was found to suggest that any of these factors were important.

Applicability of the Experimental Results

All experiments were done at atmospheric pressure. No information on the depth (pressure) dependence of these constants is available. As a rough estimate of the depth range over which the values are applicable, the known depth dependence of the dissociation constants of carbonic acid will be assumed to be about the same magnitude as for arsenic acid and will then be applied and related to the precision of the arsenic acid determinations. The constants should be applicable over the depth where the pressure effect is less than the precision of the determinations. The average precision was $\pm 3.7\%$, and the average pressure coefficient for the dissociation constants of carbonic acid (Culberson and Pytkowicz 1968) was 9% per 1000 m in the upper 1000 m at a salinity of about 35 ‰ and 10°C. Accordingly, the arsenic acid dissociation constants given here should be applicable over approximately the upper 400 m of the ocean.

Oceanic arsenate concentrations are usually about 1×10^{-8} m. The experimental concentration used in this study was about 1×10^{-3} m. Did this have an effect on the determination of K_1' , K_2' or K_3' ? The problem can be evaluated by considering the following expression for K_3' which derives from eq. (3), the definitions in Table 1 and the assumption that Mg^{2+} and Ca^{2+} are the most significant arsenate-complexing agents in natural seawater. The same

treatment can be applied to K_1' and K_2' but the effect, if any, would be most serious for K_3' , where ion pairing with divalent cations is strongest.

$$K_3' = K_3^* \left(\frac{1 + K_{MgA}^* [Mg^{2+}] + K_{CaA}^* [Ca^{2+}]}{1 + K_{MgHA}^* [Mg^{2+}] + K_{CaHA}^* [Ca^{2+}]} \right) \quad (37)$$

K^* constants vary with μ and not ionic composition. The addition of 1×10^{-3} m arsenate to 35 ‰ salinity ASW will increase μ by 0.15%, an amount too small to have a measurable effect on any of the K^* constants in (37). Since K_3^* , or that aspect of K_3' which accounts for the ionic strength effect on K_3' does not measurably change, one must ask whether the high experimental concentration would alter the degree of ion pairing between AsO_4^{3-} and the major cations. This aspect of K_3' is described by the expression in parentheses in (37), the value of which will change measurably only if there is a change in $[Mg^{2+}]$ or $[Ca^{2+}]$. Table 7 indicates that in ASW of 35 ‰ salinity, $p[H] = 8$ at 25°C, 1.6% of the total arsenate is present as AsO_4^{3-} . Even if all of this, or 1.6×10^{-5} m, were ion paired with Mg or Ca in the experimental situation, the decrease in $[Mg^{2+}]$ or $[Ca^{2+}]$, (initially about 0.05 m and 0.02 m respectively), would be 0.03% and 0.08% respectively. Therefore, it can be concluded that the high experimental arsenate concentration did not significantly effect the determination of K_3' .

SUMMARY

The apparent dissociation constants for arsenic acid have been determined in artificial seawater at various salinities and temperatures. These values may be applied under surface seawater conditions in conjunction with pH measurements made either on the free molal hydrogen or NBS scale. Differences observed between values determined in a sodium chloride solution and in artificial seawater can be attributed to ion pairing between arsenate and cations other than sodium in seawater. A comparison of the apparent dissociation constants of phosphoric and arsenic acids suggests that the former is more completely dissociated under typical seawater conditions.

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APPENDIX I.

Calibration of the Glass Electrode and Measurement of p[H]

The assumption that the glass electrode responded in a linear and Nernstian fashion over the experimental p[H] range was based on the results of acid-base titrations in 0.68 m NaCl at 25°C. Acidified solutions were bubbled with N₂, neutralized with NaOH, and titrated to about p[H]=2 with standard 1 N HCl. The electrode slope, dE/dp[H], was calculated by performing linear regression analyses on E, p[H] data pairs using the Monroe 1860 programmable calculator. Table 8 gives the experimental electrode slopes from 11 titrations over a 3-month period. The average correlation coefficient was greater than 0.9999: a correlation coefficient of 1 indicates linearity. On 21 July 75, the solution was neutralized after the HCl titration, and then titrated with 1 N NaOH to a p[OH] of about 3.2 (p[OH]=-log[OH]). Fig. 1 gives plots of E vs. p[H] and -E vs. p[OH] for the acid-base titrations of 21 July 75. The calculated slopes for the two titrations were -59.70 and 60.64 respectively compared to an ideal slope of ± 59.16 at 25°C. It is doubtful whether the actual electrode slope was significantly different from

Table 8.--The experimental slope (S) of the glass electrode determined in 0.68 m NaCl at 25°C.

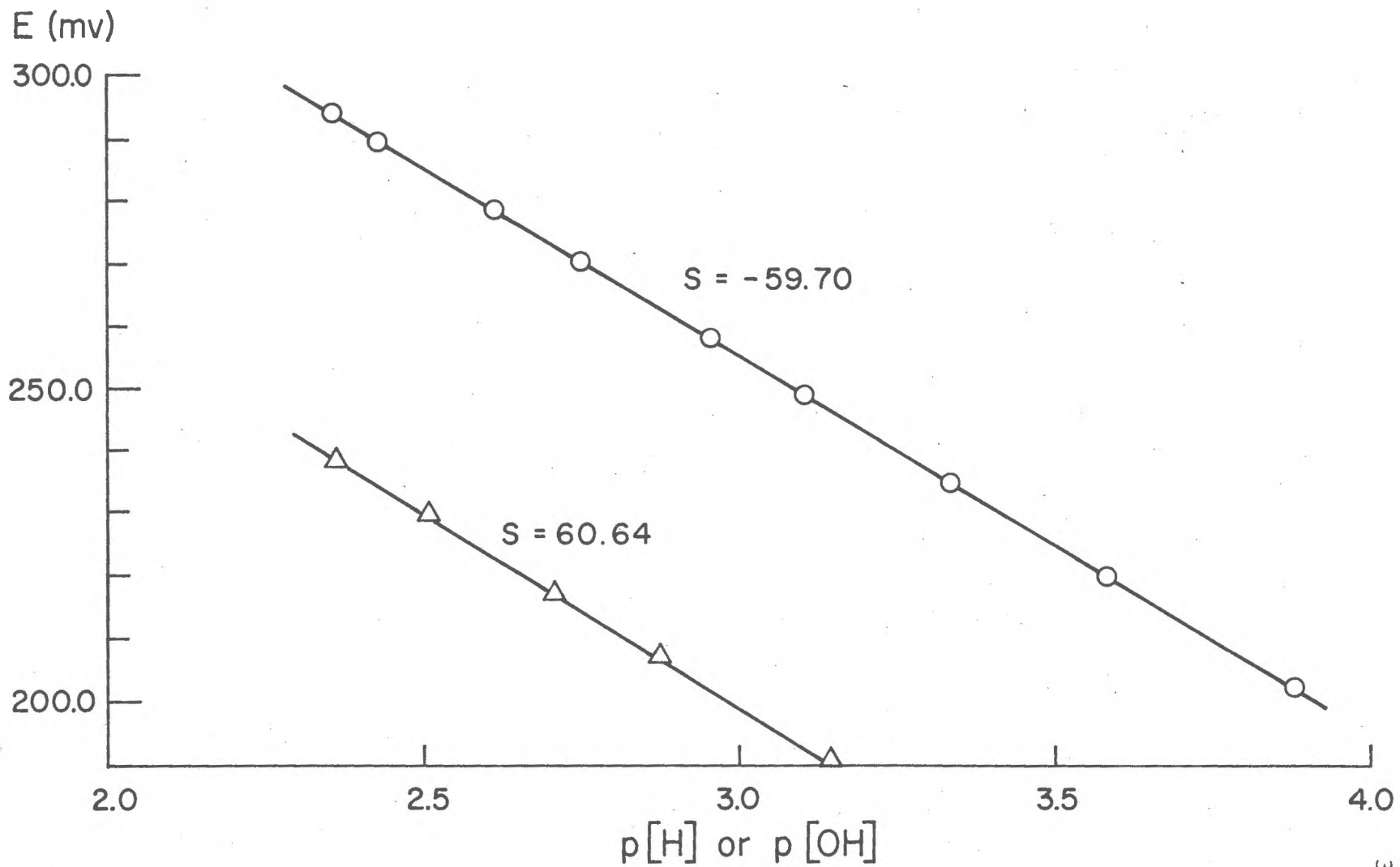
Date 1975	(S)
May 9	-61.15
June 13	-58.15
June 13	-58.60
June 18	-59.28
June 18	-59.37
July 3	-59.52
July 9	-60.54
July 18	-58.89
July 21	-59.70
July 30	-59.73
October 9	-59.82
Average	-59.52

Figure 1.--Titrations of 0.68 m NaCl with 1 N HCl and with
1 N NaOH at 25°C.

O - p[H] vs. E

Δ - p[OH] vs. -E

S - experimental slope.



Nernstian. A small amount of buffer in the solution, probably CO_3^{2-} introduced in the titrant or accidentally as atmospheric CO_2 , could have caused the observed departures from the ideal slope. Based on these results, the convention of calibrating the glass electrode at a single standard $p[\text{H}]$ was adopted.

An electrode calibration was performed before each experimental titration. Three calibrations for a determination of one set of K'_1 , K'_2 and K'_3 were compared as follows. The potential, mv_0 , in the acidified ASW ($p[\text{H}] \approx 2.6$) was more stable than that in the phthalate buffer. Differences in mv_0 between days were taken as the degree of drift in the circuit response. Table 9 gives the results of calibrations done for 30 ‰ salinity and 25°C. $p[\text{H}]_s$ was calculated according to eq. (27). E_{s_N} is the value for E_s normalized for differences in mv_0 between days, i.e., since mv_0 was 0.2 mv lower on 19 Mar. 76 and 20 Mar. 76 than on 18 Mar. 76, E_s for the two former days had to be increased by 0.2 mv to make an intercomparison possible. $p[\text{H}]_{250}$ is the $p[\text{H}]$ calculated from E_{s_N} and $p[\text{H}]_s$ for an arbitrary potential of 250 mv. $p[\text{H}]_{250}$ for the three calibrations should ideally be the same. Actually, it was found that the average $p[\text{H}]_{250}$ from the two closest calibrations was precise to ± 0.001 $p[\text{H}]$ units. This value was taken as $p[\text{H}]_s$ for the 3 titrations; in this case, $p[\text{H}]_s = 2.984$. E_s was 250 mv for 18 Mar 76 but 249.8 mv

Table 9.--Electrode calibration data for 30 ‰ and 25°C.

	18 Mar. 76	19 Mar. 76	20 Mar. 76
c	0.9886	0.9886	0.9886
wt _O	126.96	122.20	136.075
C _{HCl}	0.9745	0.9745	0.9744
V _a	0.12	0.12	0.136
p[H] _s	3.036	3.020	3.012
E _s	246.9	247.4	248.1
mv _O	266.3	266.1	266.1
E _{sN}	246.9	247.6	248.3
p[H] 250	2.984	2.979	2.983

19 Mar. 76 and 20 Mar. 76. (0.2 mv were subtracted since mv_o was 0.2 mv lower for these two days than on 18 Mar. 76.)

These calibration data were used to calculate the $p[H]$ for the titration data presented in Appendix III for 30 ‰ salinity, 25°C.

APPENDIX II.

Treatment of Possible Sources of Error

The effects of salinity changes due to pre-acidification and addition of titrant as well as micrometer delivery error have been considered previously.

The validity of the procedure for calibrating the glass electrode was examined in Appendix I. It was found that the fit of the experimental data to eq. (24) was relatively insensitive to the $p[H]$ parameter. For example, shifting $p[H]_s$ by as much as 0.03 $p[H]$ units had little effect on the quality of the fit.

An attempt was made to completely exclude CO_2 during these titrations. The air space over the test solution was flushed continuously with N_2 . Some CO_2 may have entered this space upon addition of KH_2AsO_4 but little would have dissolved due to the low $p[H]$. The rest should have been quickly flushed out of the titration vessel.

Eq. (23) requires that H_o in eq. (21) and eq. (22) be equal. If this condition does not hold, a significant error will result. By pre-acidifying a batch of ASW, it was felt that $p[H]_o$ and thus H_o would be the same for aliquots withdrawn successively. Differences in $p[H]_o$

between days could have been effected by evaporation during bubbling with N_2 . Initially, $p[H]_0$ was adjusted with concentrated HCl each day to some arbitrary value. By pre-acidifying the batch ASW, the fit was improved by more than an order of magnitude in most cases.

Artificial seawater closely resembles natural seawater in major ion composition. Thus, the apparent constants determined in artificial seawater closely reflect those interactions of the chemical species of interest with the major ions of seawater. Natural systems containing trace metal, organic or particulate constituents not present in artificial seawater might exhibit different types of interactions. At this time we have no reason to assume that such interactions would affect As more strongly than do the major cations. Additionally, it is difficult to define an average natural system. Thus, for experimental purposes, a properly prepared artificial seawater may often be the medium of choice.

APPENDIX III.

Titration Data and Results for 30 ‰ Salinity, 25°C

Complete titration data used for the determination of K'_1 , K'_2 and K'_3 in ASW of 30 ‰ salinity at 25°C are presented in Tables 10-12. The $p[H]$ was calculated according to eq. (26) using calibration data presented in Appendix I. Values for Y were calculated on the Monroe 1860 programmable calculator according to eq. (28). Computer printouts giving the regression coefficients A_1 , A_2 , A_3 , and B_1 , B_2 , and B_3 for replicate ASW_(As) titrations are included in Figs. 2-4. The coefficients are used to calculate predicted values for $OH_{(n)}$ and Y are compared to experimental values graphically and in tabular form. In the plots, \underline{O} is the observed value and \underline{P} the predicted value. A \underline{Y} indicates that the observed and predicted values agree to 1% or better.

It was necessary to omit the first $OH_{(n)}$, $[H]$ pair from the data in the ASW titration, because $OH_{(n)} = 0$ was an extreme value and biased the regression. $OH_{(n)}$ for the first $[H]_{As}$ value (corresponding to $OH_{(As)} = 0$) was calculated by interpolating between the first and second ASW titration data pairs, since $[H]_{As(1)}$ lay between $[H]_{n(1)}$

and $[H]_{n(2)}$, according to the formula,

$$OH_{(n)As1} = \left(\frac{[H]_{As(1)} - [H]_{n(1)}}{[H]_{n(2)} - [H]_{n(1)}} \right) \left(OH_{(n)2} \right), \quad (38)$$

where the subscript (As1) signifies the condition $OH_{(As)} = 0$. $[H]_n$ and $[H]_{As}$ refer to the free hydrogen concentrations in the ASW and $ASW_{(As)}$ titrations respectively.

Table 10.--Titration Data. Artificial Seawater, ASW;

Salinity = 30 ‰; 25°C; $p[H]_S = 2.984$; $E_S = 249.8$; $C_{NaOH} = 0.9967$ N; $c = .9947$; $wt_O = 136.99$.

	V_B	E	p[H]	$[H]_n$	$OH_{(n)}$
1)	0.0000	266.1	2.709	1.954×10^{-3}	0
2)	0.1160	255.8	2.883	1.309×10^{-3}	8.4329×10^{-4}
3)	0.1860	246.3	3.043	9.057×10^{-4}	1.3515×10^{-3}
4)	0.2360	236.5	3.209	6.180×10^{-4}	1.7142×10^{-3}
5)	0.2760	226.1	3.385	4.121×10^{-4}	2.0042×10^{-3}
6)	0.3020	215.9	3.557	2.773×10^{-4}	2.1926×10^{-3}
7)	0.3180	204.1	3.757	1.750×10^{-4}	2.3085×10^{-3}
8)	0.3260	193.9	3.929	1.178×10^{-4}	2.3664×10^{-3}
9)	0.3320	183.9	4.098	7.980×10^{-5}	2.4098×10^{-3}
10)	0.3370	172.3	4.294	5.082×10^{-5}	2.4461×10^{-3}
11)	0.3400	161.6	4.475	3.350×10^{-5}	2.4678×10^{-3}
12)	0.3420	152.6	4.627	2.361×10^{-5}	2.4823×10^{-3}
13)	0.3436	140.3	4.835	1.462×10^{-5}	2.4938×10^{-3}
14)	0.3448	125.8	5.080	8.318×10^{-6}	2.5025×10^{-3}
15)	0.3456	104.7	5.437	3.656×10^{-6}	2.5083×10^{-3}
16)	0.3461	79.8	5.858	1.387×10^{-6}	2.5119×10^{-3}
17)	0.3465	57.0	6.243	5.715×10^{-7}	2.5148×10^{-3}
18)	0.3469	26.4	6.760	1.738×10^{-7}	2.5177×10^{-3}
19)	0.3475	-32.6	7.758	1.746×10^{-8}	2.5221×10^{-3}
20)	0.3479	-49.4	8.042	9.078×10^{-9}	2.5250×10^{-3}
21)	0.3484	-62.3	8.260	5.495×10^{-9}	2.5286×10^{-3}
22)	0.3494	-77.0	8.508	3.105×10^{-9}	2.5358×10^{-3}
23)	0.3510	-90.8	8.741	1.816×10^{-9}	2.5474×10^{-3}
24)	0.3534	-103.1	8.949	1.125×10^{-9}	2.5648×10^{-3}

Table 11.--Titration Data. Titration I; 30 ‰ ASW_(As); 25°C; $p[H]_S = 2.984$; $E_S = 249.8$; $Z = 5.6127 \times 10^{-4}$ moles; $C_{NaOH} = 0.9967$ N; $c = .9947$; $wt_O = 131.585$.

	V_B	E	$p[H]$	$[H]_{As}$	Y
1)	0.000	259.6	2.818	1.521×10^{-3}	2.1327
2)	0.110	249.2	2.994	1.014×10^{-3}	2.0911
3)	0.182	239.6	3.156	6.982×10^{-4}	2.0582
4)	0.232	229.5	3.327	4.710×10^{-4}	2.0378
5)	0.266	219.9	3.489	3.243×10^{-4}	2.0216
6)	0.290	209.1	3.672	2.128×10^{-4}	2.0125
7)	0.306	199.4	3.836	1.459×10^{-4}	2.0043
8)	0.318	189.7	4.000	1.000×10^{-4}	1.9968
9)	0.328	179.4	4.174	6.699×10^{-5}	1.9890
10)	0.335	169.6	4.340	4.571×10^{-5}	1.9830
11)	0.342	159.5	4.510	3.090×10^{-5}	1.9751
12)	0.350	148.0	4.705	1.972×10^{-5}	1.9643
13)	0.358	139.3	4.852	1.406×10^{-5}	1.9518
14)	0.372	129.5	5.018	9.594×10^{-6}	1.9283
15)	0.402	114.5	5.271	5.358×10^{-6}	1.8765
16)	0.446	98.7	5.538	2.897×10^{-6}	1.7993
17)	0.510	83.5	5.795	1.603×10^{-6}	1.6863
18)	0.588	68.7	6.045	9.016×10^{-7}	1.5483
19)	0.670	53.3	6.306	4.943×10^{-7}	1.4032
20)	0.740	38.0	6.564	2.729×10^{-7}	1.2793
21)	0.796	22.2	6.831	1.476×10^{-7}	1.1802
22)	0.833	8.0	7.071	8.492×10^{-8}	1.1147
23)	0.853	-1.4	7.230	5.888×10^{-8}	1.0794
24)	0.865	-10.6	7.386	4.112×10^{-8}	1.0582
25)	0.875	-23.4	7.602	2.500×10^{-8}	1.0407
26)	0.882	-35.3	7.803	1.574×10^{-8}	1.0286
27)	0.887	-45.1	7.969	1.074×10^{-8}	1.0201

Table 11.--Continued

	V_B	E	p[H]	$[H]_{As}$	Y
28)	0.892	-52.5	8.094	8.054×10^{-9}	1.0117
29)	0.899	-62.5	8.263	5.458×10^{-9}	1.0000
30)	0.909	-72.3	8.429	3.724×10^{-9}	0.9834
31)	0.923	-81.8	8.589	2.576×10^{-9}	0.9601
32)	0.941	-93.7	8.790	1.622×10^{-9}	0.9312
33)	0.961	-102.2	8.934	1.164×10^{-9}	0.8989

Table 12.--Titration Data. Titration II; 30 ‰ ASW_(AS); 25°C; $p[H]_S = 2.984$; $E_S = 250.0$; $Z = 5.6377 \times 10^{-4}$ moles; $C_{NaOH} = 0.9966$ N; $c = .9947$; $wt_O = 132.96$.

	V_B	E	$p[H]$	$[H]_{AS}$	Y
1)	0.000	259.8	2.818	1.521×10^{-3}	2.1335
2)	0.110	249.7	2.989	1.026×10^{-3}	2.0901
3)	0.184	239.7	3.158	6.950×10^{-4}	2.0594
4)	0.234	229.7	3.327	4.710×10^{-4}	2.0388
5)	0.270	219.7	3.496	3.192×10^{-4}	2.0211
6)	0.294	209.9	3.662	2.178×10^{-4}	2.0094
7)	0.311	199.6	3.836	1.459×10^{-4}	2.0012
8)	0.323	189.6	4.005	9.886×10^{-5}	1.9942
9)	0.332	179.5	4.176	6.668×10^{-5}	1.9881
10)	0.340	169.0	4.353	4.436×10^{-5}	1.9807
11)	0.347	159.0	4.522	3.006×10^{-5}	1.9727
12)	0.355	148.7	4.696	2.014×10^{-5}	1.9616
13)	0.365	139.0	4.860	1.380×10^{-5}	1.9459
14)	0.379	129.0	5.029	9.354×10^{-6}	1.9225
15)	0.407	114.7	5.271	5.358×10^{-6}	1.8744
16)	0.451	99.5	5.528	2.965×10^{-6}	1.7975
17)	0.513	84.6	5.780	1.660×10^{-6}	1.6886
18)	0.591	69.6	6.033	9.268×10^{-7}	1.5513
19)	0.675	54.3	6.292	5.105×10^{-7}	1.4033
20)	0.749	39.1	6.549	2.825×10^{-7}	1.2729
21)	0.805	23.9	6.806	1.563×10^{-7}	1.1742
22)	0.845	9.2	7.054	8.831×10^{-8}	1.1038
23)	0.863	-1.1	7.228	5.916×10^{-8}	1.0721
24)	0.875	-10.7	7.391	4.064×10^{-8}	1.0510
25)	0.884	-20.6	7.558	2.767×10^{-8}	1.0353
26)	0.891	-29.4	7.708	1.963×10^{-8}	1.0232

Table 12.--Continued

	V_B	E	p[H]	$[H]_{AS}$	Y
27)	0.899	-40.5	7.894	1.276×10^{-8}	1.0094
28)	0.909	-54.4	8.129	7.430×10^{-9}	0.9925
29)	0.917	-63.8	8.288	5.152×10^{-9}	0.9792
30)	0.927	-74.3	8.466	3.420×10^{-9}	0.9628
31)	0.939	-83.7	8.625	2.371×10^{-9}	0.9433
32)	0.954	-92.2	8.768	1.706×10^{-9}	0.9190
33)	0.980	-101.7	8.929	1.178×10^{-9}	0.8766

Figure 2.--Printout of the results of the NLIN-2 program: regression on data pairs $(\text{OH}_{(n)}, [\text{H}])_i$ (excluding 1st titration point) for the conditions 30 ‰ salinity and 25°C, taken on March 20, 1976. The calculated regression coefficients A_1 , A_2 and A_3 (defined in Table 1) have been labelled. The following apply to symbols and abbreviations appearing in Figures 2-4:

O = observed value in plot

P = predicted value in plot

Y = observed and predicted values agree to 1% or better

OBS = experimental value for function

PRED = value for function from calculated regression coefficients

DIFF = OBS-PRED

N = number of data points

K = number of unknown parameters

M = number of independent variables

FF = variance ratio statistic

T = user's T

E and TAU = convergence criteria

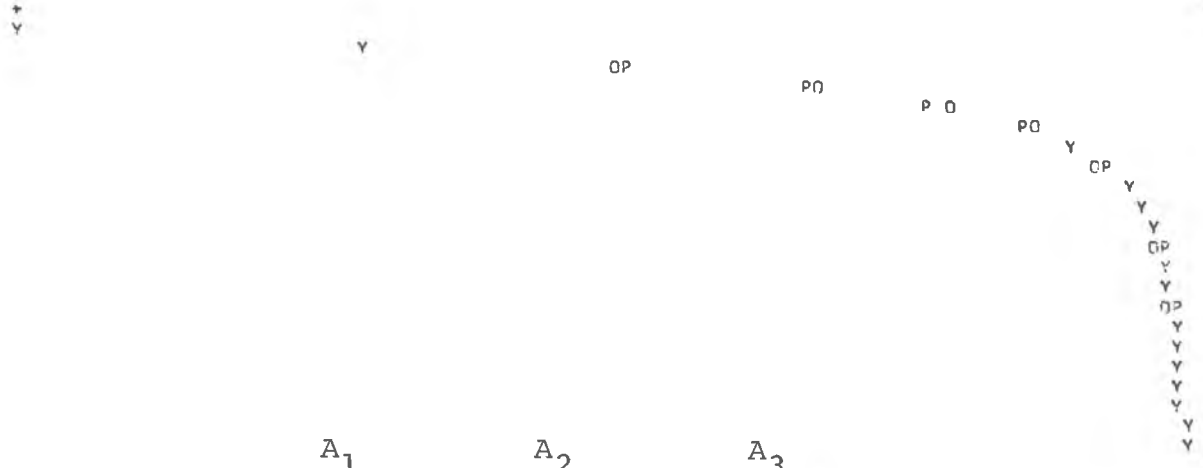
$\phi = \sum (\text{OBS}-\text{PRED})^2$

EPSILON TEST

N = 23 K = 3 P = 0 M = 1
 FF = 0.400E 01 T = 0.200E 01 E = 0.500E-04 TAU = 0.100E-02

(2) PARAMETERS 0.25173414E-02 0.54468335E-13 0.12786884E 01
 0.84E-03

0.25E-02



A₁ A₂ A₃

(2) PARAMETERS 0.25173414E-02 0.54468335E-13 0.12786884E 01

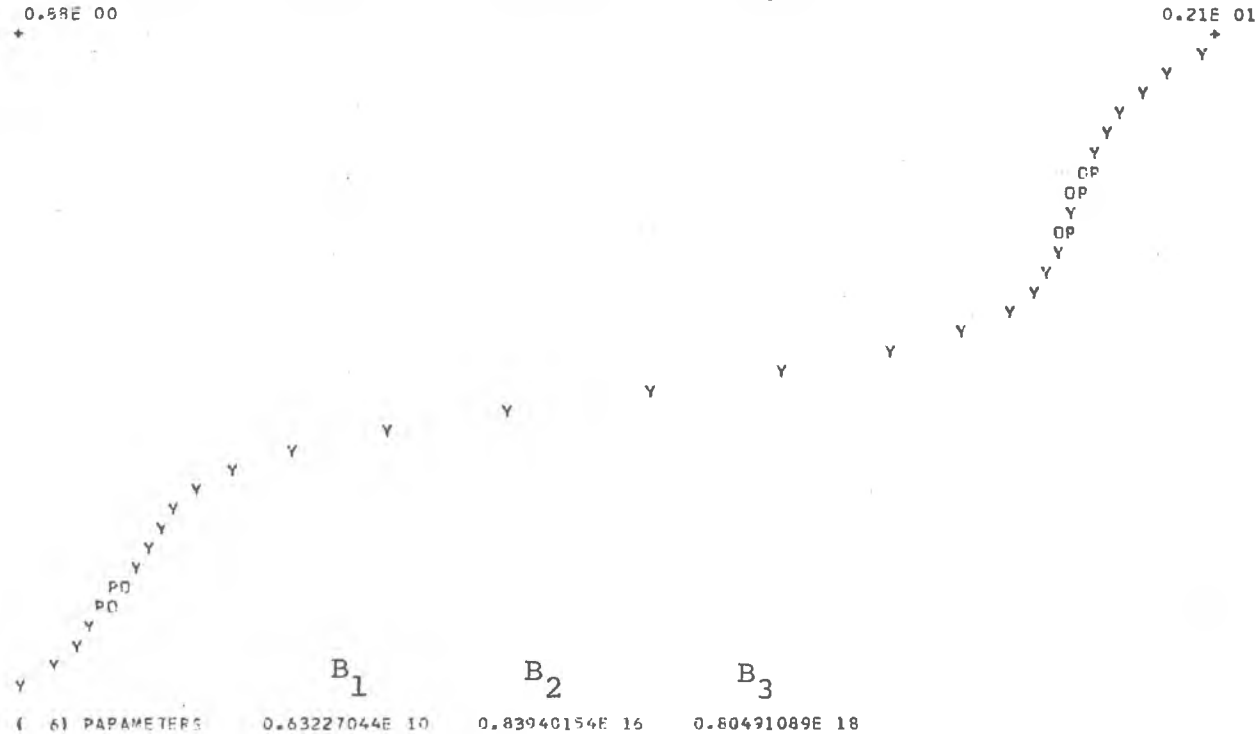
OPC	PRED	DIFF
0.84328977E-03	0.84353044E-03	-0.2486313E-06
0.13514999E-02	0.13592336E-02	-0.77337027E-05
0.17141991E-02	0.17271123E-02	-0.12912555E-04
0.20041899E-02	0.19903940E-02	0.13405926E-04
0.21925999E-02	0.21627613E-02	0.29838644E-04
0.23045000E-02	0.22993711E-02	0.14928868E-04
0.23663999E-02	0.23667121E-02	-0.31222589E-06
0.24098000E-02	0.24153024E-02	-0.55024666E-05
0.24460999E-02	0.24523593E-02	-0.62594190E-05
0.24677999E-02	0.24745066E-02	-0.67066667E-05
0.24822999E-02	0.24871539E-02	-0.48535876E-05
0.24927999E-02	0.24986507E-02	-0.48507936E-05
0.25024999E-02	0.25067118E-02	-0.42119063E-05
0.25032999E-02	0.25125811E-02	-0.43811742E-05
0.25118999E-02	0.25154068E-02	-0.37068967E-05
0.25147998E-02	0.25167058E-02	-0.19059516E-05
0.25177000E-02	0.25174324E-02	0.26752241E-06
0.25221000E-02	0.25204385E-02	0.16614795E-05
0.25249999E-02	0.25233296E-02	0.16703270E-05
0.25285999E-02	0.25272465E-02	0.13534445E-05
0.25358000E-02	0.25348794E-02	0.92061237E-06
0.25473998E-02	0.25473326E-02	0.67288056E-07
0.25648000E-02	0.25657560E-02	-0.95600262E-06

Figure 3.--Printout of the results of the NLIN-2 program:
regression on data pairs $(Y, [H]_{AS})_i$ for the conditions
30 ‰ salinity and 25°C, taken on March 18, 1976. The cal-
culated regression coefficients B_1 , B_2 and B_3 (defined by
equations 7-9) have been labelled.

EPSILON TEST

N =, 33 K = 3 P = 0 M = 1
 FF = 0.400E 01 T = 0.200E 01 E = 0.500E-04 TAU = 0.100E-02

(6) PARAMETERS 0.63227044E 10 0.83940154E 16 0.80491089E 18
 0.58E 00



(6) PARAMETERS 0.63227044E 10 0.83940154E 16 0.80491089E 18

DBS	PRFD	DIFF
0.21334991E 01	0.21267967E 01	0.67024231E-02
0.20900993E 01	0.20888414E 01	0.12578964E-02
0.20593996E 01	0.20414023E 01	-0.20027161E-02
0.20387993E 01	0.20416192E 01	-0.28200150E-02
0.20210991E 01	0.20273476E 01	-0.62484741E-02
0.20093994E 01	0.20170126E 01	-0.76131821E-02
0.20011997E 01	0.20086622E 01	-0.74625015E-02
0.19941998E 01	0.20018263E 01	-0.76265335E-02
0.19880991E 01	0.19951811E 01	-0.70819855E-02
0.19806995E 01	0.19875402E 01	-0.68407059E-02
0.19726992E 01	0.19784269E 01	-0.57277679E-02
0.19615993E 01	0.19658728E 01	-0.42734146E-02
0.19459000E 01	0.19495602E 01	-0.36602020E-02
0.19224997E 01	0.19263639E 01	-0.38642883E-02

Figure 4.--Printout of the results of the NLIN-2 program: regression on data pairs $(Y, [H]_{As})_i$ for the conditions 30 ‰ salinity and 25°C, taken on March 19, 1976. The calculated regression coefficients B_1 , B_2 and B_3 (defined by equations 7-9) have been labelled.

0.18764992E 01	0.18821525E 01	-0.56533813E-02
0.17992092E 01	0.18013620E 01	-0.20627975E-02
0.16862993E 01	0.16903820E 01	-0.40826797E-02
0.15482998E 01	0.15562353E 01	-0.79356240E-02
0.14031992E 01	0.14071541E 01	-0.39548874E-02
0.12792997E 01	0.12746773E 01	0.46224594E-02
0.11801996E 01	0.11695061E 01	0.10693550E-01
0.11146994E 01	0.11042376E 01	0.10461807E-01
0.10793991E 01	0.10736914E 01	0.57077408E-02
0.10581999E 01	0.10512409E 01	0.69569615E-02
0.10407000E 01	0.10289221E 01	0.11777878E-01
0.10285997E 01	0.10140142E 01	0.14585495E-01
0.10200996E 01	0.10039005E 01	0.16199112E-01
0.10116997E 01	0.99670634E 00	0.14902833E-01
0.10000000E 01	0.98647332E 00	0.13526678E-01
0.98339999E 00	0.97458684E 00	0.38131428E-02
0.96010000E 00	0.95997584E 00	0.12415648E-03
0.93119997E 00	0.93474811E 00	-0.35481453E-02
0.89889997E 00	0.90998739E 00	-0.11087418E-01

PHI	S E	LAMBDA	ANALYTIC PARTIALS USED
0.19928995E-02	0.81504583E-02	0.100E-07	

SINGULAR MATRIX I= 2 J= 2 PIVOT= 0.25952275E-20

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