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# The determination of the apparent dissociation constants of arsenic acid in seawater

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## ABSTRACT

The apparent dissociation constants for arsenic acid in seawater, based on a free molal hydrogen scale, were determined in artificial seawater over a range of salinities and temperatures. A comparison between constants determined in a sodium chloride solution and artificial seawater of the same ionic strength suggests that a significant amount of the reactive arsenate in seawater is ion paired with cations other than sodium. Under typical seawater conditions, arsenic acid appears to be less dissociated than its analogue, phosphoric acid. 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.

## 1. Introduction

Arsenic occurs in seawater at a concentration of about  $10$  to  $30 \times 10^{-9}$  m and appears to be primarily in the +5 oxidation state as arsenate (Ishibashi *et al.*, 1960; Johnson and Pilson, 1972; Gohda, 1974). We report here the first measurements 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. Thermodynamic dissociation constants for arsenic acid have been determined by several authors (Sillen and Martell, 1964); the most complete set of data appears to be that reported by Flis *et al.* (1959). Application of these constants 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 (Buch *et al.*, 1932; Lyman, 1956; Hansson, 1973; Mehrbach *et al.*, 1973) and phosphoric acids (Kester and Pytkowicz, 1967). Determination of the apparent dissociation constants for arsenic acid in seawater will serve as a basis for

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Table 1. Definitions, abbreviations and symbols.

1. ( ) = molal concentration, equal to free plus ion paired species
2. [ ] = molal "free" concentration
3.  $(A) = (AsO_4^{3-}) = [A] (1 + K_{MgA}^* [Mg^{2+}] + K_{CaA}^* [Ca^{2+}] + K_{NaA}^* [Na^+] + \dots)$
4.  $(HA) = (HASO_4^{2-}) = [HA] (1 + K_{MgHA}^* [Mg^{2+}] + K_{CaHA}^* [Ca^{2+}] + K_{NaHA}^* [Na^+] + \dots)$
5.  $(H_2A) = (H_2ASO_4^-) = [H_2A] (1 + K_{MgH_2A}^* [Mg^{2+}] + K_{CaH_2A}^* [Ca^{2+}] + K_{NaH_2A}^* [Na^+] + \dots)$
6.  $(H_3A) = (H_3ASO_4)$
7.  $A_1 = H_0$
8.  $A_2 = K_w (1 + K_{MOH}^* [M^{2+}])$
9.  $A_3 = 1 + K_{HSO_4^-} (SO_4^{2-}) + K_{HF} (F^-)$
10. *ASW* = artificial seawater
11. *ASW*<sub>(As)</sub> = artificial seawater to which  $KH_2AsO_4$  has been added
12.  $A_T$  = total arsenate, added as  $KH_2AsO_4$ , moles/kg (water)
13.  $B$  = an algebraic variation on  $K'$  (see equations 7, 8 and 9)
14.  $C$  = concentration of *NaOH* or *HCl* solution, ( $N$ )
15.  $C_{H_2O}$  = grams  $H_2O/ml$  in titrant solution
16. *DDW* = doubly deionized water
17.  $E_s$  = electrode potential in standard *HCl* or phthalate buffer
18.  $E_x$  = electrode potential in test solution
19.  $F = (HA) + 2(H_2A) + 3(H_3A)$ , the total hydrogen associated with arsenate
20.  $g$  = a free activity coefficient, dependent on  $T$ ,  $P$  and ionic strength, but independent of medium composition
21.  $[H_2O]$  = water formed by combination of  $H^+$  and  $OH^-$  when *NaOH* is added to test solution
22.  $(H_T)_0$  = total initial hydrogen concentration, as defined by equation 17
23.  $[H]$  = free hydrogen ion,  $H^+$ , concentration (including such forms as  $H^+$ ,  $H_3O^+$ ,  $H_5O_2^+$ , etc.)
24.  $[H]_0$  = initial free hydrogen ion concentration

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 first, second and third apparent dissociation constants reported here were based on a free molal hydrogen scale, and were determined in artificial seawater systems at various salinities and temperatures. Constants were also determined in a sodium chloride medium to make possible an evaluation of ion pairing between arsenate species and the major cations in seawater.

## 2. Theory

Definitions and abbreviations are given in Table 1.

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

Table 1 (continued).

25.  $[H]_s$  = free hydrogen ion concentration in standard  $HCl$  solution
26.  $K$  = a thermodynamic dissociation constant =  $f(T, P)$  only
27.  $K^*$  = a "free" concentration dissociation =  $f(T, P, \mu)$  defined for a complex of cation  $M$  and anion  $N$  such that  $K^*_{MN} = [MN]/[M][N]$
28.  $K'$  = an apparent dissociation constant =  $f(T, P, S \text{ } \%$ )
29.  $K_w$  =  $[H][OH]$ , the ion product of water in seawater
30.  $m$  = concentration, moles /kg  $H_2O$
31.  $[MOH]$  = sum of  $[MgOH^+]$ ,  $[CaOH^+]$  and  $[SrOH^+]$
32.  $m_{v_0}$  = electrode potential in  $ASW$  before addition of  $KH_2AsO_4$  or titrant
33.  $N$  = concentration, equivalents/liter
34.  $[OH]$  = concentration of free hydroxide ion,  $OH^-$
35.  $(OH)_{As}$  = amount of  $NaOH$  titrant added to  $ASW_{(As)}$ , ( $m$ )
36.  $(OH)_n$  = amount of  $NaOH$  titrant added to  $ASW$  without arsenate ( $m$ )
37.  $pH$  = a general term for the degree of acidity
38.  $p[H] = -\log [H]$
39.  $P$  = pressure
40.  $T$  = temperature
41.  $V_A$  = ml acid added
42.  $V_B$  = ml base added
43.  $w_{t_0}$  = initial water content by weight ( $g$ )
44.  $X$  = an empirical quantity related to hydrogen activity when  $pH$  measurements are made in concentrated electrolytes
45.  $Y = f(B_1, B_2, B_3, [H])$ , see equation 27
46.  $Z$  = moles  $KH_2AsO_4$  added
47.  $\gamma$  = a total activity coefficient
48.  $\mu$  = effective ionic strength (molal).



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,  $H_iA$ , can be derived from (1), (2) and (3).

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

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

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

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),

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

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

$$(H_T)_0 = [H]_0 + (HSO_4^-)_0 + (HF)_0 \quad (17)$$

where the subscripts denote initial concentrations.

Enough  $KH_2AsO_4$  is added to bring the solution to about  $4 \times 10^{-3}$  m in arsenate. The total hydrogen,  $(H_T)_{As}$ , in this sample,  $ASW_{(As)}$ , is given by:

$$(H_T)_{As} = (H_T)_0 + 2A_T = [H] + (HSO_4^-) + (HF) + 3(H_3A) + 2(H_2A) + (HA) \quad (18)$$

Using equation (15):

$$(H_T)_{As} = (H_T)_0 + 2A_T = [H] + (HSO_4^-) + (HF) + F \quad (19)$$

As titration with 1N NaOH proceeds, total hydrogen decreases due to combination of  $H^+$  and  $OH^-$  to form water. The decrease in  $H_T$  as  $OH^-$  is added is  $[H_2O]_{As}$ , the concentration of water formed (from  $H_T$ ) by NaOH addition. Total hydrogen in  $ASW_{(As)}$  after NaOH addition is then:

$$(H_T)_{As} = (H_T)_0 - 2A_T - [H_2O]_{As} = [H] + (HSO_4^-) + (HF) + F \quad (20)$$

The total hydrogen,  $(H_T)_n$ , in a second aliquot from the batch  $ASW$ , containing added  $OH^-$  but no arsenic is:

$$(H_T)_n = (H_T)_0 - [H_2O]_n = [H] + (HSO_4^-) + (HF) \quad (21)$$

where  $[H_2O]_n$  is the concentration of water formed in the solution containing no arsenic.

When the solution containing no arsenic is titrated to match the  $p[H]$  of the solution with arsenic, the term  $[H] + (HSO_4^-) + (HF)$  is identical in the two solutions and equations (20) and (21) may be combined to give:

$$(H_T)_{As} - (H_T)_n = 2A_T - [H_2O]_{As} + [H_2O]_n = F \quad (22)$$

Since at the initial  $pH$ ,  $[OH]_0$  and  $[MOH]_0$  are quantitatively insignificant, the total hydroxide added to each solution can be accounted for as follows:

$$(OH)_{As} = [OH]_{As} + [MOH]_{As} + [H_2O]_{As} \quad (23)$$

$$(OH)_n = [OH]_n + [MOH]_n + [H_2O]_n \quad (24)$$

For identical  $p[H]$  in each solution equations (23) and (24) may be combined to give:

$$[H_2O]_n - [H_2O]_{As} = (OH)_n - (OH)_{As} \quad (25)$$

This may be combined with equation (22):

$$F = 2A_T - (OH)_{As} + (OH)_n \quad (26)$$

By combining equations (26) and (16) we obtain a relationship between the quantities to be measured and the values of  $B$  which are to be determined:

$$Y = \frac{2A_T - (OH)_{As} + (OH)_n}{A_T} = \frac{B_1[H] + 2B_2[H]^2 + 3B_3[H]^3}{1 + B_1[H] + B_2[H]^2 + B_3[H]^3} \quad (27)$$

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 described by the equation,

$$(OH)_n = A_1 + A_2/[H]_n - A_3[H]_n \quad (28)$$

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" (URI Computer Center), based on an algorithm by Marquardt (1963), was used to solve (28) and (27) for the requisite parameters. Through iterative modification of initial estimates for  $A_1$ ,  $A_2$ ,  $A_3$ , and  $B_1$ ,  $B_2$  and  $B_3$ , the least-squares best fit to the nonlinear equations (28) and (27) was calculated using data sets  $(OH)_{(n)i}$ ,  $[H]_{(n)i}$  and  $Y_i$ ,  $[H]_{(As)i}$  respectively, obtained at each titration point ( $i$ ). 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).

### 3. 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 =  $\mu$ ), 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 the ionic strength of seawater 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 is defined for any temperature and pressure as hydrogen ion at unit activity and molality in pure water.

### 4. 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,

$$p[H]_x = p[H]_s + \frac{E_x - E_s}{S} \quad (29)$$

where  $S$  is the Nernstian slope of the glass electrode. Titrations in 0.68 m  $NaCl$  at

25°C demonstrated that the glass electrode responded linearly over the  $p[H]$  ranges 2-4 and 10-11 and that the experimental slope was within 0.06% of the Nernstian slope.

The electrodes were standardized before each experiment by measuring  $E_s$  in a standard solution of known  $HCl$  concentration. This standard solution was  $CO_2$ -free and contained sufficient  $NaCl$  to produce an effective ionic strength (Kester, 1974) equal to that of the  $ASW$  to be titrated.  $p[H]_s$  was calculated from the formula,

$$p[H]_s = -\log \left( \frac{V_A \times C_{HCl}}{wt_0 + [V_A \times C_{H_2O}]} \right) \quad (30)$$

The temperature was maintained within  $\pm 0.05^\circ C$  with a water bath circulating water through 250-ml jacketed beakers.

All solutions were acidified and bubbled with nitrogen for  $\frac{1}{2}$  hour to remove  $CO_2$ . Nitrogen was passed over solutions during experiments to prevent ingress of atmospheric  $CO_2$ . Stirring with a magnetic stirrer was maintained for the duration of each experiment.

Artificial seawater (Kester, 1966) was prepared and the salinity checked against Copenhagen water using an inductive salinometer. The initial salinity of an  $ASW$  stock solution was  $40.016 \pm 0.001\%$ , 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 Baker and Adamson Primary Standard  $Na_2CO_3$ . The  $NaOH$  titrant was prepared from Baker  $CO_2$ -free 1  $N$  "Dilute-It" and calibrated potentiometrically against Mallinckrodt Primary Standard potassium acid phthalate. The titrant was stored under nitrogen and protected by ascarite, in a polyethylene bottle surrounded except for the cap by about 2 cm of paraffin wax.

Titrations and standardization were done using 2 ml and 0.2 ml Gilmont micrometer syringes 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.

## 5. 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 0.1 g  $KH_2AsO_4$  was carefully added to each of the two aliquots and titrations to about  $p[H] = 9$  were



Table 2. The first apparent dissociation constants for arsenic acid ( $K_1' \times 10^8$ ), experimental values.

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.

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 at each  $ASW_{(As)}$  titration point ( $i$ ) from the formula:

$$Y_i = \left( \frac{2000 Z - V_{Bi} C_{NaOH}}{wt_0 + (V_{Bi} \times C_{H_2O})} + (OH)_{(n)i} \right) \frac{wt_0 + (V_{Bi} \times C_{H_2O})}{1000 Z} \quad (31)$$

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. Lowenthal (1976) gives an expanded account of these operations.

Determinations of  $K_1'$ ,  $K_2'$  and  $K_3'$  were made in ASW at 25 and 30°C at salinities of 20, 30, 35 and 40‰, at 15°C at salinities of 20, 30 and 35‰, at 5°C at salinities of 20 and 35‰, and at 30°C in 0.6733 m NaCl solution.

## 6. Results

The experimental results appear in Tables 2-4. Temperature and salinity effects were significant but not entirely consistent. Although there is little empirical or theoretical basis for predicting the effects of temperature and salinity on the interactions between arsenic acid and other seawater constituents, we think that the dissociation constants should show regular trends with changes in salinity and temperature. For this reason the  $pK'$  values calculated from  $K'$  values in Tables 2-4 were

Table 3. The second apparent dissociation constants for arsenic acid ( $K_2' \times 10^7$ ), experimental values.

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 ± 0.00
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 constants for arsenic acid ( $K_3' \times 10^{10}$ ), experimental values.

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 ± 0.00	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.

Table 5. The first apparent dissociation constants for arsenic acid ( $K_1' \times 10^3$ ), smoothed values.

T°C	Salinity (‰)				
	20	25	30	35	40
5	10.97	11.12	11.27	11.45	11.62
10	10.79	10.97	11.09	11.27	11.43
15	10.42	10.57	10.74	10.89	11.04
20	10.12	10.28	10.42	10.59	10.72
25	9.55	9.68	9.83	9.97	10.12
30	8.71	8.83	8.97	9.10	9.23

Table 6. The second apparent dissociation constants for arsenic acid ( $K_2' \times 10^7$ ), smoothed values.

T°C	Salinity (‰)				
	20	25	30	35	40
5	5.29	5.68	6.08	6.53	7.00
10	5.40	5.79	6.21	6.67	7.15
15	5.52	5.92	6.34	6.82	7.31
20	5.64	6.04	6.49	6.95	7.47
25	5.75	6.17	6.62	7.10	7.62
30	5.89	6.31	6.76	7.28	7.82

Table 7. The third apparent dissociation constants for arsenic acid ( $K_3' \times 10^{10}$ ), smoothed values.

T°C	Salinity (‰)				
	20	25	30	35	40
5	0.56	0.72	0.80	0.87	0.89
10	0.59	0.75	0.84	0.91	0.93
15	0.66	0.84	0.93	1.01	1.04
20	0.77	1.02	1.10	1.18	1.22
25	0.96	1.20	1.36	1.45	1.50
30	1.26	1.59	1.78	1.89	1.95

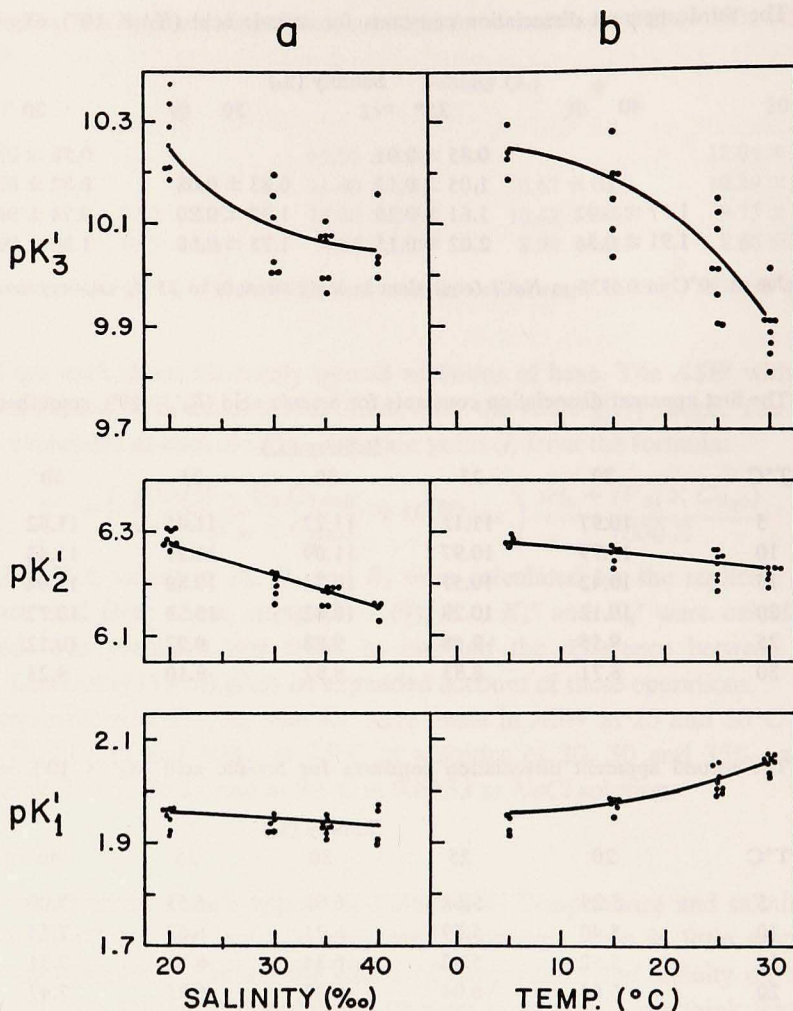


Figure 1. Plots of  $pK'_1$ ,  $pK'_2$  and  $pK'_3$  at  $5^\circ\text{C}$  v. salinity (a) and at  $20\text{‰}$  v. temperature (b). Experimental  $pK'$  values, plotted around the smoothed curves in (a), were normalized to  $5^\circ\text{C}$  according to the slopes of the curves in (b). Experimental  $pK'$  values in (b) were normalized to  $20\text{‰}$  according to the slopes of the curves in (a).

visually fitted to parallel lines as functions of temperature and salinity. A precedent for this approach can be found in Lyman (1956). Refined  $pK'$  values were generated from the graphs produced in this manner. These smoothed values (Tables 5-7) represent our best estimates of these constants.

In Figure 1, the lines used for the  $pK'$  v. salinity plots and the  $pK'$  v. temperature plots are shown. As a means of visualizing the conformity of the experimental results to the smoothed values, all experimental points were normalized to  $5^\circ\text{C}$  and

Table 8. Conversion factors ( $r$ ), where  $K'_{(NBS)} = r K'_{[H]}$ .

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.

20‰ and plotted on the graphs in Figure 1. The agreement seems reasonably good, although in some cases it seems that the slope and shape of the lines could have been slightly different. The average differences between the normalized smoothed values and the normalized experimental points were 4%, 3% and 11% for  $K'_1$ ,  $K'_2$  and  $K'_3$  respectively.

## 7. Conversion to NBS system

Since the  $pH$  electrodes were also calibrated in phthalate 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.)

$$K'_{1(NBS)} = \frac{X(H_2A)}{(H_3A)} \quad (32)$$

$$K'_{1[H]} = \frac{[H](H_2A)}{(H_3A)} \quad (33)$$

Dividing (32) by (33),

$$\frac{K'_{1(NBS)}}{K'_{1[H]}} = \frac{X}{[H]} \quad (34)$$

Rearranging (34)

$$K'_{1(NBS)} = \frac{X K'_{1[H]}}{[H]} \quad (35)$$

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

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  $[H]$  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 8.

## 8. Specific ion effects on the apparent constants

Following the approach 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 a *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

$$K_1 = K_1'_{(NaCl)} g_{H^+(NaCl)} \frac{\gamma_{H_2A(NaCl)}}{\gamma_{H_3A(NaCl)}} = K_1'_{(ASW)} g_{H^+(ASW)} \frac{\gamma_{H_2A(ASW)}}{\gamma_{H_3A(ASW)}} \quad (36)$$

Since  $\mu_{NaCl} = \mu_{ASW}$ ,  $g_{H^+(NaCl)} = g_{H^+(ASW)}$ , and as  $H_3A$  is neutrally charged and not expected to form ion pairs,  $\gamma_{H_3A(NaCl)} = \gamma_{H_3A(ASW)}$ . Therefore (36) may be arranged to give

$$\frac{\gamma_{H_2A(NaCl)}}{\gamma_{H_2A(ASW)}} = \frac{K_1'_{(ASW)}}{K_1'_{(NaCl)}} \quad (37)$$

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

$$\frac{\gamma_{HA(NaCl)}}{\gamma_{HA(ASW)}} = \frac{K_2'_{(ASW)}}{K_2'_{(NaCl)}} \times \frac{\gamma_{H_2A(NaCl)}}{\gamma_{H_2A(ASW)}} \quad (38)$$

$$\frac{\gamma_A(NaCl)}{\gamma_A(ASW)} = \frac{K_3'_{(ASW)}}{K_3'_{(NaCl)}} \times \frac{\gamma_{HA(NaCl)}}{\gamma_{HA(ASW)}} \quad (39)$$

$K_1'$ ,  $K_2'$  and  $K_3'$  were determined at 30°C in 0.6733 m *NaCl* and *ASW* of 35%. Since for any species such as *A*,

$$[A]_{ASW} \times g_{A(ASW)} = (A)_{ASW} \times \gamma_A(ASW) \quad (40)$$

and

$$[A]_{NaCl} \times g_{A(NaCl)} = (A)_{NaCl} \times \gamma_A(NaCl) \quad (41)$$

and since  $\mu$  is the same in both solutions,

$$g_{A(NaCl)} = g_{A(ASW)} \quad (42)$$

it follows that

$$\frac{\gamma_A(NaCl)}{\gamma_A(ASW)} = \frac{[A]_{NaCl}}{(A)_{NaCl}} \div \frac{[A]_{ASW}}{(A)_{ASW}} \quad (43)$$

The ratios expressed in equations (37) - (39) are therefore equal to the ratios of the fraction "free" in *NaCl* to the fraction "free" in *ASW*, in each case. Values for these ratios are given in Table 9.

Table 9. Ratio of  $\gamma$  values of  $H_2A$ ,  $HA$  and  $A$  in  $NaCl$  and  $ASW$  (35 ‰, 30°C).

	$H_2A$	$HA$	$A$
Ratio: $\frac{\gamma \text{ in } (NaCl)}{\gamma \text{ in } (ASW)}$	0.95	1.40	15.57

The value for  $\gamma_{H_2A}$  was slightly smaller in the simple salt solution than in  $ASW$ . This cannot be attributed to differences in nonspecific interactions since both solutions were at the same effective ionic strength. This indicates that there was more  $H_2A$  ion pairing with sodium in the 0.6733 m  $NaCl$  than with sodium plus the other cations in 35‰ salinity  $ASW$ , due to the higher (50%)  $[Na^+]$  in the simple salt solution.

In the case of  $\gamma_{HA}$ , although the  $[Na^+]$  was lower in the  $ASW$ ,  $\gamma_{HA(NaCl)}$  was greater than  $\gamma_{HA(ASW)}$  by a factor of 1.4, indicating that the ion pairing in  $ASW$  was dominated by factors other than  $[Na^+]$ . The results of phosphate ion pairing studies (Atlas et al., 1976) suggest that  $MgHA$  was the dominant ion pair in the  $ASW$ . By analogy with the phosphate results it seems likely that  $Mg$  is the major ion-pairing species for arsenate as well.

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 large difference between  $\gamma_{A(ASW)}$  and  $\gamma_{A(NaCl)}$  was due almost entirely to the formation of  $MgAsO_4^-$  and  $CaAsO_4^-$  ion pairs in the  $ASW$  and that most of the reactive  $AsO_4^{3-}$  in seawater is complexed with magnesium and calcium.

## 9. Comparison with phosphoric acid

In Table 10, values for the apparent dissociation constants of phosphoric acid (Kester and Pytkowicz, 1967) and arsenic acid (Tables 5-7) at 35‰ salinity and 25°C are presented with the calculated percentages of each of the dissociation products present at  $p[H] = 8$ . Phosphoric acid appears to be more completely dis-

Table 10. Comparison of arsenic acid with phosphoric acid, 35 ‰ salinity, 25°C,  $p[H] = 8$ .

	$H_3AsO_4$	$H_3PO_4^*$
$K_1' (\times 10^9)$	0.997	2.45
$K_2' (\times 10^7)$	7.10	8.7
$K_3' (\times 10^6)$	0.145	2.73
% $H_3A$	$1.4 \times 10^{-6}$	$3.25 \times 10^{-7}$
% $H_2A$	1.4	0.8
% $HA$	96.9	77.0
% $A$	1.7	22.2

\* 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.

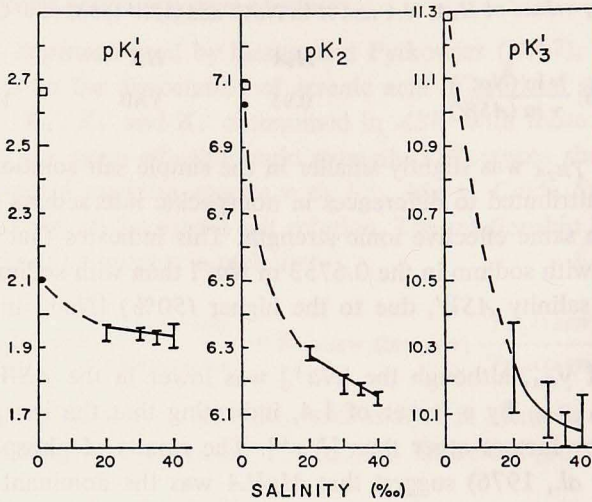


Figure 2. Smoothed curves for the apparent constants of arsenic acid shown in relationship to the thermodynamic constants determined by Agafonova and Agafonov (●) and by Flis *et al.* (□) at 5°C. The ranges of the experimental values, normalized to 5°C, are indicated by the error bars.

sociated, especially in the final dissociation, as  $K_3'$  for phosphoric acid is 19 times larger than  $K_3'$  for arsenic acid. This may reflect a higher degree of ion pairing of  $Mg^{2+}$  and  $Ca^{2+}$  with  $PO_4^{8-}$  than with  $AsO_4^{8-}$ . Nevertheless, for both arsenate and phosphate the dominant form at  $p[H]$  8 is  $HA$ .

## 10. Comparison with thermodynamic constants

Measurements of the thermodynamic dissociation constants of arsenic acid have been published by Agafonova and Agafonov (1953) and by Flis *et al.*, (1959). Those measurements are not in good agreement with each other. Both sets of data are compared in Figure 2 with our own data as a function of salinity at 5°C. For  $pK_1'$  and  $pK_2'$  the plots suggest a closer agreement of our data with those of Agafonova and Agafonov. For  $pK_3'$  only the data of Flis *et al.* are available for comparison.

## 11. 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 cali-

brate the glass electrode was reproducible to  $\pm 0.001$   $p[H]$  units on the average. Errors of  $pH$  measurements in seawater are expected to be about  $\pm 0.003$   $pH$  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 might have been caused by introduction of  $CO_3^{2-}$  or by precipitation of  $Mg(OH)_2$ . However, no evidence was found to suggest which, if any, of these factors was important.

## 12. 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  $1 \times 10^{-8}$  m. The experimental concentration used in this study was about  $4 \times 10^{-3}$  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 (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.

$$K_3' = K_3^* \left( \frac{1 + K_{MgA}^* [Mg^{2+}] + K_{CaA}^* [Ca^{2+}]}{1 + K_{MgHA}^* [Mg^{2+}] + K_{CaHA}^* [Ca^{2+}]} \right) \quad (44)$$

$K^*$  constants vary with  $\mu$  and not ionic composition. The addition of  $4 \times 10^{-3}$  m arsenate to 35‰ salinity ASW will increase  $\mu$  by about 0.6%. Since this change is too small to have a measurable effect on any of the  $K^*$  constants in (44),  $K'$  will be unaffected by the ionic strength variation accompanying addition of arsenate. One may then ask whether the high experimental concentration of arsenate would alter equation (44) by measurably changing  $[Ca^{2+}]$  or  $[Mg^{2+}]$ . Table 10 indicates that in ASW of 35‰ salinity,  $p[H] = 8$  at 25°C, 1.7% of the total arsenate is present as  $AsO_4^{3-}$ . Even if all of this, or  $7 \times 10^{-5}$  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 0.12 and 0.36% respectively. Even at  $p[H]$



= 9 the decrease would be only 1.1 and 2.8% respectively, still small relative to the experimental error in  $K_3'$ . Therefore, it can be concluded that the high experimental arsenate concentration did not significantly affect 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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