

Variation of the Apparent Dissociation Constants of Carbonic Acid With Magnesium and Calcium Concentrations in Seawater

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ABSTRACT

The effects of calcium and magnesium ion concentrations in artificial seawater (ASW) on the equilibrium state of the system $\text{H}_2\text{CO}_3\text{-H}_2\text{O}$ have been tested. The measured first and second apparent dissociation constants of carbonic acid, K'_1 and K'_2 , increase with an increase in the concentrations of calcium and magnesium in ASW. The total and free activity coefficients of HCO_3^- and CO_3^{2-} at the ionic strength of 0.718 and temperature of 25°C decrease as a function of Mg:Ca concentration ratios in ASW. The results also show that the calcium ion has a greater effect on the apparent dissociation constants of carbonic acid than magnesium, suggesting that the calcium ion associates more strongly with bicarbonate and carbonate than the magnesium ion does.

(Key words: Dissociation constant, carbonic acid, Mg, Ca, seawater)

1. INTRODUCTION

The apparent equilibrium constants of carbonic acid (Lyman, 1965; Mehrbach, 1973; Pytkowicz *et al.*, 1974) are of practical value (Feely and Chen, 1982; Chen and Drake, 1986) as long as they remain constants in the processes being considered. Such processes are photosynthesis, precipitation and dissolution of calcium carbonate, which have small effects on the major ion composition of seawater. In seawater, the apparent dissociation constants depend on the major ion composition of seawater within the pH range of oceanographic interest (Ben-Yaakov and Goldhaber, 1973; Pytkowicz, *et al.*, 1974).

In sediment reservoirs where there are physico-chemical processes that cause notable changes in the major ion composition, such as magnesium, there is a variation in the apparent dissociation constants. These processes include the diageneses of magnesian-calcite and

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dolomite (Keltz and McKenzie, 1982; Kulm *et al.*, 1984). The consumption of magnesium from interstitial water is caused by dolomitization and basalt-sediment reaction (Mcduff and Gieskes, 1976). It is suggested that marine organic matter is a significant sink for magnesium from seawater (Von Breyman, 1988). Therefore, it should be noted that reactions in pore water can affect the composition of the major ions, and generally, the apparent constants used for open ocean water cannot be applied (Pytkowicz, 1983b).

The purpose of this phase of work was to measure the variation of the apparent dissociation constants of carbonic acid in artificial seawater (ASW) having different (Mg^{2+})-to- (Ca^{2+}) ratios and the constant total ionic strength of 0.718M at 25°C. Another goal was to obtain the total and free single activity coefficients of bicarbonate and carbonate ions in the test solution.

2. THEORY OF K_1 AND K_2 DETERMINATION

In this work, the method of Weyl (1961) was modified to determine the values of the apparent dissociation constants of carbonic acid (K'_1 and K'_2). The $K'_1K'_2$ values of the test solution were first determined following the same method developed by Weyl (1961) and used by Kester and Pytkowicz (1967), Mehrbach (1973), Hawley (1973) and Pytkowicz and Hawley (1972). Then K'_1 is determined from the modified function $F(x)$:

$$F(x) = (K'_1K'_2 - x^2)/(x^2 + xK'_1 + K'_1K'_2), \quad (1)$$

where x is akin to the thermodynamic activity of hydrogen, a_H , but differs from it because the liquid junction and asymmetry potentials of pH electrodes change when they are transferred from dilute buffers to seawater (Hawley, 1973; Pytkowicz, 1983b). A further difference having a small effect, which is neglected here, occurs because an assumption is made about the activity of chloride ions when a pH is assigned to the buffer solution (Bates, 1973). Then, X is related to a_H as follows:

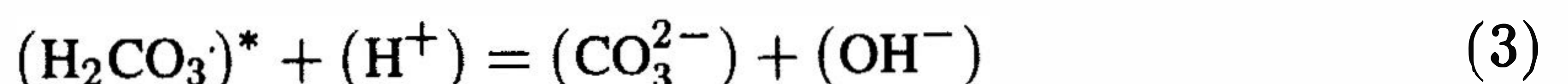
$$x = k a_H,$$

where k is constant within the reproducibility of the pH measurements. The reproducibility is high if the same types of glass electrode are used (Johnson *et al.*, 1977). K'_1 is also determined by the method used by Hawley (1973) and Pytkowicz and Hawley (1974).

The theory behind measuring the value of $K'_1K'_2$ originated from the fact that when the solution of interest is at equilibrium and the increase in HCO_3^- does not affect the equilibrium of pH, the ratio of the carbonate alkalinity to total carbon dioxide, $\text{CA}/\Sigma \text{CO}_2$, is one, and

$$\text{pH} = -\log x = 0.5(\text{p}K'_1 + \text{p}K'_2). \quad (2)$$

This pH value is defined as pH_e in this phase of work and is equivalent to point b in Figure 1. At this pH_e , the reference level of the solution is HCO_3^- and H_2O , and the proton condition is:



The function $F(x)$, introduced by Weyl (1961), is:

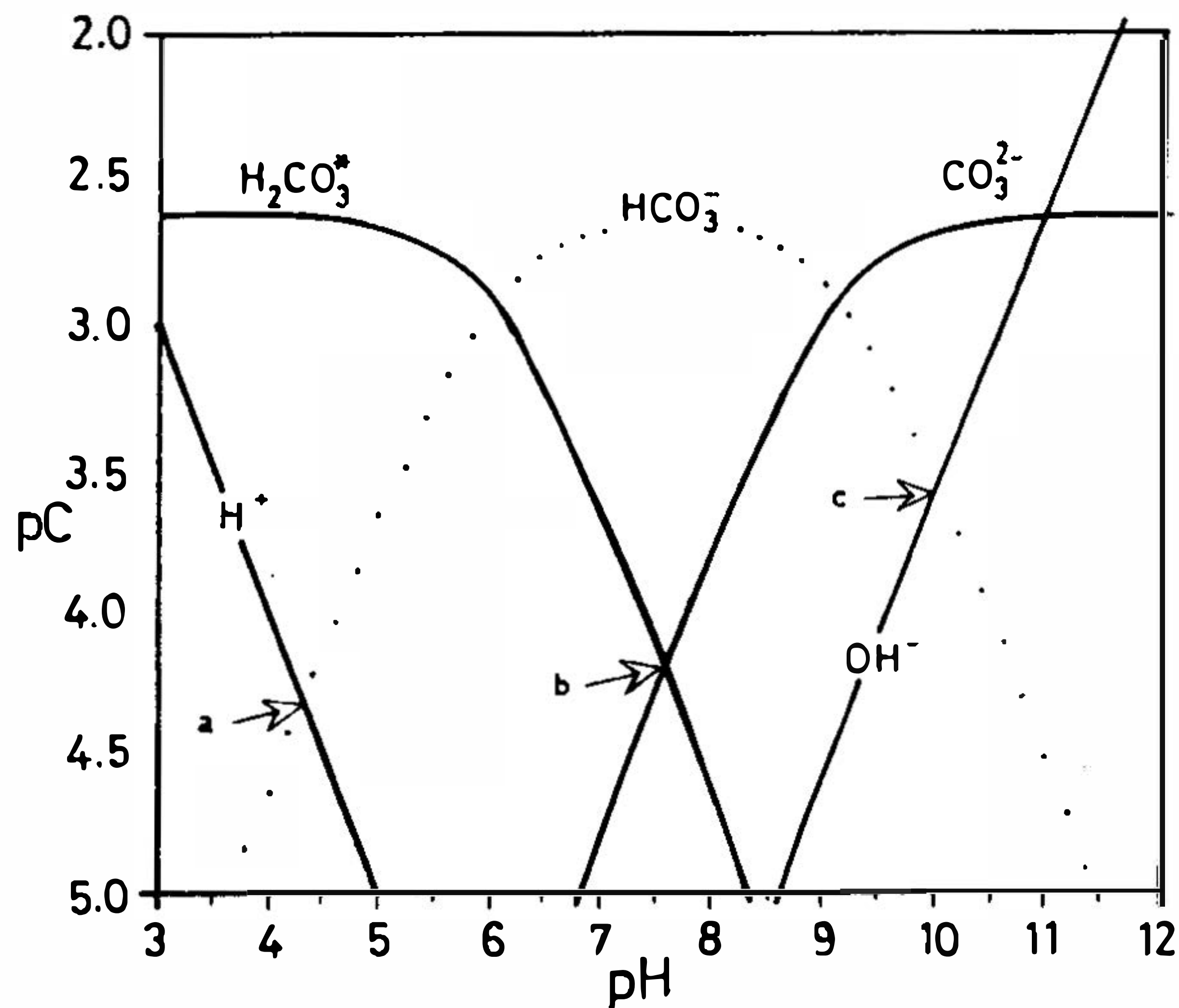


Fig. 1. pC-pH diagram of carbonic acid in seawater of 35 salinity, total CO_2 is $2.3 \text{ mmole kg}^{-1} \text{ SW}$, $K'_1 = 9.972 \times 10^{-7}$ and $K'_2 = 7.651 \times 10^{-10}$ (from Mehrbach, 1973) and $K_w = 2.399 \times 10^{-14}$ (Culberson *et al.*, 1970), showing the various equivalent points.

$$F(x) = (\text{CA}/\Sigma\text{CO}_2) - 1. \quad (4)$$

Thus equation (4) shows that $F(x) = 0$ at pH_e .

$F(x)$ was modified in this work to calculate K'_1 directly after $K'_1 K'_2$ was measured. The following equation was used:

$$K'_1 = [K'_1 K'_2 (1/F(x) - 1)/\Sigma\text{CO}_2] - [x(1 + (1/F(x)))]. \quad (5)$$

K'_1 was also determined from the graphical plot of x versus $1/\text{CA}$, following the approach developed by Hawley (1973). This approach is only applied to low pH, where only $\text{CO}_2(\text{aqueous})$, H_2CO_3 and HCO_3^- species, are dealt with, and where CO_3^{2-} is negligible.

Since the concentration of CO_3^{2-} is almost zero, carbonic acid can be treated as a monoprotic acid, making the following modification and definitions applicable:

$$\Sigma\text{CO}_2 = (\text{H}_2\text{CO}_3)^* + (\text{HCO}_3^-)_T, \quad (6)$$

where $(\text{H}_2\text{CO}_3)^*$ is the sum of $(\text{H}_2\text{CO}_3) + (\text{CO}_2)$ in solution, and the subscript T refers to total concentrations. In ASW, the total alkalinity is defined as

$$\text{TA} = (\text{HCO}_3^-)_T + (\text{OH}^-)_T - (\text{H}^+)_T. \quad (7)$$

Because borate is neglected in ASW, the carbonate alkalinity is:

$$\text{CA} = \text{TA} - (\text{OH}^-)_T + (\text{H}^+)_T = (\text{HCO}_3^-)_T. \quad (8)$$

Equations (6) and (8) yield:

$$(\text{H}^+) = (\Sigma\text{CO}_2 K'_1 / \text{CA}) - K'_1 = x. \quad (9)$$

Plotting x versus $1/CA$ gives a straight line, with the intercept at $1/CA = 0$ a negative value of K_1' , and the slope $\Sigma CO_2 K_1'$.

3. EXPERIMENTAL PROCEDURE

(Mg^{2+}), (Ca^{2+}) and (H_3BO_4)-free artificial seawater (ASW) was prepared following the formula of Kester *et al.*, (1967). This ASW with the ionic strength of 0.498M was equilibrated with laboratory pCO_2 by bubbling air through the solution for about two days. Bubbling was stopped when the measured pH was at steady-state and was not changed by further bubbling. From this ASW and the prestandardized $MgCl_2$ and $CaCl_2$ stock solutions by Mohr titration (Blaedel and Meloche, 1957), five test solutions were prepared to obtain (Mg^{2+})-to-(Ca^{2+}) concentration pairs of 0-to-0, 0-to-0.01, 0.01-to-0.01, 0.03-to-0.01 and 0.05-to-0.01 (refer to Table 2 for concentration units), for the determination of the dissociation constants of carbonic acid. These solutions had different ionic strengths, so varying amounts of reagent grade NaCl were added to maintain the ionic strength of 0.718M.

A cell was constructed from a beaker fitted in a water jack for carbonic acid equilibrium constant determination. The cell included a pH electrode (Radiometer #K2401), a reference electrode (Radiometer #G202c), a cut-off glass syringe that was gradually pushed out as the titrant was added to maintain constant pressure, a glass tube with a stopcock to serve as a passage for flushing out any excess volume, and a hole for the micrometer syringe burette (Gilmont S1200). The cell which has a volume of 82.894 ± 0.031 ml is shown in Figure 2. The water jacked beaker was connected to a water bath (VWR 1140) to maintain the temperature at $25.00 \pm 0.05^\circ C$. The electrodes were connected to a Radiometer PHM84 Research pH Meter.

Before any titration was conducted, the electrodes were standardized in two buffer solutions (NBS buffer 180f having an assigned pH of 4.006 at $25^\circ C$ and buffers 186-I-C and 186-II-C having an assigned pH of 7.415 at $25^\circ C$). The slope, S , of the electrode pair expressed in mV/pH was determined. The measured slope was compared with the theoretical one ($s = 59.155$ mV/pH at $25^\circ C$), and if it was higher than 99%, the theoretical one was usually used. The measured slopes for five different measurements are shown in Table 1.

The measured pH, pH_m , was calculated from the equation:

$$pH_m = pH_b + [(E_m - E_b)/s], \quad (10)$$

where pH_b is the pH of the standard buffer solution, E_m and E_b are the electrode potentials in the test solution and in the standard buffer solutions, respectively, and s is the slope of the electrode pair.

Table 1. The measured slopes, s , of the electrode pair from five different measurements using NBS pH buffers 4.006 and 7.415 at $25^\circ C$.

Measurement No.	s	% error
1	58.756	0.667
2	58.786	0.624
3	58.844	0.526
4	58.815	0.575
5	58.874	0.475

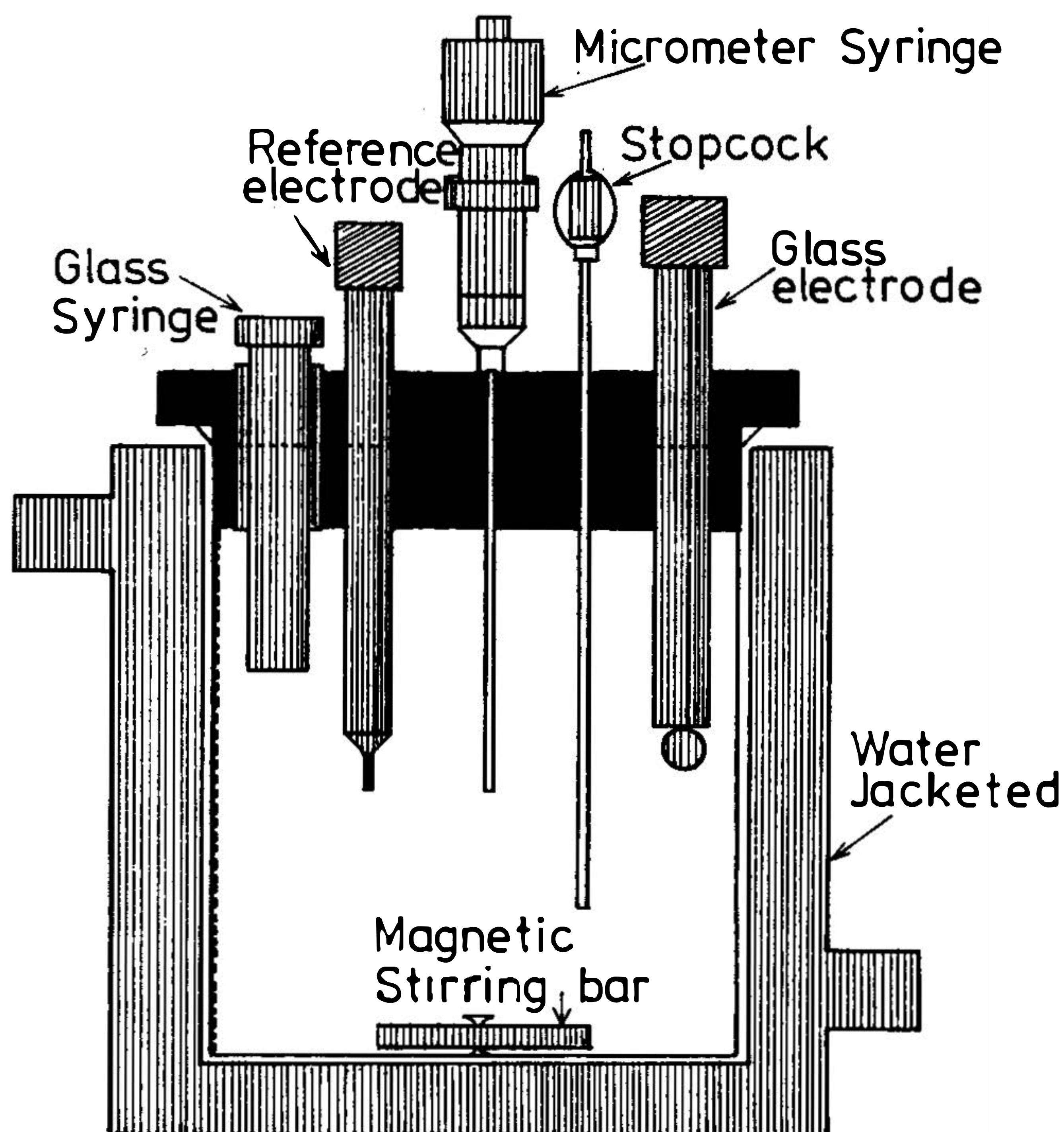


Fig. 2. The Titration Cell.

For the determination of $K'_1 K'_2$, the titration cell previously described was completely filled with the solution to avoid the exchange of CO_2 . The pH of the test solution was dropped to approximately -0.05 pH units lower than the $0.5(pK'_1 + pK'_2)$ by the addition of a few tenths of a ml of 0.1N HCl. Then, about 5 to 8 mg reagent grade NaHCO_3 was placed in a dry 2.5 ml Hamilton syringe, and about 0.5 ml of CO_2 -free distilled water was pulled into the syringe to dissolve the salt. The solution in the syringe was injected slowly into the test solution through the hole in the stopcock while stirring was maintained. After the solution was stirred for about two to three minutes, the electrode potential was recorded for two to three minutes without further stirring. Usually, about five to seven additions of NaHCO_3 were made to achieve a constant pH. The final total alkalinity of the test solution ranged from 3.49 to 5.75 meq kg^{-1} ASW.

The purity of the reagent grade NaHCO_3 is represented by the sample value of $\text{CA}/\Sigma \text{CO}_2$. Pure bicarbonate has a value of one, while a sample contaminated with carbonate has a value of more than one. Since by definition, the primary standard's $\text{CA}/\Sigma \text{CO}_2$ is exactly one, its steady-state pH is equal to $0.5(pK'_1 + pK'_2)$. The steady-state is some value greater than $0.5(pK'_1 + pK'_2)$ due to contamination with carbonate. The values of $K'_1 K'_2$ and K'_1 in 0.72M NaCl (Hawley and Pytkowicz, 1973) were substituted in the following equation:

$$\text{CA}/\Sigma \text{CO}_2 = (K'_1 10^{-pH_e} + 2K'_1 K'_2) / [(10^{-pH_e})^2 + K'_1 10^{-pH_e} + 2K'_1 K'_2]. \quad (11)$$

The value of $\text{CA}/\Sigma \text{CO}_2$ for NaHCO_3 used in this work as calculated from equation (11) was 1.0057. This was equivalent to a value of 0.0117 ± 0.001 pH unit between pH_e and $0.5(pK'_1 + pK'_2)$.

The same cell was also used for the determination of K'_1 . The cell was completely filled with the test solution, and the electrodes were allowed to equilibrate until the potential was changed by less than 0.1 mv hr^{-1} . Then, the solution was titrated with standard HCl (0.1001 N) from a calibrated syringe burette (Gilmont #S1200). The initial titration alkalinity in the titration cell were calculated from the weight of the test solution. The titration alkalinity at each point during the titration was obtained from the equivalents of alkalinity initially present minus the equivalents of HCl added. x versus $1/CA$ indicated by equation (9) is shown in Figure 3. The departure from linearity was tested from the first three titration points using the slope of x versus $1/CA$ as calculated by the least squares method. Then the fourth data point was combined with the first three, and when the slope from the successive calculation changed less than 0.5 percent, the value of the slope obtained, $\Sigma CO_2 K'_1$, was used to calculate K'_1 . K'_1 was calculated at each point on the titration curve from the expression $K'_1 = (\Sigma CO_2 K'_1 / CA)^{-x}$, and K'_1 was taken as the mean of the individual values.

From each test solution, at least two aliquots were brought to different pH values with HCl, and re-weighed amounts of sodium bicarbonate were added to the test solution. The change in the pH was recorded, and the amount of acid or base, z , required to produce the same change in pH was obtained from the titration curve of the same test solution. This had been done before. $1/F(x)$ was calculated from the moles of (HCO_3^-) and (H^+) added per kg ASW, where $F(x) = \text{moles of } (H^+) / \text{moles of } (HCO_3^-)$ (acid-base comparison) (Weyl, 1961). Then the $K'_1 K'_2$ values of the test solution obtained from pH steady-state were used to calculate K'_1 , as follows:

$$K'_1 = [K'_1 K'_2 (1/F(x) - 1)/x] - x(1 - 1/F(x)). \quad (12)$$

The K'_1 value obtained from equation (12) was introduced into the expression:

$$(F(x) - K'_1 K'_2 - x^2)/(x^2 + xK'_1 + K'_1 K'_2) = \Delta \quad (13)$$

and modified to obtain $\Delta = 0$.

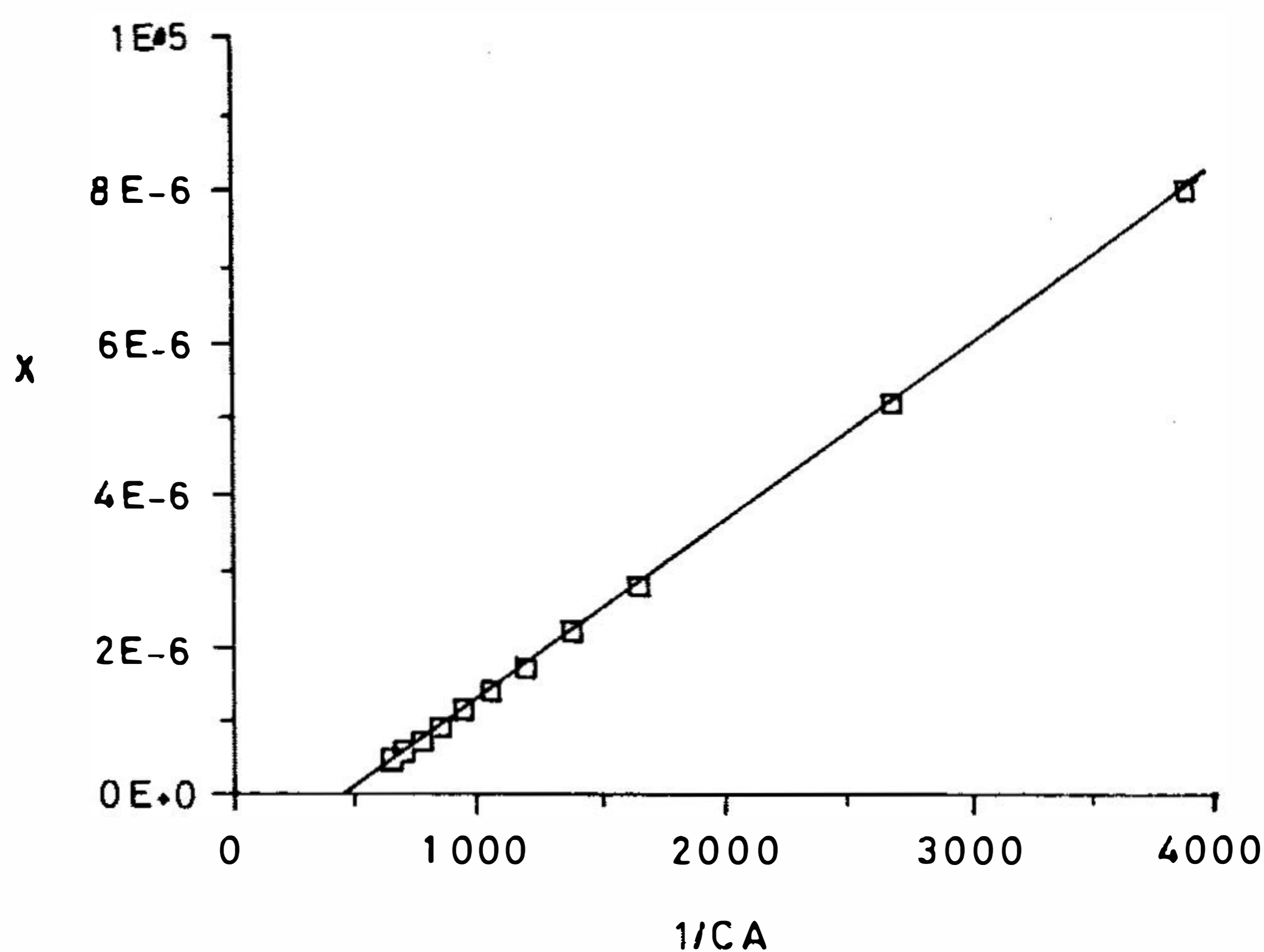


Fig. 3. Plot of x versus $1/CA$ from (Mg^{2+}) -to- (Ca^{2+}) concentration ratios equals 0-to-0.

4. RESULTS AND DISCUSSION

The results of pH_e and $K'_1K'_2$ are shown in Table 2. The values of the first apparent dissociation constants, determined by the modified Weyl's (1961) $F(x)$ function after the mean of the $K'_1K'_2$ values in Table 2 was taken, and those values from the graphical plot of x versus $1/CA$ are shown in Table 3.

The data in Table 3 shows that there is an increase in the K'_1 value with an increase in the (Mg^{2+}) -to- (Ca^{2+}) concentration ratios in solution. The results of $K'_1K'_2$ in Table 2 indicate a relationship with (Mg^{2+}) -to- (Ca^{2+}) . Both K'_1 and $K'_1K'_2$ show a positive correlation with the metal concentration in the solutions of constant ionic strength (Figures 4 and 5). The curvature in Figure 4 may be due to the formation of triple ions (Hawley, 1973). This is usually attributed to the formation of ion-pairs which decreases the activity coefficients and increases the solubility products in the same electrolyte solution (Kester, 1969; Kester and Pytkowicz, 1969; Pytkowicz, 1969 and 1983a; Pytkowicz and Hawley, 1974). The data also show that (Ca^{2+}) was relatively more effective with dissociation constants than (Mg^{2+}) , which suggests that Ca^{2+} associated with bicarbonate and carbonate more strongly than Mg^{2+} does. This was illustrated by the higher shift of the first and second ionization fractions, α_1 and α_2 , of carbonic acid in Figure 6, when only $Ca^{2+} = 9.73 \text{ mmole l}^{-1}$ was added to the test solution compared to the shift that was produced when $(Mg^{2+}) = 29.56 \text{ mmole l}^{-1}$ was added in the presence of (Ca^{2+}) . In the former, the shift increased and became obvious when the concentration of (Mg^{2+}) was five times more than that of (Ca^{2+}) .

Table 2. Determination of pH_e and $K'_1K'_2$ of carbonic acid in ASW of different (Ca^{2+}) and (Mg^{2+}) concentrations and at the total ionic strength of 0.718 at 25°C.

solution No.	(Ca^{2+})		(Mg^{2+})	pHe	$K'_1K'_2$ (10^{+16})
	mmol	kg ⁻¹	ASW		
1	0		0	7.808	2.4210
				7.811	2.3878
				7.814	2.3550
				7.810	2.3988
2	9.7060		0	7.682	4.3251
				7.686	4.2462
				7.683	4.3053
				7.682	4.3251
3	9.7117		9.6847	7.672	4.5290
				7.668	4.6132
				7.648	4.7643
				7.663	4.7206
4	9.7262		29.5603	7.650	5.0119
				7.647	5.0816
				7.648	5.0582
				7.639	5.2723
5	9.7249		48.9854	7.541	8.2794
				7.458	8.0168
				7.538	8.3946
				7.539	8.3560

Table 3. The values of $K_1'K_2'$ and K_1' of carbonic acid in ASW of various (Ca^{2+}) and (Mg^{2+}) concentrations and at the total ionic strength of 0.718 at 25°C.

solution No.	(Ca^{2+})		(Mg^{2+}) ASW	$K_1'K_2'$ (10^{+16}) (1)	K_1' (10^{+6})	
	mmol	kg ⁻¹			(2)	(3)
1	0	0	0	2.3904±0.27	1.039	1.051
					1.034	1.041
					1.053	1.037
2	9.7060	0	4.3004±0.036	1.088	1.075	
				1.069	1.084	
3	9.7117	9.6847	4.6568±0.096	1.121	1.104	
				1.097	1.103	
					1.093	
4	9.7262	29.5603	5.1060±0.123	1.118	1.119	
					1.113	
5	9.7249	48.9854	8.2617±0.166	1.169	1.169	
				1.162	1.157	
					1.144	

(1) $K_1'K_2'$ are the mean of the values in Table 2.

(2) K_1' values were determined from equations (12) and (13).

(3) K_1' values were determined from the plot of x versus $1/\text{CA}$.

Two successful approaches have been used to account for the effect of the interaction on activity coefficients. First, in the ionic-pair concept, as introduced to the mixed electrolyte solution by Garrels and Thompson (1962), association constants are determined and applied to seawater. Second, in the specific interaction model of Bronsted (1922), Guggenheim (1935) and Pitzer, (1971), the interaction terms of an unspecified nature are measured in a binary solution and applied to seawater (Leyendekkers, 1972; Robinson and Wood, 1972; Whitfield, 1973).

The total activity coefficients of bicarbonate and carbonate, $(\gamma \text{HCO}_3^-)_T$ and $(\gamma \text{CO}_3^{2-})_T$ at different magnesium-to-calcium concentration ratios were calculated following the method of Pytkowicz (1975):

$$(\gamma \text{HCO}_3^-)_T = K_1^o/K_1'(\gamma \text{CO}_2) a_w k, \quad \text{and} \quad (14)$$

$$(\gamma \text{CO}_3^{2-})_T = K_1^oK_2^o/K_1'K_2'(\gamma \text{CO}_2) a_w k. \quad (15)$$

The thermodynamic dissociation constants, K_1^o and K_2^o , used here were from Harned and Davies (1943) and from Harned and Scholes (1941). The activity coefficient of CO_2 was obtained from the expression:

$$(\gamma \text{CO}_2) = s_{DW}/s_{SW}, \quad (16)$$

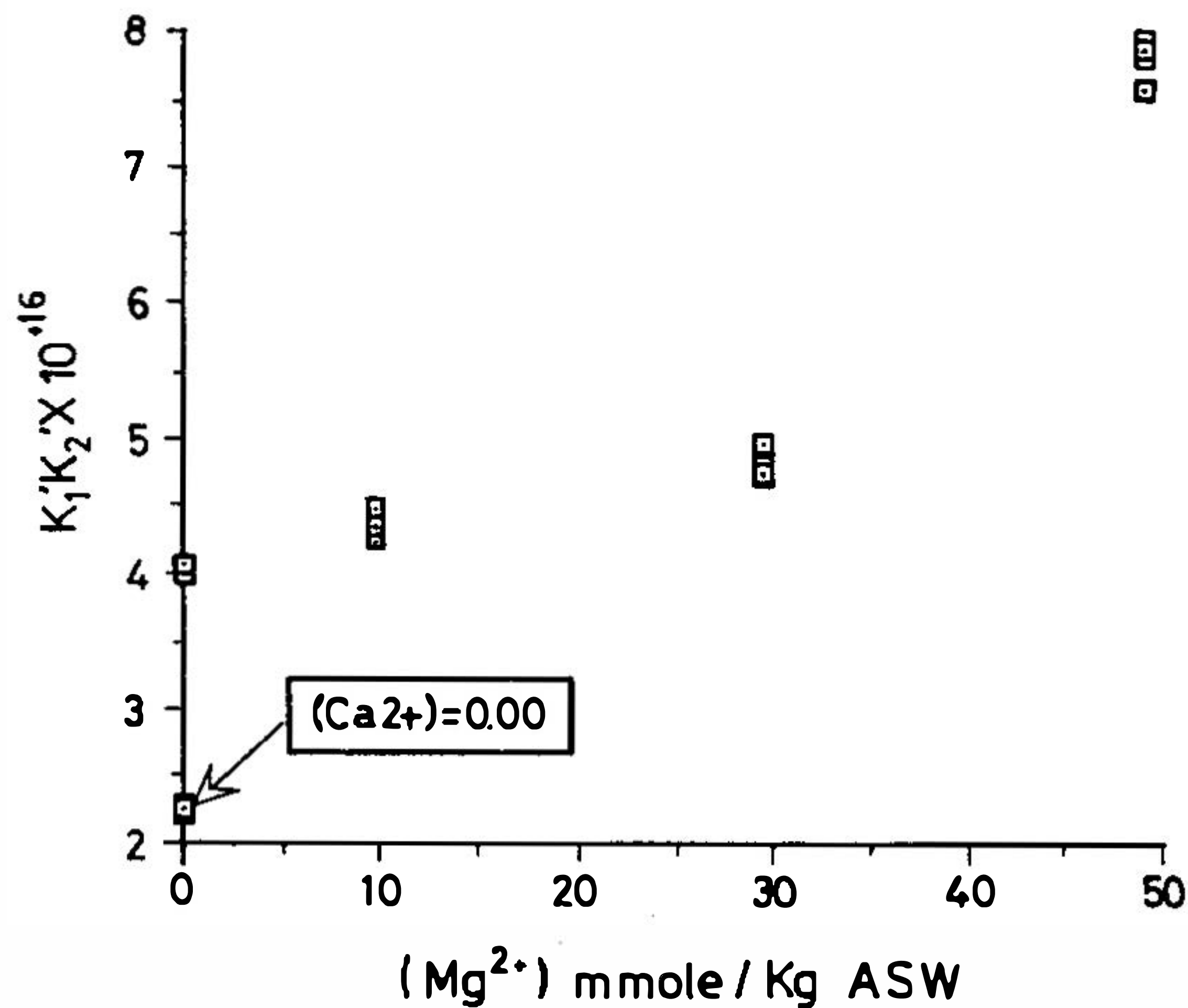


Fig. 4. The measured values of $K'_1K'_2$ of carbonic acid in ASW having different (Mg^{2+}) concentration and $9.71 \text{ mmole kg}^{-1}$ ASW and total ionic strength of 0.718 at 25°C .

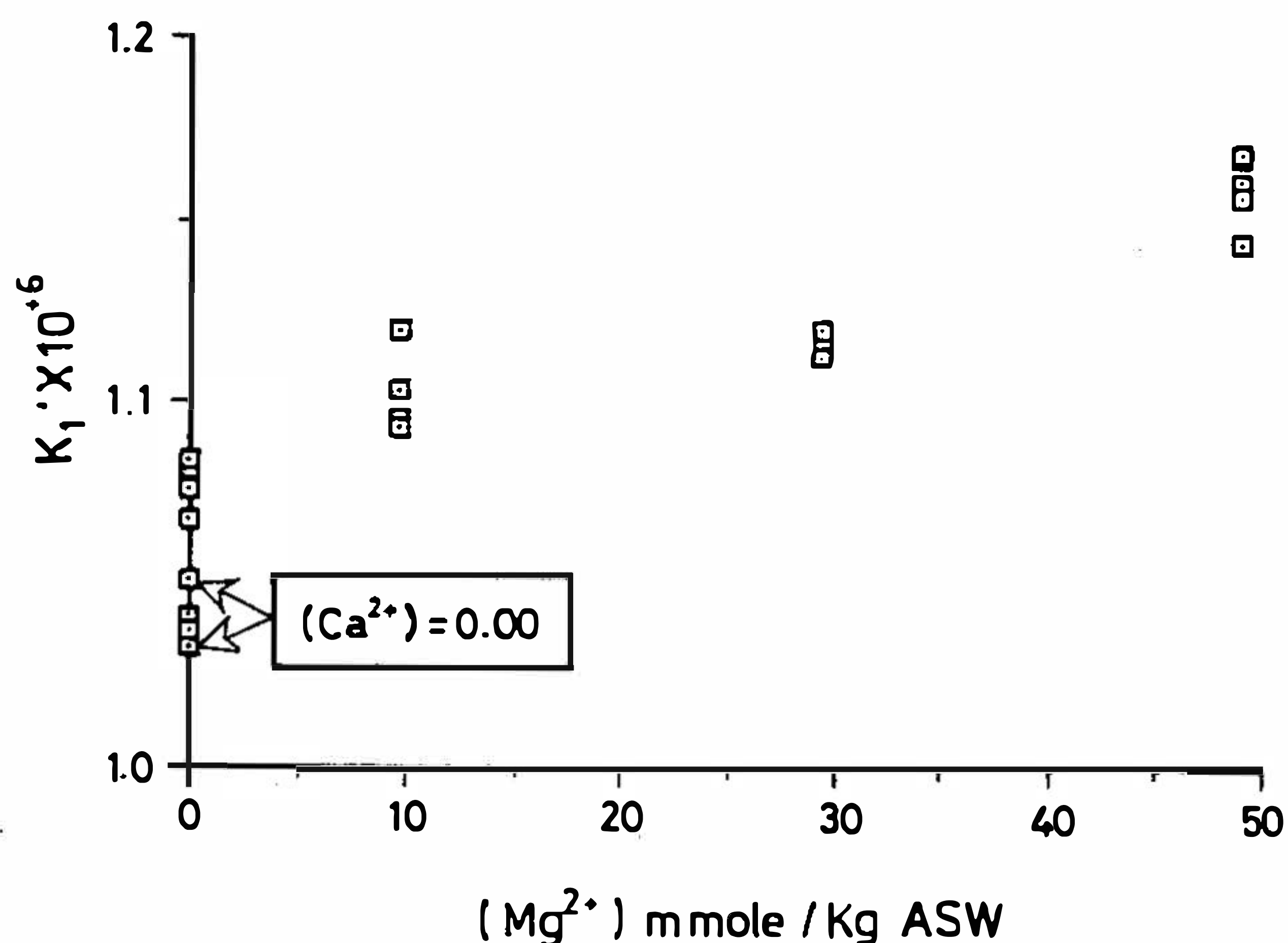


Fig. 5. The measured first dissociation constants, K'_1 , in ASW having different (Mg^{2+}) concentrations and $9.71 \text{ mmole kg}^{-1}$ ASW and total ionic strength of 0.718 at 25°C .

where s_{DW} and s_{SW} are the Bunsen coefficients of distilled water and seawater respectively, as determined by Murry and Riley (1971). The solutions were treated as seawater with different salinities. The computed activity coefficients of the CO_2 of the solutions and the values of θ , the factor which was used to convert the concentrations from $\text{mole kg}^{-1} SW$ into $\text{mole kg}^{-1} \text{H}_2\text{O}$, are shown in Table 4. The activity of water, a_w , as a function of salinity, S , in the solutions was determined from the equation of Robinson (1954) by:

$$a_w = 1 - 5.096 \times 10^{-4} S - 1.31 \times 10^{-6} S^2. \quad (17)$$

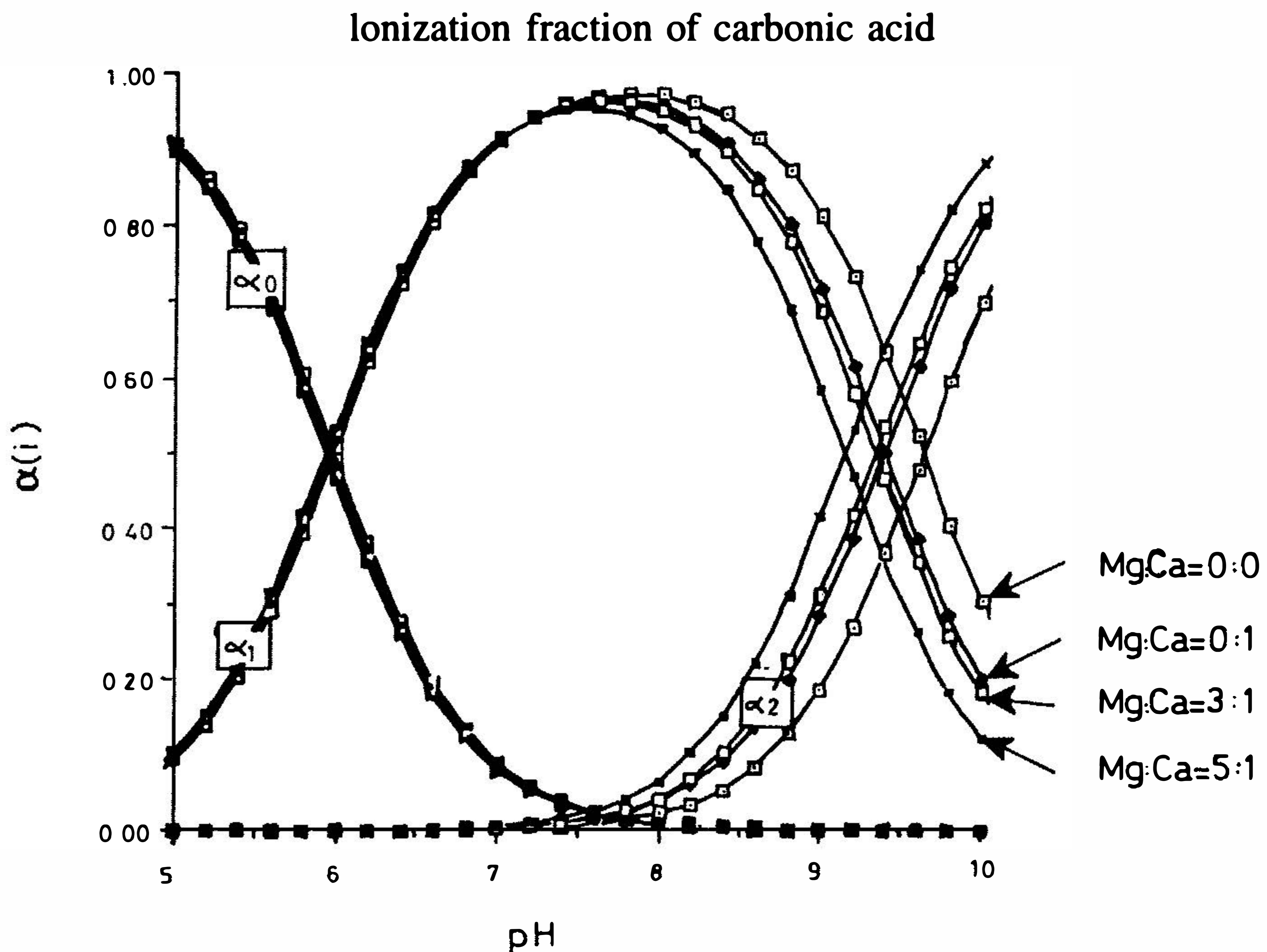


Fig. 6. The ionization fraction of carbonic acid, α_i , of different (Mg^{2+})-to- (Ca^{2+}) concentration ratios in ASW versus pH.

The factor k was estimated from the following equation:

$$\begin{aligned} K_1' &= (\text{H}^+) (\text{HCO}_3^-)_T k(\gamma \text{H}^+) / (\text{H}_2\text{CO}_3)^* \\ &= K_1'' k(\gamma \text{H}^+)_F \end{aligned} \quad (18)$$

The value of K_1'' was found to be 1.105×10^{-6} at the ionic strength of 0.718 from Harned and Bonner (1945) and that of (γH^+) was 0.866. The value of k was 1.140 for the test solutions which is in agreement with $k = 1.134$ as determined by Hawley (1973). The estimated total activity coefficients of the carbonate system are reported in Table 5 and indicate a decrease in the total activity coefficients with an increase in the major ions in the solutions resulting from the formation of ion pairs in the electrolyte solution.

Table 4. The salinity, S , the factor, θ , and the activity coefficients of CO_2 for various (Mg^{2+})-to- (Ca^{2+}) concentration ratios in the test solution of $I_T = 0.718$ and 25°C .

(Mg: Ca) solution	S	θ	(γCO_2)
0:0	41.26	0.9587	1.209
0:1	40.64	0.9594	1.205
1:1	39.27	0.9603	1.200
3:1	38.27	0.9617	1.191
5:1	36.72	0.9633	1.182

Table 5. Total activity coefficients of bicarbonate and carbonate ions in the test solutions of various (Mg²⁺)-to-(Ca²⁺) concentration ratios at 25°C and $I_T = 0.718$.

(Mg: Ca) _{solution}	(γHCO_3^-) _T	(γCO_3^{2-}) _T
0:0	0.574	0.117
0:1	0.553	0.065
1:1	0.539	0.060
3:1	0.529	0.054
5:1	0.505	0.033

Additionally, the free activity coefficients of bicarbonate and carbonate ions were estimated following the relationships:

$$(\gamma \text{HCO}_3^-)_F = (\gamma \text{HCO}_3^-)_T (\text{HCO}_3^-)_T / (\text{HCO}_3^-)_F, \quad \text{and} \quad (19)$$

$$(\gamma \text{CO}_3^{2-})_F = (\gamma \text{CO}_3^{2-})_T (\text{CO}_3^{2-})_T / (\text{CO}_3^{2-})_F. \quad (20)$$

The total concentration of bicarbonate, $(\text{HCO}_3^-)_T$, and carbonate, $(\text{CO}_3^{2-})_T$, were calculated from the pH and TA measurements. The concentrations of free bicarbonate, $(\text{HCO}_3^-)_F$, and carbonate, $(\text{CO}_3^{2-})_F$, were calculated using the MICROQL program (Westall, 1979). The association constants of ions pairs formed in the test solutions are shown in Table 6.

Table 6. The equilibrium constants of ion-pairs formation used to calculate the concentrations of free ions of bicarbonate and carbonate.

Species	Reference	Species	Reference
1. NaCl	1	13. CaCl ⁺	1
2. NaSO ₄ ⁻	2	14. CaSO ₄ [°]	2
3. NaHCO ₃ [°]	5	15. CaHCO ₃ ⁺	5
4. NaCO ₃ ⁻	5	16. CaCO ₃ [°]	5
5. NaF [°]	6	17. CaF ⁺	6
6. MgCl ⁺	1	18. KCl [°]	1
7. MgSO ₄ [°]	2	19. KSO ₄ ⁻	4
8. MgHCO ₃ ⁺	5	20. HCl [°]	1
9. MgCO ₃ [°]	5	21. H ₂ CO ₃	7
10. Mg ₂ CO ₃ ²⁺	5	22. HCO ₃ ⁻	7
11. MgCaCO ₃ ²⁺	5	23. H ₂ O	8
12. MgF ⁺	4		

1. Johnson and Pytkowicz, (1978); 2. Pytkowicz and Kester, (1968); 3. Kester and Pytkowicz, (1969); 4. Elegquist and Wedborge, (1975); Pytkowicz and Hawley, (1974); 6. Miller and Kester, (1975); 7. From Table 2 and 3; 8. Culberson and Pytkowicz, (1973).

The values of the free activity coefficients of bicarbonate and carbonate are much higher than the total activity coefficients of the same species, as shown in Table 7. They also show the same trend of decreasing with the presence of (Ca²⁺) and (Mg²⁺) ions in the solution.

Table 7. Free activity coefficients of bicarbonate and carbonate ions in the test solutions of different (Mg²⁺)-to-(Ca²⁺) concentration ratios at 25°C and $I_T = 0.718$.

(Mg: Ca) _{solution}	($\gamma_{\text{HCO}_3^-}$) _F	($\gamma_{\text{CO}_3^{2-}}$) _F
0:0	0.678	0.247
0:1	0.646	0.239
1:1	0.644	0.232
3:1	0.639	0.229
5:1	0.634	0.217

The concentration variations of major ions occur mainly in sediments, where the concentrations of magnesium and calcium in pore water are affected by various chemical processes. According to Drever, (1974), Holland, (1978), and Pytkowicz, (1983a) these processes include: the uptake of Mg²⁺ during dolomitization, ion exchange of Ca²⁺ on exchange sites of clays by Mg²⁺, Na⁺ and K⁺ formation of illite as sinks for Mg²⁺ in oceans, uptake of buricite between silicate layers of monotmorillonites, gibbsite-chloride transformation and the precipitation of sepiolite. There is also the input of Mg²⁺, such as in evaporite deposits. Sayles *et al.*, (1973) have concluded that there is about a 16% decrease in the Mg²⁺ concentration in the sediment. Therefore, according to the results in this study, a 16% drop in Mg²⁺ in the sediment causes a decrease of about 1.3% in the value of K'_1 and about a 14.1% drop in the value of K'_2 .

5. CONCLUSIONS

The variation in the apparent dissociation constants of carbonic acid which has been shown in this study, and probably that of other acids, depends upon the major ion composition of the solution at constant ionic strength. This variation is attributed to the formation of ion pairs such as CaHCO₃⁺, CaCO₃^o, Ca₂CO₃²⁺, MgHCO₃⁺, MgCO₃^o and Mg₂CO₃²⁺. This supports the validity of the ion association model as an adequate formal representation of the behavior of the activity coefficients and equilibrium constants (Pytkowicz, 1983b).

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