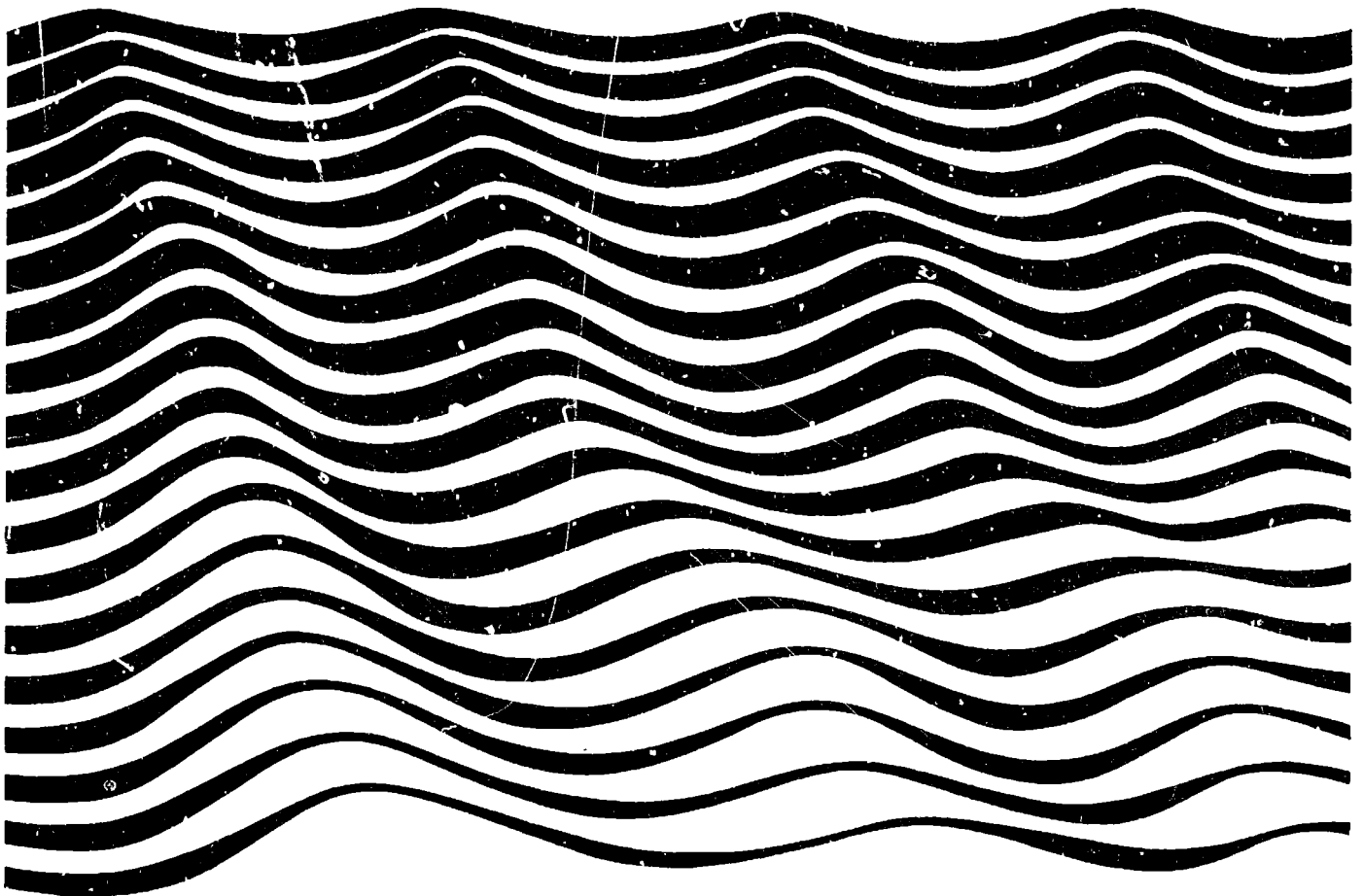


Carbon dioxide sub-group of the joint panel on oceanographic tables and standards

Report of a meeting
Miami, Florida
21-23 September 1981
sponsored by
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PREFACE

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Abstract

This report represents a summary of the discussions and recommendations, made during a meeting of the Carbon Dioxide Sub-Group of the Joint Panel on Oceanographic Tables and Standards in Miami, Florida, September 21-23, 1981.

Comparisons of the dissociation constants of carbonic acid indicate substantial agreement between various available sets of data, but it was agreed that data for the dissociation constants of boric acid needed closer scrutiny. Studies of the solubility product of calcite and aragonite in seawater still show unsatisfactory agreement, particularly for aragonite.

Recommendations are presented for a formula for the solubility of carbon dioxide, the measurement of pH, and further work on the dissociation constants of carbonic acid and boric acid, as well as on the solubility product of calcium carbonate in seawater.

1. OPENING OF THE MEETING

The meeting was opened at 10 a.m. on Monday, September 21 by the Chairman, J.M. Gieskes, at the Rosenstiel School of Marine and Atmospheric Sciences of the University of Miami. Dr. F.J. Millero, largely responsible for the organization of the meeting, welcomed the membership of the CO₂ sub-group and discussed arrangements for the meeting.

The following members were in attendance:

Dr. J.M. Gieskes (Chairman)	Scripps Institution of Oceanography Ocean Research Division, A-015 University of California, San Diego La Jolla, CA 92093	SCOR
Dr. R. Bates	Department of Chemistry University of Florida Gainesville, FL 32611	ICES
Dr. D. Dyrssen	Department of Analytical and Marine Chemistry Chalmers University of Technology and University of Göteborg S-412 96 Göteborg 5, Sweden	ICES
Dr. F.J. Millero	Rosenstiel School of Marine and Atmospheric Sciences 4600 Rickenbacker Causeway Miami, FL 33149	UNESCO
Dr. A. Poisson	Laboratoire d'Océanographie Physique Universite P. & M. Curie Tour 24, 4 Place Jussieu 75230 Paris, Cedex 05 France	ICES
Dr. R.M. Pytkowicz	School of Oceanography Oregon State University Corvallis, OR 97331,	SCOR
Dr. G. Skirrow	Department of Chemistry The University Liverpool, England U.K.	UNESCO
Dr. S. Morcos	Division of Marine Sciences 7 Place de Fontenoy 75700 Paris France	UNESCO

2. OBJECTIVES OF THE MEETING

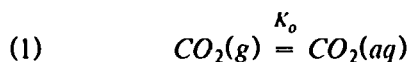
During its 9th meeting in Paris (11-13 September, 1978) the Joint Panel on Oceanographic Tables and Standards, upon suggestions by its sponsoring agencies, decided that, especially because of the increased importance of precise evaluations of carbon dioxide speciation in seawater, a sub-group of the panel should be formed to consider the information available on the thermodynamics of the CO_2 system in seawater (see also SCOR Proceedings, Vol. 17, No. 1, 1981). For these reasons a meeting was arranged in Miami, Florida on September 21-23, 1981, in which various experts, who have been involved in recent work on the thermodynamics of the carbon dioxide system could exchange their views, compare data sets, and recommend possible further work to resolve any discrepancies in these data sets.

The terms of reference as defined by the present CO_2 sub-group are as follows:

- (1) The state of knowledge of the dissociation constants of the carbonic acid system should be appraised;
- (2) Data sets on these constants should be compared when possible;
- (3) Means of improvement of thermodynamic information should be identified, i.e., further measurements and research should be indicated;
- (4) New tables should be considered.

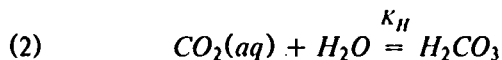
3. THERMODYNAMICS OF THE CO_2 SYSTEM

The carbon dioxide system in seawater is governed by the following equilibria:

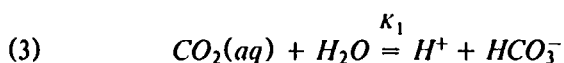


Where K_o is the solubility coefficient of carbon dioxide in seawater.

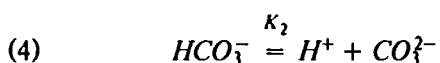
Subsequently, the dissolved gas becomes hydrated



where $K_H \sim 10^{-3}$, so that most undissociated dissolved CO_2 gas is in the $CO_2(aq)$ form. Because K_H is not well known it is a practice to set $K_H = 1$ (hydrate convention; Lewis and Randall, 1961), as a result of which $CO_2(aq)$ and H_2CO_3 are considered as one species in the following equation for the dissociation of dissolved carbon dioxide (or carbonic acid).



where K_1 is the *first* stoichiometric dissociation constant of carbonic acid, and



where K_2 is the *second* stoichiometric dissociation constant of carbonic acid.

In seawater estimates of carbon dioxide speciation often rely on estimates of the titration alkalinity (TA)

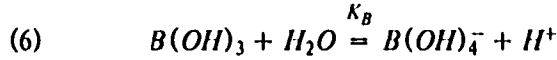
$$(5a) \quad TA = (HCO_3^-) + 2(CO_3^{2-}) + (B(OH)_4^-) + (OH^-) - (H^+)$$

Titration alkalinity generally includes minor species of carbonic acid and weaker acids (Dickson, 1981;

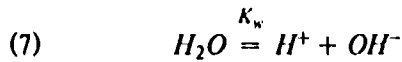
Johansson and Wedborg, 1982).

$$(5b) \quad TA = (HCO_3^-) + 2(CO_3^{2-}) + (B(OH)_4^-) + (OH^-) + (Si(OH)_3^-) + (HPO_4^{2-}) + 2(PO_4^{3-}) - (H^+) - (HSO_4^-) - (HF) - (H_3PO_4)$$

In the speciation calculations only the carbon dioxide contributions to TA, i.e. carbonate alkalinity ($CA = (HCO_3^-) + 2(CO_3^{2-})$), are considered so that correction to TA must be made for the contributions of $(B(OH)_4^-)$, (OH^-) and (H^+) . For this one needs to consider the equilibria

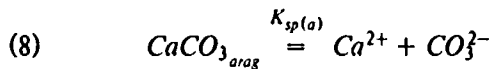


where K_B is the stoichiometric dissociation constant of boric acid, and

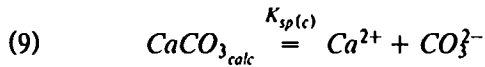


where K_w is the dissociation constant for water.

Finally, in seawater often the solubility of calcium carbonate, both of its polymorphic forms aragonite and calcite, are considered. These solubilities are governed by the following equilibria:



and



where $K_{sp(i)}$ is the stoichiometric solubility product of aragonite or calcite.

During the last few years a large amount of work has been carried out on the determination of the various equilibrium constants, particularly by the research groups associated with Dr. David Dyrssen (University of Göteborg, Sweden) and Dr. Ricardo Pytkowicz (Oregon State University). The panel has made it its task to study the data sets available from these two laboratories, because these data were considered to be more reliable than previously available information.

4. SOLUBILITY OF CARBON DIOXIDE

The ad-hoc group discussed the data available on the solubility of carbon dioxide in seawater. It was decided that the formula provided by Weiss (1974) gives the best representation of CO_2 gas solubility as a function of temperature and salinity as measured by Murray and Riley (1971) and Weiss (1974).

$$(4.1) \quad \ln K_o = A_1 + A_2(100/T) + A_3 \ln(T/100) + S[B_1 + B_2(T/100) + B_3(T/100)^2]$$

where K_o may be expressed either in moles $dm^{-3} atm^{-1}$ (referring to a dm^3 of solution at the temperature measurement and one atmosphere fugacity in the gas phase) or in moles $kg^{-1} atm^{-1}$ (referring to one kilogram of solution). T is the absolute temperature ($^{\circ}K$) and S the salinity. A_i and B_i are constants and are given in the following table:

	moles·dm ⁻³ ·atm ⁻¹	moles·kg ⁻¹ (seawater)·atm ⁻¹
A ₁	-58.093 1	-60.240 9
A ₂	90.506 9	93.451 7
A ₃	22.294 0	23.358 5
B ₁	0.027 766	0.023 517
B ₂	-0.025 888	-0.023 656
B ₃	0.005 057 8	0.004 703 6

5. COMPARISON OF DATA SETS ON K₁ AND K₂ OF CARBONIC ACID

In this section we present an analysis of the data sets available on K₁ and K₂ of carbonic acid as well as an error analysis based on possible variations between these data sets.

5.1 Comparison of dissociation constants

Measurements of the apparent (K_i^a) or stoichiometric (K_i^s) ionization constants for carbonic acid have been made by a number of workers (Buch *et al.*, 1932; Buch, 1951; Lyman, 1957; Mehrbach *et al.*, 1973; Hansson, 1972). The more recent work of Mehrbach *et al.* and of Hansson is more reliable than earlier studies, so that here only a comparison of these data sets will be presented. Before such a comparison can be made it is necessary to discuss the various pH scales used by recent workers.

5.1.1 Definition of pH

The pH value in the seawater medium has been defined in three different ways. Corresponding to these are three different values of the dissociation constants K₁ and K₂ (as well as K_B). It is convenient to distinguish these by different symbols, as follows

pH	pK (= -logK)	
pH _{NBS} ¹⁾	pK'	Mehrbach <i>et al.</i>
pH _t	pK*	Hansson
pm _H	pK _c	Bates and Culberson

1) NBS = National Bureau of Standards

Here m_H designates the concentration (molality) of *free* hydrogen ions, whereas H_t designates the *total* concentration of hydrogen ions.

Intercomparison of pm_H and pH_t is readily possible when values for the formation constants of the species HSO₄⁻ and HF are known:

$$(5.1.1.1) \quad pH_t = pm_H - \log[1 + \beta_{HSO_4} (SO_4^{2-})_t + \beta_{HF} (F^-)_t]$$

Conversion of pH_{NBS} to pH_t or pm_H is less easy, as some dependence on liquid junction structure may be involved. Nevertheless, this can be accomplished through the measurement of the quantity (γ_H)_t for the particular conditions of the experiment. Here (γ_H)_t is the apparent total hydrogen ion activity coefficient (Bates and Culberson, 1977).

$$(5.1.1.2) \quad (\gamma_H)_t = 10^{-pH(NBS)/(H^+)_t}$$

or

$$(5.1.1.3) \quad pH_t = pH_{NBS} + \log(\gamma_H)_t$$

The pH on the NBS scale yields the quantity $k_H a_H = 10^{-pH(NBS)}$, where k_H describes the effect of liquid junction potential changes when electrodes are transferred from buffers to seawater. k_H is roughly 1.13 (Hawley and Pytkowicz, 1973). In practice k_H cancels out within the reproducibility of pH measurements when dissociation constants are measured and applied in a consistent manner. The reproducibility of pH measurements is ± 0.006 (Johnson *et al.*, 1977) when glass electrodes are calibrated against hydrogen ion electrodes.

The three pH scales should lead to results which are nearly the same when k_H and $(\gamma_H)_i$ corrections are applied.

Bates (m.s.) obtained the approximate intercomparison at 25°C in seawater with salinity = 35:

$$(5.1.1.4) \quad \begin{aligned} pH_{NBS} &= p a_H - 0.076 \\ p m_H &= p a_H - 0.080 \\ pH_i &= p m_H - 0.130 \end{aligned}$$

These relationships take into account k_H and γ_H (Mehrbach *et al.*, 1973). Values of $(\gamma_H)_i$ as a function of temperature and salinity have been estimated by Mehrbach *et al.* (1973):

t °C	S	$(\gamma_H)_i$	
2.00	27.01	0.770	
		0.774	
	34.78	0.802	
13.00	26.76	0.801	
		0.813	
		0.718	
	34.76	0.731	
		0.750	
		0.755	
25.00	42.85	0.787	
		0.788	
		0.677	
	19.19	0.677	
		25.25	0.674
		0.677	
		31.49	0.684
		0.684	
		35.10	0.690
35.00	26.75	0.695	
		0.695	
		0.688	
	34.95	0.625	
		0.624	
		0.619	
		42.67	0.629

Bates and Culberson (1977) made a comparison of pH values for Tris Buffer solutions in synthetic seawater at 25°C and 35 salinity:

Buffer	pH_{NBS}	pH_i	pm_H
Tris (0.02m), Tris.HCl (0.02m)	8.208	8.072	8.207
Tris (0.04m), Tris.HCl (0.04m)		8.073	8.208
Tris (0.06m), Tris.HCl (0.06m)		8.074	8.209

It is of interest to note that pH values on the NBS and pm_H scales are very closely the same in numerical value at $S = 35$ and $t = 25^\circ\text{C}$.

In the following intercomparison of the data sets on K_1 and K_2 due corrections for differences in pH scales have been made (Bates and Culberson, 1977).

5.1.2 Intercomparison of K_1 and K_2

A comparison of the pK measurements of Hansson (1973) and Mehrbach *et al.* (1973) has been made by Bates and Culberson (1977) and by Millero (1979). Bates and Culberson (1977) converted the apparent constants of Mehrbach *et al.* (1973) to stoichiometric constants by dividing the values of K'_1 and K'_2 (Mehrbach *et al.*, 1973) by their measured values of $(\gamma_H)_i$ (see section 5.1.1). This adjusts the two studies to the same scale. A comparison of the values of pK'_1 and pK'_2 obtained by the two studies is given in the following table.

Table I
Comparison of the values of pK'_1 and pK'_2 ($\Delta pK'_i = \text{Hansson-Mehrbach}$)
 $S = 35$

$t^\circ\text{C}$	$\Delta pK'_1$	$\Delta pK'_2$
5	0.015 (0.005)	-0.006 (-0.016)
15	0.030 (0.020)	-0.016 (-0.026)
25	0.022 (0.012)	-0.016 (-0.026)
35	-0.005 (-0.015)	-0.020 (-0.030)
Mean	0.018 (0.013)	-0.015 (-0.025)

$t = 25^\circ\text{C}$

S		
20	0.014 (0.004)	-0.002 (-0.012)
25	0.018 (0.008)	0.005 (-0.005)
30	0.021 (0.011)	0.007 (-0.003)
35	0.023 (0.013)	-0.016 (-0.026)
40	0.025 (0.015)	0.002 (-0.008)
Mean	0.020 (0.010)	0.006 (0.011)

The differences in the two studies $\Delta pK'_i = pK'_i$ (Hansson) - pK'_i (Mehrbach *et al.*) shown in the above table can be compared to the estimated errors of the two data sets:

Table II
Estimated Errors of Values of pK_1^* and $pK_2^{*a)}$

	σ		Sum
	Hansson	Mehrbach	
pK_1	0.009	0.003	0.012 (0.009) ^{b)}
pK_2	0.018	0.014	0.032 (0.014) ^{b)}
$pK_1 + pK_2$	0.020 ^{b)}	0.014 ^{b)}	0.024 ^{b)}

a) Based on analysis of Millero (1979)

b) $\sigma = \sqrt{(\sigma_1)^2 + (\sigma_2)^2}$

These comparisons indicate that the values of pK_1^* obtained in these two studies agree to ± 0.02 , which can be compared to an expected error of ± 0.01 [$\Delta\sigma = \sigma$ (Hansson) + σ (Mehrbach)]. The values of pK_2^* agree to ± 0.015 , which can be compared to an expected error of ± 0.033 .

The comparison at $t = 25^\circ\text{C}$ indicates that the agreement in pK_2^* is very good, while the values of pK_1^* show larger discrepancies. Part of the differences shown in the Table I are related to the fact that Hansson used fluoride-free seawater. This yields a difference in pK_1 of ~ 0.010 (Bates and Culberson, 1977). The corrected values are shown in parentheses in Table I. These comparisons, therefore, indicate that the two data sets are internally consistent to within the experimental error of the measurements ($\Delta\sigma$).

By comparing the values $K_R = K_1/K_2$ from the two studies (Table III), it is possible to eliminate the differences caused by different pH scales.

Table III
Comparison of ΔpK_R ($pK_{R,Hansson} - pK_{R,Mehrbach}$)

$t^\circ\text{C}$	ΔpK_R (S=35)	S	ΔpK_R ($t=25^\circ\text{C}$)
0	-0.039	5	-0.014
5	-0.035	10	-0.018
10	-0.033	15	-0.020
15	-0.029	20	-0.022
20	-0.027	25	-0.022
25	-0.024	30	-0.023
30	-0.022	35	-0.024
35	-0.018	40	-0.024
40	-0.016		
Mean	-0.027		-0.021

The differences in pK_R range from -0.014 to -0.039. The average difference -0.024 compares very well with the expected differences (based on $\Delta\sigma$) of 0.034.

In summary the two independent studies appear to be in agreement to within the experimental error.

5.1.3 Equations for apparent constants at one atmosphere pressure

Millero (1979) in his summary treatment of the data sets of Hansson (1973) and Mehrbach *et al.* (1973) proposed functional relationships for the ionization constants of water, boric acid, and carbonic acid in pure water.

(5.1.3.1) $\ln K_i = A + B/T + C \ln T$

with the following constants

Table 5.1.3.I

Parameters for the temperature dependence of the ionization constants of acids in water
 $\ln K_i = A + B/T + C \ln T$

Acid	A	-B	-C	σ	Reference
H ₂ O	148.9802	13847.26	23.6521	0.0014	Harned and Owen (1958)
B(OH) ₃	148.0248	8966.90	24.4344	0.0027	Owen (1934); Manov <i>et al.</i> (1944)
CO ₂ +H ₂ O	290.9097	14554.21	45.6575	0.0024	Harned and Davis (1943)
HCO ₃ ⁻	207.6548	11843.79	33.6485	0.0033	Harned and Scholes (1941)

The salinity dependence of the apparent (Mehrbach *et al.*, 1973) or stoichiometric constants is given by

(5.1.3.2) $\ln K_i' - \ln K_i = A^1 S^{1/2} + B^1 S$

where

$A^1 = a_0 + a_1/T + a_2 \ln T$

$B^1 = b_0 + b_1/T + b_2 \ln T$

The appropriate constants are presented in Table 5.1.3.II. The constants b_1 and b_2 are not needed for the systems studied here (Millero, 1979).

Table 5.1.3.II

Parameters for the temperature and salinity dependence of apparent constants in seawater^a

$\ln K_i' - \ln K_i = (a_0 + a_1/T + a_2 \ln T)S^{1/2} + b_0 S$

Solute	a_0	a_1	a_2	$b_0 \cdot 10^2$	σ	Reference
H ₂ O	-97.9429	4149.915	14.8269	-2.3694	0.019	Hansson (1972)
	-79.2447	3298.720	12.0408	-1.9813	0.020	Culberson and Pytkowicz (1973)
B(OH) ₃	0.0473	49.10	--	--	0.049	Lyman (1957)
	0.5998	-75.25	--	-1.767	0.008	Hansson (1972)
H ₂ O+CO ₂	0.0221	34.02	--	--	0.007	Mehrbach <i>et al.</i> (1973)
	0.5709	-84.25	--	-1.632	0.021	Hansson (1972)
HCO ₃ ⁻	0.9805	-92.65	--	-3.294	0.033	Mehrbach <i>et al.</i> (1973)
	1.4853	-192.69	--	-5.058	0.042	Hansson (1972)

^aIn the salinity range $0 \leq S \leq 40$ and temperature range $0 \leq t^\circ\text{C} \leq 40^\circ$; note that most measurements were made in salinity range $S = 20-40$.

In the above tables also information is enclosed on Hansson's data on the dissociation constants of boric acid in seawater. For comparison those of Lyman (1957) are presented. In his comparison paper Millero (1979) suggests that Hansson's data may be too low by 0.15 in $\ln K_B'$. More recent ion pairing calculations by Millero (1981) indicate that the differences in $\ln K_B$ are caused by errors in the work of Lyman, not that of Hansson. At this stage we are not able to recommend a "best" set of values for K_B' .

Though on the basis of the analysis of section 5.1.2 it might be tempting to suggest an "averaging" of the data sets of Hansson and Mehrbach *et al.*, this procedure is not justified unless some more work is done on the determination of the dissociation constants K_1 and K_2 of carbonic acid (see section 7-- on recommended future work). It appears advisable to use either data set separately, using Mehrbach

et al. especially when measurements of pH on the NBS scale underly the measurement of the carbonate parameters, and using Hansson, when measurements are based on the pH_i scale.

5.1.4 *Effects of pressure on dissociation constants*

Disteche and Disteche (1967) as well as Culberson and Pytkowicz (1968) measured the effect of pressure on the dissociation constants of carbonic acid potentiometrically at 25°C. The two sets of results are in good agreement. Culberson and Pytkowicz (1968) studied the pressure effect over a range of temperatures. The results agree well with those obtained from partial molal volume data (Millero, in press).

Millero (1979) presented a formula that adequately describes the pressure dependence as a function of temperature and salinity:

$$(5.1.4.1) \quad \ln (K_i^P/K_i^0) = - (\Delta V_i/RT)P + (0.5\Delta K_i/RT)P^2$$

where

$$-\Delta V_i = a_0 + a_1 (S-34.8) + a_2 t + a_3 t^2$$

$$-10^3 \Delta K_i = b_0 + b_1 (S-34.8) + b_2 T$$

and t is in °C.

The constants are summarized in Table 5.1.4.I.

Table 5.1.4.I

Coefficients for equation (5.1.4.1) for the pressure dependence of dissociation constants K_1 , K_2 and K_B

Solute	a_0	a_1	a_2	$a_3 10^3$	b_0	b_1	b_2	$\sigma (\ln K^P/K^0)$
$B(OH)_3$	29.48	-0.295	-0.1622	2.608	2.84	-0.354	--	0.0030
H_2CO_3	25.50	0.151	-0.1271	--	3.08	0.578	-0.0877	0.0043
HCO_3^-	15.82	-0.321	0.0219	--	-1.13	0.314	0.1475	0.0042

Determined from the results of Culberson and Pytkowicz (1968).

5.2 *Preliminary Error Analysis*

Since determinations involving the marine carbonate system are to be used to detect relatively small shifts in the carbonate components ($CO_2 + H_2CO_3$, P_{CO_2} , HCO_3^- , CO_3^{2-}) it is important to have some appreciation of the confidence with which these estimates can be made.

Uncertainties in the estimates arise from

- 1) Experimental uncertainties (e.g., in determination of TA (or in CA) pH, P_{CO_2} , Σ_{CO_2})
- 2) Uncertainties associated with the values of the constants (K_1' , K_2' , K_B' -- and to a lesser extent K_w') essential to the calculations.

In Annex 1 an analysis of potential errors based on the pH/Alkalinity and pH/ Σ_{CO_2} methods is presented.

6. SOLUBILITY OF CALCIUM CARBONATE

Generally two forms of calcium carbonate are considered to be important in the ocean: aragonite and calcite.

Though many studies have been carried out on the solubilities of both these forms of $CaCO_3$ in seawater and seawater-like solutions, there is still some disagreement between data sets, primarily as a result of kinetic parameters leading to non-equilibrium steady state results. There are a series of recent

measurements of these solubilities, as well as on the pressure effects on the solubilities. After due correction for differences in salinity and composition of the equilibrium solutions there appears good agreement for calcite solubilities, but for aragonite differences are large, presumably as a result of kinetic problems in the experiments, e.g., overgrowths, apparent steady states, etc.

Recently Morse *et al.* (1980) have reviewed the data available at 25°C and salinity S=35 (Table 6.1).

Table 6.1

Summary of calcite and aragonite solubility products at 25°C and S=35

Source	K'_c ($\text{mole}^2\text{kg}^{-2}\times 10^7$)	K'_a ($\text{mole}^2\text{kg}^{-2}\times 10^7$)	K'_a/K'_c	pK'_c	pK'_a
MacIntyre (1965)	4.38 (± 0.26)	7.12 (± 0.31)	1.63 (± 0.17)	6.36	6.15
Ingle <i>et al.</i> (1973)	4.60 (± 0.10)		--	6.34	--
Berner (1976)		8.21 (± 0.25)	--	--	6.09
Plath (1979)	4.62 (± 0.10)	9.46 (± 0.49)	2.05 (± 0.15)	6.34	6.02
Morse <i>et al.</i> (1980)	4.36 (± 0.20)	6.65 (± 0.12)	1.53 (± 0.10)	6.36	6.18
Plummer and Sundquist (1982)	4.60	6.66	1.45	6.34	6.18

The agreement for calcite is encouraging, but the data for aragonite solubility are too variable. There appears a strong need for further measurements to unravel these differences, and we hesitate at this stage to recommend an established procedure to be followed for saturation state calculations.

At present, work is in progress to reevaluate the temperature dependence of the solubility products. The 25°C data of Ingle (1975) on the pressure dependence of the calcite solubility product are considered to be reliable (Millero, 1979); however, further work is needed for aragonite.

7. RECOMMENDATIONS FOR FUTURE WORK

In the following we shall briefly review the "state of the art" with respect to the various parameters governing the CO_2 system in seawater and attempt to identify priority areas for further research which will lead to a uniformly acceptable description of the thermodynamics of the CO_2 system.

7.1 Solubility of Carbon Dioxide Gas

The formula presented in section 4 is recommended for future use, and no further work appears necessary at this stage.

7.2 pH Measurements

A primary note of caution concerns the use of glass electrodes in seawater solutions. Glass electrodes should be tested against hydrogen electrodes to test their slopes versus the theoretical slopes. Next the combination of the glass electrode and the reference electrode(s) should be tested against pairs of buffers to ascertain whether the liquid-junction potentials are working well, i.e., whether the assembly has roughly ($\geq 99\%$) the theoretical slope. In actual runs only one buffer is used to avoid the effect of different liquid-junction potentials in various buffers.

The NBS (pH_{NBS}) scale serves well for kinetic and equilibrium studies, where variations in k_H (c.f., section 5.1.1) are small when compared to the uncertainties in solubilities.

When an electrode assembly is standardized with the NBS phosphate buffer a delay in attaining equilibrium of about 10 minutes is observed upon the transferring of the electrodes to seawater. For these reasons it is advisable to have available some established seawater buffers (e.g., Tris-buffers, Bates and Culberson, 1977) as secondary standards. The latter buffers will also allow a ready connection to the pH scale.

Recommendation

The sub-panel on CO_2 does recommend that further work be carried out to establish seawater buffer standards over the range of pH of seawater (7-9), and that values be established as a function of temperature (0-30°C) and salinity (S=30-40).

Furthermore, careful work should be carried out on the determination of the apparent activity coefficient of the proton to relate the pH_i , pH and pH_{NBS} (c.f. section 5.1.1) scales. These measurements should be made using a standard reference electrode/liquid junction combination. This would provide an independent check for the expected differences of dissociation constants based on the various pH-scales (pH_{NBS} and pH_i).

7.3 *Dissociation Constants*

Carbonic acid

Though the comparison of the two data sets on pK_1 and pK_2 (Section 5.1.2) showed that the data sets are internally consistent within the experimental error of the measurements the subpanel agreed that further independent determinations of these constants (on either pH scale) would be appropriate.

In particular the subpanel does recommend the redetermination of the product or the ratio of the equilibrium constants by various techniques (potentiometrically; gasometry, i.e., pCO_2 - ΣCO_2 methods). Such data over a range of temperature and salinity would serve to resolve the small differences in pK_i 's obtained in the studies of Hansson and Mehrbach *et al.*

Boric acid

The subpanel on CO_2 recommends strongly that the ionization constant of boric acid in seawater be redetermined as a function of temperature and salinity. This would clear up the differences (Millero, 1979) that exist between the work of Lyman (1957) and Hansson (1973). Such work is presently in progress.

7.4 *Carbonate solubility*

The panel wishes to take this problem under further consideration, but more careful work appears necessary in this area to unravel the causes of the differences reported in Table I of section 6 of this report.

8. MEETING OF JPOTS MEMBERS (MORCOS, MILLERO, POISSON, GIESKES) ON FUTURE OCEANOGRAPHIC TABLES

Dr. Selim Morcos discussed the plans to publish information on "the Practical Salinity Scale, 1978" in the International Marine Science (IMS) newsletter published by UNESCO (IMS Special Issue 1981-1982, Number 30).

It was noted that some questions remained concerning Part 2 of the new International Oceanographic Tables, Volume 4: "Properties derived from the equation of state of seawater". It was agreed to approach panel members N. Fofonoff and O. Mamayev on this matter.

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ANNEX I

Preliminary error analysis

Since determinations involving the marine carbonate system are to be used to detect relatively small shifts in the carbonate components ($CO_2 + H_2CO_3$, P_{CO_2} , HCO_3^- , CO_3^{2-}) it is important to have some appreciation of the confidence with which these estimates can be made.

Uncertainties in the estimates arise from

- 1) Experimental uncertainties [e.g., in determination of TA (or in CA), pH, P_{CO_2} , ΣCO_2],
- 2) Uncertainties associated with the values of the constants (K_1' , K_2' , K_B' -- and to a lesser extent K_w') essential to the calculations.

This preliminary analysis is confined to estimates made by the pH/alkalinity and pH/ ΣCO_2 methods.

pH/alkalinity method

Because of the general forms of expressions used for component calculation via the pH/alkalinity or pH/ ΣCO_2 methods, errors arising in the estimates as a consequence of a given uncertainty in one of the parameters (K_1' , K_2' , K_B' , pH, etc.) will be pH dependent. This dependency will not be severe for the relatively narrow pH range of open ocean water but may become significant in the intercomparison of waters of extreme pH range (e.g., pore waters, rock pools, estuarine waters).

Some appreciation of the severity of the pH dependence can be obtained from plots, as a function of pH, of the fractional increase (error) in the estimation of a component i ($= CO_2$, $iHCO_3^-$, CO_3^{2-} , ΣCO_2) consequent on a small increase δj in parameter j ($= K_1'$, K_2' , K_B' , pH). The fractional increase is given by

$$f_{i,j} = (\partial i / \partial j) \cdot \delta j / i$$

where $(\partial i / \partial j)$ is the rate of increase of i with j , other factors being constant, δj is the specified increase in j (1% or 0.01 pH unit), and i is the absolute value of component i .

Plots of $f_{i,j}$ values for pH/alkalinity method based estimates of CO_2 and CO_3^{2-} are shown in Figure 1a and b. In order to illustrate the general trends a somewhat extended pH range has been used. δj values of 1% (for $j \equiv K_1'$, K_2' , CA) were used; for $j \equiv$ pH, δj was 0.01 pH unit. Obvious adjustments allow the plots to be adapted for other choices of δj values. The regions of sensitivity of a particular component estimation towards uncertainties in particular parameters are evident.

Standard errors of the estimates

In practice, each carbonate component estimate is subject to errors arising from uncertainties inherent in each of the parameters involved in the expression by which the estimate is calculated. Standard errors for estimates based on the pH/alkalinity method of the carbonate components can be obtained by combining the appropriate parameter errors by the usual statistical methods. In this analysis the standard errors for K_B' , K_1' , and K_2' (Table 1) were those given by Millero (1979); that for a_H was equivalent to a pH standard error of 0.01 pH unit. As with $f_{i,j}$ values, the standard errors of the individual components are pH-dependent and have been calculated for pH values between 7.00 and 9.00 for water of $S=35$, $25^\circ C$ and $TA = 2.40 \times 10^{-3} \text{ eq. kg}^{-1}$. Some results are summarized in Table 2 and Figure 2. The calculations were made using both the Mehrbach and Hansson constants (see Millero, 1979). The calculated carbonate compositions of some of the waters are shown in Table 3.

In order to focus attention on the quantities which are likely to be of immediate interest to those attempting to follow small perturbations of the carbonate system, the standard errors for CO_2 , P_{CO_2} , HCO_3^- , and ΣCO_2 have been expressed as percentages of the estimated component, $\sigma_i' (= \sigma_i$

x 100/i). Adjustment between the NBS and SWS pH scales was made using the relationship $\text{pH(NBS)} - \text{pH(SWS)} = 0.144$ (Millero, 1979).

All σ_i values are pH dependent and, within the admittedly extended pH range considered, each has some pH region in which its value may be considered large enough to impair confidence in the study of small perturbations. The values for estimates made via the Hansson constants are somewhat larger than those based on the Mehrbach values and reflect large standard errors found for the former constants (see Table 1 and Millero, 1979). In this analysis a standard error in pH of 0.01 units was assumed. Reducing this to the value (0.003 pH unit) suggested for careful measurements (Pytkowicz *et al.*, 1966) lowers σ'_{CO_2} from about 4% to 3.3% at pH 7 and from 3.3% to 2.8% at pH 8.151. Reduction occurs also in the other σ_i values as σ_{pH} is reduced (Table 4).

In general, the component concentrations estimated using the Hansson and the Mehrbach constants agree within the standard errors of the estimates, although the CO_3^{2-} estimate differences expressed as $[\text{CO}_3^{2-}(\text{M}) - \text{CO}_3^{2-}(\text{H})] \times 100/\text{CO}_3^{2-}(\text{M})$ are less satisfactory than might be wished (4-5%).

A particularly unsatisfactory feature is the disagreement between the borate estimates obtained on the basis of the Lyman constants and those calculated via the Hansson constants (see Millero, 1979 and Table 2). This uncertainty is reflected in calculated CA values (although in a subdued way since $\text{CA} \gg \text{B(OH)}_4^-$), and is propagated through the carbonate component estimates. The B(OH)_4^- estimates differ by about 13% at pH 7 and 5% at pH 9, but the effect of this decrease on CA estimates is more than offset by the larger absolute B(OH)_4^- value at high pH values. The effect of the K'_B discrepancy is to introduce an additional uncertainty of $\sim 0.5\%$ into the CA (and carbonate component) estimates for solutions of pH close to 8. The uncertainty is lower at lower pH values and increases at higher pH values. This difficulty can be resolved only by a redetermination of the K'_B values.

Conclusions (pH/alkalinity method)

- (i) The error in the estimate of a given carbonate component consequent on a given error in one of the parameters K'_1 , K'_2 or pH is pH dependent.
- (ii) The standard error associated with the estimate of a given component as a result of the simultaneous combination of those for the various parameters associated with the estimation is pH dependent.
- (iii) For the K'_B , K'_1 , and K'_2 values (and standard errors) suggested by Millero (1979) and a σ_{pH} of 0.01 pH unit, the standard error (expressed on a percentage basis) for CO_2 (and P_{CO_2}) ranges from about 2.5% (pH 7) to 4.4% (pH 9) (Mehrbach and Lyman's constants). The corresponding values for CO_3^{2-} are 4.0% (pH 7) and 1.7% (pH 9); those for HCO_3^- are *ca.* 0.1% and 2.6% and, for ΣCO_2 , 0.2% and 0.8%. Standard errors predicted on the basis of the Hansson data are somewhat higher.
- (iv) σ_{pH} makes a significant contribution to the component standard error, particularly for $\sigma_{\text{pH}} \geq 0.01$ unit. Reduction of σ_{pH} has an especially marked effect on the standard error for CO_2 (and P_{CO_2}). These features emphasize the need for care and precision in the determination of pH.
- (v) Standard errors for B(OH)_4^- are high (particularly at low pH), those based on Lyman's constants being higher than those derived from Hansson's data. A systematic error in one of the K'_B determinations causes the B(OH)_4^- predictions of the Lyman and Hansson constants to differ markedly. However, the effect of this on CA (and carbonate component estimates) is relatively small (*ca.* 0.05%). Even so, redetermination of K'_B is desirable.

pH/ ΣCO_2 method

$f_{i,j}$ values for the pH/ ΣCO_2 method are shown in Figure 3a and b. As for the corresponding pH/alkalinity plots, an unrealistically extended pH range was used in order to show the trends. Again values of δj equivalent to 1% of K_1' and K_2' were adopted and δpH was taken to be 0.01 pH unit. The plots were drawn for calculations using the Mehrbach constants but little difference would be expected if the Hansson constants were used, and the main purpose is to demonstrate the sensitivity of certain $f_{i,j}$ values to pH within the pH range of seawater.

An examination of the relative performances of the Mehrbach and Hansson constants over the pH range 7.0 to 9.0 is summarized in Table 5 and Figure 4. The component estimates listed in Table 5 were obtained by starting with a solution of $TA = 2.40 \times 10^{-3} \text{ eq.kg}^{-1}$ (25°C, S=35) and calculating, for each pH, the ΣCO_2 value predicted by the pH/alkalinity method using the Mehrbach K_1' and K_2' constants and the Lyman K_B' constants. The ΣCO_2 for each pH was used in both sets (Mehrbach and Hansson) component estimations by the pH/ ΣCO_2 method. Adjustment between the NBS and the SWS pH scales was made as previously indicated.

The percentage difference ([component (M) - component (H)] x 100/component (M)) is shown in parentheses below each estimate. The standard errors for each estimate were obtained by the usual statistical combination of the standard errors for K_1' and K_2' (Table 1) with that for ΣCO_2 ($3 \times 10^{-6} \text{ mol kg}^{-1}$ -- see e.g., Almgren and Fonselius, 1975) and that for a_{HH} . This latter value was chosen to be equivalent to a standard error in pH measurement of 0.01 pH unit. Although this is large compared with the value considered to be attainable (ca. 0.003 pH unit -- Pytkowicz *et al.*, 1966) it was deliberately selected to avoid the possibility of obtaining overoptimistic component standard error predictions. Some idea of these predictions when lower σ_{pH} values are assumed can be obtained from Figure 5. Throughout, component standard errors are expressed as percentages of the estimated component.

Component concentrations listed in Table 5 differ only slightly from the corresponding (pH/alkalinity based) values given in Table 3* and, apart from the CO_3^{2-} estimates, the agreement between the Mehrbach and Hansson predictions is reasonable in the lower half of the pH range considered. Agreement between the CO_3^{2-} estimates is not satisfactory throughout the pH range but improves somewhat towards higher pH values. These divergences can be attributed mainly to the differences in the K_2' values of the Mehrbach and Hansson constants. When adjustment is made to a common pH scale, the 25°C K_2' value of Hansson is ca. 5% greater than that of Mehrbach. At this temperature the pH scale adjusted K_1' values differ by only ca. 0.4%. When using the pH/ ΣCO_2 expressions at low pH, K_2' has little weight for the CO_2 and HCO_3^- estimations, but has virtually its full weight in the CO_3^{2-} estimation. At high pH values CO_2 and HCO_3^- estimates are more sensitive to the choice of K_2' but as K_2' enters into both the numerator and denominator of the CO_3^{2-} expression, the sensitivity of the CO_3^{2-} estimate towards the choice of K_2' diminishes.

Standard errors of the component estimates (Table 5 and Figure 4) are pH dependent. That for CO_2 is highest at high pH values whereas that for CO_3^{2-} is highest in the low pH region. A major contributor to some of these relatively large σ_i' values is σ_{pH} (taken here to be 0.01 unit). The effect of the reduction of σ_{pH} on the overall component standard errors is shown in Figure 5 for three pH values. The marked dependence of σ'_{CO_2} on σ_{pH} and the implications this has on the need for care in pH determination should be noted.

Comment Added in Proof

In this preliminary error analysis the calculationally convenient approximation was made that in the expression

$$CA = TA - [\text{borate}] - [OH^-] + [H^+]$$

* It should be noted that the values given in Tables 3 and 5 are not equivalent to independent experimental estimates but are interlinked since the ΣCO_2 values used as the basis for Table 5 were calculated via the alkalinity values used in deriving Table 3.

the $[OH^-]$ and $[H^+]$ contributions could be ignored. This approximation affects slightly the component estimates at the higher pH values. It has no significant influence on the component standard error estimates.

In the calculation of the component standard error estimates for the pH/alkalinity method, the contribution of the standard error for the total alkalinity estimations was ignored. If this standard error is taken into account, the standard error for HCO_3^- estimation is enhanced somewhat at lower pH values. The standard errors for CO_2 , P_{CO_2} and CO_3^{2-} estimates are scarcely affected.

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TABLE 1

Ionization constants and their standard errors (25°C, S = 35) (see Millero, 1979)

	Mehrbach			Hansson		
	K	σ	σ as % of K	K	σ	σ as % of K
K' _B	2.0325×10^{-9}	1.021×10^{-10}	5	2.4407×10^{-9}	1.96×10^{-11}	0.8
K' ₁	9.9652×10^{-7}	7.00×10^{-9}	0.7	1.3847×10^{-6}	2.94×10^{-8}	2.1
K' ₂	7.7667×10^{-10}	2.61×10^{-11}	3.3	1.1403×10^{-9}	4.89×10^{-11}	4.2

Lymans K'_B values used in conjunction with the Mehrbach K'₁ and K'₂ values.

TABLE 2

Standard errors of estimates of carbonate components (see Table 3)
using Mehrbach (M) and Hansson (H) constants. (pH/alkalinity method)

($T = 25^{\circ}\text{C}$; $S = 35$; $\text{TA} = 2.400 \times 10^{-3} \text{ eq kg}^{-1}$; $\Sigma\mathcal{B} = 4.251 \times 10^{-4} \text{ mol kg}^{-1}$).
Values expressed as percentage of the estimated component concentration

	M	H	M	H	M	H	M	H	M	H
pH	7.50	7.356	7.70	7.556	8.151	8.007	8.40	8.256	8.60	8.456
B(OH)_4^-	5.2	2.3 ^o	5.02	2.26	4.3	1.98	3.66	1.71	3.06	1.45
CA	0.056	0.0219	0.084	0.033	0.177	0.072	0.23	0.098	0.26	0.113
CO_2	2.56	3.25	2.64	3.37	2.98	3.63	3.30	3.96	3.64	4.29
HCO_3^-	0.212	0.251	0.325	0.386	0.797	0.95	1.22	1.47	1.64	1.97
CO_3^{2-}	3.88	4.63	3.77	4.50	3.31	3.93	2.89	3.42	2.47	2.88
ΣCO_2	0.107	0.193	0.215	0.231	0.423	0.461	0.59	0.65	0.71	0.78
P_{CO_2}	2.56	3.25	2.64	3.37	2.98	3.63	3.30	3.96	3.64	4.29

Standard errors calculated via $\sigma_i^2 = \sum [(\partial i / \partial j)^2 \sigma_j^2]$ where j is K'_1 , K'_2 , K'_B and a_{H^+} .
Standard errors for K'_1 , K'_2 and K'_B based on analysis given by Millero (1979) - see
Table 1 above. Standard error in a_{H^+} taken to be that equivalent to a 0.01 pH unit
at the pH in question.

TABLE 3

Carbonate component estimates for various pH values using Mehrbach (M) and Hansson (H) constants
($T = 25^{\circ}\text{C}$; $S = 35$; $\text{TA} = 2.4 \times 10^{-3} \text{ eq kg}^{-1}$; $\Sigma\text{B} = 4.251 \times 10^{-4} \text{ mol kg}^{-1}$). (pH/alkalinity method)

Units of $10^{-3} \text{ mol kg}^{-1}$ or $10^{-3} \text{ eq kg}^{-1}$

	M	H	M	H	M	H	M	H	M	H
pH	7.50	7.356	7.70	7.556	8.151	8.007	8.40	8.256	8.60	8.456
B(OH)_4^-	0.0257	0.0223	0.0393	0.0343	0.095	0.084	0.144	0.130	0.190	0.174
CA	2.374	2.378	2.361	2.366	2.305	2.316	2.256	2.270	2.210	2.225
CO_2	0.0718	0.0719	0.0439	0.0439	0.0134	0.0134	0.00648	0.00644	0.00344	0.00340
HCO_3^-	2.263	2.261	2.191	2.186	1.89	1.88	1.623	1.609	1.366	1.347
CO_3^{2-}	0.0556	0.0585	0.0853	0.0896	0.2078	0.218	0.317	0.331	0.422	0.439
ΣCO_2	2.391	2.391	2.320	2.320	2.111	2.112	1.946	1.946	1.791	1.789
$\text{PCO}_2 \text{ atm} / 10^{-6}$	2528	2531	1546	1546	471	471	228	226	121	120

TABLE 4

Dependence of standard errors of component estimates of σ_{pH}
 pH 8.151, 25°C, S = 35. TA = 2.40×10^{-3} eq kg⁻¹, $\Sigma B = 4.251 \times 10^{-4}$ mol kg⁻¹.
 Mehrbach constants (+ Lyman's K'_B values). Values listed as percentages of
 the estimated component. Standard errors for K'_1 , K'_2 and K'_B as given in
 Table 1 (Millero, 1979). (pH/alkalinity method)

Component	σ_{pH}	0	0.003	0.006	0.008	0.010
B(OH)_4^-		3.90	3.94	4.05	4.16	4.30
CA		0.161	0.162	0.167	0.171	0.177
CO ₂		0.94	1.26	1.93	2.44	2.98
HCO ₃ ⁻		0.62	0.64	0.69	0.74	0.797
CO ₃ ²⁻		2.75	2.81	2.90	3.11	3.31
ΣCO_2		0.32	0.33	0.36	0.39	0.42

TABLE 5

Comparison of compositions and component standard errors estimated via Mehrbach (M) and Hansson (H) apparent constants (pH/ ΣCO_2 method).
 25°C , $S = 35$. Standard errors expressed on a percentage basis.
 Concentrations in units of 10^{-5} mol kg $^{-1}$

pH	M	H	M	H	M	H	M	H	M	H	M	H	M	H
pH	7.00	6.856	7.50	7.356	7.70	7.556	8.151	8.007	8.40	8.256	8.60	8.456	9.00	8.856
CO_2	0.236	0.237	0.0718	0.0719	0.0439	0.0439	0.0134	0.0134	0.00648	0.00644	0.00344	0.00341	8.31×10^{-4}	8.14×10^{-4}
	(-)		(-)		(-)		(0.3)		(0.62)		(0.87)		(1.56)	
HCO_3^-	2.355	2.354	2.263	2.260	2.191	2.186	1.890	1.880	1.62	1.609	1.366	1.348	0.828	0.809
	(0.04)		(0.130)		(0.23)		(0.53)		(0.68)		(1.32)		(2.29)	
CO_3^{2-}	0.0183	0.0193	0.0556	0.0585	0.0853	0.0897	0.208	0.218	0.317	0.331	0.422	0.439	0.643	0.662
	(-5.5)		(-5.2)		(-5.16)		(-4.81)		(-4.41)		(-4.02)		(-2.95)	
<u>Standard errors</u>														
σ'_{CO_2}	2.23	2.88	2.42	3.10	2.48	3.17	2.66	3.35	2.85	3.52	3.09	3.74	3.73	4.433
$\sigma_{\text{HCO}_3^-}$	0.23	0.298	0.15	0.176	0.18	0.219	0.42	0.516	0.68	0.84	0.98	1.21	1.80	2.21
$\sigma_{\text{CO}_3^{2-}}$	4.18	4.95	4.03	4.80	3.96	4.72	3.69	4.39	3.43	4.06	3.14	3.70	2.31	2.69

Component estimates made for a seawater of $\text{TA} = 2.41 \times 10^{-3}$ eq kg $^{-1}$ by first calculating ΣCO_2 at each (NBS) pH using Mehrbach (+ Lyman's K'_B) constants. This ΣCO_2 was then used in subsequent pH/ ΣCO_2 component calculations using both M and H. constants. Component standard errors calculated via $\sigma_i^2 = \sum[(\partial i/\partial j)^2 \sigma_j^2]$ where j is K'_1 , K'_2 , a_H and ΣCO_2 , and expressed as $\sigma'_i (= \sigma_i \times 100/i)$. NBS and SWS scales related via $\text{pH(NBS)} - \text{pH(SWS)} = 0.144$.

Figure 1a. $f_{CO_2, J}$ and $f_{CO_3^{2-}, J}$ values for the pH/alkalinity method.

25°C, S=35 ; Meinbach constants used; δ_{pH} 0.01 unit.

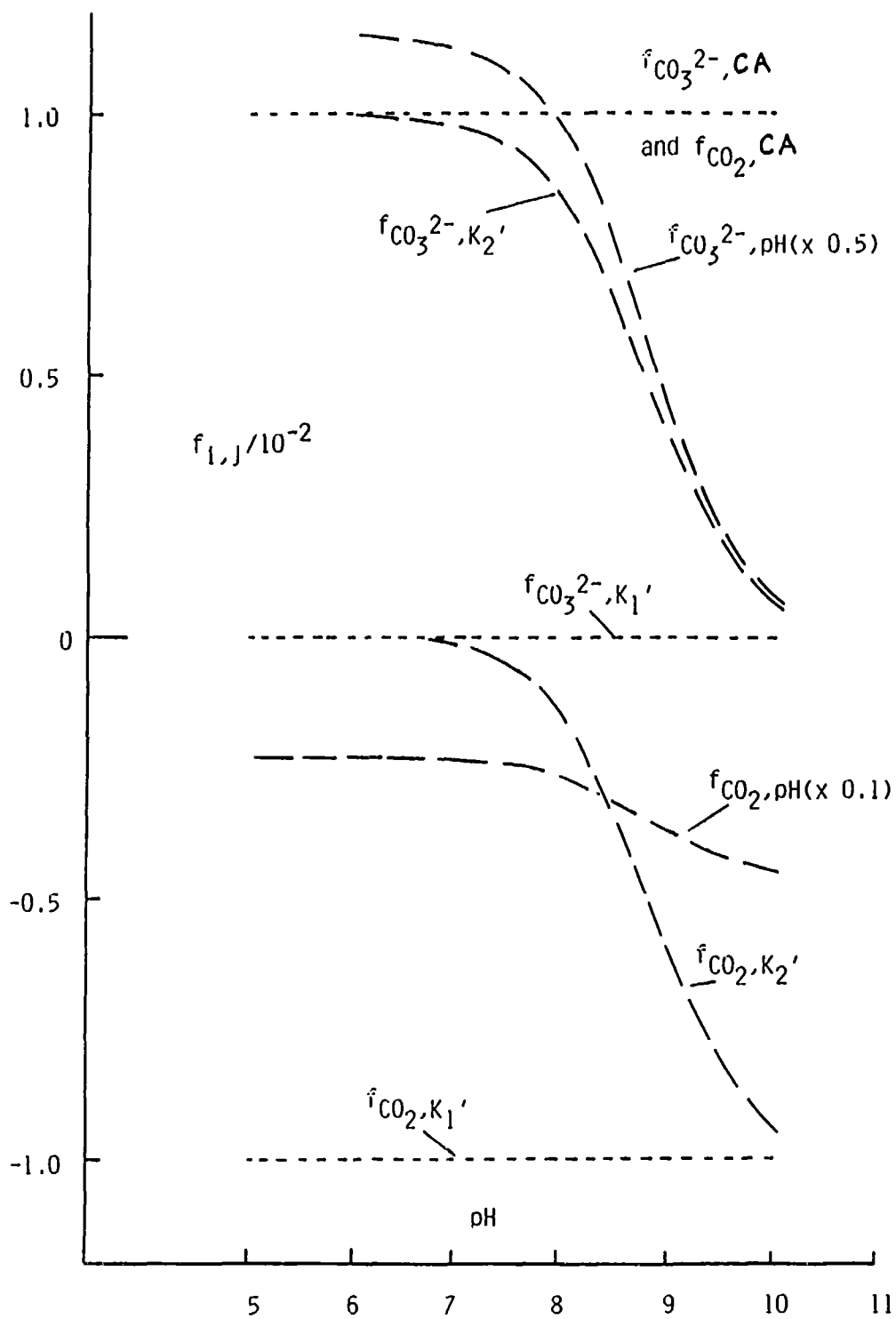


Figure 1b. $f_{\text{HCO}_3^-,j}$ values for the pH/alkalinity method.

25°C, $S=35$, Mehrbach constants used. $\delta_{\text{pH}} 0.01$ unit

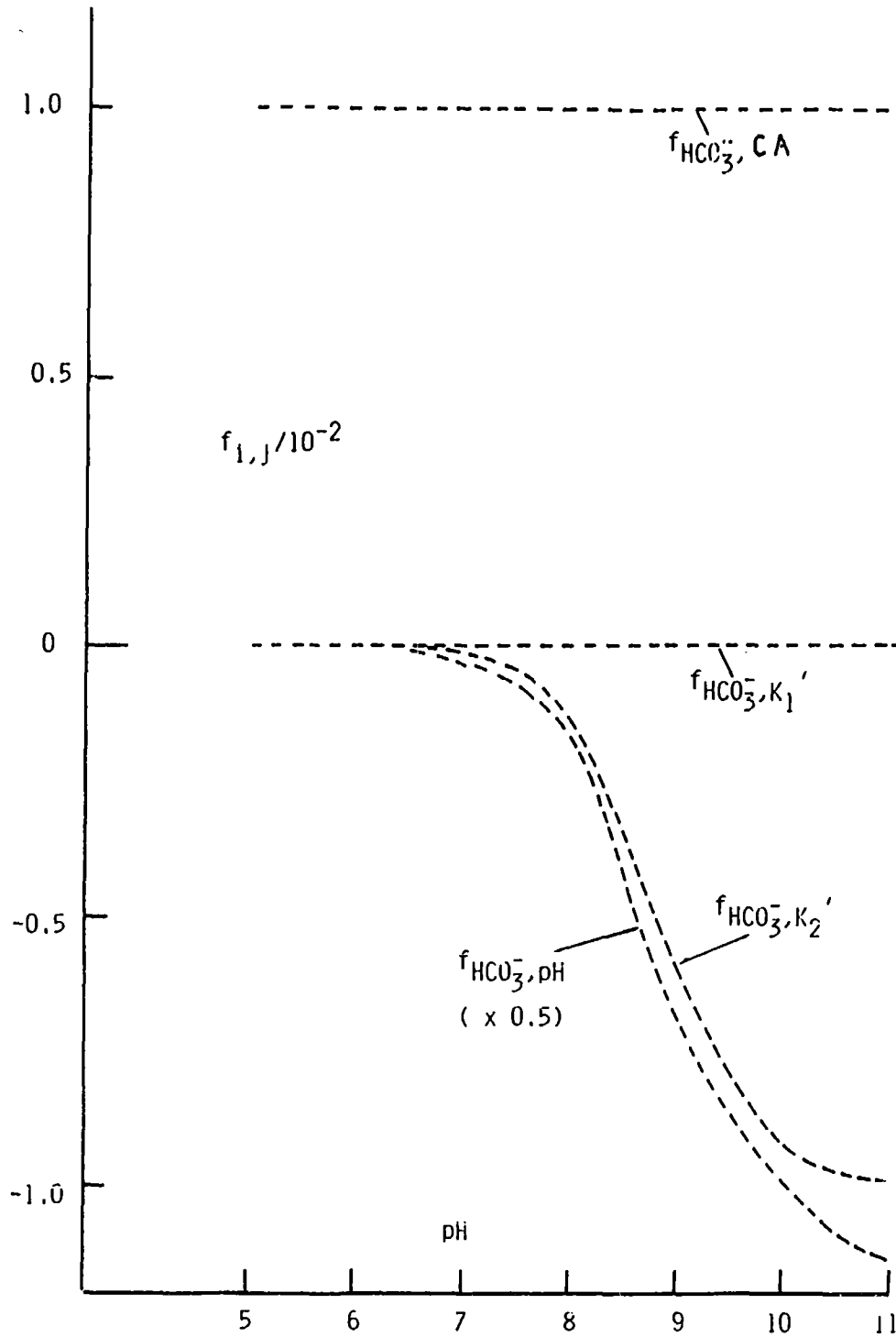


Figure 2 Dependence of σ_i' values on pH (pH/alkalinity method)

$25^{\circ}\text{C}, S=35; \text{TA} = 2.40 \times 10^{-3} \text{eq kg}^{-1}$.

Solid lines - Mehrbach constants (+Lyman's K'_B)

Broken lines - Hansson constants

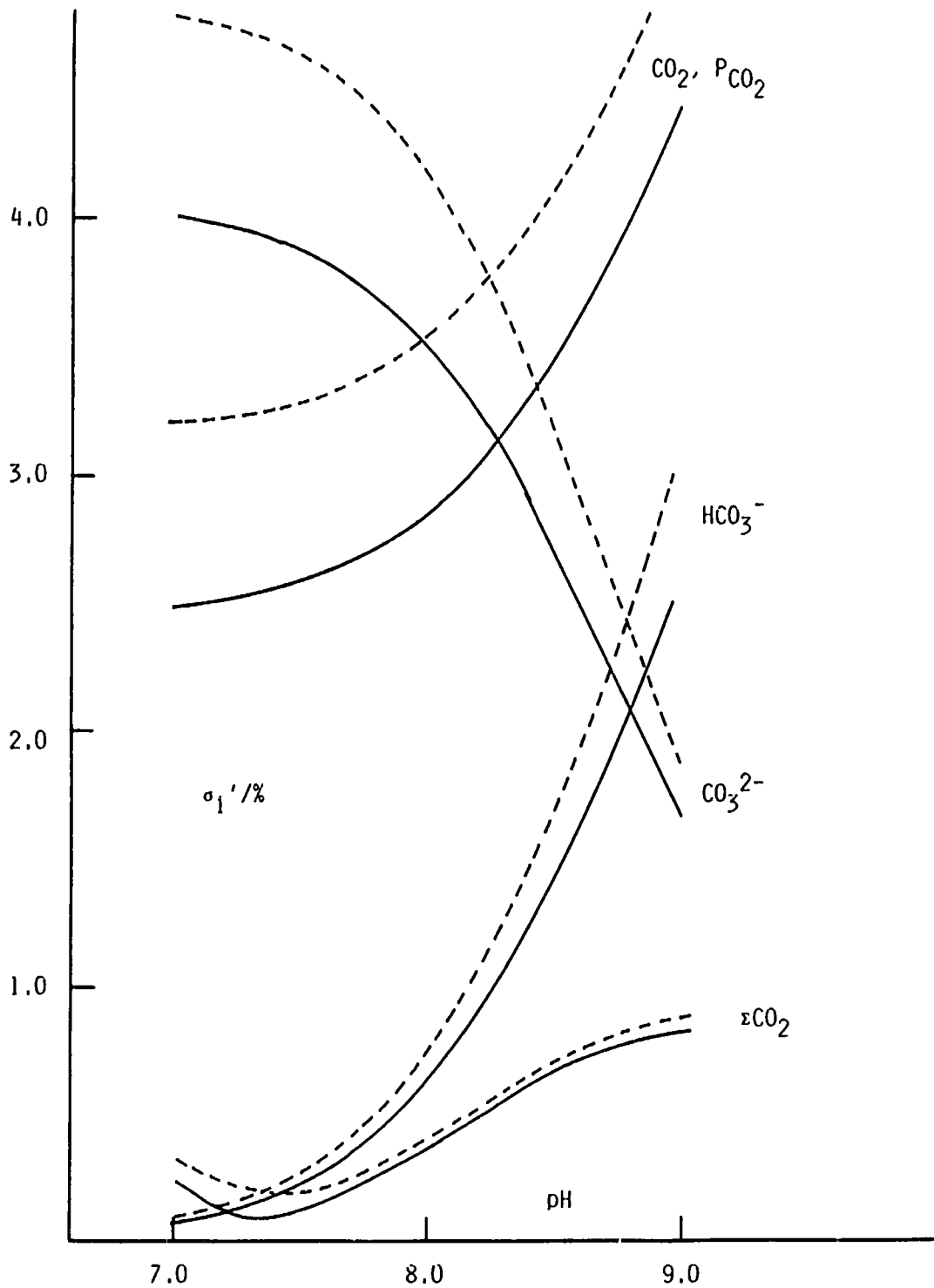


Figure 3a $f_{\text{CO}_2, j}$ and $f_{\text{CO}_3^{2-}, j}$ values for the pH/ ϵCO_2 method
 25°C, $S=35$; Mehrbach constants used.

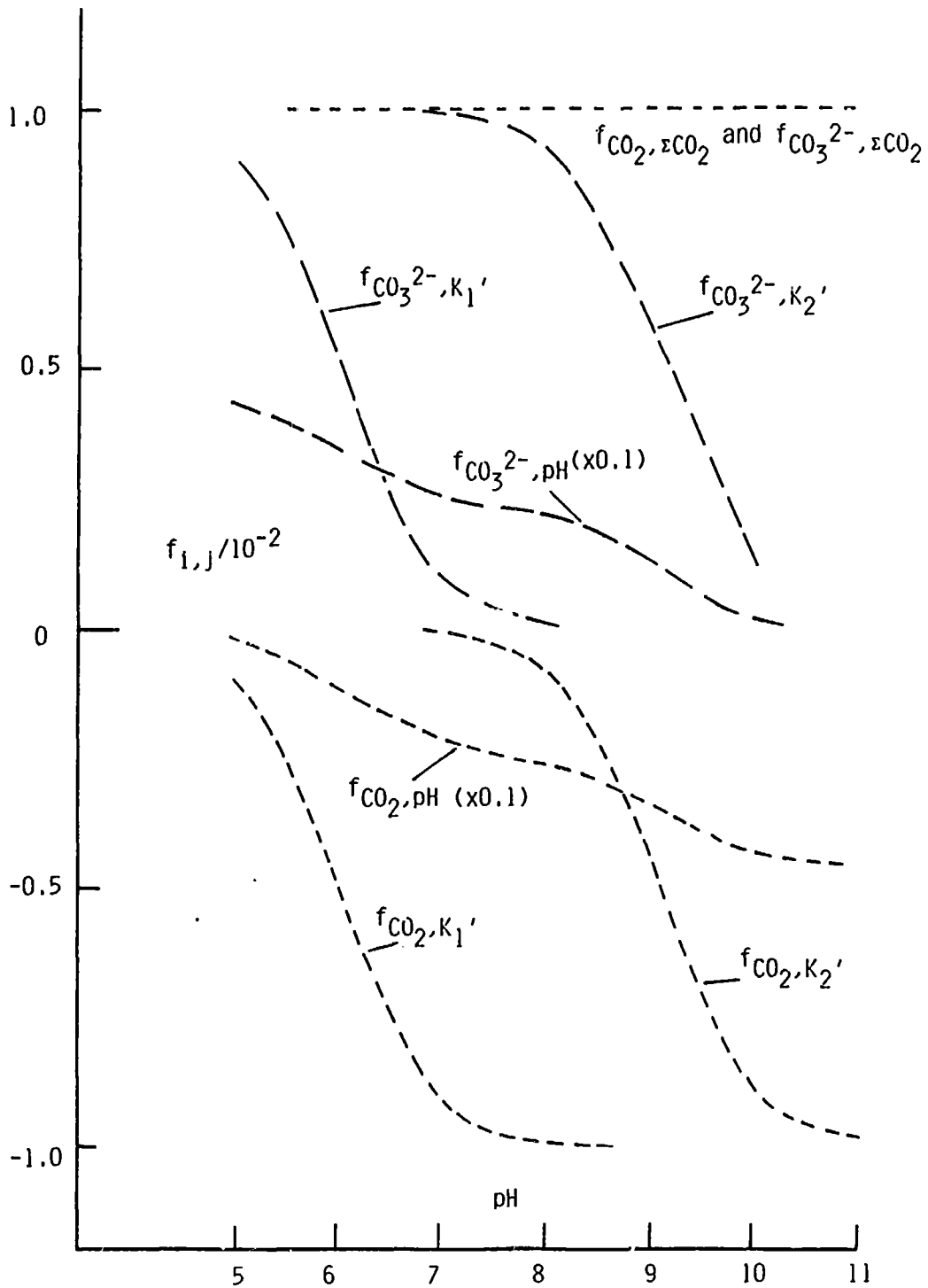


Figure 3b $f_{\text{HCO}_3^-, j}$ values for the pH/ ΣCO_2 method
 25°C, $S = 35$; Mehrbach constants used.

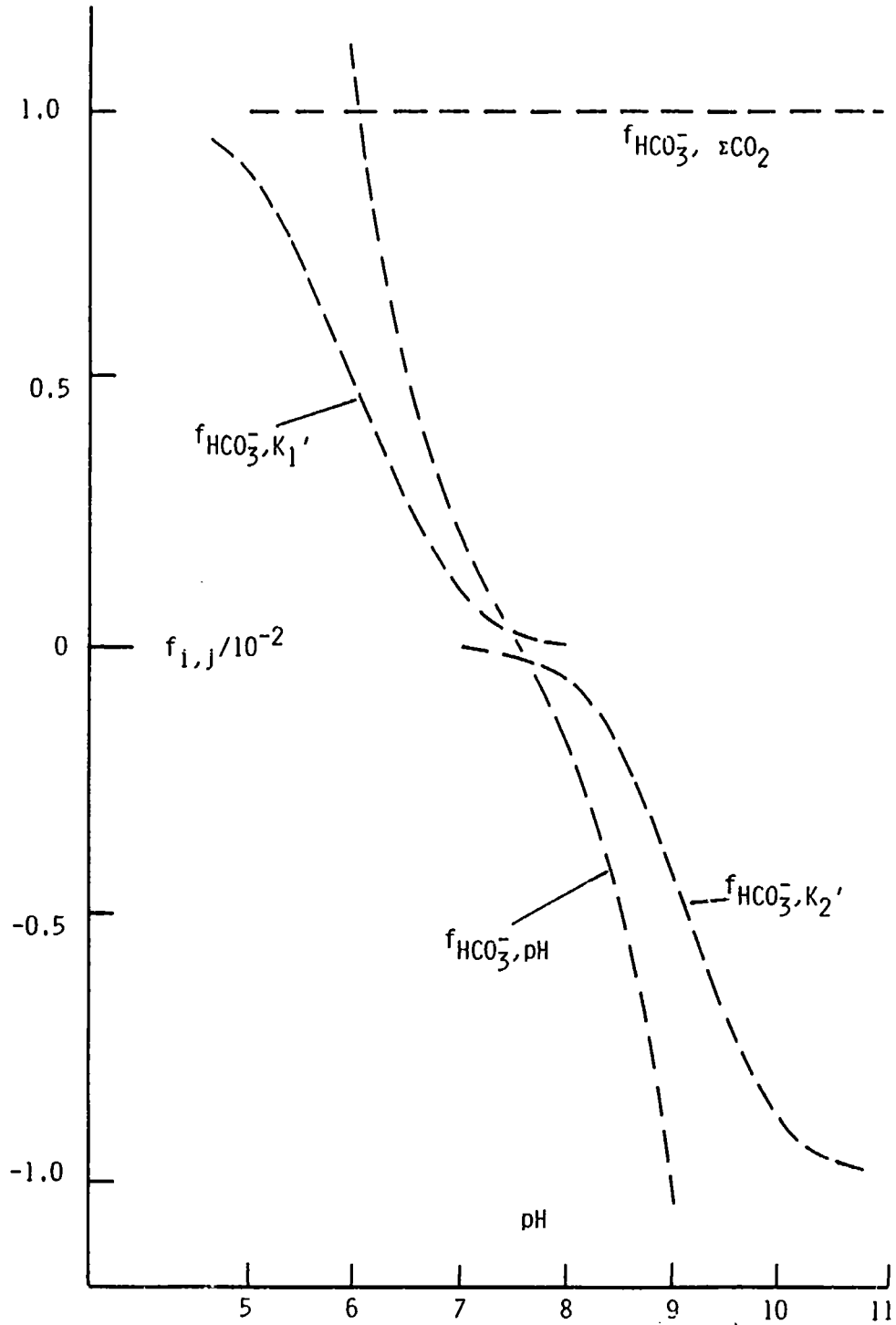


Figure 4 Dependence of σ_1' values on pH (pH/ ΣCO_2 method)

25°C , $S=35$, $\delta_{\text{pH}} 0.01$ pH unit.

Solid lines - Mehrbach constants

Broken lines - Hansson constants.

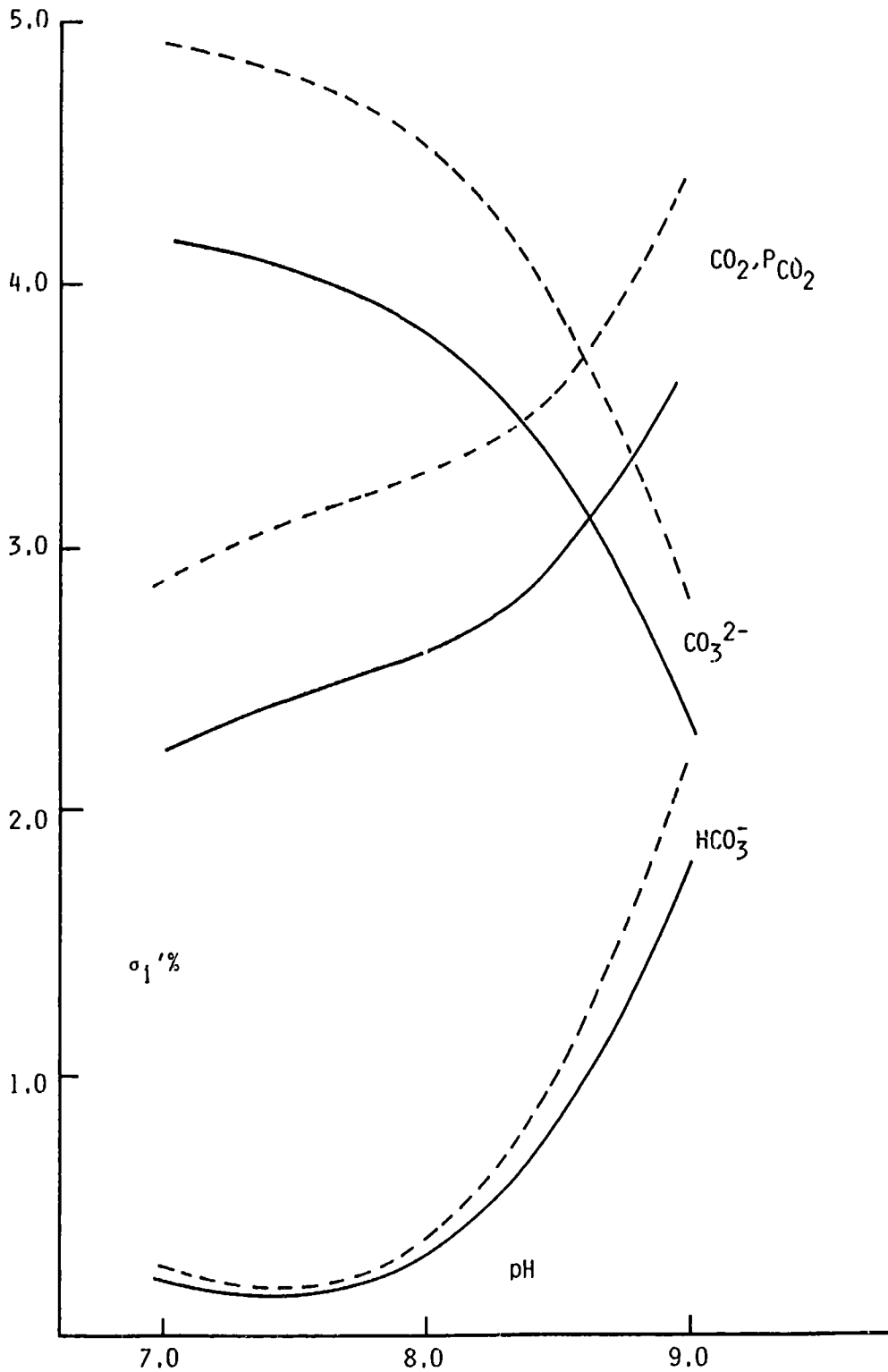
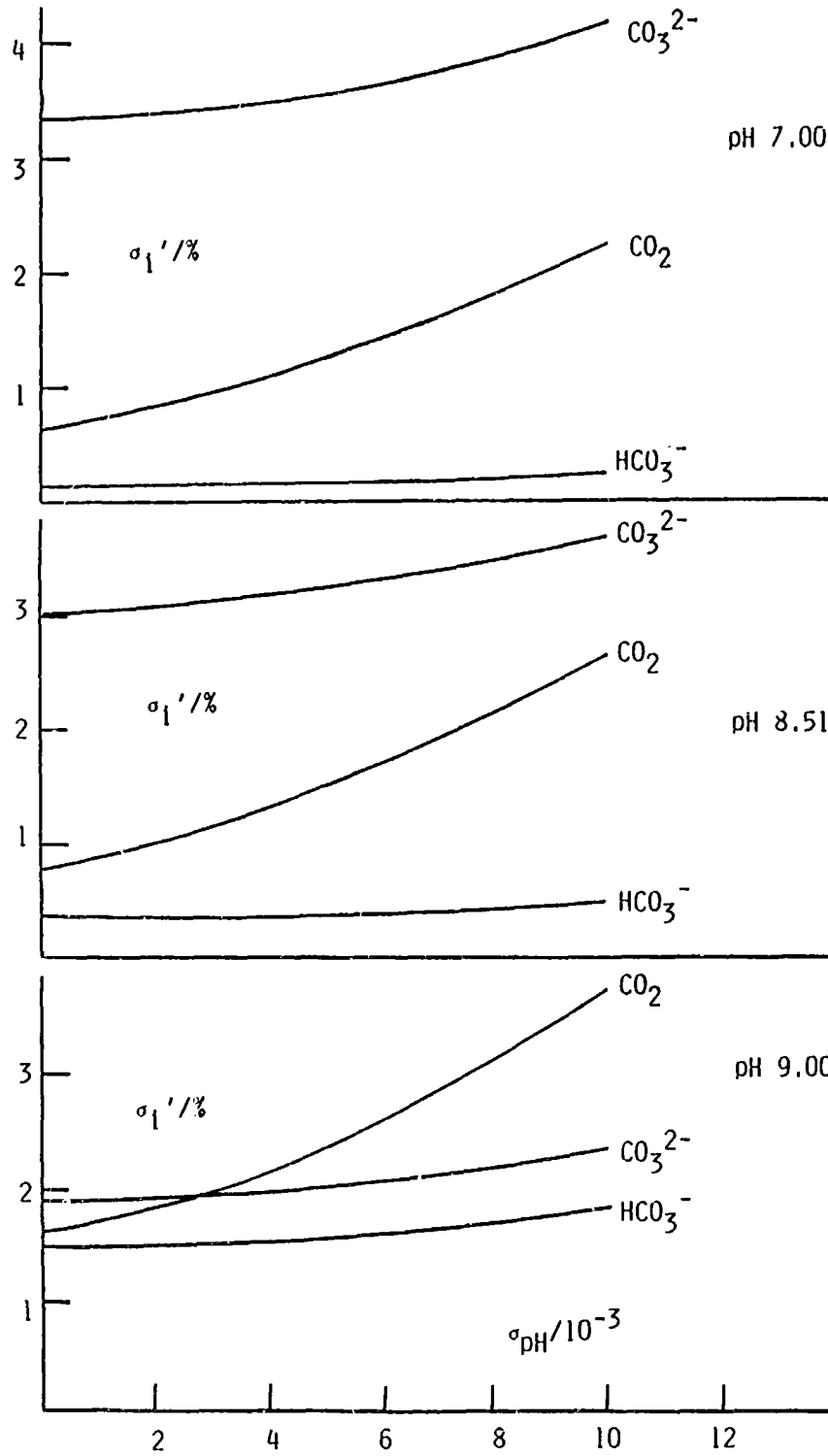


Figure 5 Dependence of σ_1' values on σ_{pH} (pH/ \pm CO₂ method)
 25°C, S = 35 ; Mehrbach constants used.



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Collected reports of the joint panel on oceanographic tables and standards, 1964-1969			International Oceanographic Tables, Vol. 3		
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Eighth report of the joint panel on oceanographic tables and standards, Woods Hole, U.S.A., sponsored by Unesco, ICES, SCOR, IAPSO			International Oceanographic Tables, Vol. 4. (To be published)		
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