

The solubilities of calcite, aragonite and vaterite in CO₂-H₂O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O

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Abstract—Calculations based on approximately 350 new measurements (Ca-PCO₂) of the solubilities of calcite, aragonite and vaterite in CO₂-H₂O solutions between 0 and 90°C indicate the following values for the log of the equilibrium constants K_C , K_A , and K_V respectively, for the reaction $\text{CaCO}_3(\text{s}) = \text{Ca}^{2+} + \text{CO}_3^{2-}$:

$$\log K_C = -171.9065 - 0.077993T + 2839.319/T + 71.595 \log T$$

$$\log K_A = -171.9773 - 0.077993T + 2903.293/T + 71.595 \log T$$

$$\log K_V = -172.1295 - 0.077993T + 3074.688/T + 71.595 \log T$$

where T is in °K. At 25°C the logarithms of the equilibrium constants are -8.480 ± 0.020 , -8.336 ± 0.020 and -7.913 ± 0.020 for calcite, aragonite and vaterite, respectively.

The equilibrium constants are internally consistent with an aqueous model that includes the CaHCO_3^+ and CaCO_3^0 ion pairs, revised analytical expressions for CO₂-H₂O equilibria, and extended Debye-Hückel individual ion activity coefficients. Using this aqueous model, the equilibrium constant of aragonite shows no PCO₂-dependence if the CaHCO_3^+ association constant is

$$\log K_{\text{CaHCO}_3^+} = 1209.120 + 0.31294T - 34765.05/T - 478.782 \log T$$

between 0 and 90°C, corresponding to the value $\log K_{\text{CaHCO}_3^+} = 1.11 \pm 0.07$ at 25°C. The CaCO_3^0 association constant was measured potentiometrically to be

$$\log K_{\text{CaCO}_3^0} = -1228.732 - 0.299444T + 35512.75/T + 485.818 \log T$$

between 5 and 80°C, yielding $\log K_{\text{CaCO}_3^0} = 3.22 \pm 0.14$ at 25°C.

The CO₂-H₂O equilibria have been critically evaluated and new empirical expressions for the temperature dependence of K_H , K_1 and K_2 are

$$\log K_H = 108.3865 + 0.01985076T - 6919.53/T - 40.45154 \log T + 669365./T^2,$$

$$\log K_1 = -356.3094 - 0.06091964T + 21834.37/T + 126.8339 \log T - 1684915./T^2$$

and

$$\log K_2 = -107.8871 - 0.03252849T + 5151.79/T + 38.92561 \log T - 563713.9/T^2$$

which may be used to at least 250°C. These expressions hold for 1 atm. total pressure between 0 and 100°C and follow the vapor pressure curve of water at higher temperatures.

Extensive measurements of the pH of Ca-HCO₃ solutions at 25°C and 0.956 atm PCO₂ using different compositions of the reference electrode filling solution show that measured differences in pH are closely approximated by differences in liquid-junction potential as calculated by the Henderson equation. Liquid-junction corrected pH measurements agree with the calculated pH within 0.003-0.011 pH.

Earlier arguments suggesting that the CaHCO_3^+ ion pair should not be included in the CaCO₃-CO₂-H₂O aqueous model were based on less accurate calcite solubility data. The CaHCO_3^+ ion pair must be included in the aqueous model to account for the observed PCO₂-dependence of aragonite solubility between 317 ppm CO₂ and 100% CO₂.

Previous literature on the solubility of CaCO₃ polymorphs have been critically evaluated using the aqueous model and the results are compared.

INTRODUCTION

ALTHOUGH there is an extensive literature on the solubility of calcite in CO₂-H₂O solutions, few studies have been carried out at temperatures above 50°C and below 15°C. Earlier literature on experimental calcite solubility at 25°C was critically evaluated by Langmuir (1968) and solubilities between 0 and 50°C by Jacobson and Langmuir (1974) who added

new solubility measurements and examined ion pairing in the system CaCO₃-CO₂-H₂O.

Jacobson and Langmuir (1974) drew special attention to several problems in the aqueous model used to describe the thermodynamic properties of Ca-HCO₃ solutions. In evaluating the PCO₂-dependence of calcite solubility (25°C), Jacobson and Langmuir (1974) found that the calcite equilibrium constant (K_C) calculated from the data of Frear and Johnston

(1929), Schloesing (1872), Engel (1888) and Haehnel (1924) varied as a function of total calcium in solution (and thus as a function of PCO_2) if the CaHCO_3^+ ion pair was assumed to form in Ca-HCO_3 solutions. The PCO_2 -dependence of K_C calculated from these data was less if CaHCO_3^+ was ignored in calculating K_C . As discussed by Jacobson and Langmuir (1974), this observation is in direct contradiction to numerous experimental studies supporting the formation of CaHCO_3^+ (Garrels and Thompson, 1962; Nakayama, 1968; Reardon, 1974; Jacobson and Langmuir, 1974; Larson *et al.*, 1976).

Langmuir (1968) pointed out that the measured pH at calcite equilibrium in CO_2 -saturated water at 25°C and one atm total pressure was 0.01–0.02 pH units too high for significant amounts of CaHCO_3^+ to be present in solution. Calculated solubilities were found to be 10 percent too high if the measured pH was used assuming the presence of CaHCO_3^+ (Plummer and Mackenzie, 1974; Christ *et al.*, 1974).

The calculated equilibrium constant depends on the particular aqueous model used to evaluate the solubility data. Uncertainties in the formation of CaHCO_3^+ alone introduce differences of 0.1 log K_C units in the calculated equilibrium constant at 25°C. Jacobson and Langmuir (1974) published two analytical expressions for the temperature dependence of K_C (0–50°C) depending on whether the CaHCO_3^+ ion pair is included (or excluded) in the aqueous model. Analytical expressions for the temperature dependence of K_C beyond 50°C are not available.

Other problems in defining the temperature-dependence of the aqueous model for the $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system are:

(1) The analytical expressions for the temperature-dependence of the Henry's law constant for CO_2 and the first and second dissociation constants of carbonic acid most frequently used (Harned and Davis, 1943; Harned and Scholes, 1941) are valid only between 0 and 50°C.

(2) The temperature dependence of the formation of CaHCO_3^+ above 50°C is not well known.

(3) There are no reliable data beyond 50°C on the formation of the CaCO_3^0 ion pair, and, except at 25°C, log $K_{\text{CaCO}_3^0}$ is not well defined between 0 and 50°C.

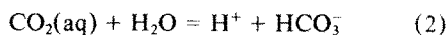
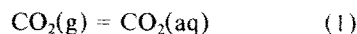
In contrast to calcite there are very few studies of aragonite solubility suitable for calculating equilibrium constants (Backstrom, 1921; Siebert *et al.*, 1974; Berner, 1976). Most equilibrium studies of aragonite have focused on the free energy difference between calcite and aragonite (see for example Jamieson, 1953; Rock and Gordon, 1976). There is only one published determination of vaterite solubility (Turnbull, 1973).

The present study attempts to resolve major problems in the aqueous model for the system $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ between 0 and 90°C, and adds detailed

measurements of the solubilities of calcite, aragonite and vaterite in $\text{CO}_2\text{-H}_2\text{O}$ solutions to approximately 90°C.

$\text{CO}_2\text{-H}_2\text{O}$ EQUILIBRIA

Reactions in the $\text{CO}_2\text{-H}_2\text{O}$ system are based on three equilibria



and



where $\text{CO}_2(\text{aq})$ is defined as $\text{CO}_2^0 + \text{H}_2\text{CO}_3^0$. The equilibrium constants for reactions (1–3) are defined as

$$K_H = \frac{m_{\text{CO}_2(\text{aq})}\gamma_{\text{CO}_2(\text{aq})}}{\text{PCO}_2\gamma_{\text{CO}_2(\text{g})}} = \frac{a_{\text{CO}_2(\text{aq})}}{f_{\text{CO}_2(\text{g})}} \quad (4)$$

$$K_1 = \frac{a_{\text{H}^+}a_{\text{HCO}_3^-}}{a_{\text{CO}_2(\text{aq})}a_{\text{H}_2\text{O}}} \quad (5)$$

$$K_2 = \frac{a_{\text{H}^+}a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad (6)$$

where m_i , γ_i , a_i , and f_i denote molality, activity coefficient, activity and fugacity of the i th species. The term $\gamma_{\text{CO}_2(\text{g})}$ denotes the fugacity coefficient of CO_2 .

Values of the Henry's law constant, K_H , for CO_2 and the first and second dissociation constants, K_1 and K_2 , for $\text{CO}_2(\text{aq})$ are relatively well known between 0 and 50°C owing largely to the works of Harned and Davis (1943), Harned and Bonner (1945), Harned and Scholes (1941), and Murray and Riley (1971) as evaluated by Weiss (1974). There are few studies of these equilibria (particularly K_1 and K_2) at temperatures higher than 50°C.

In order to evaluate our CaCO_3 solubility data, reliable interpolation formulae for the temperature-dependence of K_H , K_1 , and K_2 between 0 and 90°C and 1 atm total pressure are required.

Henry's law constant for $\text{CO}_2(\text{g})$

The Henry's law constant for $\text{CO}_2(\text{g})$ is derived from measurements of CO_2 gas solubility in water. There is a large literature on experimental CO_2 gas solubility in water, particularly between 0 and 40°C (see for example Markham and Kobe, 1941; Battino and Clever, 1966; Wilhelm *et al.*, 1977), but relatively few studies have correctly stated the Henry's law constant, as derived from the gas solubility data. Depending on the units of reporting CO_2 gas solubility measurements, corrections in defining K_H may require (1) appropriate values for the molar volume of CO_2 gas (a non-ideal gas), (2) correcting for the ionization of $\text{CO}_2(\text{aq})$ to H^+ and HCO_3^- in water, (3) inclusion of the fugacity coefficient for CO_2 , (4) unit corrections to the molal scale, and (5) corrections for the density of CO_2 -saturated water. The problem of defining K_H is complicated by the varied units used in reporting gas solubility and the requirement of defining the appropriate corrections as a function of temperature.

Weiss (1974) presents a careful statement of the problem of deriving K_H from CO_2 solubility measurements in water and sea water between 0 and 40°C. Our final selection of

experimental CO₂-water solubility data has been guided in part by the work of Weiss (1974) and by the study of Berg and Vanderzee (1978) who critically evaluated the CO₂-water solubility literature at 25°C.

One of the most frequently cited sources of CO₂-water solubility data (Harned and Davis, 1943) was judged less reliable by Berg and Vanderzee (1978) than other sources (such as Morrison and Billett, 1952; Weiss, 1974) owing to potential errors in the titration method used by Harned and Davis (1943) to determine total CO₂ in solution. For this reason we have not included the CO₂-solubility data of Harned and Davis (1943) in our final analysis.

In a recent review of gas solubilities, Wilhelm *et al.* (1977) fitted the CO₂ solubility data (0–35°C) of Murray and Riley (1971) (as corrected by Weiss, 1974) with only the higher temperature portion (42–75°C) of the data of Morrison and Billett (1952). Unfortunately, corrections for the non-ideal behavior of CO₂ gas and ionization of CO₂(aq) were not made by Wilhelm *et al.*, (1977) to the data of Morrison and Billett (1952) and these data are therefore internally inconsistent with the Murray and Riley (1971) data that were properly corrected by Weiss (1974). The analytical expression of Wilhelm *et al.* (1977) for CO₂ solubility in water deviates from published values of K_H by several percent at the low and high extremes of the fit (0–80°C).

Our analysis of K_H as a function of temperature is based on data of Morrison and Billett (1952), Murray and Riley (1971) as evaluated by Weiss (1974), the evaluation of Houghton *et al.* (1957), Malinin (1959), as given by Ryzhenko (1963), and Ellis and Golding (1963).

Morrison and Billett (1952) report the solubility of CO₂(g) in water at S.T.P. and a total gas pressure of 1 atm between 13.3 and 74.7°C. Berg and Vanderzee (1978) concluded that the experiments of Morrison and Billett (1952) were actually at 1 atm PCO₂ rather than 1 atm total pressure.

The Henry's law constant, on the molal scale, is derived from the data of Morrison and Billett (1952) by

$$K_H = \frac{S_0(1 - \beta)T}{V_m \gamma_{CO_2(g)}(273.15)} \quad (7)$$

where S_0 is the measured solubility (reported as cc CO₂(g)/kg H₂O), the term $(1 - \beta)$ accounts for the ionization of CO₂(aq) to H⁺ and HCO₃⁻, T is temperature in °K, V_m is the molar volume of CO₂(g) (cc atm/mol), $\gamma_{CO_2(g)}$ is the fugacity coefficient of CO₂(g) and the constant 273.15 has the unit of °K.

The term $(1 - \beta)$ is defined with sufficient accuracy from CO₂ solubility in water, ΣCO_2 , and the first dissociation constant for CO₂(aq), K_1 ,

$$1 - \beta \approx 1 - \frac{\sqrt{K_1 \Sigma CO_2}}{\Sigma CO_2} \quad (8)$$

The terms K_1 and ΣCO_2 are functions of temperature and were sufficiently defined by the expressions of Harned and Davis (1943). Further hydrolysis of CO₂(aq) to CO₃²⁻ is negligible in CO₂-H₂O solutions and was ignored.

The molar volume of a non-ideal gas at 1 atm total pressure can be expressed by

$$V_m = V_{(T)}^* + B_{(T)} \quad (9)$$

(see Weiss, 1974) where $V_{(T)}^*$ is the molar volume of the ideal gas at 1 atm total pressure and temperature T , $B_{(T)}$ is the second virial coefficient of CO₂(g) as a function of temperature. At one atm total pressure, $V_{(T)}^* = RT$ where R is the gas constant (82.056 cc atm mol⁻¹ °K⁻¹). We have used the expression for $B_{(T)}$ given by MacCormack and Schneider (1950) which is reliable between 0 and 600°C. At one atm total pressure, V_m is (MacCormack and Schnei-

Table 1. Definition of K_H from the CO₂-solubility data of Morrison and Billett (1952)

t °C	s ₀ ¹	1 - β ²	V _m ³	γ _{CO₂} ⁴	K _H ⁵
13.3	1059.	0.99723	23367.	0.99388	0.04769
14.9	1010.	0.99712	23500.	0.99400	0.04547
17.6	927.	0.99692	23725.	0.99420	0.04170
19.8	873.	0.99677	23908.	0.99436	0.03926
25.8	744.7	0.99634	24406.	0.99476	0.03345
29.8	662.2	0.99606	24738.	0.99500	0.02972
30.3	660.0	0.99602	24780.	0.99503	0.02962
33.2	615.2	0.99583	25021.	0.99520	0.02759
34.3	606.7	0.99576	25112.	0.99526	0.02721
34.6	599.8	0.99574	25137.	0.99528	0.02690
42.5	502.0	0.99527	25792.	0.99568	0.02248
46.4	465.0	0.99506	26115.	0.99587	0.02081
48.4	455.0	0.99497	26281.	0.99596	0.02036
51.1	425.6	0.99485	26505.	0.99608	0.01904
54.3	404.6	0.99473	26770.	0.99621	0.01809
63.1	346.1	0.99448	27498.	0.99655	0.01546
68.2	327.3	0.99440	27920.	0.99674	0.01462
72.4	306.9	0.99437	28268.	0.99688	0.01370
74.7	300.6	0.99437	28458.	0.99695	0.01342

¹ CO₂ solubility in water at STP in cc/kg H₂O at 1 atm PCO₂ (Morrison and Billett, 1952).

² Eqn (8).

³ Eqns (9)–(10).

⁴ Eqn (11).

⁵ Henry's law constant for CO₂ at atm total pressure as defined by eqn (4) and calculated from the data of Morrison and Billett (1952) using eqn (7).

der, 1950)

$$V_m = 82.056T + 22265.(3.9386 \times 10^{-3} - 1.0790$$

$$\times 10^{-6} T - 2.0787/T - 0.6002 \times 10^5/T^3). \quad (10)$$

A temperature-dependent expression for the fugacity coefficient of CO₂, γ_{CO_2} , was taken from Houghton *et al.* (1957) and truncated at the P/RT level

$$\ln \gamma_{CO_2} = 1/RT(0.10476 - 61.0102/T - 660000./T^3 - 2.47 \times 10^{27}/T^{12}) \quad (11)$$

which is reliable to 4 significant figures at 1 atm total pressure. Table 1 summarizes our calculations of K_H using the data of Morrison and Billett (1952) and Eqns. (7)–(11).

Weiss (1974) has correctly defined K_H from the CO₂-H₂O solubility data of Murray and Riley (1971). The second virial coefficient of CO₂(g) used by Weiss (1974) agrees well with that of MacCormack and Schneider (1950) over the experimental temperature range of Murray and Riley (1971), (1–35°C), but is limited to a range of applicability between –8 and 47°C.

The only correction required to the evaluation of Weiss (1974) was conversion of K_H from molar to molal units. In this case it was necessary to divide K_H (molar scale) by the ratio C_i/m_i , where C_i denotes molarity of CO₂-saturated water and m_i is the molality of CO₂-saturated water. The term C_i/m_i has units of kg H₂O/l CO₂-saturated solution and was computed as a function of temperature using the CO₂ solubility data of Harned and Davis (1943) and the density of CO₂-saturated solutions given by Parkinson and DeNevers (1969). Values of K_H (molal scale) were calculated every 2°C between 0 and 36°C, and at the experimental temperatures of Murray and Riley (1971) using the

Table 2. Values of K_H , K_1 , and K_2 for the $\text{CO}_2\text{-H}_2\text{O}$ system at one atm total pressure¹

$t^\circ\text{C}$	Log K_H	s	Ref.	$t^\circ\text{C}$	Log K_H	s	Ref.	$t^\circ\text{C}$	Log K_H	s	Ref.	$t^\circ\text{C}$	Log K_H	s	Ref.
13.3	-1.3216	.005	2	10.0	-1.2693	.005	3	30.0	-1.5230	.005	4	235.0	-2.0480	.020	7
14.9	-1.3423	.005	2	15.0	-1.3407	.005	3	32.0	-1.5441	.005	4	261.0	-1.9460	.020	7
17.6	-1.3799	.005	2	20.0	-1.4064	.005	3	34.0	-1.5645	.005	4	261.0	-1.9460	.020	7
19.8	-1.4060	.005	2	25.0	-1.4671	.005	3	36.0	-1.5842	.005	4	265.0	-1.9460	.020	7
25.8	-1.4756	.005	2	32.0	-1.5441	.005	3	0.0	-1.0951	.010	5	265.0	-1.9370	.020	7
29.8	-1.5270	.005	2	35.0	-1.5745	.005	3	10.0	-1.2618	.010	5	309.0	-1.8120	.020	7
30.3	-1.5284	.005	2	0.0	-1.1090	.005	4	15.0	-1.3515	.010	5	309.0	-1.8350	.020	7
33.2	-1.5592	.005	2	2.0	-1.1431	.005	4	20.0	-1.4152	.010	5	309.0	-1.8350	.020	7
34.3	-1.5653	.005	2	4.0	-1.1761	.005	4	25.0	-1.4715	.010	5	334.0	-1.7330	.020	7
34.6	-1.5702	.005	2	6.0	-1.2082	.005	4	35.0	-1.5805	.010	5	334.0	-1.7330	.020	7
42.5	-1.6482	.005	2	8.0	-1.2393	.005	4	50.0	-1.7201	.010	5	100.0	-1.9720	.020	8
46.4	-1.6817	.005	2	10.0	-1.2693	.005	4	75.0	-1.8611	.010	5	125.0	-2.0340	.020	8
48.4	-1.6912	.005	2	12.0	-1.2985	.005	4	100.0	-1.9855	.010	5	150.0	-2.0750	.020	8
51.1	-1.7203	.005	2	14.0	-1.3268	.005	4	100.0	-1.9730	.020	6	175.0	-2.0880	.020	8
54.3	-1.7426	.005	2	16.0	-1.3542	.005	4	156.0	-2.0790	.020	6	200.0	-2.0620	.020	8
63.1	-1.8108	.005	2	18.0	-1.3808	.005	4	200.0	-2.0810	.020	6	225.0	-2.0260	.020	8
68.2	-1.8351	.005	2	20.0	-1.4065	.005	4	177.0	-2.0940	.020	7	250.0	-1.9800	.020	8
72.4	-1.8633	.005	2	22.0	-1.4313	.005	4	202.0	-2.0480	.020	7	275.0	-1.9180	.020	8
74.7	-1.8722	.005	2	24.0	-1.4554	.005	4	204.0	-2.0410	.020	7	300.0	-1.8470	.020	8
1.0	-1.1269	.005	3	26.0	-1.4787	.005	4	229.0	-2.0260	.020	7	325.0	-1.7470	.020	8
5.0	-1.1923	.005	3	28.0	-1.5013	.005	4	229.0	-2.0110	.020	7				

$t^\circ\text{C}$	Log K_1	s	Ref.	$t^\circ\text{C}$	Log K_1	s	Ref.	$t^\circ\text{C}$	Log K_1	s	Ref.	$t^\circ\text{C}$	Log K_1	s	Ref.
25.0	-6.3470	.005	9	25.0	-6.3514	.002	11	99.4	-6.4200	.020	12	5.0	-6.5140	.005	13
25.0	-6.3500	.005	10	30.0	-6.3270	.002	11	100.4	-6.4170	.020	12	15.0	-6.4210	.005	13
0.0	-6.5773	.002	11	35.0	-6.3086	.002	11	150.0	-6.7620	.050	12	25.0	-6.3489	.005	13
5.0	-6.5171	.002	11	40.0	-6.2960	.002	11	200.1	-7.2420	.050	12	35.0	-6.3104	.005	13
10.0	-6.4647	.002	11	45.0	-6.2891	.002	11	200.5	-7.2600	.050	12	45.0	-6.2939	.005	13
15.0	-6.4200	.002	11	50.0	-6.2873	.002	11	250.1	-7.7850	.100	12	100.0	-6.4650	.050	14
20.0	-6.3825	.002	11	25.0	-6.3650	.020	12	250.2	-7.7850	.100	12	156.0	-6.8100	.100	14
												200.0	-7.1430	.200	14

$t^\circ\text{C}$	Log K_2	s	Ref.	$t^\circ\text{C}$	Log K_2	s	Ref.	$t^\circ\text{C}$	Log K_2	s	Ref.	$t^\circ\text{C}$	Log K_2	s	Ref.
25.0	-10.3200	.010	15	0.0	-10.6250	.003	17	25.0	-10.3290	.003	17	50.0	-10.1720	.003	17
60.0	-10.1790	.050	16	5.0	-10.5570	.003	17	30.0	-10.2900	.003	17	100.0	-10.1370	.100	18
70.0	-10.1530	.050	16	10.0	-10.4900	.003	17	35.0	-10.2500	.003	17	156.0	-10.4090	.100	18
80.0	-10.1420	.050	16	15.0	-10.4300	.003	17	40.0	-10.2200	.003	17	218.0	-10.9590	.100	18
90.0	-10.1400	.050	16	20.0	-10.3770	.003	17	45.0	-10.1950	.003	17				

¹ s is the estimated standard deviation of the experimental log K value used in refining the regression coefficients of Table 3.

² Morrison and Billett (1952) as corrected in Table 1.

³ Weiss (1974) molar analytical expression at the experimental temperatures of Murray and Riley (1971), corrected to the molal scale.

⁴ Weiss (1974) molar analytical expression based on the data of Murray and Riley (1971) in molal units.

⁵ Houghton *et al.* (1957) corrected to the molal scale.

⁶ Malinin (1959) as given by Ryzhenko (1963) and corrected to the molal scale.

⁷ Ellis and Golding (1963) corrected to the molal scale.

⁸ Recommended (smoothed) values from Table 7 of Ellis and Golding (1963) corrected to the molal scale.

⁹ Curry and Hazelton (1938).

¹⁰ Nasanen *et al.* (1961).

¹¹ Harned and Bonner (1945).

¹² Read (1975).

¹³ Nasanen (1947).

¹⁴ Ryzhenko (1963).

¹⁵ Nasanen (1946).

¹⁶ Cuta and Strafelda (1954).

¹⁷ Harned and Scholes (1941).

analytical expression (molar scale) given by Weiss (1974) and the units conversion described above.

Houghton *et al.* (1957) have presented a careful analysis of some of the earlier data, and tabulate values of the mole fraction of CO_2 in water, X_{CO_2} , at 0, 10, 15, 20, 25, 35, 50, 75, and 100°C between 1 and 36 atm PCO_2 . Although the experimental data on which these results are based are not as accurate as those of Morrison and Billett (1952) and Murray and Riley (1971), they were included in the total

data set owing to the lack of additional data at 75 and 100°C . The mole fraction solubility data (X) at 1 atm were converted from the mole fraction scale to molal scale using

$$K_H = \frac{10^3 X}{18.015 - 18.015X} \quad (12)$$

where 18.015 is the molecular weight of water.

To better define the regression analysis between 75 and

100°C, higher temperature data of Malinin (1959), as cited by Ryzhenko (1963) at 100, 156 and 200°C, and data of Ellis and Golding (1963) between 177 and 334°C were included. The solubility data of Malinin (1959) were converted from molar to molal units using the reported solubility and assuming the density of CO₂-saturated water is that of pure water at the temperature of the experiment. The only change made to the Ellis and Golding (1963) data was conversion from mole fraction to molal scale.

The selected data set for K_H with estimates of their standard deviations is summarized in Table 2.

First and second dissociation constants of CO₂(aq)

Analytical expressions for the temperature dependence of K_1 and K_2 given by Harned and Davis (1943), Harned and Bonner (1945) and Harned and Scholes (1941) may be used only to 50°C. Other analytical expressions for the temperature dependence of K_1 and K_2 were reported by Ryzhenko (1963) who combined several measurements of these constants between 100 and 200°C (Ryzhenko, 1963) with the data of Harned and Davis (1943) and Harned and Scholes (1941). Ryzhenko's analytical expression for K_1 deviates from the data of Harned and Davis (1943) by as much as 0.03 log K_1 (at 25°C) even though the measurements of Harned and Davis (1943) are probably precise within ± 0.005 log K or better. Ryzhenko's analytical expression for K_2 is in reasonable agreement with the data of Harned and Scholes (1941) except at temperatures between 0 and 10°C where departures as large as 0.01 log K are found.

In defining K_1 between 0 and 50°C we have relied on the careful EMF measurements of Harned and Davis (1943) as refined by Harned and Bonner (1945). Several other measurements of K_1 in this temperature range appear to be of nearly equal quality and were included (Curry and Hazelton, 1938; Näsänen *et al.*, 1961; Näsänen, 1947). We have not included measurements of Shedlovsky and MacInnes (1935), MacInnes and Belcher (1933, 1935) and Ellis (1959a) because these data do not appear to be of the quality of those of Harned and Davis (1943) and Harned and Bonner (1945).

Higher temperature measurements of K_1 using conductivity techniques were reported by Ryzhenko (1963) (100–200°C) and Read (1975) (100–250°C, with one measurement at 25°C). Both studies yield values that agree reasonably well where the data coincide, but because of the more extensive range in temperature, the Read (1975) data were weighted slightly higher in the regression analysis (as discussed below).

Other than the EMF measurements of Harned and Scholes (1941) (0–50°C), there are very few additional measurements of K_2 reported in the literature. Measurements of K_2 at 25°C of MacInnes and Belcher (1933, 1935) depart significantly from the data of Harned and Scholes (1941). Data of Čižka and Štráfelda (1954) (60–90°C) and Ryzhenko (1963) (100–219°C) were included with larger estimates of uncertainty.

The final data sets and estimated uncertainties compiled for K_1 and K_2 are summarized in Table 2.

Regression analysis

Temperature-dependent expressions for log K_H , log K_1 and log K_2 were computed using the data of Table 2 and the computer program FITIT (Head, 1970). The fitting procedure uses estimates of the standard deviation of each data point as a weighting factor in refining regression coefficients. In the fitting procedure, smaller estimates of the standard deviation cause the computed fit to more closely predict the experimental value. The standard deviations of experimental data given in Table 2 were chosen in part so that the computed regression curve would closely describe measurements judged by us to be of higher quality.

The temperature dependencies of all three equilibrium constants were effectively described by an equation of the form

$$\log K = A + BT + C/T + D \log T + E/T^2 \quad (13)$$

where A , B , C , D , and E are constants (Table 3) and T is temperature in °K. The terms in Eqn. (13) follow from an assumed Maier and Kelly (1932) form to the temperature dependence of the heat capacity of reaction. Additional terms in the expression for log K , required by more complicated equations for the form of the heat capacity (Haas and Fisher, 1976) were not warranted over the temperature range of the published data (0–350°C for K_H , 0–250°C for K_1 , and 0–220°C for K_2). Fits of slightly lesser quality were obtained using expressions excluding the E , or B and E terms of Eqn. (13).

Figures 1–3 compare the experimental values of K_H , K_1 and K_2 respectively with the appropriate regression curve defined by Eqn. (13) and the constants of Table 3. The curves describe the experimental data within the standard deviations of Table 2. The regression curves imply the following values for ΔH° for reactions (1)–(3) respectively, at 298.15°K and 1 atm total pressure: –4776., 2177., and 3561. cal mol^{–1}. These values compare well with the recent calorimetric measurements of ΔH° for reaction (1) (–4720 \pm 40 cal mol^{–1}) of Berg and Vanderzee (1978) and the recent evaluation of ΔH° for reactions (2) and (3) given by Berg and Vanderzee (1978) (2188. \pm 15 and 3513. \pm 25 cal mol^{–1}), respectively.

INDIVIDUAL ION ACTIVITY COEFFICIENTS

Modified Debye-Hückel equations of Truesdell and Jones (1974) were used to calculate $\gamma_{Ca^{2+}}$, $\gamma_{HCO_3^-}$ and $\gamma_{CO_3^{2-}}$. The equation is of the form

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}} + b_i/I \quad (14)$$

where A and B are constants defined by Hamer

Table 3: Constants for calculation of K_H , K_1 , and K_2 as a function of temperature¹

	A	B	C	D	E
Log K_H	108.3865	0.01985076	–6919.53	–40.4515	669365.
Log K_1	–356.3094	–0.06091964	21834.37	126.8339	–1684915.
Log K_2	–107.8871	–0.03252849	5151.79	38.9256	–563713.9

¹ Log $K = A + BT + C/T + D \log T + E/T^2$, where K is on the molal scale at one atm total pressure and temperature °K. The expression for K_H describes the data of Table 2 between 0 and 334°C within the estimated standard deviations given. The expression for K_1 is valid between 0 and 250°C within the estimated experimental uncertainties. The expression for K_2 may be used between 0 and 218°C within the experimental uncertainties. Sufficient significant figures are given for log K to round to the nearest 0.001 log K over the temperature range of the data.

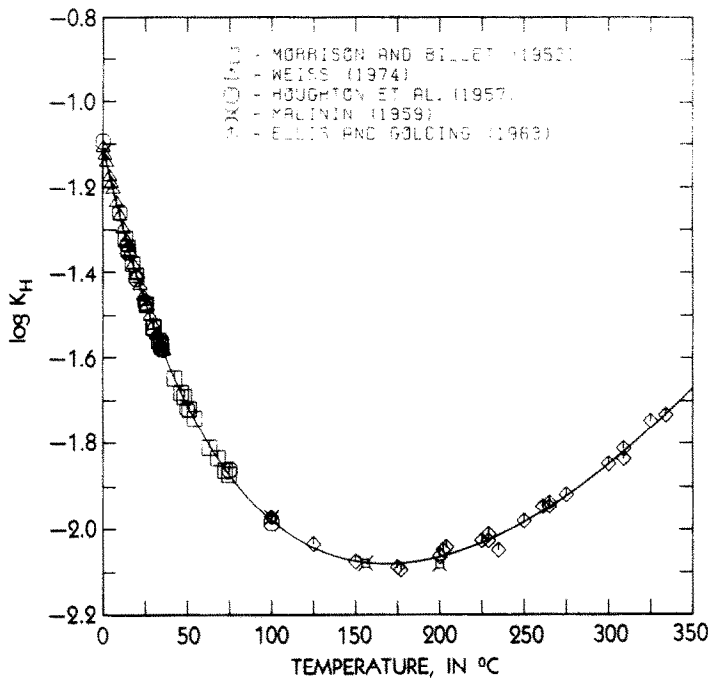


FIG. 1. $\log K_H$ as a function of temperature in $^{\circ}\text{C}$. The curve is given by Eqn. (13) and the constants of Table 3.

(1968) as a function of temperature, density and dielectric constant of water (see Truesdell and Jones, 1974), z_i is the charge on the i th ion, I is the ionic strength ($I = \frac{1}{2} \sum m_i z_i^2$), and a_i and b_i are parameters

specific to individual ions and were estimated by Truesdell and Jones (1974) from experimental data. Values of a_i and b_i for Ca^{2+} are 5.0 and 0.165, respectively, as derived from CaCl_2 -KCl mean salt data

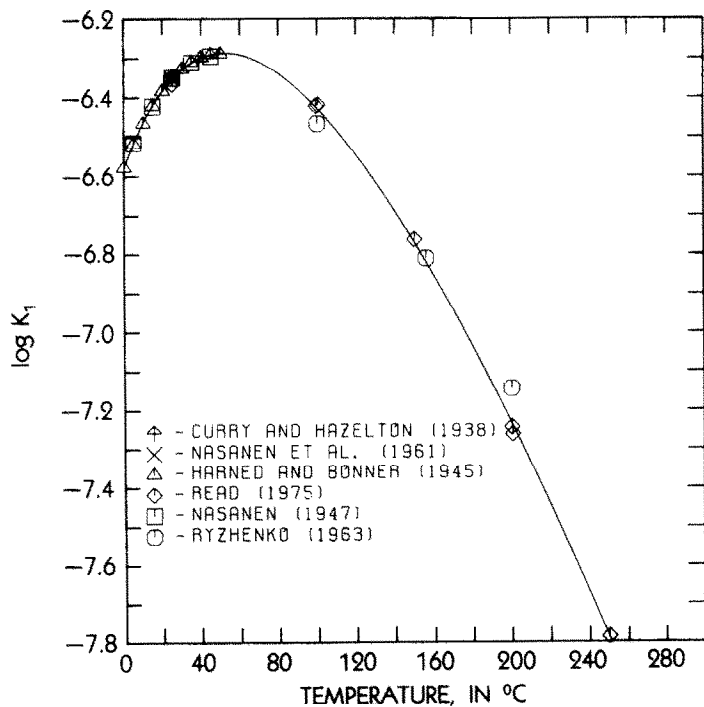


FIG. 2. $\log K_1$ as a function of temperature in $^{\circ}\text{C}$. The curve is given by Eqn. (13) and the constants of Table 3.

and use of the MacInnes assumption (MacInnes, 1919). For both HCO_3^- and CO_3^{2-} , a_i and b_i are 5.4 and 0.0, based on the experimental data of Walker *et al.* (1927).

Individual ion activity coefficients of H^+ and OH^- have been calculated from the Debye-Hückel equation

$$\log \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + B\bar{a}_i\sqrt{I}} \quad (15)$$

(Robinson and Stokes, 1955) where the terms are as in Eqn. (14) except \bar{a}_i which is the ion size parameter equal to 9.0 for H^+ and 3.5 for OH^- (Kielland, 1937).

The activity coefficient of CaHCO_3^+ was assumed equal to that of HCO_3^- . The activity coefficient of CaCO_3^0 was calculated from the expression of Reedson and Langmuir (1976)

$$\log \gamma_{\text{CaCO}_3^0} = -0.5I. \quad (16)$$

Several alternative models for calculation of individual ion activity coefficients were considered. The Debye-Hückel equation was rejected for the major species (Ca^{2+} , HCO_3^-) because most of the solutions are at ionic strengths beyond the range of reliability of Debye-Hückel theory ($I \leq 0.01$). Negligible uncertainties result from use of the Debye-Hückel equation for H^+ and OH^- species in our calculations.

The Davies equation (Davies, 1962)

$$\log \gamma_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad (17)$$

while qualitatively accounting for trends in activity coefficients at low and high ionic strengths distin-

guishes between individual ions only on the basis of charge.

The computed equilibrium constants of CaCO_3 polymorphs are not very sensitive to uncertainties in $\gamma_{\text{CaHCO}_3^+}$ and $\gamma_{\text{CaCO}_3^0}$. For example changing the activity coefficient model given above to calculate $\gamma_{\text{CaHCO}_3^+}$ from the Debye-Hückel equation (using $\bar{a}_i = 6.0$) and assuming $\gamma_{\text{CaCO}_3^0} = 1.0$ causes deviations of less than 0.001 log K (K_C , K_A , K_V) units.

Figure 4 compares differences in log K that result if other alternative activity coefficient models are used in calculation of log K from our solubility data. The uncertainties in log K due to alternative activity coefficient models vary with the total calcium concentration in solution. The total calcium concentration varies inversely with temperature and directly with PCO_2 of the experiment. Although the calculations of Fig. 4 were made at 25°C, the relationships vary less than 0.001 log K units between 0 and 80°C for a given total calcium concentration.

Because solubilities are higher at lower temperatures and higher PCO_2 , the uncertainties in log K due to activity coefficients will tend to be larger for the solubility data under these conditions than for data at low PCO_2 and high temperatures.

THE CaHCO_3^+ ASSOCIATION CONSTANT

The formation of the ion pairs CaHCO_3^+ and CaCO_3^0 in Ca-HCO_3 solutions was first suggested by Greenwald (1941), and since then there has been an increasing number of attempts to measure the equilibrium constants for the association reactions

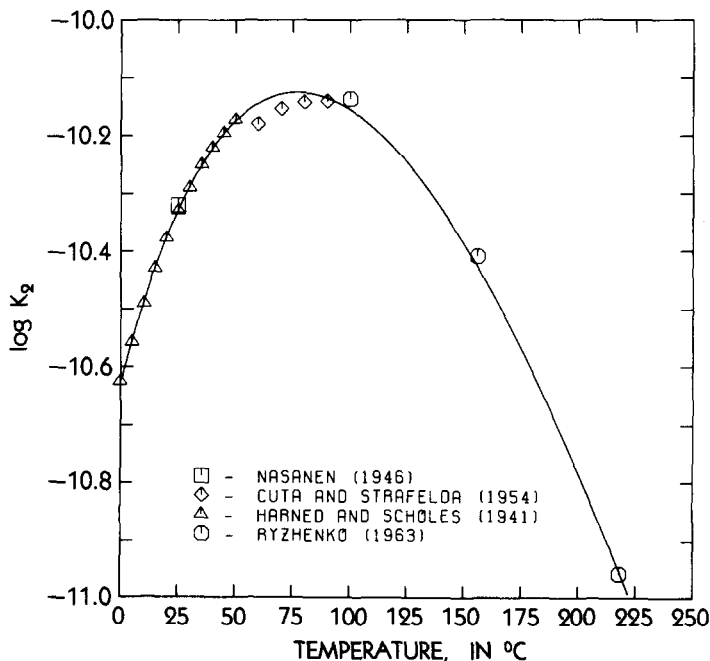


FIG. 3. Log K_2 as a function of temperature in °C. The curve is given by Eqn. (13) and the constants of Table 3.

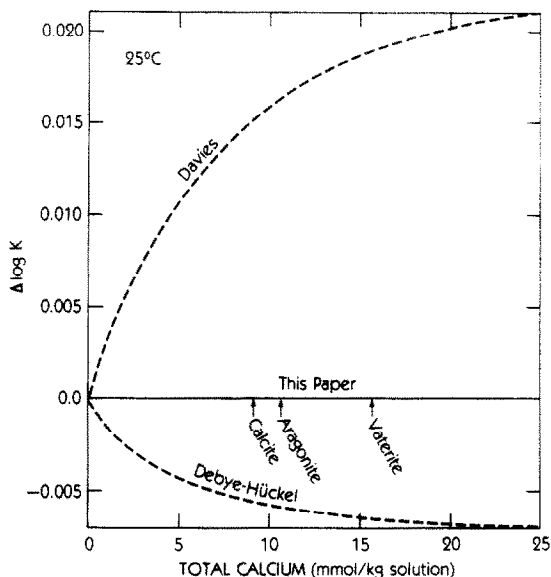


FIG. 4. Deviations in $\log K$ for calcite, aragonite and vaterite at 25°C resulting from alternate models of individual ion activity coefficients relative to the activity coefficient model of this paper (see text). $\Delta \log K = \log K$ (this paper) $-\log K$ (based on alternative activity coefficient model). The line marked Davies uses the equation of Davies (1962) with 0.31 term for charged species and 1.0 for the activity coefficient of CaCO_3 . The line marked Debye-Hückel uses the Debye-Hückel equation for all charged species and assumes $\gamma_{\text{CaCO}_3} = 1.0$. The relationships shown are nearly independent of temperature with difference from those shown of generally less than $\pm 0.001 \log K$ between 0 and 90°C. The solubilities of calcite, aragonite and vaterite at 25°C and 0.95 atm PCO_2 are shown.

and



There is little evidence supporting the formation of higher order complexes in Ca-HCO_3 solutions.

The association constant for the formation of CaHCO_3^+ is defined from reaction (18) as

$$K_{\text{CaHCO}_3^+} = \frac{a_{\text{CaHCO}_3^+}}{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}}. \quad (20)$$

$K_{\text{CaHCO}_3^+}$ has been measured as a function of temperature by Jacobson and Langmuir (1974), Reardon (1974), Martynova *et al.* (1974), and Larson *et al.* (1976) (see Fig. 5), using a variety of methods (Table 4). Jacobson and Langmuir (1974) determined $K_{\text{CaHCO}_3^+}$ from conductance measurements of dilute calcium-bicarbonate solutions. Reardon's (1974) values were calculated from pH measurements of CaCl_2 solutions at known PCO_2 . Martynova *et al.* (1974) computed $K_{\text{CaHCO}_3^+}$ from pH, pCa^{2+} , and total calcium measurements at calcite equilibrium in contact with air. Larson *et al.* (1976) used potentiometric titration procedures. Larson *et al.* (1976) found trends in $K_{\text{CaHCO}_3^+}$ during a particular titration run and chose to exclude initial values which showed the greatest change in $K_{\text{CaHCO}_3^+}$.

The agreement in experimental values of $K_{\text{CaHCO}_3^+}$ is generally not better than $\pm 0.2 \log K_{\text{CaHCO}_3^+}$ between 0 and 90°C (Fig. 5).

Several arguments have been made previously suggesting the absence of CaHCO_3^+ in Ca-HCO_3 solutions. Langmuir (1968) showed that if the measured pH (6.02, Garrels *et al.*, 1960; 6.03, Langmuir, 1964) in equilibrium with calcite in CO_2 -saturated water at 25°C is used with the assumed PCO_2 (0.97 atm) to calculate total calcium, the calculated and measured total calcium concentrations agree only if the CaHCO_3^+ ion pair is neglected. If the measured pH (6.02) in equilibrium with calcite at 0.97 atm. PCO_2 and 25°C is used, the calculated solubility of calcite is 9.8 mMol/l (assuming the presence of CaHCO_3^+) rather than the observed value (9.1

Table 4: Measurements of the association constant for CaHCO_3^+ at 25°C and one atm total pressure¹

Source	Composition	Method	log K _{CaHCO₃⁺}
Greenwald (1941)	KHCO ₃ -KCl	titration	1.05-1.62 ²
	KHCO ₃ -CaCl ₂	Solubility	
	CaCO ₃ -KCl		
	CaCO ₃ -KHCO ₃		
Nakayama (1968)	CaCO ₃ -CO ₂	pH, pCa ²⁺	1.25 ± .02
Nakayama (1968)	CaCl ₂ -CO ₂	pH	1.27 ± .03
Martynova <i>et al.</i> (1974)	CaCO ₃ -CO ₂	pH, pCa ²⁺	1.30 ³
Jacobson and Langmuir (1974)	CaCO ₃ -CO ₂	Conductance	1.0 ± .05
Reardon (1974)	CaCl ₂ -CO ₂	pH	1.14 ± .05
Larson <i>et al.</i> (1976)	KHCO ₃ -Ca(ClO ₄) ₂	titration	1.25
This paper	CaCO ₃ -CO ₂	pH	1.28 ± .06
This paper	CaCO ₃ -CO ₂	solubility	1.11 ± .07 ⁴

$$^1 K_{\text{CaHCO}_3^+} = \frac{a_{\text{CaHCO}_3^+}}{a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}}.$$

² As re-calculated by Jacobson and Langmuir (1974). Using the same data, Garrels and Thompson (1962) estimated $\log K_{\text{CaHCO}_3^+} = 1.26$. The data of Greenwald (1941) are at 22°C.

³ $\log K_{\text{CaHCO}_3^+} = 1.27$ at 22°C. Value at 25°C is derived from an assumed linear fit to reported K values between 22 and 98°C.

⁴ Smoothed value at 25°C as given by eqn (43). Experimental value at 25°C is 1.14.

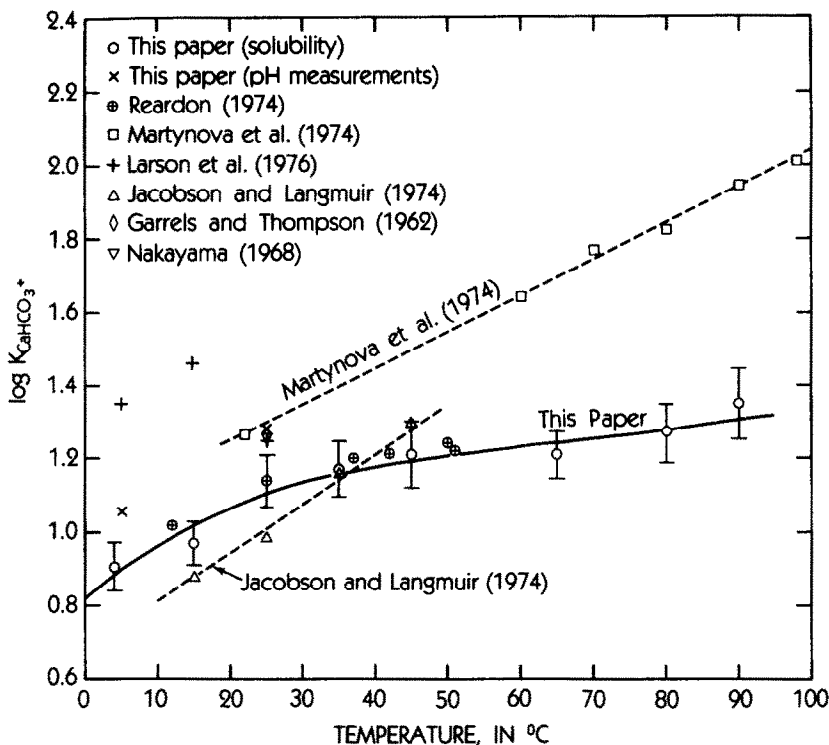


FIG. 5. Summary of experimental values of the association constant for CaHCO_3^* as a function of temperature. Data from this study are based on aragonite solubility and pH measurements of Ca-HCO_3 solutions.

mMol/l). Berner (1976) also chose to ignore CaHCO_3^* in calculation of K_C and K_A from his calcite and aragonite solubility measurements citing a similar argument.

Jacobson and Langmuir (1974) observed that trends in K_C calculated from calcite solubility as a function of total calcium (and thus PCO_2) were less if CaHCO_3^* was ignored in the calculation. Their observation was based, however, on the older solubility data (Schloesing, 1872; Engle, 1888; Haehnel, 1924; Frear and Johnston, 1929) which may not be of sufficient accuracy to test the aqueous model.

Christ *et al.* (1974) pointed out that there is little justification for equating the measured pH with the thermodynamic value. Calculating K_C from the measured solubility (9.1 mMol/l) and for a range of PCO_2 , they found that the calculated thermodynamic pH varies between 6.01 and 5.99 if PCO_2 varies from 0.94 to 0.97 atm and CaHCO_3^* is assumed present.

Because we have little basis for judging which published values of $K_{\text{CaHCO}_3^*}$ are more accurate (Fig. 5), or whether we are even justified in including the ion pair in the aqueous model, two separate experimental studies were initiated: (1) detailed measurement of the pH of Ca-HCO_3 solutions (0–16 mMol/l Ca_T) at 25°C and 5.3°C with correction for liquid junction errors, and (2) measurement of the solubility of aragonite as a function of PCO_2 and temperature.

Both experimental studies, while helping to resolve earlier problems in the Ca-HCO_3 aqueous model, lead to independent determinations of $K_{\text{CaHCO}_3^*}$, the first directly as a potentiometric method and the second indirectly through minimization of computed trends (variance) in K_A as a function of PCO_2 . The second method is similar to the analysis of Jacobson and Langmuir (1974) except that aragonite was used rather than calcite, and only our new solubility data were evaluated.

pH MEASUREMENTS OF CALCIUM-BICARBONATE SOLUTIONS

Experimental

Calcium-bicarbonate solutions were prepared by dissolution of synthetic vaterite (prepared by the methods of Turnbull, 1973 and McConnell, 1960) in CO_2 -saturated water at 5°C. After several hours the solution was filtered under CO_2 pressure through a 0.45 μm filter, again saturated with CO_2 and stored in glass at approximately 1°C. The stock Ca-HCO_3 solution contained approximately 16.0 mMol/l total calcium and was stable for several days as demonstrated by constant total calcium concentrations. Except for one run at 5.3°C, all pH measurements were at 25°C.

pH was measured with a single glass electrode (Fisher #13-639-1)¹ which was calibrated against four separate single-junction Ag-AgCl reference electrodes (Orion 90-01). Fresh NBS standards (0.05 m potassium hydrogen phthalate, pH 4.004 at 25°C, and a solution 0.025 m with respect to both KH_2PO_4 and Na_2HPO_4 , pH 6.863 at 25°C) were used to calibrate each electrode pair before and after each run. A single pole 4-position rotary ceramic switch was used to connect each reference electrode to the Orion model 801

¹ The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

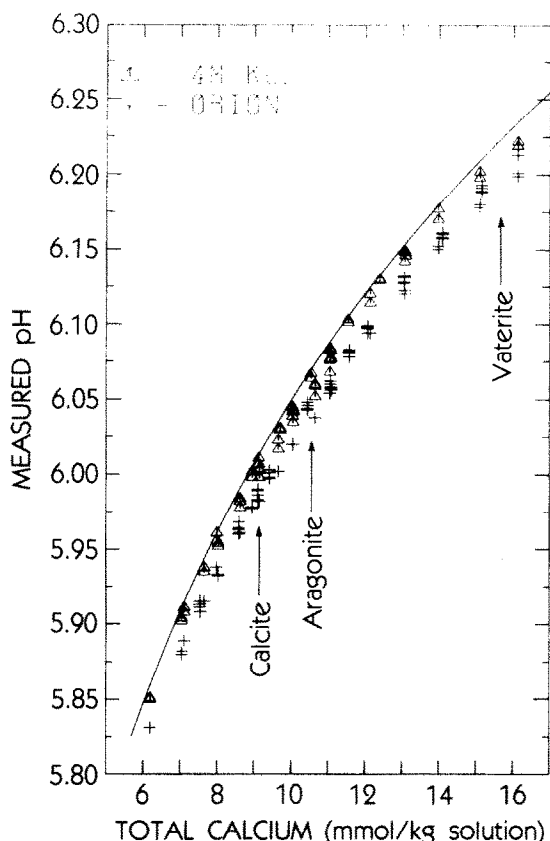


FIG. 6. Measured pH of Ca-HCO₃ solutions at 25°C and 0.956 atm. PCO₂ using Orion and 4 M KCl reference filling solutions. Each point is the average of 2–4 values obtained from multiple reference electrodes calibrated against the same glass electrode. The solid line denotes the theoretical (thermodynamic) pH calculated using the aqueous model of this paper. The solubilities of calcite, aragonite and vaterite at 25°C and 0.956 atm PCO₂ are shown.

pH meter which was read to the nearest 0.1 mV. The electrodes had typical slopes of 98.7 to 99.5 percent of the theoretical response. pH measurements were corrected for assumed linear drifts between the initial and final calibration which ranged from 0.03 to 0.3 mV/hr.

Filling solutions in the reference electrodes were either 4 M KCl (saturated with AgCl) or the Orion filling solution (90-00-01). The salt composition of the Orion filling solution is 1.70 M KNO₃, 0.64 M KCl, and 0.06 M NaCl. By using reference electrodes of several filling solution compositions in a single run, differences in pH measured against reference electrodes of different filling solution composition could be compared with calculated pH differences expected from differing liquid junction errors at the reference electrode-solution contact. These measurements provide an indirect test of the validity of the Henderson equation (Bates, 1973) for estimating the magnitude of liquid junction errors in our pH measurements of Ca-HCO₃ solutions.

The one liter, pyrex, jacketed reaction vessel was filled with approximately 700 ml of initial Ca-HCO₃ solution maintained at $\pm 0.05^\circ\text{C}$ with Haake (FE and FK2) constant temperature circulators. The reaction vessel was fitted with a Plexiglas lid with holes for insertion of a gas dispersion tube, electrodes (four reference and one glass through a single rubber stopper). Another stoppered hole was used for adding and removing solution. The solution was stirred magnetically and a stream of pure CO₂ gas pre-saturated with water at the experimental temperature was bubbled

into the solution (≈ 0.5 l/min) at an average bubbler depth of 10 mm. Approximately 20 minutes was required for the electrodes to reach a steady millivolt value in each new solution. The duration of runs ranged from 3.5 to 6 hours including approximately 2 hours (total) for electrode calibration.

During a typical run the composition of the starting Ca-HCO₃ solution was changed approximately 12 times through successive removal and addition of more dilute or more concentrated Ca-HCO₃ solution. New solution added to the reaction vessel had been filtered and pre-saturated with CO₂ at the experimental temperature to minimize equilibration times. In working with the more concentrated Ca-HCO₃ solutions (10–16 mmol/l Ca_T), care was taken to rinse electrodes, reaction vessel, lid, and dispersion tube with filtered water in order to minimize dust contamination which promotes nucleation of calcium carbonate in the metastable solutions.

The electrode readings were made in unstirred solutions with the bubbler raised over the solution. Once stable, all four electrode pairs could be read rapidly through use of the ceramic switch. Room barometric pressure was recorded for each new solution for calculation of PCO₂. Total calcium was determined for each solution by EDTA titration as described in a later section of this paper.

Results

Figure 6 compares the pH of Ca-HCO₃ solutions at 25°C and an average PCO₂ of 0.956 atm as determined using the 4 M KCl and Orion reference filling solutions. The pH was typically 0.02 pH units lower for electrode pairs using the Orion filling solution. At calcite equilibrium in CO₂-saturated water at 25°C (Fig. 6) the measured pH is 6.004 ± 0.005 if the reference electrode contains 4 M KCl, and is near 5.984 ± 0.005 if the Orion filling solution is used in the reference electrode.

The solid curve on Fig. 6 shows the calculated thermodynamic pH based on the total calcium-PCO₂ data and aqueous model adopted in this paper. Specifically, we calculated pH at 25°C and 0.956 atm. PCO₂ for each experimental total calcium using (1) the CO₂-H₂O equilibrium constants of Table 3, (2) the activity coefficient model presented earlier, (3) $\log K_{\text{CaHCO}_3^+}$ and $\log K_{\text{CaCO}_3}$ of 1.11 and 3.22 respectively (see later sections of this paper for documentation of these two constants).

The calculated (thermodynamic) pH agrees well with pH measurements using 4 M KCl, but is significantly higher relative to pH measurements using the Orion filling solution.

Liquid-junction corrections

pH measurements are subject to a number of uncertainties (Bates, 1973). Some of these uncertainties are related to glass electrode-reference electrode response properties and are identified in the equation

$$\text{pH}_x = \text{pH}_s + \frac{(E_x - E_s)}{S} - \frac{(E_j)_x - (E_j)_s}{S} + \frac{(E_a)_x - (E_a)_s}{S} \quad (21)$$

(after Hawley, 1973) where E is the potential of a pH sensitive glass electrode-reference electrode pair, E_j is the liquid-junction potential developed at the salt bridge-bulk solution interface, and E_a is the salt error developed at the pH sensitive glass membrane owing to the response of the glass to ions other than H⁺. The subscripts x and s refer to the test solution and standard buffer solution. S is the slope of the electrode pair, in mv/pH. If for test solutions $(E_j)_x - (E_j)_s$ and $(E_a)_x - (E_a)_s$ are zero, the pH of the test solution can be determined as accurately as that of the

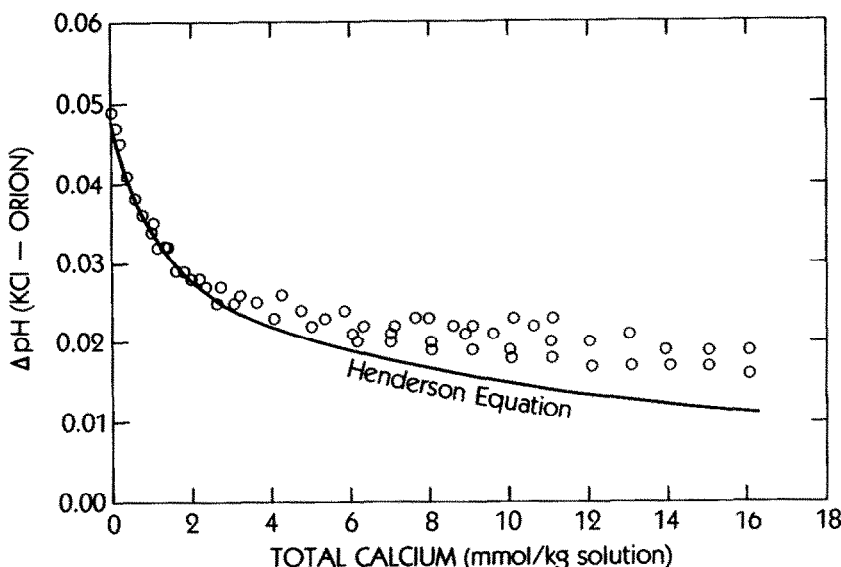


FIG. 7. Comparison of the measured differences in pH of Ca-HCO₃ solutions at 25°C and 0.956 atm PCO₂ between electrodes using 4 M KCl and Orion reference filling solutions with theoretical differences in pH due to liquid junction potential errors as calculated by the Henderson equation.

standard solution

$$pH_x = pH_r + \frac{(E_x - E_r)}{S} \quad (22)$$

However, in mixed electrolyte solutions, due to compositional differences between the test solution and buffer solution, the quantity $(E_j)_x - (E_j)_r$ is usually not zero, and to a lesser extent, the quantity $(E_a)_x - (E_a)_r$ may also differ from zero. The calculations of Hawley (1973) suggest that $(E_a)_x - (E_a)_r$ is small relative to $(E_j)_x - (E_j)_r$, and since we have no data for estimating values of E_a , we will consider only the liquid junction errors.

If liquid junction errors account for all deviations from the thermodynamic pH, the measured pH, pH_m , is then related to the thermodynamic pH, pH_t , by

$$pH_t = pH_m - \frac{(E_j)_x - (E_j)_r}{S} = pH_m + \Delta pH_j \quad (23)$$

where

$$\Delta pH_j = - \frac{(E_j)_x - (E_j)_r}{S}$$

To estimate pH_t , we have calculated values of $(E_j)_x$ and $(E_j)_r$ using the Henderson equation (Bates, 1973), and the limiting ionic conductance data of Robinson and Stokes (1955), and Picknett (1968, 1973).

Figure 7 compares differences in the measured pH of Ca-HCO₃ solutions ($\Delta pH_m = pH_{(4\text{ M KCl})} - pH_{(Orion)}$) at 25°C, 0.956 atm PCO₂ and total calcium concentrations of 0–16 mMol/kg soln with pH differences calculated using the Henderson equation, ΔpH_{Calc} , where

ΔpH_{Calc}

$$= \left[\frac{(E_j)_x - (E_j)_r}{S} \right]_{4\text{ M KCl}} - \left[\frac{(E_j)_x - (E_j)_r}{S} \right]_{Orion} \quad (24)$$

The observed pH differences, ΔpH_m , vary from 0.049 pH at 0.1 mMol/kg total calcium to 0.018 pH at 16.0 mMol/kg total calcium (Fig. 7). The observed pH differences are closely approximated by the Henderson equation for total calcium concentrations between 0 and 3 mMol/kg, but show systematic departures, the calculated differences less than the observed differences at higher total calcium con-

centrations. The maximum deviation between ΔpH_m and ΔpH_{Calc} is 0.005 pH at 16 mMol/kg total calcium (Fig. 7).

The results of Fig. 7 suggest that differences in junction potentials are reasonably well defined by the Henderson equation under the present experimental conditions. However, we do not know if absolute values of E_j calculated from the Henderson equation are accurate because only differences in E_j can be measured. Because of the encouraging results in ΔpH_{Calc} , we have calculated $(E_j)_x$ and $(E_j)_r$,

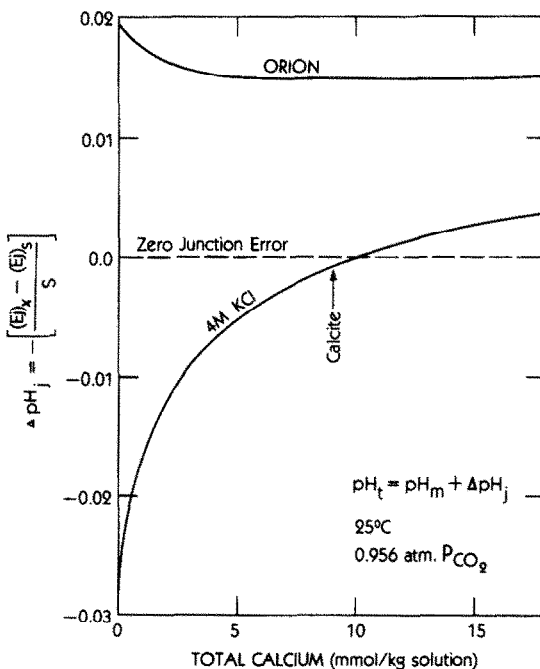


FIG. 8. Estimated liquid junction errors in the pH, ΔpH_j , of Ca-HCO₃ solutions at 25°C and 0.956 atm PCO₂ for Orion and 4 M KCl reference filling solutions, as calculated from the Henderson equation. The thermodynamic pH is estimated by adding ΔpH_j to the measured pH (pH_m).

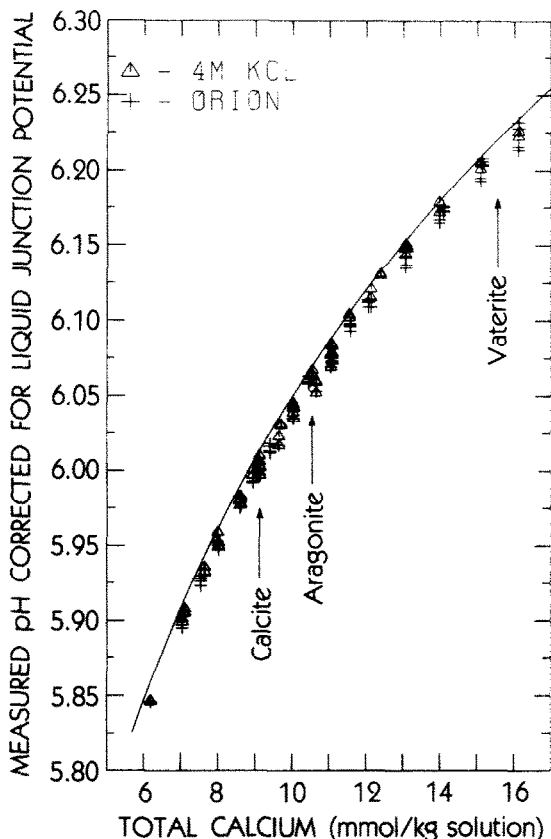


Fig. 9. Comparison of the measured pH (corrected for liquid junction potential errors) of Ca-HCO₃ solutions at 25°C and 0.956 atm PCO₂ with the theoretical thermodynamic pH (solid curve) calculated using the aqueous model of this paper. Results are shown for reference electrodes containing Orion and 4 M KCl filling solution. Compare with uncorrected pH measurements of Fig. 7.

using the Henderson equation for correction of individual pH measurements.

Values of ΔpH_j are summarized in Fig. 8 for Ca-HCO₃ solutions at 25°C as calculated from the Henderson equation for reference filling solutions of 4 M KCl and the Orion filling solution. These values were used to correct the measured pH via Eqn. (23).

Figure 9 shows close agreement among junction-corrected pH measurements. The pH measurements obtained using the 4 M KCl filling solution were little changed because ΔpH_j is small for the 4 M KCl - Ca-HCO₃ solution interface between 6 and 16 mmol/kg total calcium. Larger corrections, 0.015 pH, are required if the Orion filling solution is used in Ca-HCO₃ solutions.

The junction-corrected pH measurements (Fig. 9) agree well with the theoretical calculated pH. At calcite equilibrium in CO₂-saturated H₂O at 25°C, the calculated pH given by the present aqueous model is 6.011, which compares with 6.000–6.008 based on the junction-corrected pH measurements for both Orion and 4 M KCl filling solutions. While previously published measurements of the equilibrium pH have been above the calculated thermodynamic pH, our junction-corrected pH measurements are slightly below the calculated thermodynamic pH. The uncertainty in the NBS buffers alone is ±0.005 pH so the agreement in calculated and measured pH is well within the uncertainty of the data.

The results of Fig. 9 indicate that the measured pH at calcite equilibrium in CO₂-saturated water is not as high as previously measured (6.02–6.03). Reasons for the discrepancy between measurements are not clear, but we note

that most earlier pH measurements were made on stirred calcite suspensions, rather than the stationary, filtered solutions used here. Furthermore, earlier measurements may not have been calibrated against NBS standards and were not corrected for liquid junction errors.

Potentiometric determination of K_{CaHCO_3}

The association constant for CaHCO₃⁺ (Eqn. 20) has been calculated from our pH-PCO₂-Ca_T data at 25°C and 5.3°C, using both the junction-corrected and measured pH. For each set of pH, PCO₂ and Ca_T, the activities of CO₂(aq), HCO₃⁻, CO₃²⁻, H⁺ and OH⁻ are defined by pH and PCO₂ from

$$a_{\text{CO}_2(\text{aq})} = K_{\text{H}} \text{PCO}_2 \quad (25)$$

$$a_{\text{H}^+} = 10^{-\text{pH}} \quad (26)$$

$$a_{\text{HCO}_3^-} = \frac{K_1 a_{\text{CO}_2(\text{aq})}}{a_{\text{H}^+}} \quad (27)$$

$$a_{\text{CO}_3^{2-}} = \frac{K_2 a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \quad (28)$$

and

$$a_{\text{OH}^-} = \frac{K_{\text{w}}}{a_{\text{H}^+}} \quad (29)$$

where K_{w} is the equilibrium constant for the reaction H₂O = H⁺ + OH⁻ and the activity of H₂O and fugacity coefficient of CO₂ are taken as unity.

The molality of free calcium ion is defined by charge balance

$$m_{\text{Ca}^{2+}} = \frac{1}{2} \left[\frac{a_{\text{HCO}_3^-}}{\gamma_{\text{HCO}_3^-}} + \frac{2a_{\text{CO}_3^{2-}}}{\gamma_{\text{CO}_3^{2-}}} + \frac{a_{\text{OH}^-}}{\gamma_{\text{OH}^-}} - \frac{a_{\text{H}^+}}{\gamma_{\text{H}^+}} - m_{\text{CaHCO}_3^+} \right] \quad (30)$$

The molality of CaCO₃⁰ is defined by the mass action equation for reaction (19)

$$m_{\text{CaCO}_3^0} = \frac{K_{\text{CaCO}_3^0} m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{\gamma_{\text{CaCO}_3^0}} \quad (31)$$

The molality of CaHCO₃⁺ is found from the mass balance on dissolved calcium

$$m_{\text{CaHCO}_3^+} = \text{Ca}_T - m_{\text{Ca}^{2+}} - m_{\text{CaCO}_3^0} \quad (32)$$

and then $K_{\text{CaHCO}_3^+}$ is

$$K_{\text{CaHCO}_3^+} = \frac{m_{\text{CaHCO}_3^+} \gamma_{\text{CaHCO}_3^+}}{m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}} \quad (33)$$

In calculating $K_{\text{CaHCO}_3^+}$ from pH-PCO₂-Ca_T data, K_{H} , K_1 , and K_2 were taken from Table 3, K_{w} was taken from Sweeton *et al.* (1974), $K_{\text{CaCO}_3^0}$ was consistent with the results of this paper (Eqn. 53) and activity coefficients were as defined earlier. An iterative procedure was used to solve Eqns. (25)–(33).

All pH-measurement data may be obtained from NAPS.²

² See NAPS document No. 03946 for 18 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance \$4.00 for microfiche copy or for photocopy; \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material. \$1.50 for postage of any microfiche orders.

The calculated results are summarized in Table 5. The average $\log K_{\text{CaHCO}_3^+}$ from 62 junction-corrected pH measurements using the 4 M KCl filling solution is $1.25 (\pm 0.06)$ which compares with $1.32 (\pm 0.05)$ from 79 junction-corrected measurements using the Orion filling solution, where the \pm value denotes the standard deviation of the total number of measurements. Although the agreement in $\log K_{\text{CaHCO}_3^+}$ for the two filling solutions is not perfect using junction-corrected pH data, the disparity is larger if the junction correction is not made. For example $\log K_{\text{CaHCO}_3^+}$ from run 11 using the uncorrected pH is $1.25 (\pm 0.09)$ for 4 M KCl filling solution (compares to 1.27 ± 0.08 if pH is corrected for liquid junction) and 1.53 ± 0.03 for the Orion filling solution (compares to 1.34 ± 0.05 if pH is corrected for liquid junction errors).

In one run at 5.3°C $\log K_{\text{CaHCO}_3^+}$ was found to be 1.06 ± 0.04 based on 21 junction-corrected pH measurements using the 4 M KCl filling solution and total calcium concentration of 11.9–13.0 mMol/kg soln.

Our potentiometric method for determining $\log K_{\text{CaHCO}_3^+}$ differs from most previous studies because only the $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system was studied, thus avoiding the possibility of additional complexing (such as KHCO_3 , CaCl^+ , etc.). The results do depend slightly on the value of K_{CaCO_3} . We have added new measurements of K_{CaCO_3} (discussed in a later section of this paper) which have been used in conjunction with the potentiometric data and aragonite solubility data (discussed below) to simultaneously define both $K_{\text{CaHCO}_3^+}$ and K_{CaCO_3} .

DETERMINATION OF $K_{\text{CaHCO}_3^+}$ FROM THE PCO_2 -DEPENDENCE OF ARAGONITE SOLUBILITY

Another method of determining $K_{\text{CaHCO}_3^+}$ (and K_A) in the system $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ follows from the measurement of aragonite solubility in water over a wide range of PCO_2 and temperature. In this method $K_{\text{CaHCO}_3^+}$ is defined at each temperature as the value giving no trend in the calculated aragonite equilibrium constant ($K_A = a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}}$) over a wide range of gas compositions (317 ppm CO_2 –100% CO_2). Details of the experimental method are given in the next section of this paper where all the solubility measurements are discussed.

Aragonite was chosen for determination of $K_{\text{CaHCO}_3^+}$ because its solubility behavior demonstrated fewer experimental problems in stirred $\text{CO}_2\text{-H}_2\text{O}$ solutions. An advantage of determining $K_{\text{CaHCO}_3^+}$ from solubility measurements is that electrodes are not required. The final value of $K_{\text{CaHCO}_3^+}$ and K_A at a given temperature depends on (1) the measurements of Ca_T and PCO_2 which are very well defined (see later discussion), (2) the aqueous model for the $\text{CO}_2\text{-H}_2\text{O}$

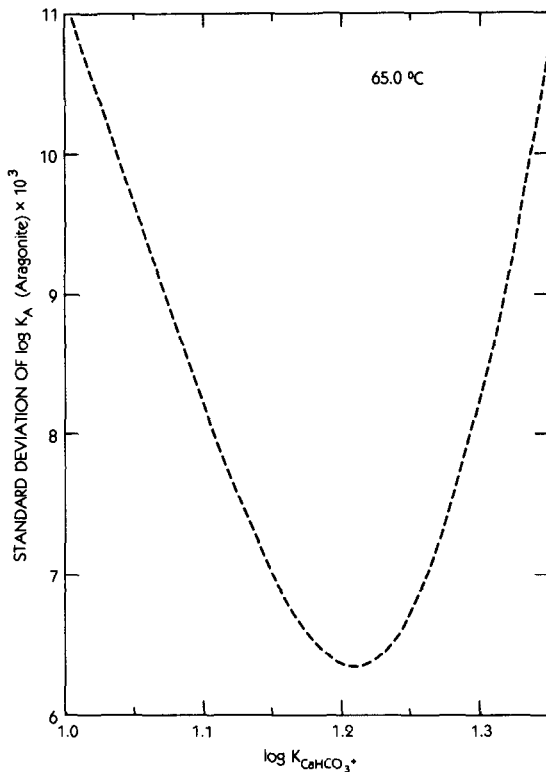


FIG. 10. Illustration of the minimization technique used to define $\log K_{\text{CaHCO}_3^+}$ from aragonite solubility measurements over a range of PCO_2 . The standard deviation of $\log K_A$ for all aragonite solubility measurements at 65°C (17 measurements between $10^{-0.13}$ and $10^{-3.5}$ atm PCO_2) is shown as a function of assumed values of $\log K_{\text{CaHCO}_3^+}$. The minimum in the standard deviation defines $\log K_{\text{CaHCO}_3^+}$ as 1.21 at 65°C .

system and activity coefficients defined above, and (3) to a lesser degree on K_{CaCO_3} . The values of $K_{\text{CaHCO}_3^+}$ reported in this study are consistent with our measurements of K_{CaCO_3} (Eqn. 53).

The equilibria and equations used to find K_A for an assumed value of $K_{\text{CaHCO}_3^+}$ are as follows:

$$a_{\text{CO}_2(\text{aq})} = K_H \text{PCO}_2 \quad (34)$$

$$a_{\text{HCO}_3^-} = m_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} \quad (35)$$

$$a_{\text{H}^+} = \frac{K_1 a_{\text{CO}_2(\text{aq})}}{a_{\text{HCO}_3^-}} \quad (36)$$

$$a_{\text{CO}_3^{2-}} = \frac{K_2 a_{\text{HCO}_3^-}}{a_{\text{H}^+}} \quad (37)$$

$$m_{\text{Ca}^{2+}} = \frac{\text{Ca}_T}{1 + \gamma_{\text{Ca}^{2+}} \left(\frac{K_{\text{CaHCO}_3^+} a_{\text{HCO}_3^-}}{\gamma_{\text{CaHCO}_3^+}} + \frac{K_{\text{CaCO}_3} a_{\text{CO}_3^{2-}}}{\gamma_{\text{CaCO}_3}} \right)} \quad (38)$$

$$m_{\text{OH}^-} = \frac{K_w}{a_{\text{H}^+} \gamma_{\text{OH}^-}} \quad (39)$$

$$m_{\text{CaHCO}_3^+} = \frac{K_{\text{CaHCO}_3^+} m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} a_{\text{HCO}_3^-}}{\gamma_{\text{CaHCO}_3^+}} \quad (40)$$

$$m_{\text{CaCO}_3} = \frac{K_{\text{CaCO}_3} m_{\text{Ca}^{2+}} \gamma_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{\gamma_{\text{CaCO}_3}} \quad (41)$$

Table 5: Average values of $K_{\text{CaHCO}_3^+}$ at 25°C calculated from liquid-junction-corrected pH measurements of CO_2 -saturated Ca-HCO_3 solutions.

Run	Total points	Ref. soln.	Ca_T mMol/kg	Log K	Std. dev.
IV	14	4M KCl	9.1–13.1	1.21	0.04
V	48	Orion	7.5–16.1	1.30	0.06
VII	21	4M KCl	6.2–16.1	1.25	0.07
VII	22	Orion	6.2–16.1	1.36	0.03
XI	27	4M KCl	7.1–11.0	1.27	0.08
XI	9	Orion	7.1–11.0	1.34	0.05
Ave.	62	4M KCl	6.2–16.1	1.25	0.06
Ave.	79	Orion	6.2–16.1	1.32	0.05

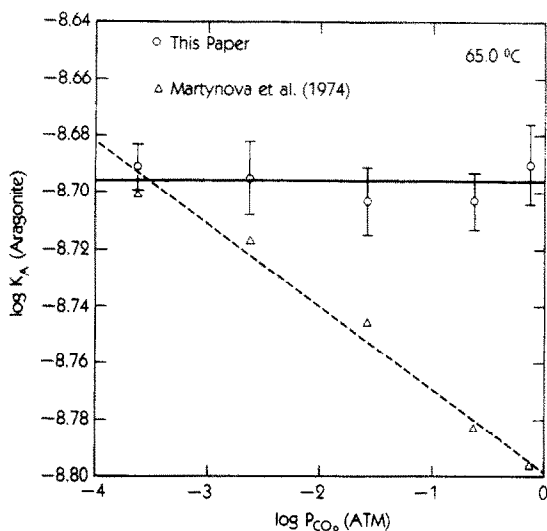


FIG. 11. Comparison of calculated values of $\log K_A$ at 65°C from solubility measurements between $10^{-0.13}$ and $10^{-3.5}$ atm PCO_2 using the aqueous model of this paper and the experimental value of $\log K_{\text{CaHCO}_3^+}$ taken from Martynova *et al.* (1974). Using the value $\log K_{\text{CaHCO}_3^+} = 1.21$, derived from Fig. 10, little or no trend in $\log K_A$ remains as a function of PCO_2 defining $\log K_A$ at 65°C as -8.70 .

and

$$m_{\text{HCO}_3^-} = 2m_{\text{Ca}^{2+}} + m_{\text{CaHCO}_3^+} + m_{\text{H}^+} - m_{\text{OH}^-} - 2m_{\text{CO}_3^{2-}} \quad (42)$$

In the iterative solution of Eqns. (34)–(42), the $m_{\text{HCO}_3^-}$ was initialized as 2Ca_T . At any temperature a value of $K_{\text{CaHCO}_3^+}$ was assumed and all aragonite solubility measurements for each PCO_2 were solved for K_A . The mean and standard deviation of K_A was then calculated for the corresponding value of $K_{\text{CaHCO}_3^+}$. A new value of $K_{\text{CaHCO}_3^+}$ was assumed and the same solubility data were again solved for K_A , and a new mean and standard deviation defined. This procedure continued until a minimum in the standard deviation of K_A values as a function of $K_{\text{CaHCO}_3^+}$ was found. As an example, Fig. 10 shows the standard deviation of K_A values at 65°C as a function of assumed values of $K_{\text{CaHCO}_3^+}$. The aragonite solubility data (between 317 ppm CO_2 and 100% CO_2) show no PCO_2 -dependence when $\log K_{\text{CaHCO}_3^+}$ is near 1.21 at 65°C (Fig. 10). Values of $\log K_{\text{CaHCO}_3^+}$ found in this way are summarized in Fig. 5 and compared with other published values of the constant.

As a means of demonstrating the sensitivity of the solubility method in defining $K_{\text{CaHCO}_3^+}$ we again use the 65°C solubility data, and value of $K_{\text{CaHCO}_3^+}$ consistent with the data of Martynova *et al.* (1974) ($\log K_{\text{CaHCO}_3^+} = 1.69$). Figure 11 shows that large trends in K_A are found if $\log K_{\text{CaHCO}_3^+}$ is 1.69, but little or no trend is observed as a function of PCO_2 in K_A if $\log K_{\text{CaHCO}_3^+}$ is near 1.21. The error bars shown in Fig. 11 denote the uncertainty in calculated K_A due to the uncertainty in the CO_2 analysis of the gas used.

In addition to defining $K_{\text{CaHCO}_3^+}$ at 65°C, Fig. 11 shows that $\log K_A$ is near -8.70 at 65°C.

The aragonite solubility measurements are summarized in a later section of this paper (Tables 11–13) with the calcite and vaterite solubility measurements.

Table 6 summarizes values of $\log K_{\text{CaHCO}_3^+}$ and $\log K_A$ found via the aragonite solubility method. The temperature dependence of $\log K_{\text{CaHCO}_3^+}$ between 0 and 90°C is given by

$$\log K_{\text{CaHCO}_3^+} = 1209.120 + 0.312947 - 34765.05/T - 478.782 \log T \quad (43)$$

where T is in °K.

Figure 5 shows reasonably good agreement between our results and those of Jacobson and Langmuir (1974), between 15 and 45°C, and Reardon (1974), between 10 and 50°C. Poor agreement is found with the results of Martynova *et al.* (1974) and Larson *et al.* (1976). $\log K_{\text{CaHCO}_3^+}$ based on our junction-corrected pH measurements using 4 M KCl filling solution at 5.3°C and 25°C are approximately 0.1 $\log K_{\text{CaHCO}_3^+}$ units higher than that found by the solubility method (Fig. 5).

In examining previously published calcite solubility data, Jacobson and Langmuir (1974) found trends in $\log K_C$ as a function of total calcium in solution when they assumed CaHCO_3^+ formed in CaHCO_3 solutions at 25°C. These trends were less if formation of CaHCO_3^+ was ignored in calculation of K_C . In evaluating our aragonite solubility data we have found just the opposite, that is, it is necessary to assume the presence of CaHCO_3^+ to eliminate trends in the calculated K_A as a function of total calcium in solution (PCO_2). The observation of Jacobson and Langmuir (1974) is based mainly on very early experimental studies for which determination of PCO_2 and total calcium may be less certain. In addition, we have found calcite solubility measurements far more difficult to reproduce due to apparent

Table 6: Summary of $\log K_{\text{CaHCO}_3^+}$ and $\log K_A$ calculated from aragonite solubility data as a function of PCO_2 .

t °C	Exp. $\log K_{\text{CaHCO}_3^+}$	Est. ¹ Error	Calc. ² $\log K_{\text{CaHCO}_3^+}$	Calc. $\log K_{\text{Arag.}}$
4.4 ³	0.91	0.06	0.89	-8.23
15.1	0.97	0.06	1.02	-8.27
25.0	1.14	0.07	1.11	-8.34
35.0	1.17	0.07	1.16	-8.40
45.0	1.21	0.10	1.19	-8.48
65.0	1.21	0.06	1.24	-8.70
80.0	1.27	0.08	1.28	-8.89
90.0	1.35	0.10	1.31	-9.02

¹ Calculated as 10 times the standard deviation of $\log K_A$ at the minimum value corresponding to the experimental value of $\log K$ of CaHCO_3^+ . See text for discussion of minimization procedure.

² Calculated from eqn (43).

³ Average of data at 4.9 and 3.9°C.

grinding of surfaces in stirred solutions (see description of the solubility experiments) which may account for problems with some of the earlier solubility data for calcite.

THE CaCO_3^0 ASSOCIATION CONSTANT

The association constant for the formation of CaCO_3^0 is defined from reaction (19) as

$$K_{\text{CaCO}_3^0} = \frac{a_{\text{CaCO}_3^0}}{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}} \quad (44)$$

The temperature-dependence of $K_{\text{CaCO}_3^0}$ was measured by Reardon and Langmuir (1974) between 4 and 53°C from pH measurements of CaCl_2 - K_2CO_3 solutions, by Larson *et al.* (1976) using a titration procedure at 5, 15 and 25°C, and by Martynova *et al.* (1974) between 22 and 98°C based on pH, total calcium, and calcium ion electrode measurements at calcite saturation in equilibrium with air. The results of Martynova *et al.* (1974) are in reasonable agreement at 25°C with the measurement of Nakayama

(1968), but do not agree with Reardon and Langmuir (1974) and Larson *et al.* (1976). Lafon (1970) argued that the value of $K_{\text{CaCO}_3^0}$ given by Nakayama (1968) is in error owing to uncertainties in the least squares regression on which it is based. The reliability of the calcium-selective electrode used by Martynova *et al.* (1974) was not demonstrated and may be seriously questioned because of (1) possible HCO_3^- interference with electrode response, (2) the high temperatures of the experiment lead to poor electrode behavior, and (3) the low slope of the Ca^{2+} -electrode (29 mv/decade change in $a_{\text{Ca}^{2+}}$) requires more precise measurements. Values of K_C calculated by Martynova *et al.* (1974) from their pH, pCa measurements at the PCO_2 of air (using K_1 and K_2 of Ryzhenko, 1963) are as much as 0.6 log K units more stable than the values reported here. Because of these uncertainties, we have excluded the results of Nakayama (1968) and Martynova *et al.* (1974) in Table 7 and Fig. 12.

For the remaining data (Reardon and Langmuir, 1974; Larson *et al.*, 1976) $K_{\text{CaCO}_3^0}$ is not well defined

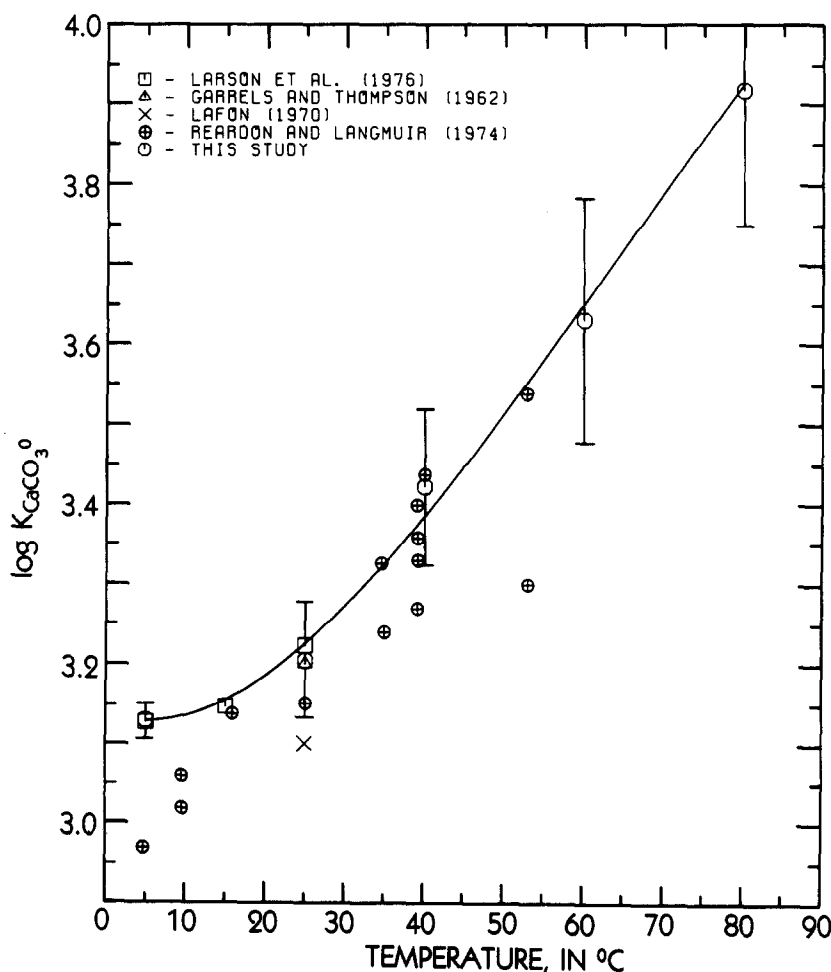


FIG. 12. Comparison of experimental values of $\log K_{\text{CaCO}_3^0}$ as a function of temperature. The point from Reardon and Langmuir (1974) at 25°C is an average of 31 measurements. The curve was calculated from the results of this study (Eqn. 53). The error bars show one standard deviation of the average value from Table 8.

Table 7: Measurements of the association constant for CaCO_3^0 at 25°C and one atm total pressure¹

Source	Composition	Method	$\log K_{\text{CaCO}_3^0}$
Greenwald (1941)	$\text{CaCO}_3\text{-KHCO}_3$	solubility	3.0 ²
Garrels and Thompson (1962)	$\text{M}_2\text{CO}_3\text{-CaCl}_2$ ³	titration	3.2
Nakayama (1968)	$\text{CaCO}_3\text{-CO}_2$	pH, pCa^{2+}	4.483
Lafon (1970)	CaCO_3	solubility	$3.1 \pm .3^4$
Martynova et al. (1974)	$\text{CaCO}_3\text{-CO}_2$	pH, pCa^{2+}	4.39 ⁵
Reardon and Langmuir (1974)	$\text{K}_2\text{CO}_3\text{-CaCl}_2$	titration	$3.15 \pm .08$
Larson et al. (1976)	$\text{K}_2\text{CO}_3\text{-KHCO}_3\text{-Ca(ClO}_4)_2$	titration	$3.22 \pm .05$
This paper	$\text{K}_2\text{CO}_3\text{-CaCl}_2$	pH	$3.22^{6 \pm} .14$

$$^1 K_{\text{CaCO}_3^0} = \frac{a_{\text{CaCO}_3^0}}{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}.$$

² Taken from Lafon (1970).

³ The particular carbonate salt used by Garrels and Thompson (1962) was not identified.

⁴ Assuming $\log K_C = -8.40$, and the calcite solubility data of Grezes and Basset (1965).

⁵ 22°C.

⁶ Smoothed value at 25°C as given by eqn (53). Experimental value is 3.20 at 25°C.

as a function of temperature (only 9 measurements between 25 and 53°C). The two determinations of K_{CaCO_3} at 53°C (Reardon and Langmuir, 1974) differ by 0.23 log K units. Between 5 and 25°C the values of Larson *et al.* (1976) average about 0.1 log K units larger than those of Reardon and Langmuir (1974) (Fig. 12). Depending upon assumed linear and non-linear extrapolations of the data of Reardon and Langmuir (1974) to 90°C, uncertainties of as much as 0.5 log K_{CaCO_3} can result. In attempting to improve estimates of log K_{CaCO_3} at higher temperatures, we have made new measurements of K_{CaCO_3} to approximately 80°C and repeated some of the measurements of Reardon and Langmuir (1974) at lower temperatures.

POTENTIOMETRIC DETERMINATION OF $K_{\text{CaCO}_3^0}$

Reardon and Langmuir (1974) determined K_{CaCO_3} from pH measurements of $\text{K}_2\text{CO}_3\text{-CaCl}_2\text{-HCl}$ solutions near pH 9.5. Our determinations of K_{CaCO_3} have basically followed their method, but with several modifications including (1) additional precautions to insure a reaction system closed to atmospheric CO_2 , and (2) redundant pH measurements using multiple electrodes in each solution.

The experimental procedure was as follows. To a known weight of freshly prepared CO_2 -free water (≈ 800 g) a known weight of (solid) standard K_2CO_3 (≈ 0.260 g) was added, followed by a known weight and volume of 1.000 M HCl solution (1.4–1.6 g). The CO_2 -free water was prepared using Continental Water Conditioners, Inc. charcoal and ion-exchange columns and has a resistance greater than 18 M Ω . The experiments were performed in one liter water-jacketed reaction vessels with Plexiglas lids which have holes for insertion of electrodes (through rubber stoppers) and entry holes for adding weighed aliquots of 0.025 M CO_2 -free CaCl_2 solution. A purified nitrogen atmosphere was maintained over the solution throughout the experiments (≈ 0.2 l N_2/min) to exclude air. The solutions were

stirred with a magnetic stirrer and maintained at constant temperature ($\pm 0.05^\circ\text{C}$) with Haake (FE and FK2) circulators. Several Fisher (13-639-1) and Sargent Welch (S-30070-10) combination electrodes were read to 0.1 mv using the Orion 855 electrode switch and 801 pH meter. The reference electrode contained 4 M KCl filling solution. Electrode calibration was with the NBS borax (pH 9.183 at 25°C) and phthalate (pH 4.004 at 25°C) buffers at the experimental temperatures using standard pH values given by NBS and Bates (1962).

After calibration the electrodes were washed and inserted in the reaction vessel. At least 30 minutes were required to obtain readings stable to 0.1 mv for the starting solution. All electrode readings were made on stationary (unstirred) solutions.

Total carbon in the reaction vessel was determined from the weight of K_2CO_3 used to prepare the starting solution and verified by calculation using the initial pH and alkalinity determinations (to the methyl orange endpoint). Weighed aliquots of the CaCl_2 solution were added to the starting solution and pH was determined for each electrode. At low temperatures (0–25°C) four successive additions of CaCl_2 solution were made to each starting solution without nucleating CaCO_3 , as verified by stable pH readings and EDTA titration for total calcium. At higher temperatures (60–80°C) only one addition of CaCl_2 solution could be made without nucleating CaCO_3 , as demonstrated by stable pH readings for 5–10 minutes. At these higher temperatures pH was recorded for each electrode until nucleation of CaCO_3 occurred as indicated by an abrupt decrease in pH.

The electrodes were calibrated again at the end of each run and pH measurements were corrected for assumed linear drifts. All concentrations were corrected for dilution and reported on the molal scale.

The equilibria and equations used to evaluate K_{CaCO_3} are as follows.

$$\frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{CO}_2(\text{aq})} a_{\text{H}_2\text{O}}} = K_1 \quad (45)$$

$$\frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} = K_2 \quad (46)$$

$$\frac{a_{\text{CaOH}^+}}{a_{\text{Ca}^{2+}}a_{\text{OH}^-}} = K_{\text{CaOH}^+} \quad (47)$$

$$\frac{a_{\text{CaHCO}_3^+}}{a_{\text{Ca}^{2+}}a_{\text{HCO}_3^-}} = K_{\text{CaHCO}_3^+} \quad (48)$$

$$\frac{a_{\text{H}^+}a_{\text{OH}^-}}{a_{\text{H}_2\text{O}}} = K_w \quad (49)$$

$$C_T = m_{\text{CO}_2(\text{aq})} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} + m_{\text{CaHCO}_3^+} + m_{\text{CaCO}_3} \quad (50)$$

$$\text{Ca}_T = m_{\text{Ca}^{2+}} + m_{\text{CaHCO}_3^+} + m_{\text{CaOH}^+} + m_{\text{CaCO}_3} \quad (51)$$

$$m_{\text{H}^+} + 2m_{\text{Ca}^{2+}} + m_{\text{CaHCO}_3^+} + m_{\text{CaOH}^+} + K_T - 2m_{\text{CO}_3^{2-}} - m_{\text{OH}^-} - m_{\text{HCO}_3^-} - \text{Cl}_T = 0 \quad (52)$$

where $\text{Cl}_T = \text{HCl} + 2\text{Ca}_T$, and $K_T = 2\text{K}_2\text{CO}_3$, where HCl , Ca_T and K_2CO_3 denote the moles of HCl , CaCl_2 and K_2CO_3 added.

The association constant for CaCO_3^0 is then defined by Eqn. (44). In solving Eqns. (44)–(52) for K_{CaCO_3} , the equilibrium constants K_1 and K_2 were as defined in Table 3, K_{CaOH^+} was taken from Smith and Martell (1976), $K_{\text{CaHCO}_3^+}$ was taken from the present study (Eqn. 43), $K_{\text{H}_2\text{O}}$ was that of Sweeton *et al.* (1974) and $a_{\text{H}_2\text{O}}$ was taken as unity. Individual ion activity coefficients were defined earlier except γ_{CaOH^+} which was calculated from the Debye-Hückel equation using $\hat{a}_{\text{CaOH}^+} = 6.0$. The total molalities of carbon, C_T , chloride, Cl_T , calcium, Ca_T , and potassium, K_T , are known and a_{H^+} was measured. The eight remaining unknowns ($m_{\text{CO}_2(\text{aq})}$, $m_{\text{HCO}_3^-}$, $m_{\text{CO}_3^{2-}}$, m_{OH^-} , $m_{\text{CaHCO}_3^+}$, m_{CaOH^+} , m_{CaCO_3} , and $m_{\text{Ca}^{2+}}$) were then

Table 8. Summary of experimental data and calculated values of $-\log K_{\text{CaCO}_3^0}$ (pK) between 5 and 80°C.¹

Run	t°C	HCl	K ₂ CO ₃	CaCl ₂	pH	pK	Run	t°C	HCl	K ₂ CO ₃	CaCl ₂	pH	pK
19	5.0	2.732	2.616	3.515	9.861	3.11	4	40.0	2.741	2.623	3.563	9.430	3.40
19	5.0	2.732	2.616	3.515	9.854	3.17	4	40.0	2.741	2.623	3.563	9.445	3.25
19	5.0	2.737	2.621	3.221	9.807	3.09	4	40.0	2.744	2.625	3.374	9.400	3.36
19	5.0	2.737	2.621	3.221	9.794	3.16	4	40.0	2.744	2.625	3.374	9.390	3.42
19	5.0	2.742	2.627	3.049	9.752	3.09	4	40.0	2.744	2.625	3.374	9.410	3.29
19	5.0	2.742	2.627	3.049	9.740	3.13	5	40.0	2.744	2.647	3.529	9.313	3.49
19	5.0	2.748	2.632	2.929	9.709	3.10	5	40.0	2.744	2.647	3.529	9.307	3.53
19	5.0	2.748	2.632	2.929	9.692	3.15	5	40.0	2.744	2.647	3.529	9.308	3.53
19	5.0	2.753	2.637	2.837	9.662	3.12	5	40.0	2.749	2.652	3.232	9.240	3.42
19	5.0	2.753	2.637	2.837	9.656	3.13	5	40.0	2.749	2.652	3.232	9.233	3.45
19	5.0	2.758	2.642	2.763	9.633	3.10	5	40.0	2.749	2.652	3.232	9.231	3.46
19	5.0	2.758	2.642	2.763	9.619	3.14	6	40.0	2.750	2.680	3.532	9.136	3.59
20	5.0	2.748	2.662	3.054	9.595	3.13	6	40.0	2.750	2.680	3.532	9.131	3.61
20	5.0	2.748	2.662	3.054	9.594	3.13	6	40.0	2.750	2.680	3.532	9.137	3.58
20	5.0	2.743	2.657	3.225	9.644	3.15	6	40.0	2.755	2.686	3.235	9.066	3.44
20	5.0	2.743	2.657	3.225	9.645	3.15	6	40.0	2.755	2.686	3.235	9.058	3.47
20	5.0	2.753	2.667	2.934	9.549	3.13	6	40.0	2.755	2.686	3.235	9.064	3.45
20	5.0	2.753	2.667	2.934	9.548	3.13	10	60.0	2.749	2.644	3.533	9.126	3.75
20	5.0	2.759	2.672	2.842	9.513	3.13	10	60.0	2.749	2.644	3.533	9.080	4.03
20	5.0	2.759	2.672	2.842	9.506	3.14	10	60.0	2.749	2.644	3.533	9.106	3.88
20	5.0	2.764	2.677	2.768	9.481	3.12	10	60.0	2.754	2.649	3.237	9.053	3.63
20	5.0	2.764	2.677	2.768	9.476	3.13	10	60.0	2.754	2.649	3.237	9.052	3.63
1	25.0	2.763	2.620	4.310	9.752	3.12	11	60.0	2.755	2.645	3.544	9.145	3.78
1	25.0	2.773	2.631	3.200	9.634	3.15	11	60.0	2.755	2.645	3.544	9.178	3.54
1	25.0	2.773	2.631	3.200	9.636	3.14	11	60.0	2.755	2.645	3.544	9.195	3.38
1	25.0	2.773	2.631	3.200	9.640	3.12	11	60.0	2.760	2.650	3.248	9.057	3.71
2	25.0	2.726	2.678	3.515	9.156	3.32	11	60.0	2.760	2.650	3.248	9.076	3.64
2	25.0	2.726	2.678	3.515	9.174	3.22	11	60.0	2.760	2.650	3.248	9.096	3.56
2	25.0	2.732	2.683	3.222	9.082	3.32	12	60.0	2.731	2.623	3.515	9.139	3.78
2	25.0	2.732	2.683	3.222	9.089	3.30	12	60.0	2.731	2.623	3.515	9.169	3.56
2	25.0	2.732	2.683	3.222	9.105	3.24	12	60.0	2.731	2.623	3.515	9.146	3.73
2	25.0	2.737	2.689	3.051	9.027	3.26	8	60.0	2.748	2.634	3.534	9.213	3.38
2	25.0	2.737	2.689	3.051	9.034	3.24	8	60.0	2.748	2.634	3.534	9.193	3.56
2	25.0	2.737	2.689	3.051	9.049	3.19	8	60.0	2.748	2.634	3.534	9.195	3.55
2	25.0	2.742	2.694	2.931	8.982	3.24	8	60.0	2.753	2.639	3.237	9.142	3.43
2	25.0	2.742	2.694	2.931	8.989	3.22	8	60.0	2.753	2.639	3.237	9.112	3.56
2	25.0	2.742	2.694	2.931	9.003	3.19	8	60.0	2.753	2.639	3.237	9.123	3.52
2	25.0	2.747	2.699	2.840	8.943	3.23	13	80.0	2.729	2.617	3.523	8.960	3.87
2	25.0	2.742	2.699	2.840	8.943	3.12	13	80.0	2.729	2.617	3.523	8.957	3.89
2	25.0	2.742	2.699	2.840	8.963	3.07	13	80.0	2.729	2.617	3.523	8.946	3.97
3	40.0	2.763	2.633	3.539	9.490	3.19	13	80.0	2.729	2.617	3.523	8.940	4.01
3	40.0	2.763	2.633	3.539	9.470	3.39	14	80.0	2.744	2.621	3.529	8.973	4.07
3	40.0	2.763	2.633	3.539	9.470	3.39	14	80.0	2.744	2.621	3.529	8.962	4.16
3	40.0	2.768	2.638	3.244	9.420	3.28	14	80.0	2.744	2.621	3.529	9.003	3.84
3	40.0	2.768	2.638	3.244	9.390	3.43	14	80.0	2.744	2.621	3.529	8.962	4.16
3	40.0	2.768	2.638	3.244	9.400	3.38	18	80.0	2.739	2.652	3.532	8.822	3.93
4	40.0	2.739	2.620	3.833	9.470	3.39	17	80.0	2.727	2.597	3.507	9.014	4.02
4	40.0	2.739	2.620	3.833	9.470	3.39	17	80.0	2.727	2.597	3.507	9.059	3.63
4	40.0	2.739	2.620	3.833	9.460	3.56	17	80.0	2.727	2.597	3.507	9.045	3.76
4	40.0	2.741	2.623	3.563	9.444	3.26	17	80.0	2.727	2.597	3.507	9.061	3.61

¹ HCl, K₂CO₃, and CaCl₂ are -log molality of HCl, K₂CO₃ and CaCl₂ in solution.

Table 9: Recommended values of $K_{\text{CaCO}_3^0}$ between 5 and 80°C.

t °C	Exp. log K CaCO ₃ ⁰	No. Meas.	Std. dev.	Calc. ¹ log K CaCO ₃ ⁰
5.5	3.13	22	0.02	3.13
25.0	3.20	18	0.07	3.22
40.0	3.42	27	0.11	3.38
60.0	3.63	20	0.16	3.65
80.0	3.92	13	0.18	3.92

¹ Calculated from eqn (53).

solved via Eqns. (45)–(52). The particular iterative scheme used to define K_{CaCO_3} combined Eqns. (45)–(52) to form a quadratic expression for $m_{\text{Ca}^{2+}}$.

As equations (44)–(52) show, calculation of K_{CaCO_3} from our potentiometric data depends on $K_{\text{CaHCO}_3^+}$, and, as defined earlier from aragonite solubility, (Eqns. 34–42), calculation of $K_{\text{CaHCO}_3^+}$ depends on K_{CaCO_3} . The final values of K_{CaCO_3} and $K_{\text{CaHCO}_3^+}$ reported here were derived from an iterative procedure, using both the potentiometric data for CaCO_3^0 (Table 8) and the aragonite solubility data as a function of PCO_2 . The iteration procedure began by arbitrarily defining a temperature-dependent analytical expression for $K_{\text{CaHCO}_3^+}$. This expression was then used to calculate K_{CaCO_3} from the potentiometric data. These calculations then defined an analytical expression for K_{CaCO_3} which was used to define $K_{\text{CaHCO}_3^+}$ from the aragonite solubility data as a function of PCO_2 using the minimization procedure discussed above. A new analytical expression for $K_{\text{CaHCO}_3^+}$ was defined and used to solve again the potentiometric data for K_{CaCO_3} . This procedure was rapidly convergent and defined the temperature dependence of K_{CaCO_3} and $K_{\text{CaHCO}_3^+}$ within the precision of the experimental data in two iterations. Liquid junction errors in the pH measurements for K_{CaCO_3} were negligible and ignored.

The experimental results and calculation of K_{CaCO_3} are summarized in Table 8. The temperature dependence of K_{CaCO_3} is best described by

$$\log K_{\text{CaCO}_3^0} = -1228.732 - 0.299444T \\ + 35512.75/T + 485.818 \log T \quad (53)$$

between 5 and 80°C. Table 9 summarizes mean experimental values of $\log K_{\text{CaCO}_3}$, standard deviations and values calculated from Eqn. (53). These values are compared with published experimental values of $\log K_{\text{CaCO}_3}$ in Fig. 12 showing good agreement with results of Larson *et al.* (1976), Garrels and Thompson (1962) and much of the data of Reardon and Langmuir (1974).

The increase in the standard deviation of our $\text{pK}_{\text{CaCO}_3}$ values with temperature shown in Fig. 12 is due almost entirely to differing values of pH measured from 2 or 3 separately calibrated electrodes in the solution (Table 8). The maximum differences in pH between separate electrodes in the same solution

averaged 0.01 to 0.02 pH between 5 and 40°C corresponding to a relatively higher precision in calculated values of $\text{pK}_{\text{CaCO}_3}$. At 80°C maximum pH differences between separate electrodes averaged 0.04 pH resulting in a wider range of calculated equilibrium constants. Our calculated values of $\text{pK}_{\text{CaCO}_3}$ would suggest higher precision if based on a single electrode pair, but because there was no evidence favoring one particular electrode pair, all pH measurements for a single solution were included in our evaluation (Table 8).

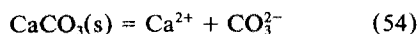
SUMMARY OF THE AQUEOUS MODEL AND MODEL UNCERTAINTIES

All results of this study are internally consistent with the following aqueous model. The equilibrium constants for the $\text{CO}_2\text{-H}_2\text{O}$ system, K_H (Eqn. 4), K_1 (Eqn. 5), and K_2 (Eqn. 6), have the form of Eqn. (13) where regression coefficients are given in Table 3. The equilibrium constant for the dissociation of water was taken from Sweeton *et al.* (1974). The equilibrium constant for CaHCO_3^+ (Eqn. 20) is defined by Eqn. (43) to 90°C and the equilibrium constant for CaCO_3^0 (Eqn. 44) is given by Eqn. (53) to 80°C. The activity of water is taken as unity. Activity coefficients of Ca^{2+} , HCO_3^- and CO_3^{2-} are defined by equations similar to Eqn. (14) as given by Truesdell and Jones (1974). The activity coefficient of CaHCO_3^+ has been equated to $\gamma_{\text{HCO}_3^-}$. The activity coefficients of H^+ and OH^- are calculated from the Debye-Hückel equation (Eqn. 15), and γ_{CaCO_3} has been computed from Eqn. (16) as given by Reardon and Langmuir (1976).

Estimates of uncertainties in the aqueous model are summarized in Table 10 between 0 and 80°C along with the implied uncertainty in the calcite (or aragonite, or vaterite) equilibrium constants. The largest uncertainties in $\log K$ follow from uncertainty in $\log K_{\text{CaHCO}_3^+}$. Even large uncertainties in $\log K_{\text{CaCO}_3}$ contribute only very small errors in $\log K$ for the pH range of our experiments (pH 6–8). Uncertainties in activity coefficients were estimated from the calculations of Fig. 4. The cumulative uncertainty in $\log K$ resulting from uncertainties in the aqueous model contribute approximately ± 0.02 to $\pm 0.03 \log K$ units between 0 and 50°C, and approximately $\pm 0.07 \log K$ units at 80°C (Table 10).

DETERMINATION OF THE EQUILIBRIUM CONSTANTS OF CALCITE, ARAGONITE AND VATERITE

The equilibrium constants of calcite, K_C , aragonite, K_A , and vaterite, K_V are defined for the reaction



where

$$K = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \quad (55)$$

The equilibrium constant is calculated on the molal

scale using the measured solubility and the aqueous model.

The usual measurements of CaCO_3 solubility include two or more of either pH, PCO_2 , Ca_T , or total alkalinity, A_T . If the charge balance criteria is included in the aqueous model, the equilibrium constant may be calculated from (1) pH and PCO_2 , (2) pH and A_T , (3) pH and Ca_T , (4) PCO_2 and A_T , or (5) PCO_2 and Ca_T . If the charge balance criterion is not used, the equilibrium constants may be calculated from pH, A_T and Ca_T ; or PCO_2 , A_T and Ca_T . PCO_2 is usually not measured directly but is calculated from knowledge of the gas composition, barometric pressure, and corrections for the vapor pressure of water and the bubble depth. Most solubility studies of calcite and aragonite in CO_2 - H_2O solutions have used CO_2 partial pressures greater than 0.10 atm, for which gas composition can be known to 1.0% or better of the reported composition. For tanks of "pure" CO_2 , the gas composition is typically 99.9% CO_2 or better. For 100% CO_2 , PCO_2 can be calculated to $\pm 0.1\%$ or better. Total calcium and total alkalinity can be determined by titration to better than 0.5%. Larger errors in K follow from pH-based data (particularly pH- Ca_T and pH- PCO_2) because the measured pH must be known within several thousandths to be on par with the more reliable PCO_2 , Ca_T and alkalinity data. In addition, the measured pH is subject to liquid junction errors and may differ significantly from the thermodynamic value. Thus greater accuracy is expected from PCO_2 - Ca_T or PCO_2 - A_T measurements rather than pH-based data (Langmuir, 1968).

All solubility determinations reported here are based on PCO_2 - Ca_T measurements. The equilibrium constants of calcite, aragonite and vaterite were calculated using Eqns. (34)–(42) and Eqn. (55), the

PCO_2 - Ca_T measurements, and the aqueous model presented above. Uncertainties of $\pm 0.1\%$ in PCO_2 and $\pm 0.5\%$ in Ca_T lead to an estimate of the analytical uncertainty in $\log K$ of $\pm 0.005 \log K$ units.

SOLUBILITY MEASUREMENTS

General procedures

Most experiments were performed in jacketed one liter pyrex reaction vessels maintained to within 0.05°C of the desired temperature by circulating water through the jackets with Haake (FE and FK2) constant temperature circulating pumps. The reaction vessels were covered with Plexiglas lids with holes for insertion of thermometer, polyethylene impeller for stirring, gas dispersion tube, and for sampling the solution. The holes were closed with rubber stoppers when not in use. The stirring rate was usually 260 rpm or less.

Commercial CO_2 gas or mixtures of CO_2 - N_2 were bubbled through at least one flask of deionized water at the same temperature as the reaction vessel to regulate the temperature of the gas and saturate the gas with water vapor prior to bubbling into the reaction vessel.

Samples were withdrawn from the reaction vessels with plastic syringes preheated to the experimental temperature and rapidly forced through $0.45 \mu\text{m}$ filters into pre-weighed Teflon beakers containing water at room temperature. The samples were immediately and rapidly weighed to the nearest mg by difference and titrated with EDTA for Ca_T using an ultraprecision Roger Gilmont Instruments, Inc. 2.5 ml micrometer buret. The reproducibility of the calcium analyses suggests there is little room for error in the sampling and analytical procedures.

Generally, samples were taken only when the room barometric pressure was stable and did not change more than 1 mm Hg for at least 2–3 hours. Once equilibrium was established, total calcium determinations were precise enough (at temperatures $\leq 25^\circ\text{C}$) to delineate variations in room barometric pressure.

Reaction times to reach equilibrium varied with temperature, PCO_2 , and surface area of the solid. Using 100% CO_2 , constant total calcium concentrations were reached in approximately 6 hours near 0°C and after about 1 hour

Table 10: Summary of uncertainties in the aqueous model for the system CaCO_3 - CO_2 - H_2O and estimates of uncertainties in calculated calcite, aragonite and vaterite equilibrium constants between 0 and 80°C .

Estimated Uncertainties							
t°C	log K _H	log K ₁	log K ₂	log K ₊ CaHCO ₃	log K _o CaCO ₃	γ ₁ ¹	
0.0	±0.005	±0.002	±0.003	±0.05	±0.05	±2%	
25.0	±0.005	±0.002	±0.003	±0.05	±0.05	±2%	
50.0	±0.005	±0.002	±0.003	±0.05	±0.10	±2%	
80.0	±0.010	±0.010	±0.020	±0.10	±0.20	±2%	
t°C	Corresponding error in log K					Cumulative error in log K ₁	
0.0	±0.005	±0.002	±0.003	±0.008	0.000	±0.005	±0.023
25.0	±0.005	±0.002	±0.003	±0.010	0.000	±0.005	±0.025
50.0	±0.005	±0.002	±0.003	±0.012	0.000	±0.005	±0.027
80.0	±0.010	±0.010	±0.020	±0.027	±0.002	±0.005	±0.074

¹ The estimated magnitude of error in $\gamma_{\text{Ca}^{2+}}$ at calcite equilibrium in CO_2 saturated water is based on the difference between the Debye-Hückel and Truesdell and Jones (1974) equations.

at 60°C for calcite and aragonite. Much longer times were required to reach equilibrium with calcite and aragonite at lower PCO_2 ranging from 1–2 days at 25°C and 317 ppm CO_2 . At 1 atm PCO_2 vaterite reaches equilibrium within 2 hours at 0°C, and within 15 minutes at 80°C. After equilibrium was established, calcite and aragonite-saturated solutions were sampled for several days (at 1 atm PCO_2) and as long as 52 days (aragonite at 0°C and 317 ppm CO_2). From the particle size and amounts of calcite, aragonite and vaterite used in the experiments, total reaction surface areas ranged from 3.6–12.5 m^2/l , 12–25 m^2/l and 80–160 m^2/l for these materials, respectively. Normally, the larger surface areas were used at lower temperatures.

Most of the solubility measurements were reversed daily by normal variations in barometric pressure. Several calcite solubility measurements were approached from supersaturations of more than 1 mMol/kg total calcium by adding calcite to a solution previously saturated with aragonite (and subsequently filtered to remove the aragonite), or by increasing temperature. Similar attempts to approach aragonite and vaterite equilibrium from supersaturation resulted in nucleation of calcite, as evidenced by steady decreases in total calcium (Turnbull, 1973).

Analytical method

Calcium was determined by EDTA titration using the fluorescence endpoint of calcein indicator by the procedure of Diehl (1964). The 0.001 M EDTA was prepared by dilution of Fisher Scientific Co. 0.1000 \pm 0.0005 M EDTA (SO-S-412). The diluted EDTA was standardized against J. T. Baker Chemical Co. calcium standard solution (4760) and Ultrex CaCO_3 (4-4918). The concentration of the EDTA was determined to an accuracy of better than 0.1%.

The gas phase

Commercial, liquified 100% CO_2 and CO_2 - N_2 gas mixtures were used. The CO_2 compositions of the mixtures were determined gravimetrically or by gas chromatography by Air Products, Inc.

The CO_2 partial pressure was calculated from the measured room barometric pressure using the equation

$$\text{PCO}_2 = \left(\frac{B - V + 0.4h/D}{760} \right) X_{\text{CO}_2} \quad (56)$$

where B is the measured barometric pressure in mm Hg, corrected for room temperature and latitude, V is the vapor pressure of water at the experimental temperature in mm Hg, h is the depth in mm of the gas bubbler in the reaction vessel, D is the specific gravity of mercury (13.6) and X_{CO_2} is the volume fraction of CO_2 in the gas. V was assumed to be the saturation vapor pressure of water at the experimental temperature. The supersaturation factor for CO_2 , the term $0.4h/D$ was experimentally determined for use in the hydrogen electrode (Hill and Ives, 1949), but is not known for CO_2 . The theoretical maximum value is $0.5h/D$. Equation (56) was found to be experimentally valid for CO_2 . The solubility of aragonite was determined in 3 solutions with the gas dispersion tube at depths of 100 mm, 10 mm, and 0 mm (above the solution). In all cases, after correction for the CO_2 supersaturation factor, the same calculated aragonite equilibrium constants were obtained. When CO_2 was not bubbled into the solution, very long times were required to reach equilibrium.

CO_2 bubbling rates through gas dispersion tubes from less than 10 ml per minute to more than 1 liter per minute were evaluated. Erratic, low results were obtained for the solubility of aragonite at CO_2 flow rates of less than 10 ml per minute, probably because at those very slow bubbling rates, air diffuses into the open space above the solution reducing the CO_2 partial pressure. For CO_2 flow rates of

30–800 ml per minute, a constant value was obtained for the solubility of aragonite, as determined by calcium analysis. The pH observed during bubbling decreased with increasing CO_2 flow rates. As total calcium was not affected by this bubbling, the decrease in apparent pH was attributed to streaming potentials. At one atm total pressure, PCO_2 is independent of the CO_2 bubbling rate and does not vary from 0.8 to 1.2 atm as suggested by Jacobson and Langmuir (1974).

Stirring effects

The stirring effect on the solubility of calcite was investigated from 50 to 2700 rpm. Very high stirring rates can substantially increase the apparent solubility of calcite. The significance of the stirring effect increases with the calcite particle size. The apparent solubility of calcite rhombs of 177–420 μm size reaches a steady-state solubility of 9.56 mMol/kg of solution at 0.96 atm PCO_2 , 25°C and 1800 rpm as compared to the expected 9.1 mMol/kg. This apparent solubility increases to 9.99 mMol/kg soln at 2700 rpm. As stirring continues, this steady state value slowly decreases over a period of several days to the previous value when the stirring was again decreased to 1800 rpm. The steady state solubility of 20 μm calcite rhombs, similar to those used in our solubility measurements, is 9.30 mMol/kg soln at 1800 rpm. For the 20 μm size rhombs used here, the stirring effect is negligible below 500 rpm. All solubility measurements used particles less than or equal to 20 μm size at 260 rpm. The grinding, resulting from the rapid stirring, and possibly the formation of some aragonite is believed to be responsible for the higher apparent solubilities at higher stirring rates (Goujon and Mutaftschiev, 1976; Cabrol *et al.*, 1978). Violent agitation caused by very rapid bubbling of CO_2 causes a similar but less pronounced enhancement of the solubility of calcite. No stirring effects were observed for aragonite.

Water

The presence of unknown impurities that are not removed by ion-exchange can increase the apparent solubility of calcite at 25° and 45°C (1 atm PCO_2) by as much as 0.1 mMol/kg soln. Reproducible results were obtained by passing the water through an activated charcoal column, prior to distillation or ion-exchange. The measured solubility of calcite using water passed through a charcoal column followed by two ion-exchange columns is identical at 25, 45, and 65°C and 100% CO_2 with results obtained using Fisher Scientific Co. high pressure liquid chromatography water (W-5).

Calcite

Reagent grade calcite, low in alkalis, was used in all the dissolution runs and was obtained from J. T. Baker Chemical Co. (1-1294) and Fisher Scientific Co. (C-65). The Baker and Fisher calcites have surface areas of 0.19 and 0.70 m^2/g , respectively. All surface areas were determined by a modified single-point BET method using argon as the adsorbate by Micromeritics Instruments, Inc. The Fisher, and to a lesser degree, the Baker calcites gave erratic results initially. However, the performance of both these materials was greatly improved after recrystallization of the calcites at 65°C and 100% CO_2 for a period of at least 48 hours. After recrystallization, both materials gave consistently identical results. This treatment may have improved the crystallinity of the calcites by healing surface defects, or may have improved the surface purity of the material.

Aragonite

The aragonites used in this study were precipitated from artificial sea water at 75°C by the procedures described by

Kinsman and Holland (1969) and Angus *et al.* (1979). The aragonites were aged at least 24 hours at 75°C in sulfate-free artificial sea water and consisted entirely of needles 20–30 μm long and 3–4 μm wide with surface areas of 1.20 m^2/g . Strontium and magnesium were the two major impurities with concentrations of 150 and 500 ppm, respectively.

These aragonites were found to be free of any other phases by X-ray diffraction analyses and optical microscopic examination. Angus *et al.* (1979) using electron spin resonance spectroscopy have shown that aragonites prepared by this method are free from trace calcite and structural imperfections (strain) that are common in aragonites prepared by other methods.

Vaterite

Vaterites, free from all other carbonate phases, were prepared by the procedures of Turnbull (1973) at 25°C and McConnell (1960) at 65°C. Both solids consisted of spherules 4–6 μm in diameter. The material prepared at 65°C approached equilibrium very slowly and was used in only

two runs. The vaterite prepared at 25°C had a surface area of 7.2 m^2/g , reached equilibrium rapidly, and was used in most of the solubility experiments. The experimental procedures used to achieve chemical equilibrium with vaterite are described in detail by Turnbull (1973).

RESULTS

The experimental solubility data for calcite, aragonite and vaterite are summarized in Tables 11–13 along with the calculated pH and equilibrium constants based on the aqueous model presented above. The calculated equilibrium constants are shown as a function of temperature in Fig. 13 to 100°C. The data of Tables 11–13 and Fig. 13 show that at a given temperature most measurements are reproduced within $\pm 0.01 \log K$. This variation is twice that expected from uncertainties in the analytical procedures and may reflect other uncertainties beyond our control, such as trace impurities and crystal im-

Table 11. Summary of experimental solubility data for calcite in $\text{CO}_2\text{--H}_2\text{O}$ solutions.¹

$t^\circ\text{C}$	PCO_2 atm.	Total calcium	Calc. pH	$\log K_c$	$t^\circ\text{C}$	PCO_2 atm.	Total calcium	Calc. pH	$\log K_c$	$t^\circ\text{C}$	PCO_2 atm.	Total calcium	Calc. pH	$\log K_c$
0.1	.9843	14.33	6.061	-8.371	15.1	.9686	11.19	6.034	-8.404	54.5	.2512	3.30	6.391	-8.699
0.1	.9838	14.34	6.062	-8.370	15.1	.9687	11.19	6.033	-8.404	54.8	.8172	5.16	6.061	-8.699
0.1	.9893	14.38	6.061	-8.369	24.6	.9480	9.10	6.014	-8.489	54.8	.8172	5.20	6.064	-8.691
0.1	.9892	14.37	6.060	-8.370	25.0	.9497	9.11	6.016	-8.483	54.8	.8172	5.16	6.061	-8.699
0.2	.9339	14.01	6.076	-8.371	25.0	.9486	9.07	6.015	-8.487	54.8	.8200	5.10	6.055	-8.714
0.2	.9739	13.98	6.057	-8.392	25.0	.9487	9.07	6.015	-8.487	54.8	.8200	5.20	6.063	-8.692
0.3	.9763	13.97	6.056	-8.392	25.0	.9476	9.07	6.015	-8.487	54.8	.8200	5.23	6.065	-8.686
0.3	.9816	14.04	6.055	-8.389	25.0	.9478	9.15	6.018	-8.477	54.8	.8199	5.17	6.061	-8.699
0.3	.9816	14.05	6.056	-8.388	25.0	.9478	9.10	6.016	-8.483	54.8	.8199	5.11	6.056	-8.712
3.8	.9800	13.40	6.050	-8.383	25.1	.2880	5.68	6.346	-8.490	55.0	0.8336	5.14	6.053	-8.710
3.8	.9831	13.23	6.043	-8.398	25.1	.2880	5.70	6.347	-8.486	55.0	0.8332	5.19	6.057	-8.699
3.8	.9747	13.35	6.051	-8.385	25.5	.9477	8.99	6.015	-8.490	55.0	0.8325	5.17	6.055	-8.703
3.8	.9767	13.22	6.046	-8.396	25.5	.9493	9.01	6.015	-8.488	55.0	0.8321	5.16	6.055	-8.705
3.8	.9822	13.18	6.042	-8.402	25.5	.9491	9.04	6.016	-8.485	55.2	.8232	5.21	6.065	-8.688
3.8	.9800	13.32	6.047	-8.389	25.5	.9493	8.98	6.013	-8.492	57.6	.8263	4.91	6.058	-8.732
3.8	.9774	13.20	6.045	-8.398	35.0	.9280	7.48	6.011	-8.562	57.6	.8251	4.92	6.059	-8.730
3.8	.9814	13.20	6.043	-8.400	35.0	.9283	7.54	6.015	-8.553	64.5	.7561	4.29	6.096	-8.783
3.8	.9817	13.31	6.046	-8.391	35.0	.9293	7.48	6.011	-8.562	64.7	0.7508	4.32	6.103	-8.770
3.8	.9836	13.23	6.043	-8.398	35.0	.2825	4.81	6.351	-8.540	64.7	0.7508	4.33	6.104	-8.767
3.8	.9878	13.22	6.041	-8.401	35.0	.2821	4.79	6.350	-8.544	64.7	.2292	2.70	6.428	-8.794
3.8	.9850	13.28	6.044	-8.395	35.0	.2821	4.80	6.351	-8.542	64.9	.2303	2.68	6.424	-8.803
3.8	.9825	13.16	6.041	-8.404	35.0	.9280	7.49	6.012	-8.560	65.0	.2226	2.60	6.428	-8.822
3.8	.9823	13.23	6.044	-8.398	35.0	.9281	7.50	6.013	-8.558	65.0	.2226	2.61	6.429	-8.818
3.8	.9770	13.14	6.043	-8.403	35.1	.9208	7.51	6.017	-8.553	65.1	.7347	4.27	6.111	-8.770
3.8	.9732	13.15	6.045	-8.401	37.8	.9262	7.27	6.020	-8.558	72.4	.6846	3.59	6.130	-8.876
3.8	.9719	13.09	6.044	-8.405	38.0	.9264	7.25	6.020	-8.559	73.0	0.6401	3.30	6.130	-8.938
3.8	.9754	13.11	6.043	-8.405	45.0	.8872	6.19	6.026	-8.635	73.0	0.6388	3.33	6.135	-8.927
3.8	.9732	13.32	6.050	-8.386	45.0	.8872	6.2	6.026	-8.633	73.0	0.6382	3.325	6.134	-8.928
3.8	.9776	13.14	6.043	-8.403	45.0	.8849	6.22	6.029	-8.628	73.0	0.6379	3.32	6.134	-8.930
4.6	.9686	13.28	6.054	-8.375	45.0	.8838	6.27	6.032	-8.619	74.9	.1845	2.07	6.495	-8.925
4.6	.9829	13.27	6.048	-8.382	45.0	.8834	6.25	6.031	-8.622	74.9	.1847	2.11	6.502	-8.903
4.6	.9676	13.31	6.056	-8.372	45.0	0.8952	6.251	6.026	-8.628	75.2	.6021	3.23	6.165	-8.919
4.6	.9663	13.28	6.055	-8.374	45.0	0.8962	6.249	6.025	-8.629	75.2	.6028	3.31	6.175	-8.892
5.0	.9724	13.18	6.051	-8.379	45.0	0.8959	6.255	6.025	-8.628	75.4	.5995	3.21	6.166	-8.923
5.0	.9714	13.17	6.051	-8.379	45.0	0.8938	6.26	6.027	-8.626	75.4	.5995	3.21	6.166	-8.923
5.0	.9703	13.19	6.052	-8.377	45.1	.8812	6.24	6.032	-8.622	75.4	.5988	3.22	6.168	-8.919
9.9	.9670	11.87	6.033	-8.416	45.1	.8808	6.20	6.030	-8.629	80.1	0.5170	2.77	6.209	-8.994
9.9	.9683	11.89	6.033	-8.414	45.1	.8800	6.19	6.030	-8.630	80.1	0.5170	2.76	6.208	-8.998
9.9	.9707	11.98	6.035	-8.407	45.1	.8799	6.20	6.030	-8.628	80.1	0.5170	2.77	6.209	-8.994
9.9	.9703	11.99	6.035	-8.406	45.1	.8843	6.21	6.029	-8.629	81.0	.5064	2.72	6.218	-9.000
9.9	.9703	11.97	6.034	-8.408	45.1	.8833	6.20	6.029	-8.630	81.7	.4895	2.67	6.231	-9.002
10.0	.9720	11.97	6.034	-8.408	45.1	.8829	6.21	6.030	-8.628	82.0	.4853	2.62	6.229	-9.018
10.0	.9720	11.93	6.033	-8.412	51.0	.8587	5.63	6.046	-8.662	88.5	.3425	2.06	6.336	-9.104
10.0	.9730	11.97	6.034	-8.408	51.2	.8574	5.61	6.047	-8.663	89.7	.3130	1.92	6.356	-9.140
14.7	.9629	11.01	6.028	-8.425	51.6	.8451	5.58	6.054	-8.659	89.7	0.3082	1.91	6.360	-9.139
14.7	.9630	11.02	6.028	-8.424	51.6	.8455	5.53	6.050	-8.669	89.7	0.3082	1.92	6.363	-9.133
15.1	.9575	11.13	6.036	-8.405	54.5	.2514	3.26	6.386	-8.713	89.7	0.3091	1.91	6.359	-9.140

¹ Total calcium is in mmol/kg of solution. Owing to uncertainties in gas compositions, PCO_2 values are uncertain in the 4th significant figure reported.

Table 12. Summary of experimental solubility data for aragonite in CO₂-H₂O solutions.¹

t°C	PO ₂ atm ²	Total calcium	Calc. pH	Log K _A	t°C	PO ₂ atm ²	Total calcium	Calc. pH	Log K _A	t°C	PO ₂ atm ²	Total calcium	Calc. pH	Log K _A	t°C	PO ₂ atm ²	Total calcium	Calc. pH	Log K _A
0.7	.9821	16.22	6.113	-8.225	25.0	.2911	6.55	6.398	-8.337	44.9	.8939	7.15	6.079	-8.480	65.0	0.002216	0.565	7.782	-8.686
0.7	.9822	16.10	6.110	-8.233	25.0	.2961	6.60	6.393	-8.335	44.9	.8933	7.27	6.085	-8.462	65.0	0.002239	0.5529	7.769	-8.716
0.7	.9812	16.20	6.114	-8.223	25.0	.2890	6.56	6.401	-8.332	44.9	.8930	7.26	6.085	-8.463	65.0	0.002237	0.5563	7.771	-8.708
0.7	.9808	16.24	6.113	-8.225	25.0	.2890	6.56	6.401	-8.332	44.9	.8929	7.20	6.082	-8.472	65.0	.002252	.569	7.778	-8.684
0.7	.9819	16.10	6.110	-8.233	25.0	.2909	6.58	6.400	-8.331	44.9	.8925	7.24	6.084	-8.466	65.0	.002238	.571	7.782	-8.677
0.7	.9824	16.17	6.112	-8.228	25.0	.2893	6.56	6.401	-8.332	44.9	.8916	7.23	6.084	-8.467	65.0	0.0002407	0.2790	8.402	-8.697
0.7	.9824	16.23	6.113	-8.224	25.0	.2877	6.59	6.405	-8.325	44.9	.8919	7.17	6.081	-8.476	65.0	0.0002405	0.2805	8.404	-8.690
3.9	.2993	9.62	6.432	-8.236	25.0	.2869	6.56	6.402	-8.332	44.9	.2707	4.473	6.410	-8.487	65.0	0.0002404	0.2778	8.401	-8.701
3.9	.2988	9.66	6.435	-8.230	25.0	.03028	2.763	7.030	-8.346	44.9	.2701	4.487	6.412	-8.482	65.0	.0002360	.2805	8.412	-8.684
3.9	.02608	3.904	7.126	-8.209	25.0	.03036	2.767	7.029	-8.345	44.9	.26943	4.459	6.411	-8.488	65.0	.0002359	.2807	8.412	-8.683
3.9	.02603	3.887	7.125	-8.213	25.0	.03045	2.772	7.029	-8.344	44.9	.02564	1.882	7.079	-8.472	80.0	0.5241	3.110	6.249	-8.868
3.9	.002963	1.737	7.731	-8.234	25.0	.03011	2.759	7.032	-8.345	44.9	.02558	1.872	7.078	-8.477	80.0	0.5243	3.126	6.251	-8.863
3.9	.002978	1.734	7.731	-8.236	25.0	.03024	2.810	7.037	-8.325	44.9	.02552	1.849	7.073	-8.491	80.0	0.5249	3.130	6.251	-8.862
4.9	.9801	15.28	6.106	-8.222	25.0	.002920	1.190	7.693	-8.343	44.9	.02548	1.841	7.072	-8.495	80.0	0.5253	3.090	6.245	-8.877
4.9	.9796	15.21	6.104	-8.227	25.0	.002912	1.195	7.696	-8.337	44.9	.02543	1.831	7.071	-8.501	80.0	0.5222	3.08	6.247	-8.878
4.9	.9804	15.04	6.099	-8.239	25.0	.002909	1.193	7.696	-8.338	44.9	.002698	0.856	7.723	-8.456	80.0	0.5222	3.08	6.247	-8.878
4.9	.9803	15.03	6.099	-8.240	25.0	.002909	1.202	7.699	-8.329	44.9	.002692	0.849	7.721	-8.465	80.0	0.5222	3.09	6.248	-8.874
4.9	.9800	15.22	6.104	-8.226	25.0	.002929	1.196	7.694	-8.338	44.9	.002685	0.832	7.713	-8.488	80.0	0.5221	3.09	6.248	-8.874
4.9	.9800	15.24	6.105	-8.225	25.0	.002896	1.193	7.698	-8.336	55.0	0.8400	5.765	6.095	-8.586	80.0	0.1592	1.970	6.579	-8.883
4.9	.9797	14.97	6.098	-8.244	25.0	.002894	1.190	7.697	-8.339	55.0	0.8400	5.768	6.095	-8.585	80.0	0.1594	1.963	6.577	-8.887
4.9	.9782	15.00	6.099	-8.241	25.0	.000310	.5538	8.340	-8.329	55.0	0.8351	5.733	6.095	-8.590	80.0	0.1576	1.986	6.587	-8.869
15.1	.9534	12.46	6.083	-8.280	25.0	.000310	.5542	8.341	-8.327	55.0	0.8308	5.737	6.098	-8.587	80.0	0.1577	1.965	6.582	-8.881
15.1	.9529	12.45	6.083	-8.281	25.0	.0003075	.5496	8.344	-8.331	55.0	0.8351	5.733	6.095	-8.590	80.0	0.1576	1.986	6.587	-8.869
15.1	.9513	12.45	6.079	-8.285	25.0	.0003075	.5539	8.338	-8.330	55.0	0.8308	5.737	6.098	-8.587	80.0	0.1577	1.965	6.582	-8.881
15.1	.9578	12.46	6.081	-8.282	25.0	.0003035	.5533	8.343	-8.327	55.0	0.8351	5.733	6.095	-8.590	80.0	0.1576	1.986	6.587	-8.869
15.1	.9578	12.47	6.081	-8.282	25.0	.0003035	.5544	8.340	-8.328	65.0	0.7479	4.69	6.140	-8.674	80.0	0.01639	0.865	7.221	-8.890
15.1	.9578	12.47	6.081	-8.282	25.0	.0003087	.5550	8.337	-8.330	65.0	0.7479	4.69	6.140	-8.674	80.0	0.01639	0.865	7.221	-8.890
15.1	.9536	12.45	6.082	-8.281	35.0	.9329	8.82	6.074	-8.384	65.0	0.7479	4.69	6.140	-8.674	80.0	0.01563	0.398	7.893	-8.872
15.1	.2988	7.96	6.408	-8.271	35.0	.9330	8.72	6.070	-8.396	65.0	0.7479	4.68	6.139	-8.676	80.0	0.01563	0.401	7.896	-8.864
15.1	.0.2986	7.94	6.408	-8.274	35.0	.9330	8.82	6.074	-8.384	65.0	0.7486	4.557	6.128	-8.706	90.0	0.3051	2.129	6.411	-9.007
15.1	.0.2982	8.01	6.412	-8.263	35.0	.9322	8.69	6.069	-8.399	65.0	0.7488	4.543	6.127	-8.710	90.0	0.3043	2.125	6.412	-9.008
15.1	.0.2938	7.97	6.416	-8.263	35.0	.9316	8.80	6.074	-8.385	65.0	0.7443	4.541	6.129	-8.708	90.0	0.3064	2.133	6.410	-9.007
15.1	.0.2938	7.96	6.416	-8.264	35.0	.9317	8.66	6.068	-8.403	65.0	0.7512	4.61	6.131	-8.695	90.0	0.3131	2.115	6.397	-9.026
15.1	.002892	1.430	7.717	-8.266	35.0	.9328	8.85	6.076	-8.380	65.0	0.7509	4.609	6.131	-8.695	90.0	0.3034	2.145	6.417	-8.996
15.1	.002891	1.430	7.717	-8.266	35.0	.9333	8.62	6.065	-8.409	65.0	0.7512	4.608	6.131	-8.695	90.0	0.3031	2.128	6.414	-9.005
15.1	.0003023	.649	8.356	-8.274	35.0	.9329	8.82	6.074	-8.384	65.0	0.7512	4.608	6.131	-8.695	90.0	0.3031	2.145	6.417	-8.996
15.1	.0003023	.649	8.356	-8.274	35.0	.9330	8.72	6.070	-8.396	65.0	0.7512	4.608	6.131	-8.695	90.0	0.3031	2.145	6.417	-8.996
15.1	.0003022	.652	8.358	-8.268	35.0	.9330	8.82	6.074	-8.384	65.0	0.7512	4.608	6.131	-8.695	90.0	0.3031	2.145	6.417	-8.996
15.1	.0003047	.652	8.355	-8.272	35.0	.9322	8.69	6.069	-8.399	65.0	0.7512	4.608	6.131	-8.695	90.0	0.3031	2.145	6.417	-8.996
25.0	.9545	10.63	6.074	-8.317	35.0	.9316	8.80	6.074	-8.385	65.0	0.7443	4.541	6.129	-8.708	90.0	0.3064	2.133	6.410	-9.007
25.0	.9541	10.59	6.073	-8.321	35.0	.9317	8.66	6.068	-8.403	65.0	0.7512	4.61	6.131	-8.695	90.0	0.3131	2.115	6.397	-9.026
25.0	.9551	10.51	6.070	-8.330	35.0	.9328	8.85	6.076	-8.380	65.0	0.7509	4.609	6.131	-8.695	90.0	0.3034	2.145	6.417	-8.996
25.0	.9554	10.62	6.074	-8.319	35.0	.9333	8.62	6.065	-8.409	65.0	0.7512	4.608	6.131	-8.695	90.0	0.3031	2.145	6.417	-8.996
25.0	.9542	10.59	6.073	-8.321	35.0	.2770	5.37	6.404	-8.408	65.0	0.02058	1.201	7.140	-8.710	90.0	0.09004	1.297	6.736	-9.065
25.0	.9541	10.56	6.072	-8.324	35.0	.2772	5.36	6.403	-8.410	65.0	0.02059	1.200	7.140	-8.711	90.0	0.08988	1.308	6.740	-9.054
25.0	.9532	10.58	6.073	-8.322	35.0	.02623	2.24	7.071	-8.396	65.0	0.02057	1.213	7.144	-8.698	90.0	0.09521	0.5996	7.381	-9.043
25.0	.9528	10.55	6.072	-8.325	35.0	.02625	2.23	7.069	-8.401	65.0	0.02348	1.274	7.108	-8.696	90.0	0.09519	0.6098	7.388	-9.023
25.0	.2904	6.52	6.397	-8.341	35.0	.002761	.999	7.709	-8.396	65.0	0.02348	1.274	7.108	-8.696	90.0	0.09519	0.6098	7.388	-9.023
25.0	.2903	6.53	6.398	-8.339	35.0	.002763	.997	7.708	-8.399	65.0	0.02217	0.558	7.776	-8.701	90.0	0.09507	0.6133	7.391	-9.015
25.0	.2900	6.53	6.398	-8.338	35.0	.002763	.999	7.709	-8.397	65.0	0.02218	0.559	7.777	-8.699	90.0	0.09507	0.6133	7.391	-9.015
25.0	.2900	6.53	6.398	-8.338	35.0	.002763	.999	7.709	-8.397	65.0	0.02218	0.559	7.777	-8.699	90.0	0.09507	0.6133	7.391	-9.015
25.0	.2900	6.53	6.398	-8.338	35.0	.002763	.999	7.709	-8.397	65.0	0.02218	0.559	7.777	-8.699	90.0	0.09507	0.6133	7.391	-9.015
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25.0	.2900	6.53	6.398	-8.338	35.0	.002763	.999	7.709	-8.397	65.0	0.02218	0.559	7.777	-8.699	90.0	0.09507	0.6133	7.391	-9.015
25.0	.2900	6.53	6.398	-8.338	35.0	.002763	.999	7.709	-8.397	65.0	0.02218	0.559	7.777	-8.699	90.0	0.09507	0.6133	7.391	-9.015
25.0	.2900	6.53	6.398	-8.338	35.0	.002763	.999	7.709	-8.397	65.0	0.02218	0.55							

perfections. Experimental errors are estimated as ± 0.01 to ± 0.02 between 0 and 40°C, and increase to approximately ± 0.02 to ± 0.03 at 90°C.

Table 14 summarizes average values of $\log K_C$, $\log K_A$, and $\log K_V$ at the experimental temperatures along with the estimated experimental error. The data of Table 14 were fitted simultaneously to an equation of the form

$$\log K = A + BT + C/T + D \log T \quad (57)$$

using the estimated experimental error for each temperature and the constraint of an assumed common heat capacity for the calcite, aragonite and vaterite dissociation reactions. The regression coefficients are summarized in Table 15. Table 14 compares calculated values of $\log K$ with the experimental values.

The thermodynamic properties of the dissociation reactions of calcite, aragonite and vaterite (reaction 54) at one atm total pressure may be calculated using appropriate thermodynamic expressions and the regression coefficients of Table 15. Relations for the standard Gibbs free energy, enthalpy, heat capacity and entropy of reaction, ΔG_r^0 , ΔH_r^0 , ΔC_{pr}^0 , and ΔS_r^0 are, respectively

$$\begin{aligned} \Delta G_r^0 &= -RT \ln K \\ &= -\alpha R \left(AT + BT^2 + C + \frac{DT \ln T}{\alpha} \right) \end{aligned} \quad (58)$$

$$\begin{aligned} \Delta H_r^0 &= RT^2 d \ln K / dT \\ &= \alpha R \left(BT^2 - C + \frac{DT}{\alpha} \right) \end{aligned} \quad (59)$$

$$\Delta C_{pr}^0 = \frac{\partial \Delta H_r^0}{\partial T} = \alpha R \left(2BT + \frac{D}{\alpha} \right) \quad (60)$$

and

$$\begin{aligned} \Delta S_r^0 &= \frac{-\partial \Delta G_r^0}{\partial T} \\ &= \alpha R \left(A + 2BT + \frac{D}{\alpha} (1 + \ln T) \right) \end{aligned} \quad (61)$$

Table 13. Summary of experimental solubility¹ data for vaterite in CO₂-H₂O solutions.

t°C	PCO ₂ atm.	Total Calcium	Calc. pH	Log K _A
0.0	.9895	25.80	6.290	-7.739
15.3	.9833	19.05	6.236	-7.837
25.1	.9632	15.71	6.223	-7.902
25.1	.9620	15.73	6.224	-7.900
35.0	.9412	12.40	6.203	-8.021
45.0	.9005	9.92	6.204	-8.127
55.0	.8391	7.96	6.222	-8.232
65.0	.7516	6.22	6.250	-8.364
80.0	.5279	4.09	6.355	-8.563
80.0	.5195	4.02	6.355	-8.576
90.0	.3018	2.80	6.526	-8.690

¹ Total calcium is in mMol/kg solution. Owing to uncertainties in gas composition, reported PCO₂ values are uncertain in the 4th significant figure.

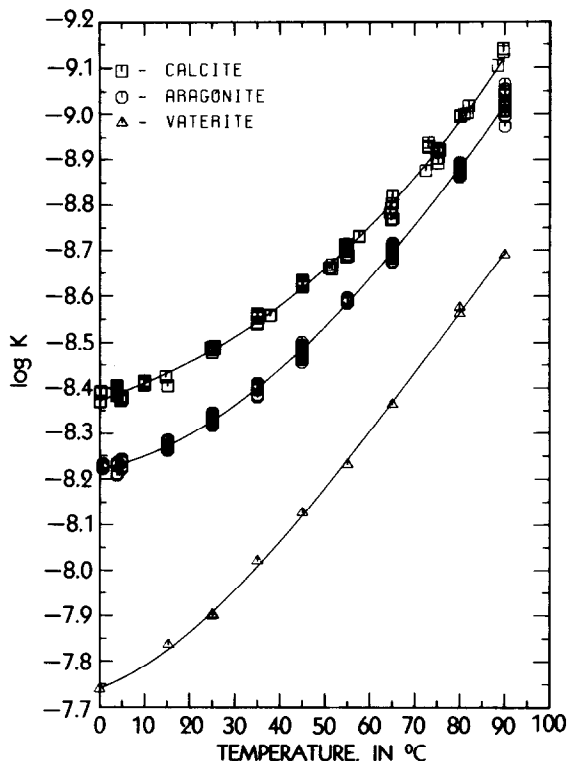


FIG. 13. Summary of $\log K$ for calcite, aragonite and vaterite between 0 and 90°C based on the solubility measurements and aqueous model of this study. Approximately 350 measurements are included in the computer-drawn plot. The curves were calculated from the fits to these data given by Eqn. (57) and coefficients of Table 15.

where α is 2.302585 and R is the gas constant ($=1.987165 \text{ cal K}^{-1} \text{ mol}^{-1}$), T is in °K, and the constants A , B , C , and D are summarized in Table 15 for calcite, aragonite and vaterite. Equations (57)–(61) may be used between 0 and 90°C.

Calculated values of ΔG_r^0 , ΔH_r^0 , ΔC_{pr}^0 and ΔS_r^0 for calcite, aragonite and vaterite dissociation are summarized in Table 16 at 25°C and one atm total pressure. The calculated free energy differences between calcite and aragonite, and calcite and vaterite at 25°C are 196 and 772 cal mol⁻¹. The free energy difference between calcite and aragonite corresponds to the ratio K_A/K_C of 1.39 at 25°C.

COMPARISON WITH PREVIOUS WORK

The free energy difference between calcite and aragonite at 25°C reported here ($196 \pm 30 \text{ cal mol}^{-1}$) is in reasonable agreement with 230 cal mol^{-1} based on the results of Jamieson (1953) as given by Broecker and Takahashi (1976), 232 cal mol^{-1} (Langmuir, 1964; Berner, 1976) and 218 cal mol^{-1} (Christ *et al.*, 1974). Measurements of the solubility of calcite and aragonite in sea water indicate a wide variability in the free energy difference (425 cal mol^{-1} , Plath and Pytkowicz, 1980; 288 cal mol^{-1} , MacIntyre, 1965, as recalculated by Morse *et al.*, 1980; 250 cal mol^{-1} , Morse *et al.*, 1980), and may

Table 14. Summary of average experimental and calculated values of $\log K_C$, $\log K_A$ and $\log K_V$ ¹

Calcite				Aragonite			
t °C	Exp. Log K_C	Std. dev.	Calc. Log K_C	t °C	Exp. Log K_A	Std. dev.	Calc. Log K_A
0.2	-8.379	0.011	-8.382	0.7	-8.226	0.0036	-8.220
3.8	-8.397	0.007	-8.391	3.9	-8.226	0.0121	-8.231
4.6	-8.376	0.020	-8.393	4.9	-8.234	0.0081	-8.235
5.0	-8.378	0.020	-8.394	15.1	-8.274	0.0078	-8.279
10.0	-8.410	0.004	-8.410	25.0	-8.332	0.0077	-8.336
14.7	-8.425	0.020	-8.429	35.0	-8.395	0.0099	-8.406
15.1	-8.404	0.020	-8.431	44.9	-8.474	0.0128	-8.488
24.6	-8.489	0.020	-8.478	55.0	-8.590	0.0041	-8.585
25.0	-8.485	0.004	-8.480	65.0	-8.698	0.0119	-8.693
25.5	-8.489	0.003	-8.483	80.0	-8.876	0.0089	-8.878
35.0	-8.553	0.009	-8.543	90.0	-9.021	0.0214	-9.016
37.8	-8.558	0.020	-8.563				
38.0	-8.559	0.020	-8.565				
45.0	-8.628	0.004	-8.620				
51.1	-8.663	0.020	-8.673				
51.6	-8.664	0.020	-8.677				
54.5	-8.706	0.020	-8.704				
54.8	-8.699	0.010	-8.707				
55.0	-8.704	0.005	-8.709				
55.2	-8.688	0.020	-8.711				
57.6	-8.731	0.020	-8.735				
64.6	-8.779	0.012	-8.807				
65.0	-8.803	0.024	-8.812				
72.4	-8.876	0.020	-8.895				
73.0	-8.931	0.020	-8.903				
74.9	-8.914	0.020	-8.925				
75.2	-8.906	0.030	-8.929				
75.4	-8.922	0.020	-8.931				
80.1	-8.995	0.020	-8.990				
81.0	-9.000	0.020	-9.001				
81.7	-9.002	0.020	-9.010				
82.0	-9.018	0.020	-9.014				
88.5	-9.104	0.020	-9.101				
89.7	-9.138	0.010	-9.118				

Vaterite			
t °C	Exp. Log K_V	Std. dev.	Calc. Log K_V
0.0	-7.739	0.020	-7.743
15.3	-7.837	0.020	-7.838
25.1	-7.902	0.005	-7.914
35.0	-8.021	0.020	-8.002
45.0	-8.127	0.020	-8.103
55.0	-8.232	0.020	-8.215
65.0	-8.364	0.030	-8.339
80.0	-8.570	0.030	-8.545
90.0	-8.690	0.020	-8.697

¹ These values used in the regression analysis of Table 15.

be caused by the formation of an unstable (temporary) surface coating of magnesian calcite on aragonite surfaces in sea water, as discussed by Plummer and Sundquist (1982). Calcite and aragonite solubility studies in sea water of duration greater than 10 days (Morse *et al.*, 1980) closely approach our results (Plummer and Sundquist, 1982).³

Using a novel electrode method, Rock and Gordon (1976) found the free energy difference between calcite and aragonite to be 330 ± 8 cal mol⁻¹, and the difference between calcite and vaterite was found to be 881 ± 15 cal mol⁻¹. Turnbull (1973) found the free energy difference between calcite and vaterite at 25°C (based on solubility studies) to be 790 ± 25 cal mol⁻¹, which is nearly identical to our value (772 ± 30 cal mol⁻¹). It appears, then, that there is a systematic error of approximately 100 cal mol⁻¹ in the method of Rock and Gordon (1976).

Calculated thermodynamic properties of the calcite dissociation reaction at 25°C agree reasonably well with the results of Jacobson and Langmuir (1974) who reported $\Delta H_r^0 = -2585 \pm 300$ cal mol⁻¹, and $\Delta S_r^0 = -47.4 \pm 1.0$ cal mol⁻¹ deg⁻¹, as compared with -2297 ± 300 cal mol⁻¹ and -46.5 ± 2.0 cal mol⁻¹ deg⁻¹ given in Table 16. Larger differences are found in the derived ΔC_p^0 , which depend on the second derivative of $\log K$ with respect to temperature. Jacobson and Langmuir (1974) reported the value for

the heat capacity of reaction for calcite of -109 ± 2 cal mol⁻¹ deg⁻¹ at 25°C which compares with -70.5 ± 4.0 cal mol⁻¹ deg⁻¹ given by Eqn. (60).

From heat capacity measurements, Staveley and Linford (1969) found that the molar entropy of calcite exceeds that of aragonite by 0.89 ± 0.05 cal mol⁻¹ deg⁻¹ at 25°C which compares with -0.3 ± 2.0 calculated from the data of Table 16.

Figures 14 and 15 compare experimental determinations of $\log K_C$ and $\log K_A$ (re-calculated from the original measurements and internally consistent with our aqueous model), with our results (solid line). A large range of values of K_C is demonstrated (Fig. 14). Calcite solubility studies agreeing well with the present work include Jacobson and Langmuir (1974), at 5, 15, 35, and 50°C in CO₂-saturated water, Shternina (1945) at 25°C and PCO₂'s of 0.06 to 0.97 atm, Engle (1888) at 16°C and 1 to 6 atm PCO₂, Shternina and Frolova (1952) at 25°C and 0.10 to 0.97 atm PCO₂, and Turnbull (1973) at 25°C and 0.97 atm PCO₂. A supplementary table² summarizes our re-calculation of much of the calcite solubility literature. In our re-calculation, CO₂ partial pressures greater than 1 atm. were corrected to fugacity using the formula of Houghton *et al.* (1957).

Other calculations (not included in the NAPS supplement) indicate that several extensive calcite solubility studies (notably Miller, 1952; Ellis, 1959b, 1963; Sipple and Glover, 1964; and to a lesser extent Segnit *et al.*, 1962) did not reach equilibrium at "low" pressures (≤ 10 atm) and "low" temperatures ($\leq 100^\circ\text{C}$), where their results may be compared with ours (Fig. 14). Experiments of Miller (1952), Segnit *et al.* (1962) and Ellis (1959b, 1963) were all similar in that a single crystal or several single crystals of calcite were placed in a water-filled liner within a constant-temperature hydrothermal bomb and pressurized with CO₂ gas.

Miller (1952) assumed equilibrium was established after 8–12 hours in most runs because in trial runs of longer duration, no further dissolution could be detected by weight loss of a single plate of Iceland spar. Runs of Ellis (1959b, 1963) at 100°C and Segnit *et al.* (1962) at 75 and 100°C were of generally 1–2 days duration. Segnit *et al.* (1962) apparently reversed solubilities above 100°C by varying PCO₂, but it was uncertain whether runs at 75 and 100°C were reversed (Segnit *et al.*, 1962). In a different experiment, Sipple and Glover (1964) passed CO₂-H₂O solutions (1.0×10^{-2} and 0.33×10^{-2} molal

Table 15: Temperature dependence of $\log K_C$, $\log K_A$ and $\log K_V$ ¹

Mineral	A	B	C	D
Calcite	-171.9065	-0.077993	2839.319	71.595
Aragonite	-171.9773	-0.077993	2903.293	71.595
Vaterite	-172.1295	-0.077993	3074.688	71.595

¹ $\log K = A + BT + C/T + D \log T$, where T is in °K, and $\log K$ is internally consistent with the aqueous model of this paper. Because the heat capacities of calcite and aragonite, and presumably vaterite, are nearly equal between 0 and 90°C (Robie *et al.*, 1978), the equilibrium constants of calcite, aragonite and vaterite were regressed simultaneously with the constraint that the B and D parameters be identical for all three reactions. The fits may be used between 0 and 90°C.

³ Values of K_C and K_A used by Plummer and Sundquist (1982) differ slightly from those given here, but their conclusions are unchanged.

Table 16: Thermodynamic properties of the dissociation reactions of calcite, aragonite, and vaterite at 25°C and 1 atm. total pressure¹

Mineral	log K	K/K _C	ΔG _r ⁰	ΔH _r ⁰	ΔC _{pr} ⁰	ΔS _r ⁰
Calcite	-8.480±0.020	1.0	11568±27	-2297±300	-70.5±4.0	-46.5±2.0
Aragonite	-8.336±0.020	1.39±0.1	11372±27	-2589±300	-70.5±4.0	-46.8±2.0
Vaterite	-7.913±0.020	3.69±0.3	10796±27	-3774±300	-70.5±4.0	-47.5±2.0

¹ Calculated from the regression coefficients of Table 15 and eqns (57)-(61). Units are cal/mol for ΔG_r⁰, and ΔH_r⁰, and cal/mole/deg for ΔC_{pr}⁰ and ΔS_r⁰. Uncertainties are based on estimated errors of ±0.02 log K at 0°C and ±0.04 log K at 90°C. 1 cal = 4.1840 joules.

CO₂) through pressurized columns packed with calcite crystals (60–325 mesh) at a flow rate of 50 ml/hr. They assumed equilibrium was established be-

cause no decrease in dissolved calcium was noted at substantially higher flow rates.

Thermodynamic calculations using the aqueous

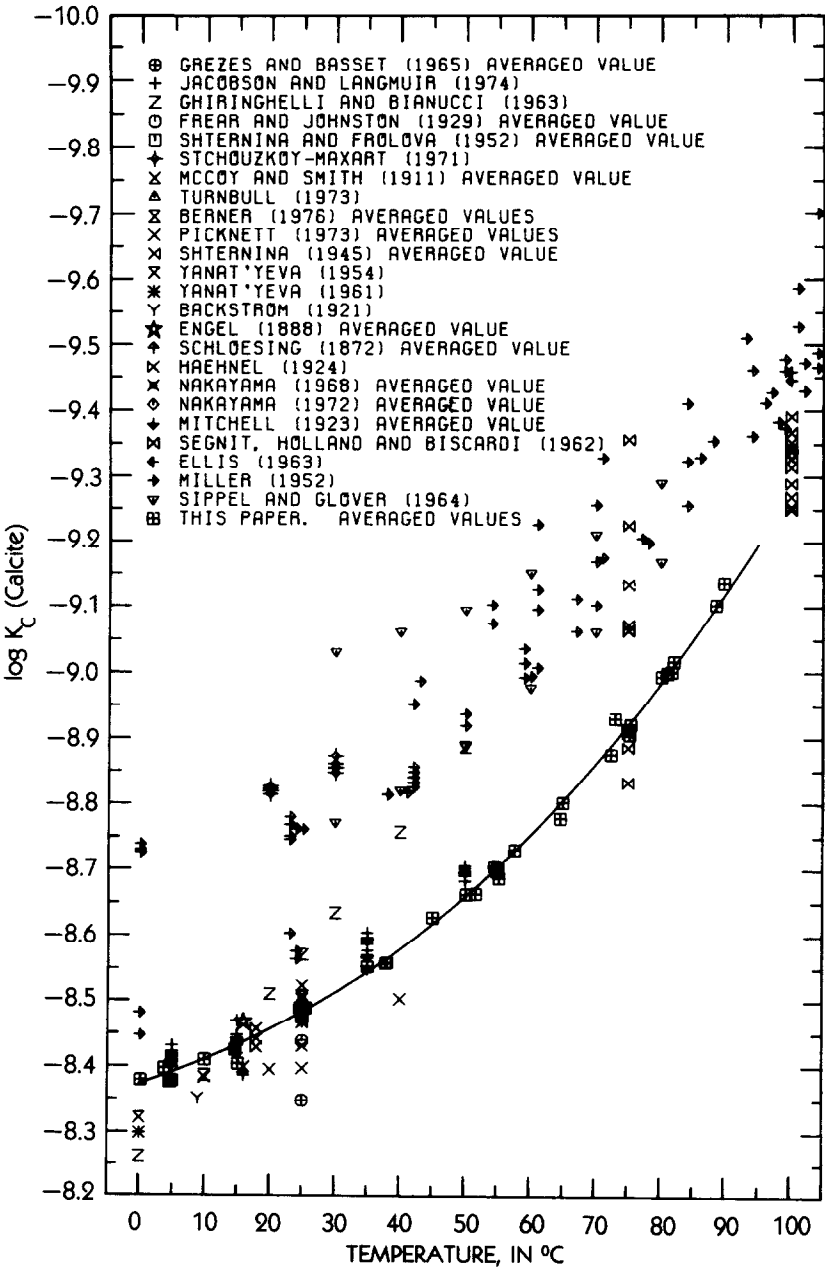


FIG. 14. Comparison of previous determinations of log K for calcite (re-calculated from the original data to be internally consistent with the aqueous model of this paper) as a function of temperature. The curve is based on the results of this paper (Eqn. 57).

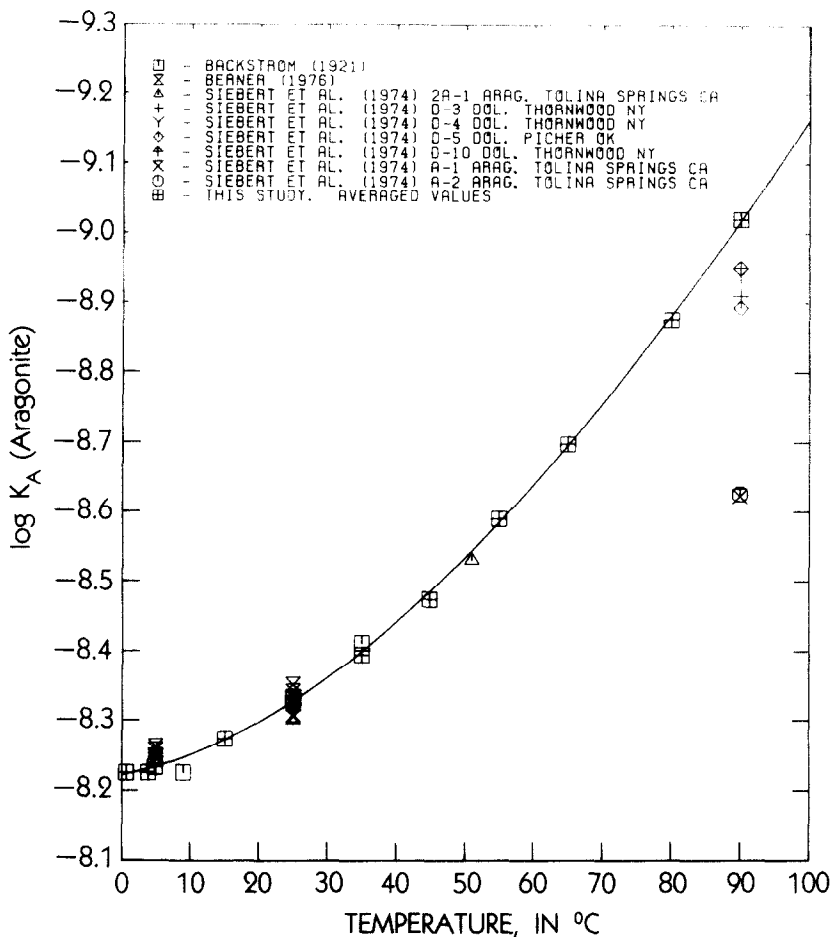


FIG. 15. Comparison of previous determinations of $\log K$ for aragonite (re-calculated from the original data to be internally consistent with the aqueous model of this paper) as a function of temperature. The curve is based on the results of this paper (Eqn. 57).

model of this paper and portions of the data of Miller (1952), Ellis (1959b, 1963), Segnit *et al.* (1962) and Sipple and Glover (1964) show reasonably consistent results among these authors, but systematically smaller values of the calcite equilibrium constant relative to our values. Data of Miller (1952) between 0 and 100°C and 1–10 atm PCO_2 indicate $\log K_C$ values ~ 0.3 smaller (more negative) than our values. Most of the data of Segnit *et al.* (1962) imply $\log K_C$ values at 1 atm total pressure and 75°C which are 0.2–0.4 $\log K_C$ less than our values. Data of Segnit *et al.*, (1962) at 100°C are closer to our values. Data of Ellis (1959b, 1963) at 100°C and 1–12 atm PCO_2 are about 0.18 $\log K_C$ units less than our value. Calculations using the data of Sipple and Glover (1964), assuming their column experiment was closed to an external source of CO_2 gas, average $0.22 \pm 0.04 \log K_C$ units less than our values between 30 and 80°C (at 3.45 atm total pressure) for one initial CO_2 - H_2O solution (1.0×10^{-2} m CO_2) and 0.52 to 0.31 $\log K_C$ units less for the other initial CO_2 - H_2O solution (0.33×10^{-2} m CO_2).

Except for the data of Segnit *et al.* (1962) at 100°C, these undersaturations are significant and

beyond experimental error. For example, calculations using the reaction simulation program PHREEQE (Parkhurst *et al.* 1980), our aqueous model, and our calcite equilibrium constants indicate that the observed solubilities of Ellis (1959b, 1963) in water at 100°C are 15% too low. Larger deviations are found in the data of Miller (1952). The most likely explanation for the discrepancy is failure to establish equilibrium in hydrothermal bombs at low temperatures ($\leq 100^\circ\text{C}$).

Several factors are prevalent in the hydrothermal bomb calcite solubility studies that would favor undersaturated solutions. (1) The calcite surface area that was available for reaction was approximately 1,000 to 10,000 times less than in our experiments. (2) Metal impurities in solution (from condensation and/or corrosion of the steel bombs) are known to strongly inhibit the rate of calcite dissolution even at trace levels (Erga and Terjesen, 1956; Terjesen *et al.*, 1961; Nestaas and Terjesen, 1969). Adsorption of metals on calcite surfaces can effectively stop reaction giving a false indication of equilibrium. Experiments using low reactant surface areas are most susceptible to inhibition because very low levels of

metal contamination can effectively block all surface reaction sites for dissolution.

In contrast to the wide range of values reported for K_C , the relatively limited number of aragonite solubility studies show close agreement with the present study (Fig. 15). Our re-calculation of the experimental solubility determination for aragonite is included in the NAPS supplement. Siebert *et al.* (1974) reported the formation of aragonite in their dolomite solubility studies at 51 and 90°C. Values of the equilibrium constant of aragonite calculated from their dolomite solubility data using the aqueous model of this paper and the magnesium speciation data of WATEQF (Plummer *et al.*, 1976) are in close agreement with the aragonite results of this paper (Fig. 15). Curiously, solubility runs of Siebert *et al.* (1974) using only aragonite at 90°C in $MgCl_2$ solutions are approximately 0.3 log K units more soluble than aragonite (Fig. 15). The aragonite equilibrium constant derived from the pH- Ca_T data of Browman and Hastings (1937) averages 0.08 log K units more stable than our value at 38°C.

The vaterite solubility determination of Turnbull (1973) at 25°C is in complete agreement with the results of this paper.

CONCLUSIONS

(1) The CO_2 - H_2O equilibria have been critically evaluated and new empirical expressions for the temperature-dependence of K_H , K_1 , and K_2 (as defined by Eqns. (4)–(6)) are

$$\log K_H = 108.3865 + 0.01985076T - 6919.53/T \\ - 40.45154 \log T + 669365./T^2,$$

$$\log K_1 = -356.3094 - 0.06091964T \\ + 21834.37/T + 126.8339 \log T - 1684915./T^2$$

and

$$\log K_2 = -107.8871 - 0.03252894T + 5151.79/T \\ + 38.92561 \log T - 563713.9/T^2,$$

which may be used to at least 250°C.

(2) Earlier arguments suggesting that the $CaHCO_3^+$ ion pair should not be included in the $CaCO_3$ - CO_2 - H_2O aqueous model are incorrect and based on erroneous calcite solubility data. The $CaHCO_3^+$ ion pair must be included in the aqueous model in order to account for our observed PCO_2 -dependence of aragonite solubility. The temperature-dependence of the $CaHCO_3^+$ association constant was derived from measurements of aragonite solubility as a function of PCO_2 and temperature, and is given by

$$\log K_{CaHCO_3^+} = 1209.120 + 0.31294T \\ - 34765.05/T - 478.782 \log T$$

between 0 and 90°C.

(3) Differences in the measured equilibrium pH, when different electrolyte reference filling solutions are used, are closely approximated by differences in liquid-junction potential calculated by the Henderson equation. Liquid-junction corrected equilibrium pH measurements agree with calculated (thermodynamic) pH values within 0.003 to 0.011 pH at 25°C.

(4) The temperature-dependence of the association constant for $CaCO_3^0$ has been measured potentiometrically and is given by

$$\log K_{CaCO_3^0} = -1228.732 - 0.299444T \\ + 35512.75/T + 485.818 \log T$$

between 5 and 80°C.

(5) Individual ion activity coefficients required for use with the above equilibria are based largely on extended Debye-Hückel expressions of Truesdell and Jones (1974), as summarized in the text.

(6) Based on approximately 350 new solubility measurements of calcite, aragonite and vaterite in CO_2 - H_2O solutions between 0 and 90°C, and the aqueous model of this paper,

$$\log K_C = -171.9065 - 0.077993T \\ + 2839.319/T + 71.595 \log T,$$

$$\log K_A = -171.9773 - 0.077993T \\ + 2903.293/T + 71.595 \log T,$$

and

$$\log K_V = -172.1295 - 0.077993T \\ + 3074.688/T + 71.595 \log T.$$

(7) These results support many of the earlier measurements of ion pairing and $CaCO_3$ solubility in the system $CaCO_3$ - CO_2 - H_2O . Most calcite solubility experiments conducted in hydrothermal bombs at temperatures below 100°C appear not to have reached equilibrium owing to low calcite surface areas and/or the possibility of foreign metal ion inhibition. Using our results, reliable calculations of calcite, aragonite and vaterite equilibria can be made to 90°C.

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REFERENCES

- Angus J. G., Raynor J. B. and Robson M. (1979) Reliability of experimental partition coefficients in carbonate systems: Evidence for inhomogeneous distribution of impurity cations. *Chem. Geol.* **27**, 181–205.
 Backstrom H. L. J. (1921) On the solubilities of calcite and aragonite. *Medd. Vetenskapsakad. Nobel Inst.* **4**, 1–11.
 Bates R. G. (1962) Revised standard values for pH mea-

- surements from 0 to 95°C. *U.S. Natl. Bur. Standards Jour. Res.* **66A**, 179–184.
- Bates R. G. (1973) *Determination of pH*. 2nd edn. John Wiley & Sons.
- Battino R. and Clever H. L. (1966) The solubility of gases in liquids. *Chem. Rev.* **66**, 395–463.
- Berg R. L. and Vanderzee C. E. (1978) The thermodynamics of carbon dioxide: (a) the standard enthalpies of solution of $\text{Na}_2\text{CO}_3(\text{s})$, $\text{NaHCO}_3(\text{s})$, and $\text{CO}_2(\text{g})$ in water at 298.15 K; (b) the standard enthalpies of formation, standard Gibbs energies of formation, and standard entropies of $\text{CO}_2(\text{aq})$, $\text{HCO}_3^-(\text{aq})$, $\text{CO}_3^{2-}(\text{aq})$, $\text{NaHCO}_3(\text{s})$, $\text{Na}_2\text{CO}_3(\text{s})$, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(\text{s})$. *J. Chem. Thermodynamics* **10**, 1113–1136.
- Berner R. A. (1976) The solubility of calcite and aragonite in seawater at atmospheric pressure and 34.5‰ salinity. *Amer. J. Sci.* **276**, 713–730.
- Broecker W. S. and Takahashi T. (1976) The solubility of calcite in seawater. In *Thermodynamics in Geology* (ed. D. G. Fraser) pp. 365–379, D. Reidel.
- Browman A. A. and Hastings A. B. (1937) Solubility of aragonite in salt solutions. *J. Biol. Chem.* **119**, 241–246.
- Cabrol P., Coudray J., Dandurand J. L. and Schott J. (1978) Sur la possibilité de transformation naturelle calcite \rightarrow aragonite dans les conditions ordinaires de température et de pression; reproduction expérimentale du phénomène. *Compt. Rend.* **287**, D411–414.
- Christ C. L., Hostetler P. B. and Siebert R. M. (1974) Stabilities of calcite and aragonite. *J. Res. U.S. Geol. Survey* **2**, 175–184.
- Curry J. and Hazelton C. L. (1938) The first thermodynamic ionization constant of deuterio-carbonic acid at 25°C. *J. Amer. Chem. Soc.* **60**, 2773–2776.
- Čüta F. and Stráfelda F. (1954) The second dissociation constant of carbonic acid between 60 and 90°C. *Chem. Listy* **48**, 1308–1313.
- Davies C. W. (1962) *Ion Association*. Butterworths, London.
- Diehl H. (1964) Calcein, calmagite, and o,o'-dihydroxyazobenzene titrimetric, colorimetric, and fluorometric reagents for calcium and magnesium. The G. Frederick Smith Company, Columbus, Ohio.
- Ellis A. J. (1959a) The effect of pressure on the first dissociation constant of "carbonic acid". *J. Chem. Soc.* 3689–3699.
- Ellis A. J. (1959b) The solubility of calcite in carbon dioxide solutions. *Amer. J. Sci.* **257**, 354–365.
- Ellis A. J. (1963) The solubility of calcite in sodium chloride solutions at high temperatures. *Amer. J. Sci.* **261**, 259–267.
- Ellis A. J. and Golding R. M. (1963) The solubility of carbon dioxide above 100°C in water and in sodium chloride solutions. *Amer. J. Sci.* **261**, 46–60.
- Engel M. (1888) Sur la loi de M. Schloesing relative à la solution des carbonates à la faveur de l'acide carboniques. *Ann. Chim. Phys. 6th ser.* **13**, 344–387.
- Erga O. and Terjesen S. G. (1956) Kinetics of the heterogeneous reaction of calcium bicarbonate formation, with special reference to copper ion inhibition. *Acta Chem. Scand.* **10**, 872–874.
- Frear C. L. and Johnston J. (1929) The solubility of calcium carbonate (calcite) in certain aqueous solutions at 25°C. *J. Amer. Chem. Soc.* **51**, 2082–2093.
- Garrels R. M., Thompson M. E. and Siever R. (1960) Stability of some carbonates at 25°C and one atmosphere total pressure. *Amer. J. Sci.* **258**, 402–418.
- Garrels R. M. and Thompson M. E. (1962) A chemical model for seawater at 25°C and one atmosphere total pressure. *Amer. J. Sci.* **258**, 402–418.
- Ghiringhelli L. and Bianucci G. (1963) The solubility product of calcium carbonate in aqueous solutions from 0 to 50°C. *Annali di Idrologia* **1**, 36–42.
- Goujon G. and Mutaftschiev B. (1976) On the crystallinity and the stoichiometry of the calcite surface. *J. Colloid Interface Sci.* **57**, 148–161.
- Greenwald I. (1941) The dissociation of calcium and magnesium carbonates and bicarbonates. *J. Biol. Chem.* **141**, 789–796.
- Grezes G. and Basset M. (1965) Contribution à l'étude de la solubilité du carbonate de calcium. *Compt. Rend.* **260**, 869–872.
- Haas J. L., Jr. and Fisher J. R. (1976) Simultaneous evaluation and correlation of thermodynamic data. *Amer. J. Sci.* **276**, 525–545.
- Haehnel O. (1924) Solubility of calcium carbonate. *J. Prakt. Chem.* **107**, 165–176.
- Hamer W. J. (1968) Theoretical mean activity coefficients of strong electrolytes in aqueous solutions from 0 to 100°C. *U.S. Natl. Bur. Standards, Natl. Standard Reference Data Ser.* **24**, 271 p.
- Harned H. S. and Bonner F. T. (1945) The first ionization of carbonic acid in aqueous solutions of sodium chloride. *J. Amer. Chem. Soc.* **67**, 1026–1031.
- Harned H. S. and Davis R., Jr. (1943) The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50°C. *J. Amer. Chem. Soc.* **65**, 2030–2037.
- Harned H. S. and Scholes S. R., Jr. (1941) The ionization constant of HCO_3^- from 0 to 50°C. *J. Amer. Chem. Soc.* **63**, 1706–1709.
- Hawley J. E. (1973) Bicarbonate and carbonate ion association with sodium, magnesium and calcium at 25°C and 0.72 ionic strength. Ph.D. Dissertation, Oregon State Univ.
- Head J. H. (1970) FITIT, A computer program to least squares fit non-linear theories. U.S. Air Force Academy, Tech. Report 70-5. Available from Quantum Chemistry Program Exchange, Program #230, Dept. Chemistry, Indiana Univ., Bloomington, Ind.
- Hills G. J. and Ives D. J. G. (1949) The hydrogen electrode. *Nature* **163**, 997.
- Houghton G., McLean A. M. and Ritchie P. D. (1957) Compressibility, fugacity, and water-solubility of carbon dioxide in the region 0–36 atm. and 0–100°C. *Chem. Eng. Sci.* **6**, 132–137.
- Jacobson R. L. and Langmuir D. (1974) Dissociation constants of calcite and CaHCO_3^+ from 0 to 50°C. *Geochim. Cosmochim. Acta* **38**, 301–318.
- Jamieson J. C. (1953) Phase equilibrium in the system calcite-aragonite. *J. Chem. Phys.* **21**, 1385–1390.
- Kielland J. (1937) Individual activity coefficients of ions in aqueous solutions. *J. Amer. Chem. Soc.* **59**, 1675–1678.
- Kinsman D. J. J. and Holland H. D. (1969) The co-precipitation of cations with CaCO_3 —IV. The co-precipitation of Sr^{2+} with aragonite between 16° and 96°C. *Geochim. Cosmochim. Acta* **33**, 1–17.
- Lafon G. M. (1970) Calcium complexing with carbonate ion in aqueous solutions at 25°C and 1 atmosphere. *Geochim. Cosmochim. Acta* **34**, 935–940.
- Langmuir D. (1964) Stability of carbonates in the system $\text{CaO-MgO-CO}_2\text{-H}_2\text{O}$. Ph.D. Dissertation, Harvard Univ.
- Langmuir D. (1968) Stability of calcite based on aqueous solubility measurements. *Geochim. Cosmochim. Acta* **32**, 835–851.
- Larson T. E., Sollo F. W., Jr. and McGurk F. F. (1976) Complexes affecting the solubility of calcium carbonate in water—Phase II. UIUW-WRC-76-0108.
- MacCormack K. E. and Schneider W. G. (1950) Compressibility of gases at high temperatures. IV. Carbon dioxide in the temperature range 0°–600°C, and pressures up to 50 atmospheres. *J. Chem. Phys.* **18**, 1269–1272.
- MacInnes D. A. (1919) The activities of the ions of strong electrolytes. *J. Amer. Chem. Soc.* **41**, 1086–1092.
- MacInnes D. A. and Belcher D. (1933) The thermodynamic

- ionization constants of carbonic acid. *J. Amer. Chem. Soc.* **55**, 2630–2646.
- MacInnes D. A. and Belcher D. (1935) The thermodynamic ionization constants of carbonic acid at 38°C from electromotive force measurements. *J. Amer. Chem. Soc.* **57**, 1683–1685.
- MacIntyre W. G. (1965) The temperature variation of the solubility products of calcium carbonate in seawater. *Fisheries Research Board of Canada Manuscript Report Series*, 200, 153p.
- Maier C. G. and Kelly K. K. (1932) An equation for the representation of high temperature heat content data. *J. Amer. Chem. Soc.* **54**, 3243–3246.
- Malinin S. D. (1959) The system $\text{H}_2\text{O}-\text{CO}_2$ at high temperatures and pressures. *Geochemistry* (1959), 292–306 (English).
- Markham A. E. and Kobe K. A. (1941) The solubility of gases in liquids. *Chem. Rev.* **28**, 519–588.
- Martynova O. I., Vasina L. G. and Pozdniakova S. A. (1974) Dissociation constants of certain scale forming salts. *Desalination* **15**, 259–265.
- McConnell J. D. C. (1960) Vaterite from Ballycraigy, Larne, Northern Ireland. *Mineral. Mag.* **32**, 534–544.
- McCoy H. N. and Smith H. J. (1911) Equilibrium between alkali-earth carbonates, carbon dioxide and water. *J. Amer. Chem. Soc.* **33**, 468–473.
- Miller J. P. (1952) A portion of the system calcium carbonate–carbon dioxide–water, with geological implications. *Amer. J. Sci.* **250**, 161–203.
- Mitchell A. E. (1923) Studies on the dolomite system.—Part II. *J. Amer. Chem. Soc.* **123**, 1887–1904.
- Morrison T. J. and Billett F. (1952) The salting-out of non-electrolytes. Part II. The effect of variation in non-electrolyte. *J. Chem. Soc.* 3819–3822.
- Morse J. W., Mucci A. and Millero F. J. (1980) The solubility of calcite and aragonite in seawater of 35‰ salinity at 25°C and atmospheric pressure. *Geochim. Cosmochim. Acta* **44**, 85–94.
- Murray C. N. and Riley J. P. (1971) The solubility of gases in distilled water and sea water—IV. Carbon dioxide. *Deep-Sea Res.* **18**, 533–541.
- Nakayama F. S. (1968) Calcium activity, complex and ion-pair in saturated CaCO_3 solutions. *Soil Sci.* **106**, 429–434.
- Nakayama F. S. (1972) A simple method for estimating the solubility product of calcium carbonate. *Soil Sci.* **113**, 456–457.
- Näsänen R. (1946) Zur Einwirkung der Saure—und Basenzusätze auf die Fallungskurve von Bariumcarbonat. *Suomen Kemistilehti*, B19, 90, 24–26.
- Näsänen R. (1947) Potentiometric study on the first ionization of carbonic acid in aqueous solutions of sodium chloride. *Acta Chem. Scand.* **1**, 204–209.
- Näsänen R., Merilainen P. and Leppanen K. (1961) Potentiometric determination of the solubility product of lead carbonate. *Acta Chem. Scand.* **15**, 913–918.
- Nestaas I. and Terjesen S. G. (1969) The inhibiting effect of scandium ions upon the dissolution of calcium carbonate. *Acta Chem. Scand.* **23**, 2519–2531.
- Parkhurst D. L., Thorstenson D. C. and Plummer L. N. (1980) PHREEQE-A computer program for geochemical calculations. *U.S. Geol. Survey Water Res. Invest.* 80–96. NTIS PB-81 167 801.
- Parkinson W. J. and DeNevers N. (1969) Partial molal volume of carbon dioxide in water solutions. *Ind. Eng. Chem. Fund.* **8**, 709–713.
- Picknett R. G. (1968) Liquid junction potential between dilute electrolyte and saturated potassium chloride. *Trans. Faraday Soc.* **64**, 1059–1069.
- Picknett R. G. (1973) Saturated calcite solutions from 10 to 40°C: A theoretical study evaluating the solubility product and other constants. *Trans. Cave Res. Group Great Britain* **15**, 67–80.
- Plath D. C. and Pytkowicz R. M. (1980) The solubility of aragonite in seawater at 25.0°C and 32.62‰ salinity. *Marine Chem.* **10**, 3–7.
- Plummer L. N. and Mackenzie F. T. (1974) Predicting mineral solubility from rate data: Application to the dissolution of magnesian calcites. *Amer. J. Sci.* **274**, 61–83.
- Plummer L. N. and Sundquist E. T. (1982) Total individual ion activity coefficients of calcium and carbonate in seawater at 25°C and 35‰ salinity, and implications to the agreement between apparent and thermodynamic constants of calcite and aragonite. *Geochim. Cosmochim. Acta* **46**, 247–258.
- Plummer L. N., Jones B. F. and Truesdell A. H. (1976) WATEQF—A FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. *U.S. Geol. Survey Water Res. Invest.* 76–13.
- Read A. J. (1975) The first ionization constant of carbonic acid from 25 to 250°C and to 2000 bar. *J. Solution Chem.* **4**, 53–70.
- Reardon E. J. (1974) Thermodynamic properties of some sulfate, carbonate and bicarbonate ion pairs. Ph.D. Dissertation, The Pennsylvania State Univ.
- Reardon E. J. and Langmuir D. (1974) Thermodynamic properties of the ion pairs MgCO_3^0 and CaCO_3^0 from 10 to 50°C. *Amer. J. Sci.* **274**, 599–612.
- Reardon E. J. and Langmuir D. (1976) Activity coefficients of MgCO_3^0 and CaSO_4^0 ion pairs as a function of ionic strength. *Geochim. Cosmochim. Acta* **40**, 549–554.
- Robinson R. A. and Stokes R. H. (1955) *Electrolyte Solutions*. 2nd edn. (revised) Butterworths, London.
- Robie, R. A., Hemingway, B. S. and Fisher, J. R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pascals) pressure and at higher temperatures. *U.S. Geol. Survey Bull.* **1452**, 456p.
- Rock P. A. and Gordon A. Z. (1976) Determination of Gibbs energies for solid-solid phase transitions in electrochemical double cells without liquid junction: calcite, aragonite and vaterite. *J. Amer. Chem. Soc.* **98**, 2364–2365.
- Ryzhenko B. N. (1963) Determination of dissociation constants of carbonic acid and the degree of hydrolysis of the CO_3^{2-} and HCO_3^- ions in solutions of alkali carbonates and bicarbonates at elevated temperatures. *Geochemistry*, No. 2, 151–164.
- Schloesing T. (1872) Sur la dissolution du carbonate de chaux par l'acide carbonique. *Compt. Rend.* **74**, 1552–1556.
- Segnit E. R., Holland H. D. and Biscardi C. J. (1962) The solubility of calcite in aqueous solutions—I. The solubility of calcite in water between 75°C and 200°C at CO_2 pressures up to 60 atm. *Geochim. Cosmochim. Acta* **26**, 1301–1331.
- Shedlovsky T. and MacInnes D. A. (1935) The first ionization constant of carbonic acid, 0 to 38°C, from conductance measurements. *J. Amer. Chem. Soc.* **57**, 1705–1710.
- Shternina E. B. (1945) Determination of the solubility of calcite in aqueous solutions. *Dokl. Akad. Nauk. SSSR* **50**, 261–264.
- Shternina E. B. and Frolova E. V. (1952) The solubility of calcite in the presence of CO_2 and NaCl . *Izv. Sektor. Fiz-Khim. Anal. Inst. Obshchei Neorg. Kim., Akad. Nauk. SSSR* **21**, 271–287.
- Siebert R. M., Hostetler P. B. and Christ C. L. (1974) Activity-product constants of aragonite at 90°C and 51°C. *U.S. Geol. Survey J. Res.* **2**, 447–455.
- Sipple R. F. and Glover E. D. (1964) The solution alteration of carbonate rocks, the effect of temperature and pressure. *Geochim. Cosmochim. Acta* **28**, 1401–1417.
- Smith R. M. and Martell A. E. (1976) *Critical Stability*

- Constants-Volume 4: Inorganic Complexes*. Plenum Press, N.Y., 257p.
- Staveley L. A. K. and Linford R. G. (1969) The heat capacity and entropy of calcite and aragonite, and their interpretation. *J. Chem. Thermodynamics* **1**, 1-11.
- Stchouzkoy-Maxart T. (1971) Solubility of calcite in water in the presence of carbon dioxide. *Mezhdunar. Geokhim. Kongr.* **4**, 326-337.
- Sweeton F. H., Mesmer R. E. and Baes C. F., Jr. (1974) Activity measurements at elevated temperatures. VII Dissociation of water. *J. Solution Chem.* **3**, 191-214.
- Terjesen S. G., Erga O., Thorsen G. and Ve A. (1961) Phase boundary processes as rate determining steps in reactions between solids and liquids. The inhibitory action of metal ions on the formation of calcium bicarbonate by the reaction of calcite with aqueous carbon dioxide. *Chem. Eng. Sci.* **14**, 277-289.
- Truesdell A. H. and Jones B. F. (1974) WATEQ, A computer program for calculating chemical equilibria of natural waters. *U.S. Geol. Survey J. Res.* **2**, 233-248.
- Turnbull A. G. (1973) A thermochemical study of vaterite. *Geochim. Cosmochim. Acta* **37**, 1593-1601.
- Walker A. C., Bray U. B. and Johnston J. (1927) Equilibrium in solutions of alkali carbonates. *J. Amer. Chem. Soc.* **49**, 1235-1256.
- Weiss R. F. (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chem.* **2**, 203-215.
- Wilhelm E., Battino R. and Wilcock R. J. (1977) Low-pressure solubility of gases in liquid water. *Chem. Rev.* **77**, 219-262.
- Yanat'yeva O. K. (1954) Solubility in the system $\text{CaCO}_3\text{-MgCO}_3\text{-H}_2\text{O}$ at different temperatures and pressures of CO_2 . *Dokl. Akad. Nauk. SSSR* **96**, 777-779.
- Yanat'yeva O. K. (1961) Metastable equilibria in the calcium carbonate-magnesium carbonate water system. *Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk.* 180-182.