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THE SOLUBILITY OF CALCITE IN SODIUM CHLORIDE SOLUTIONS AT HIGH TEMPERATURES

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ABSTRACT. The solubility of calcite has been determined at controlled carbon dioxide pressures in sodium chloride solutions of 0.2, 0.5, and 1.0 molal for temperatures between 120° and 320°C. Recent solubility results for carbon dioxide in water and salt solutions, together with earlier information on calcite solubility in water, have been used to interpret the results. The solubility of calcite in natural hydrothermal solutions was found to be significantly higher than in salt solutions of comparable ionic strength. Complexing of calcium with silica is suspected.

The solubility product for calcite is given for temperatures between 25° to 250° and also the values of the mean activity coefficient for the calcium and bicarbonate ions over the same temperature interval and ionic strengths up to molal.

INTRODUCTION

In connection with the Geothermal Power project at Wairakei, New Zealand, it was necessary to investigate the conditions leading to deposition of calcite in bore pipes passing hot water solutions to the surface from depths of 2000 to 3000 feet.

The solubility of calcite in water has been reported by the author (Ellis, 1959) for temperatures up to 300°C, and in water and calcium chloride solutions up to 200° by Holland, Segnit, and Oxburgh (1960). Holland analyzed the solution in contact with calcite at controlled carbon dioxide pressures, whereas the author's work was based on the loss of weight of a calcite crystal in a closed carbon dioxide-water system. The two sets of results were in good agreement.

Now that information is available on the solubility of carbon dioxide in sodium chloride solutions (Ellis and Golding, 1963), adequate interpretation can be made of a set of results for calcite solubility in salt solutions obtained three years ago. The earlier values for calcite solubility in water (Ellis, 1959) have been recalculated using the improved values for carbon dioxide solubility in water. The corrections to the figures reported previously are small, compared with the accuracy of the calcite solubility method, and range from zero at 100° up to 10 percent at 300°.

From the effect of dissolved salt on the solubility of calcite the mean activity coefficients for the calcium and bicarbonate ions have been calculated for temperatures up to 250° and ionic strengths up to one molal. Values of the thermodynamic solubility product for calcite have been obtained for temperatures up to 300°. The solubility of calcite at 250° in analyzed water samples from drillholes at Wairakei has also been determined and is compared with the values obtained for sodium chloride solutions.

EXPERIMENTAL

The crystal loss of weight method was applied again, using the technique described in the earlier paper (Ellis, 1959). The calcite crystals used were from the sample for which an analysis was reported. After each run it was necessary to boil the crystal in distilled water to remove the adhering salt before the crystal was dried and reweighed. A correction was made for the few micrograms of calcite dissolved in the standardized cleaning procedure. A bomb of volume 104.5 cc at 20° was used, to which was added 50 cc of the salt solution and carbon dioxide to give an initial pressure in the vapor space of 150 psia. The partial pressure of carbon dioxide, p_{CO_2}, which was calculated from the solubility of the gas in the salt solution at a particular temperature, varied with temperature for a given initial mixture in the bomb. The calcite solubility results were corrected to a carbon dioxide partial pressure of 12 atmospheres, making use of the fact that the calcite dissolved was proportional to the cube root of p_{CO_2}.

In the earlier paper the relationship between calcite solubility and carbon dioxide pressure was given

$$[Ca^{++}]^3 = P\,K'_1\,B\,p_{CO_2}\alpha \,/\, 4\,K_2\,\gamma_{\pm}{}^3 \qquad (1)$$

$[Ca^{++}]$ is the solubility of calcite measured as the molal calcium concentration (moles Ca^{++}/1000 g water), $P = (Ca^{++})\ (CO_3'')$ is the activity solubility product, $B = [CO_2]/\alpha\ p_{CO_2}$, K'_1 and K_2 are the first apparent and

TABLE 1

Solubility of calcite in sodium chloride solutions at $p_{CO_2} = 12$ atmospheres (solubilities in millimoles $CaCO_3$/1000 grams H_2O)

	Temperature (°C)	Solubility	Temperature (°C)	Solubility
0.2 m NaCl				
	119	6.50	201	2.17
	126	6.06	205	1.94
	142	5.04	217	1.73
	143	4.81	220	1.74
	154	4.48	228	1.68
	165	3.40	245	1.22
	172	3.32	249	1.19
	176	2.75	251	1.02
	185	2.42	275	0.82
	188	2.71	278	0.67
	197	2.45		
0.5 m NaCl				
	124	7.65	224	2.20
	142	6.12	231	2.19
	161	5.10	255	1.76
	176	4.24	263	1.45
	177	4.11	272	1.41
	204	2.82		
1 m NaCl				
	131	7.78	221	3.00
	137	7.25	223	3.02
	152	6.52	242	2.60
	164	5.74	258	2.17
	174	4.96	274	1.94
	182	4.70	290	1.60
	203	3.94	320	1.40
	218	3.15	322	1.32

second dissociation constants for "carbonic acid", $\gamma_{\pm}$ is the mean ion activity coefficient for the calcium and bicarbonate ions, and α is the fugacity coefficient for carbon dioxide at p_{CO_2} and the temperature. The predicted proportionality between the calcium concentration and the cube root of p_{CO_2} was demonstrated with the earlier solubility results. The proportionality also existed in the results of Miller (1952) for the solubility of calcite in 0.5 m sodium chloride solutions up to 100°, but only where the ionic strength of calcium bicarbonate did not exceed about 0.05 molal.

RESULTS

Water and salt solutions.—Solubility values for calcite are given in table 1 for sodium chloride solutions of 0.2, 0.5, and 1.0 molal, at $p_{CO_2} = 12$ atmospheres, and temperatures between 120° and 320°. Table 2 gives calcite solubilities in carbon dioxide-water solutions recalculated from Ellis (1959), using the improved solubility values for carbon dioxide in water. The changes required are small and do not significantly change the agreement with Holland, Segnit, and Oxburgh's (1960) results.

TABLE 2

Solubility of calcite in water-carbon dioxide solutions at given values of p_{CO_2}. Recalculated from the results of Ellis (1959) using the carbon dioxide solubility values of Ellis and Golding (1963) (solubilities in millimoles $CaCO_3/1000$ g H_2O)

T°C	100	125	150	175	200	225	250	275	300
p_{CO_2} (atm)									
1	2.16	1.42	0.94	0.60	0.40	0.27	0.15	0.08	0.06
4	3.60	2.44	1.58	0.97	0.63	0.39	0.24	0.13	0.09
12	5.55	3.57	2.21	1.44	0.91	0.59	0.36	0.20	0.12
62	—	—	4.05	2.55	1.52	0.89	0.51	0.28	0.14

The results for calcite solubility in water and in salt solutions at $p_{CO_2} = 12$ atmospheres are summarized in figure 1. Miller's results for 0.5 m NaCl solutions interpolate to a value of 8.9 millimoles $CaCO_3$/kg water at this gas pressure and 100°C, which is about 10 percent lower than is indicated by the present results. However, Holland, Segnit, and Oxburgh (1960) showed that Miller's technique of quenching a run caused a tendency for redeposition of calcite on the crystal that would result in low solubilities.

Natural hydrothermal solutions.—The solubility of calcite in natural hydrothermal solutions from drillholes at Wairakei, New Zealand, was determined to test whether the results for salt solutions adequately represented the solubilities in natural solutions of the same ionic strength. The waters used were of similar composition, and typical complete analyses were reported by Ellis (1961). Major ion constituents in ppm were Cl', 2200; SO_4'', 35; F', 7:5; Br', 5.5; Na^+, 1300; K^+, 220; Li^+, 13; Ca^{++}, 10-40; Mg^{++}, 2. Silica as SiO_2 and boric acid as HBO_2 were respectively 600 and 110 ppm, and the pH of the water cooled after collection in the atmosphere was approximately 8.5. The

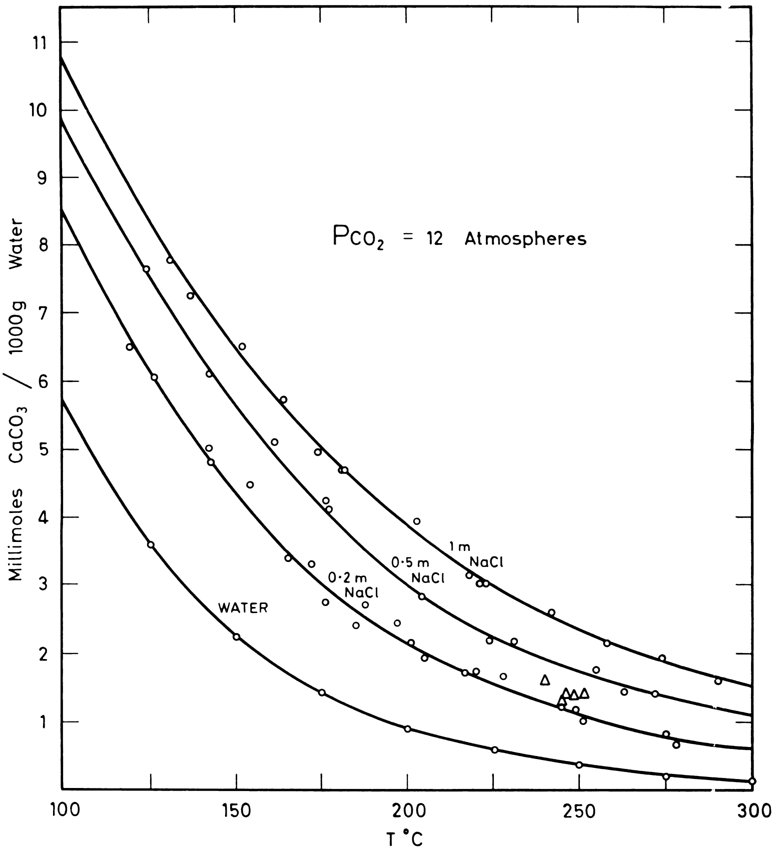

Fig. 1. Solubility of calcite in water and in sodium chloride solutions at a carbon dioxide pressure of 12 atmospheres. Triangles mark solubilities in Wairakei thermal waters (see table 3).

concentration of bicarbonate in the cooled slightly alkaline water ranged from 10 to 50 ppm but, as pointed out by Wilson (1961), in the presence of an appreciable carbon dioxide pressure the bicarbonate concentration is increased by the equivalent of the borate and silicate ions present at room temperatures and pH. This correction amounts to approximately 40 ppm HCO'_3 for waters of the above composition.

Table 3 gives the solubility of calcite at $p_{CO_2} = 12$ atmospheres in five natural thermal waters at about 250°, which is the temperature of the underground water tapped by the drillholes at Wairakei. To obtain the product $[Ca^{++}]\ [HCO'_3]^2 = C$, the calcium and bicarbonate concentrations resulting from solution of the calcite crystal in the thermal waters were added to the natural concentrations of these ions. For a given p_{CO_2} and temperature, C is a constant for a given solvent, and for calcite solution in pure water or sodium chloride solutions $C = [Ca^{++}]^3$. The solubilities, $C^{1/3}$ in table 3, have been included in figure 1 as points marked with triangles.

TABLE 3

Solubility of calcite in natural thermal waters
(concentrations in millimoles/1000g water)

Drillhole No. Water Source	T°C	Corrected Natural $[HCO'_3]$	Natural $[Ca^{++}]$	Solubility of $CaCO_3$	$[Ca^{++}]\,[HCO'_3]^2 = C$	$C^{1/3}$	p_{CO_2}	$C^{1/3}$ at p_{CO_2} 12 atm
18	248	0.97	0.52	0.45	3.4	1.5	15.9	1.4
20	251	1.00	0.25	0.59	4.0	1.6	16.0	1.4
28	240	1.39	0.37	0.55	5.7	1.8	15.6	1.6
40	246	1.10	0.60	0.39	3.5	1.5	15.8	1.4
67	245	1.13	0.33	0.41	2.8	1.4	15.8	1.3

The solubility values are higher than expected for a sodium chloride solution at a comparable ionic strength of about 0.06. The true value of the bicarbonate ion concentration in the waters at 250° is rather uncertain, but a slight excess solubility is still found if the bicarbonate values as analyzed, which are definitely too low, are used in the calculation. The interaction of calcium with silica, which is present at ten times the molal calcium concentration, possibly accounts for the extra solubility. To obtain a more accurate expression for calcite solubility in natural hydrothermal solutions silica should be considered as a separate variable.

ACTIVITY COEFFICIENTS FOR CALCIUM BICARBONATE SOLUTIONS

From equation (1)

$$[Ca^{++}] = \frac{n}{\gamma_\pm}(B\,\alpha\,p_{CO_2})^{1/3} = \frac{n'}{\gamma_\pm}\left(\frac{p_{CO_2}'\alpha}{K}\right)^{1/3} \qquad (2)$$

n and n′ are constants for a given temperature and K is the Henry's Law gas solubility constant expressed in terms of atmospheres/moles CO_2 per 1000 g H_2O. At constant temperature the following relationship applies:

$$\log\left[\frac{Ca}{Ca'}\right] = \log\frac{\gamma_\pm'}{\gamma_\pm} + \tfrac{1}{3}\log\frac{K'\,\alpha\,p_{CO_2}}{K} \qquad (3)$$

The primed quantities are those in absence of added salt at a partial pressure of carbon dioxide of one atmosphere where α can be taken as unity.

$$\text{If } \log\left[\frac{Ca}{Ca'}\right] + \tfrac{1}{3}\log\frac{K}{K'\,p_{CO_2}\,\alpha} = \log\frac{\gamma_\pm'}{\gamma_\pm} \qquad (3a)$$

is plotted against the square root of ionic strength $\mu^{1/2}$ (where μ is the molality NaCl + 3 times molality of $Ca(HCO_3)_2$), it is possible to make a short extrapolation to $\mu = 0$ and obtain values of $\gamma_\pm$ relative to $\gamma_\pm = 1$ at infinite dilution. This has been done in figure 2. For each salt concentration and carbon dioxide pressure the appropriate value of K from Ellis and Golding (1963) was used together with values of α calculated by Majumdar and Roy (1956).

The curve representing $\log \frac{\gamma_\pm'}{\gamma_\pm}$ versus $\mu^{1/2}$ at each temperature fitted smoothly at low concentrations to the limiting slope predicted by the simple

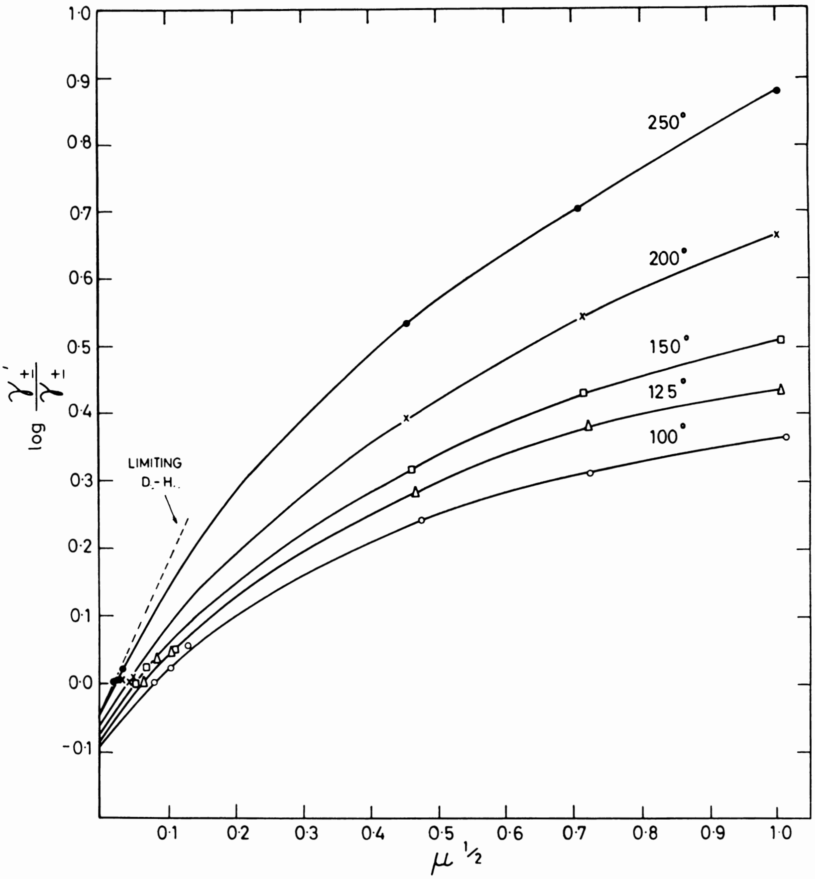

Fig. 2. Extrapolation of values of $\log\frac{\gamma'_\pm}{\gamma_\pm}$ to zero ionic strength. Dotted line shows limiting slope predicted for a 2-1 electrolyte in water at 250° by the Debye-Hückel equation.

Debye-Hückel equation for 2-1 electrolytes, $\log \gamma_\pm = -2A\,\mu^{1/2}$. A is a constant related to the temperature and the dielectric constant of the solvent, and for water has the values 0.606 at 100° and 1.12 at 250°. The limiting Debye-Hückel slope for 250° is shown as a dotted line on figure 2.

The graph reaches the limiting Debye-Hückel slope at ionic strengths of about 10^{-3}m. Similar behavior was found by Stoughton and Lietzke (1960) in a study of silver sulphate solubility at high temperature in the presence of added salts. Figure 3 gives the variation of $\gamma_\pm$ with $\mu^{1/2}$ for a range of temperatures. Previous values of $\gamma_\pm$ for calcium bicarbonate in sodium chloride solutions at 25° by Frear and Johnson (1929) follow the trend of the present results at high salt concentrations. At low ionic strengths their values are high in relation to the present set of activity coefficients, and the limiting Debye-Hückel law is not obeyed.

SOLUBILITY PRODUCT FOR CALCITE

From knowledge of the variation of $\gamma_{\pm}$ with concentration at a particular temperature the values of y′ were calculated from the solubility results for calcite in CO_2-water solutions.

$$y' = [Ca^{++}]^3 \gamma_{\pm}^3/\alpha\, p_{CO_2} = P\, K_1'/4K\, K_2 \qquad (4)$$

Table 4 gives the mean values of y′ and the calculated values for P assuming that the ratio K_2/K_1', which is equal to about 1.25×10^{-4} at 100°, remains constant up to 250° (Ellis and Fyfe, 1957). K was taken from Ellis and Golding (1963). y′ was approximately constant for p_{CO_2} equal to 1, 4, and 12 atmospheres, but the 62 atmosphere results tended to be low.

TABLE 4

Solubility product for calcite

T°C	25°	100°	125°	150°	200°	250°
$10^{10}y'$ (moles^3 liters^{-3} atm^{-1})	3900	52	16	4.8	0.42	0.024
K (atm kg moles^{-1})	29	93	109	119	115	95
10^{11} P	480*	24	8.7	2.9	0.24	0.011
ΔG°_s (kcal/mole)	11.3	16.4	18.3	20.4	25.2	31.0

* From Frear and Johnston (1929)

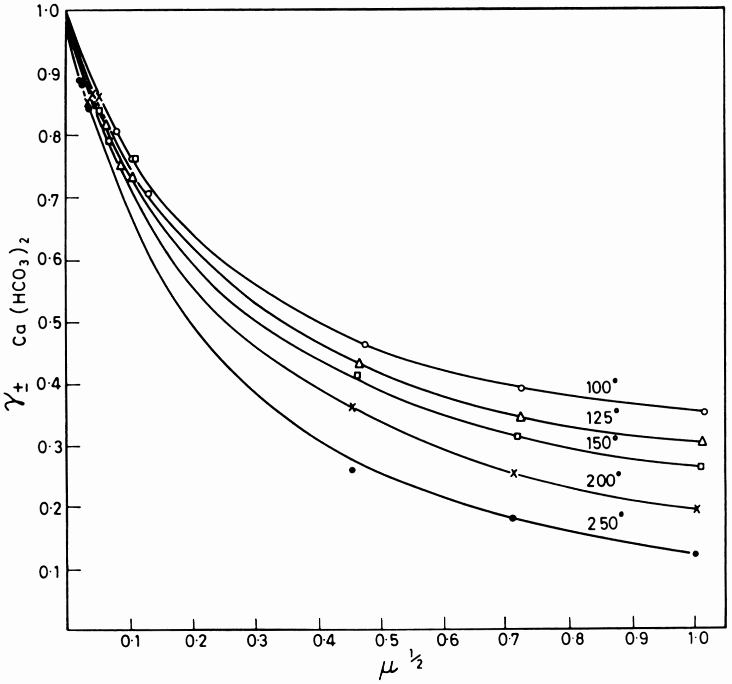

Fig. 3. Values of the mean activity coefficient $\gamma_{\pm}$ for calcium bicarbonate solutions for ionic strengths up to 1 molal and temperatures between 100° and 250°.

APPLICATION OF RESULTS

The results were used by the author (1959) to examine the possibility of calcite precipitation from natural hot water rising to the surface in a bore pipe and separating into a mixture of steam and water. A comparison of the calcite precipitating tendency for three N.Z. hydrothermal systems was given recently (Ellis, 1961) using analytical information from the complete steam and water discharges from drillholes.

It is also of interest to see whether in a closed system calcite could be deposited during the cooling to atmospheric temperature (20°) of a hot liquid initially saturated with calcite. An example will be taken of a sealed rock cavity, completely filled with the saturated liquid at an elevated temperature. In a salt solution at any temperature from equation (4)

$$[Ca^{++}]\ [HCO'_3]^2 = y'\ \alpha\ p_{CO_2}\ /\gamma_{\pm}{}^3$$

$$\text{or, } [Ca^{++}]\ [HCO'_3]^2 = y'\ [CO_2]\ K/\gamma_{\pm}{}^3$$

A vapor phase appears when the liquid in the cavity is cooled, and the concentration of carbon dioxide in the liquid phase and the value of p_{CO_2} can be calculated from available solubility information for carbon dioxide. At constant p_{CO_2} the solubility of calcite falls with increasing temperature both in water and in molal sodium chloride solution. As this trend shows no sign of reversing at higher salt concentrations, the increase in $\gamma_{\pm}{}^3$ with decreasing temperature for a given solution is never as great as the corresponding increase in y′. Any calcite precipitation must result from a lowering of carbon dioxide pressure in the system. For the formation of a vapor phase on cooling the concentration of carbon dioxide in the liquid is given by the expression

$$[CO_2]^{20}/[CO_2]^T = \frac{\lambda\ \rho^T/\rho^{20}}{1-(\rho^T/\rho^{20})\ (1-\lambda)}$$

λ is the Ostwald was solubility coefficient at 20°, and at appreciable carbon dioxide pressures $\lambda = \lambda^\circ \alpha z$, where λ° is the limiting distribution coefficient at low gas pressures. Sweigert, Weber, and Allen (1946) gave values of the compressibility factor z over a wide range of pressures and temperatures.

At low gas pressures where α and z are approximately unity, the carbon dioxide pressure falls on cooling to 20° by a factor that rises to a maximum of about five for an intial temperature of 175°, the temperature where K is a maximum. This factor is similar for water and the salt solutions. The comparable increases in calcite solubility in the temperature interval 175° to 20° expressed as the product $[Ca^{++}][HCO'_3]^2$ are by factors of 5200 for water and 450 for molal salt solution. There is no temperature interval over which the decrease in solubility due to lowering of gas pressure outweighs the increase in calcite solubility with falling temperature.

At high gas pressures the low values of the fugacity coefficient α and compressibility factor z at 20° cause $[CO_2]^{20}/[CO_2]^T$ and $p_{CO_2}{}^{20}/p_{CO_2\,T}$ to be lower than for the previous example. For $p_{CO_2} = 50$ atmospheres at 20° the value of αz is about 0.4. This is still not sufficient to reverse the solubility behavior over any temperature interval at the salt concentrations that were examined.

The effects of higher salt concentrations and of the complexing action of calcite with silica, for example, remain to be investigated, but loss of carbon dioxide from the system seems to be the usual mechanism for calcite deposition with decreasing temperature in natural hydrothermal fluids.

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