The results obtained are satisfactorily explained by a reaction mechanism based upon a dissociation of the primarily excited molecule as a primary process and not one involving an activated molecule. Agreement is obtained if the dissociation is either into N_2H_3 and H or $2NH_2$. Thermal calculations for the various primary and secondary processes discussed are given. The nature of the absorption spectrum is in accord with such a mechanism if the idea of Bonhoeffer and Farkas be accepted.

PRINCETON, NEW JERSEY

THE SOLUBILITY OF CALCIUM CARBONATE (CALCITE) IN CERTAIN AQUEOUS SOLUTIONS AT 25°[1]

BY G. L. FREAR[2] AND JOHN JOHNSTON

The solubility of calcium carbonate in aqueous solutions, as influenced by the partial pressure of carbon dioxide in the system and by the presence of other salts, is of interest because of its significance in relation to the problem of scale formation in steam boilers and pipes, to the study of bone calcification and of blood equilibria in physiological systems, and to a better understanding of the process of deposition of carbonates under geological conditions. The work to be presented comprises precise determinations of the solubility of calcite at 25° in the presence of carbon dioxide at pressures varying from 0.0003 to 1.0 atmosphere, in water and in a series of solutions of sodium chloride and of calcium sulfate, including solutions saturated also with respect to gypsum ($CaSO_4 \cdot 2H_2O$).

The papers on the solubility of calcium carbonate in water, prior to 1915, have been reviewed in an earlier paper;[3] since that time a number of other contributions have been published.[4] A plot of all of the data,

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[1] From the dissertation presented by G. L. Frear to the Graduate School of Yale University, June, 1926, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1925–1926; Sterling Fellow, 1926–1927.

[3] Johnston, THIS JOURNAL, 37, 2001 (1915).

[4] (a) Cavazzi, Gazz. chim. ital., II 46, 122 (1916); solubility of $CaCO_3$ in water at 0–15° and 1 atm. of CO_2; (b) Bäckström, Z. physik. Chem., 97, 179 (1921), solubility of calcite and aragonite at 9, 25 and 35° and approximately 1 atm. of CO_2; see also Bäckström, THIS JOURNAL, 47, 2432, 2443 (1925); (c) Mitchell, J. Chem. Soc., 123, 1887 (1923), solubility of calcite, and of calcite with nesquehonite ($MgCO_3 \cdot 3H_2O$), at 25° and 4–24 atm. of CO_2; (d) Haehnel, J. prakt. Chem., 107, 165 (1924), solubility of $CaCO_3$ in water at 18° and 10–56 atm. of CO_2, and up to 50° at 56 atm.; (e) Hastings, Murray and Sendroy, J. Biol. Chem., 71, 723 (1927), solubility of $CaCO_3$ at 38° in some solutions of NaCl and in serum; (f) with respect to the three crystal forms of $CaCO_3$, see Johnston, Merwin and Williamson, Am. J. Sci., 41, 473 (1916); Gibson, Wyckoff and Merwin, Am. J. Sci., 10, 325 (1925); (g) W. D. Kline, "Dissertation," Yale University, 1923.

including Kline's results (presented later, in Table III), leads to the following values.[5]

TABLE I

THE SOLUBILITY OF CALCITE AT 25°

CO_2, partial pressure, atm.	0.00032	0.001	0.01	0.1	1.0	10
$CaCO_3$, millimoles per kilo water	0.53	0.78	1.7	3.9	9.0	22.5

The temperature coefficient of the solubility is, within the accuracy of the measurements, independent of the partial pressure of carbon dioxide, particularly in the range 0.0003–1 atm.; consequently it suffices to give the ratio r of the solubility at $t°$ to that at 25°.

TABLE II

THE RATIO (r) OF THE SOLUBILITY AT $t°$ TO THAT AT 25°

t	0°	10°	20°	25°	30°	50°
r	1.8	1.4	1.1	1.0	0.9	0.6

These values of r are on the line $\log r = 830/T - 2.78$; this formula, when extrapolated to 100°, yields results in harmony with analyses of waters from boilers.

In presenting our results we shall adopt a notation made use of in a previous paper,[6] dealing with equilibrium in solutions of alkali carbonates in terms of activities. The activity of carbonic acid (H_2CO_3)[7] may be written

$$(H_2CO_3) = \gamma\lambda cP \qquad (1)$$

where P is the partial pressure, in atmospheres, of carbon dioxide in the gas phase in equilibrium with the solution; c is the total molal concentration of carbon dioxide in the solution when P is unity and γ and λ are the activity coefficients of H_2CO_3 and of water, respectively. We also write

$$(H^+)(HCO_3^-)/(H_2CO_3) = K_1$$
$$(H^+)(CO_3^-)/(HCO_3^-) = K_2$$
$$(Ca^{++})(CO_3^-) = K_C$$

K_C being the activity product constant for calcium carbonate (calcite); whence by combination with (1)

$$(Ca^{++})(HCO_3^-)^2/P = \gamma\lambda cK_CK_1/K_2 \qquad (2)$$

If α_1 and α_2 denote the activity coefficients of Ca^{++} and HCO_3^-, respectively, and m_1 and m_2 the corresponding molalities, Equation 2 may be written

$$P/m_1m_2^2 = \alpha_1\alpha_2^2(K_2/(K_1K_C\gamma\lambda c)) = f'(m) \qquad (3a)$$

Determinations, in a series of equilibrated solutions, of the quantities P, m_1 and m_2 enable one to calculate directly the corresponding value of the function $f'(m)$. Equation 3a may be more conveniently expressed

[5] With respect to the solubility at smaller pressure, see Johnston and Williamson, THIS JOURNAL, **38**, 975 (1916).

[6] Walker, Bray and Johnston, *ibid.*, **49**, 1235 (1927).

[7] Parentheses denote an activity; brackets, a concentration.

in terms of the mean molality m and the mean activity coefficient α of $Ca(HCO_3)_2$. By definition $m = \sqrt[3]{m_1 m_2^2}$ and $\alpha = \sqrt[3]{\alpha_1 \alpha_2^2}$. It follows that

$$P^{1/3}/m = \alpha \sqrt[3]{K_2/(K_1 K_C \gamma \lambda c)} = f(m) \tag{3}$$

The function $f(m)$ contains a factor $K_2/K_1 K_C$ independent of concentration; as m and P approach zero, α_1 and α_2 by definition approach unity; when $m_1 = 0$, c_0 is the solubility of carbon dioxide in water and we have $c_0 \gamma_0 \lambda_0 = c \gamma \lambda$. Thus by plotting $f(m)$, evaluated directly from the experimental results, against the concentration, we are enabled to estimate $f(0)$, the value of $f(m)$ obtained by extrapolation to zero concentration of salt and, since $(\alpha_1 \alpha_2^2)_m/(\alpha_1 \alpha_2^2)_0 = f(m)/f(0)$, by substitution of the appropriate values of the other factors, to calculate, from the intercept $f(0)$, the actual solubility product of calcite applicable at any pressure within the range of solutions investigated if the assumption is made that $(\alpha_2)_0$ is equal to unity, which probably is not seriously in error and is the best approximation than can be made at the present time. In this connection it is important to note that at very small pressures of CO_2, probably of the order of 10^{-14} atm.,[5] the relative amount of Ca^{++} associated with OH^- so far exceeds that present in solution as carbonate and bicarbonate that $Ca(OH)_2$ becomes the stable solid phase in place of $CaCO_3$; thus $f(0)$ is merely a virtual quantity, but this fact does not diminish its significance or interfere with the process of extrapolation.

If, besides calcite, gypsum is in equilibrium with the solution, the additional solid phase imposes the further condition defining the solubility product of gypsum K_G, *i. e.*,

$$(Ca^{++})(SO_4^-) = K_G$$

By combination of this condition with relations similar to those developed above, and correcting for incomplete ionization, Stieglitz[8] calculated the saturating concentration of calcium carbonate and of calcium sulfate in sea water as functions of the partial pressure of CO_2 in the atmosphere. Provided that no change in the nature of the solid phases occurs, the equality of the ratios must be valid

$$(CO_3^-)/(SO_4^-) = K_C/K_G \tag{4}$$

However, there is some mineralogical evidence of the possibility of reaction between $CaSO_4$ and $CaCO_3$ (possibly as aragonite) under appropriate conditions with the formation of a solid solution or a double salt, in which event deviations from Equation 4 are to be expected. Thus Doss[9] found that certain fresh water limestones and tuffs contain appre-

[8] J. Stieglitz, "The Relation of Equilibrium between the Carbon Dioxide of the Atmosphere and the Calcium Sulfate, Calcium Carbonate, and Calcium Bicarbonate in Water Solutions in Contact with It" in "The Tidal and Other Problems" by T. C. Chamberlin, *et al.* Carnegie Inst. Publ. No. 107 (1909).

[9] B. Doss, "Neues Jahrbuch für Mineralogie und Geologie," **1897,** Vol. I, p. 105.

ciable quantities of sulfate and of water in proportions approximately equal to their ratio in pure gypsum; the inclusions visible at 2000 diameters' magnification accounted for not more than one-twentieth of the sulfate present. Vater[10] prepared calcite crystals in gypsum solutions and observed that they possessed a high sulfate content which he thought could not be attributed to inclusions of the mother liquor or to ingrown crystals of gypsum.

Little information for the solution of this problem is to be obtained from the results of Shipley and McHaffie[11] in their attempt to investigate, by means of electrometric titration, the influence of calcium sulfate on the hydrogen-ion concentration of carbonate solutions; failure to recognize the interdependence of the equilibria involved in this system led these authors to the unwarranted conclusions that the ionization constants of carbonic acid vary and that alkaline earth bicarbonates do not exist in aqueous solutions.

In unsaturated solutions of $CaSO_4$, the solubility of $CaCO_3$ depends upon the common ion effect and upon the influence of the total ion concentration on the activities of the chemical species involved in the equilibrium. Solubility determinations in solutions of hetero-ionic salts are of interest for the study of the influence of ionic strength on these activities. At best the data of Cameron and his co-workers[12] and of Seyler and Lloyd[13] are of merely qualitative significance as experimental conditions were insufficiently controlled.

The Solubility of Calcite in Water at 25°.[14]—Mixtures of air and carbon dioxide in fixed proportions[15] were passed through reaction flasks, of the type used for the equilibration of solutions of alkali carbonates,[6] containing calcite crystals in contact with conductivity water. After equilibrium had been attained, the partial pressure of carbon dioxide and the total molality of base in solution[16] were determined; the mean results are assembled in the first two columns of Table III. The third column gives the bicarbonate molality $[HCO_3^-]$; the fourth, the ionic strength $\mu = (2[Ca^{++}] + 2[CO_3^{--}] + \frac{1}{2}[HCO_3^-])$; and the last, the function $f(m) = P^{1/3}/m$. The bicarbonate molality was arrived at by deducting from the calcium molality $[Ca^{++}]$ an amount equivalent to the carbonate molality $[CO_3^{--}]$, that of hydroxyl $[OH^-]$ being negligible at the partial pressure of carbon dioxide in these experiments. The correction, which in no case exceeds 2%, may be estimated with sufficient accuracy by introducing into Equation 3 the extrapolated value of $\gamma \lambda_c K_1/K_2$ (which is 310)[6] and the activity coeffi-

[10] Vater, *Z. Krist.*, **21**, 460 (1893).

[11] Shipley and McHaffie, *J. Soc. Chem. Ind.*, **42**, 310T, 321T (1923).

[12] Cameron, Bell and Robinson, *J. Phys. Chem.*, **11**, 414 (1907); Cameron and Robinson, *ibid.*, **11**, 577 (1907).

[13] Seyler and Lloyd, *J. Chem. Soc.*, **95**, 1347 (1909).

[14] Experimental work by Dr. W. D. Kline.

[15] For the method of preparation and analysis of such mixtures, see Johnston and Walker, THIS JOURNAL, **47**, 1807 (1925).

[16] See Johnston, *ibid.*, **38**, 947 (1916); Walker, Bray and Johnston, *ibid.*, **49**, 1235 (1927).

cient of $MgSO_4$ and of $Ba(IO_3)_2$[17] as approximations to that of $CaCO_3$ and $Ca(HCO_3)_2$ at corresponding ionic strengths; when P exceeds 0.01, the correction is less than the experimental uncertainty in the determination of total base, and so may be neglected. The results so calculated are, we venture to believe, more reliable than any hitherto available.

TABLE III

EXPERIMENTAL REDETERMINATIONS (BY W. D. KLINE) OF THE SOLUBILITY OF CALCITE IN WATER AT 25°

Partial press. of CO_2, atm., P	Calcium mol., mml./ kilo H_2O, 1000 [Ca^{++}]	Bicarb. mol., mml./ kilo, H_2O, 1000 [HCO_3^-]	Ionic strength μ	Log $f(m) =$ log $P^{1/3}/m$
0.00031	0.52	1.02	0.00157	1.9194
.00038	0.56	1.10	.00169	1.9162
.00093	0.76	1.50	.00229	1.9119
.00334	1.17	2.32	.00352	1.9082
.00690	1.51	3.01	.00454	1.9009
.0160	2.01	4.01	.00603	1.8983
.0432	2.87	5.74	.00861	1.8866
.1116	4.03	8.06	.01209	1.8766
.9684	8.91	17.82	.02673	1.8448

The Solubility of Calcite in Aqueous Solutions of Calcium Sulfate and of Sodium Chloride.—Calcite for the following experiments was prepared by adding dropwise with constant stirring a solution of ammonium bicarbonate to a purified solution of calcium chloride; after the precipitation had been completed, ammonium chloride was added and the mixture was stirred continuously for several hours at 80°. The product after thorough washing was heated in a Rose crucible in a stream of carbon dioxide to remove any remaining traces of ammonium salts. Examination with a petrographic microscope showed crystals of calcite ranging in average dimensions from 0.01 to 0.1 mm.

Natural gypsum, the analysis of which indicated a high purity, was split into small blocks, the fine particles being removed by screening. Sodium chloride was recrystallized from commercial "c. p." stock.

In all of the experiments conducted at roughly one atmosphere of carbon dioxide the procedure employed was very similar to that outlined in the preceding section. In the earlier experiments with lower partial pressures of carbon dioxide, equilibrium was established by causing a motor-driven circulating pump, consisting of mercury valves with a mercury column as piston, to pass a mixture of air and carbon dioxide continuously around a closed glass system consisting of a one-liter pyrex glass reaction flask in series with a group of gas-sampling pipets in parallel with one another. In order to avoid rubber connections, the various parts of the system were joined to one another through mercury seals. The reaction flask was clamped in an air thermostat maintained at a temperature of $25 \pm 0.05°$. The approach to equilibrium was observed by analyzing the gas phase at intervals; ordinarily a week was allowed for the system to attain equilibrium.

As the circulating system just described did not establish equilibrium so rapidly as had been anticipated, and as the arrangement for sampling was not quite satisfactory, a different form of apparatus (Fig. 1) was devised and used in the later work. The

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[17] As given by Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 344, 375.

purpose of this device is to cause the solution to pass repeatedly back and forth through a filter containing the solid phase so that the movement of the liquid provides the pump action for circulating the gas. The two 200-cc. bulbs (A, A') are joined to a short neck B into each end of which is sealed a perforated glass plate to serve as a partition preventing any of the solid phase from passing into either bulb. Midway between the plates the neck is provided with a wide glass-stoppered side-tube for introducing the crystals of the saturating solute and, if necessary, the wads of cotton to act as filters.[18] Sealed through the ends of the bulbs, Tubes D and D' are connected by ground-glass joints with the opposite ends of Pipet C, which is provided with suitable stopcocks for isolating a sample of the gas phase. A cam, driven by an electric motor through a train of speed reducers and connected to the equilibrium apparatus through suitable gearing, causes the apparatus to turn from an initially vertical posicion through a half revolution, to remain upright long enough to allow most of the solution to filter from one bulb to the other and then to return to its original position, where there is another pause before the cycle is repeated. Intermittent oscillation is employed in preference to interrupted rotation as it permits the apparatus to be mounted so that the cylindrical axis of the pipet never occupies a lower level than the solution in the bulbs; thus the danger of blocking the passage of the gas to and through the pipet with solution is avoided. The gas displaced from the lower bulb by the inflowing solution forces an equal volume to bubble from the pipet into the solution in the upper bulb through the upturned tips of Tubes D, D'. This combination of filtration and bubbling affords ample contact of the liquid with the solid and the gas phases without danger of pulverizing the crystals. Trial experiments with calcite at various partial pressures of carbon dioxide indicated that equilibrium conditions are attained in two to three days when the volume of the solution is 100 cc., the weight of calcite is 2 g. and filtration is in progress

Fig. 1.—Equilibration apparatus.

four minutes of the five in each cycle. The apparatus may be conveniently mounted in a water thermostat. At the end of a run the motion is stopped so as to allow the solution to run completely into the bulb A', the stopcocks on the pipet are closed and the apparatus is removed bodily from the thermostat. The pipet is then disconnected at the ground joints and samples of the equilibrium solution are allowed to run through Stopcock E into tared glass-stoppered flasks containing known weights of standard hydrochloric acid. The stopcock, E, permits regulation of the sample size so as to bring the contents of the titration flasks nearly to the end-point. Owing to the strong tendency of calcium bicarbonate solutions to remain supersaturated when not in contact with solid $CaCO_3$, there is little opportunity for the solution to change in concentration while the samples are being withdrawn.
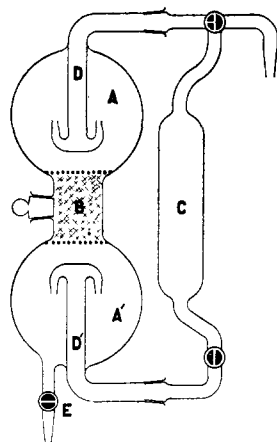
The data in Table IV were obtained from runs of three or four days' duration. The partial pressure of carbon dioxide in the gas phase was determined by measuring the volume of gas before and after absorption in potassium hydroxide solution; from the known capacity of the pipet

[18] When the crystals of the saturating solute are sufficiently large, the cotton may be dispensed with so as to avoid delay in the attainment to equilibrium from absorption effects.

the partial pressure of carbon dioxide could then be computed. The total base content of the solution was then determined in duplicate samples by the customary method except that care was taken to saturate the titrated solution with carbon dioxide gas immediately prior to the addition of the final few drops of standard reagent, the purpose of this precaution being to avoid difficulty in case the carbon dioxide liberated in the titration should be insufficient completely to saturate the mixture. For the determination of sulfate concentrations, precipitation as barium sulfate according to the directions of Johnston and Adams[19] was employed. Sodium chloride concentrations were determined by analysis for chloride either gravimetrically or volumetrically with ammonium thiocyanate and silver nitrate.

The results of the experiments on the solubility of calcite in saturated and in unsaturated calcium sulfate solutions are given in Table IV, which does not include the less precise results secured by means of the mercury circulating pump method except at partial pressures of carbon dioxide under which no corresponding measurements by the improved method were made. The first three columns list the mean experimental determinations of the partial pressure of carbon dioxide in atmospheres and the coexisting molalities of calcium bicarbonate and of calcium sulfate, re-

TABLE IV

ANALYSES OF SOLUTIONS SATURATED WITH BOTH CALCITE AND GYPSUM AT 25°

Partial press., of CO_2, atm., P	Bicarb. mol. mml./kilo H_2O $1000[Ca(HCO_3)_2]$	Sulfate mol. mml./kilo H_2O $1000[CaSO_4]$	μ	$\operatorname{Log} f(m)$
0.121[a]	3.11	14.43	0.0671	1.750
.167[a]	3.56	14.24	.0676	1.756
.270	4.34	13.99	.0690	1.764
.431	5.31	13.48	.0698	1.770
.598	6.22	13.25	.0717	1.766
.652	6.42	13.27	.0723	1.768
.728[a]	6.71	13.41	.0738	1.767
.770[a]	6.95	13.46	.0747	1.764
.897[a]	7.40	13.60	.0766	1.763
.916[a]	7.53	13.41	.0762	1.762
.957	7.51	13.20	.0753	1.770
.963	7.55	13.20	.0754	1.769
.960	7.55	12.98	.0748	1.771
.953	7.58	13.17	.0754	1.767
.966	7.85	8.51[b]	.0576	1.793
.962	8.30	4.13[b]	.0414	1.816

[a] By mercury circulating pump method. The uncertainty in these measurements proves to be in the sulfate rather than in the carbonate concentration; the reason for this is not clear.

[b] Not saturated with respect to gypsum.

[19] Johnston and Adams, THIS JOURNAL, 33, 829 (1911).

spectively; the fourth column gives the ionic strength; and the last column contains the values of log $f(m)$ where, as before, $f(m) = P^{1/3}/m$, both experimentally determined.

In Table V are brought together, likewise, the best results of the solubility determinations on calcite in sodium chloride solutions. In most of these experiments the method used was to bubble a stream of carbon dioxide through the salt solution in contact with calcite crystals; the oscillating equilibration apparatus, which was developed later, was employed in the single experiment indicated by the asterisk. A number of results for more concentrated salt solutions than are shown in Table V have not been included because, apparently, complete equilibrium was not attained in spite of the fact that a period of a week was allowed before the final sample was taken. This slowness was especially noticeable in the more concentrated salt solutions, and consequently these results are less concordant. The experimental procedure offers less likelihood of supersaturation than of incomplete saturation, so that the points indicating higher solubility are apparently the more reliable; the single result obtained with the improved form of apparatus is in conformity with this view. The work of Cameron Bell and Robinson[12] indicates a higher solubility than we have observed; their method, however, offers some possibility of supersaturation and their solid phase may not have been pure calcite which, being the most stable, is the least soluble of the three forms of calcium carbonate.

TABLE V

SOLUBILITY OF CALCITE IN SODIUM CHLORIDE SOLUTIONS AT 25°

Partial press. of CO_2, atm., P	Bicarb. mol. mml./ kilo H_2O $1000[Ca(HCO_3)_2]$	Chloride mol. mml./ kilo H_2O $1000[NaCl]$	μ	Log $f(m)$
0.965	8.96	3.79	0.0307	1.842
.965	9.37	14.8	.0429	1.822
.965	9.67	34.8	.0638	1.809
.962	10.70	82.8	.115	1.764
.958	12.41	236	.273	1.699
.963	12.34	297	.334	1.703
.953	14.73	599	.643	1.624
.968	14.67	816	.860	1.628
.955*	15.55	878	.925	1.601
.953	14.55	1089	1.133	1.630
.968	16.18	1154	1.203	1.585

Discussion of Results

The last column of Table III shows again that the concentration of calcium bicarbonate in solution varies roughly as the cube root of the partial pressure of carbon dioxide through the range investigated. Indeed a plot of $[Ca(HCO_3)_2]$ against $P^{1/3}$ is the most convenient method of

interpolating to ascertain the solubility of calcite at any pressure of carbon dioxide, the graph being nearly linear. When this is done for the data in Table III and IV, we obtain the results listed in Table VI; it also gives, in the fifth column, the saturation concentration $[CaSO_4]$ which diminishes as P, and hence $[Ca(HCO_3)_2]$ increases.

TABLE VI

COMPARISON OF SOLUBILITY OF CALCITE IN WATER AND IN SOLUTIONS SATURATED ALSO WITH GYPSUM, AT A SERIES OF VALUES OF P

		Solubility (millimoles per kilo) of			
		Calcite in		$CaSO_4$ in	
$P^{1/3}$	P	H_2O s	$H_2O-CaSO_4$ s'	$H_2O-CaCO_3$ s''	$s's''/s$
0.5	0.125	4.21	3.16	14.35	10.8
.6	.216	5.13	3.97	14.10	10.9
.7	.343	6.08	4.80	13.83	10.9
.8	.528	7.06	5.76	13.53	11.0
.9	.729	8.04	6.72	13.22	11.1
1.0	1.000	9.02	7.70	12.91	11.0

In order to compare the influence of a change in P upon the solubility of calcite in water and in a calcium sulfate solution of constant concentration, we must make some allowance for the change in the latter which actually occurs when the solution is in contact with solid gypsum. This we have done by computing the quotient in the last column of Table VI; its degree of constancy proves that, for any value of P within this range, the ratio of solubility of calcite in a (dilute) salt solution of constant concentration to that in water is independent of the partial pressure of carbon dioxide. That this is valid follows from Equation 2, for by setting up the corresponding expression for a definite salt solution, and dividing one by the other, we find the ratio of solubilities to be equal to a quotient of corresponding activity coefficients, and this quotient we would expect to be, in general, independent of P. In other words, the solubility of calcite in a given salt solution, if measured at a single partial pressure of carbon dioxide, may readily be calculated for any other pressure through the corresponding slope of the curve in water alone. For this reason we did not trouble to make measurements in sodium chloride solutions except at a single pressure; Table V shows that the influence of salt concentration is very marked, the solubility in 1 molal sodium chloride being practically double that in absence of the salt.

The experimental data are also conveniently treated on the basis of the function $f(m)$. Equation 3 may be written

$$\log f(m) = \log \alpha + \tfrac{1}{3} \log (K_2/K_1\gamma\lambda c) - \tfrac{1}{3} \log K_C$$

where it is evident that $f(m)$ varies directly as α, since the other terms are constant. As the activity coefficient α is dependent upon the ionic strength, it is of interest to plot the several experimental values of $\log f(m)$ against the square root of the ionic strength; when this is done, the lines

for the calcium sulfate and sodium chloride solutions converge to, and then coincide with, the line representing the solubility in absence of other salts.

The value of $f(0)$, derived by extrapolation of this curve to zero ionic strength, is 87.5 ± 0.5. From Equation 3, since α is now virtually unity, $f(0) = (K_2/K_1\gamma\lambda c)^{1/3} (1/K_C)^{1/3} = (\varphi_0)^{1/3}(1/K_C)^{1/3}$; the value of the first factor φ_0 is, from the work of Walker, Bray and Johnston,[6] 310, and therefore K_C, the solubility product constant of calcite in terms of activities is 4.82×10^{-9} at $25°$. The difference between this value and that calculated by McCoy and Smith[20] (9.3×10^{-9}), by Osaka[21] (7.24×10^{-9}) and by Mitchell[4c] (5.88×10^{-9}) is attributable to the different values assumed for the constants and coefficients in the first factor in the equation above.

By applying the expression

$$\log f(0) + \log \alpha = \log f(m)$$

which is derived from Equation 3, to interpolated values of $\log f(m)$ at even values of the total ionic strength, we obtain the activity coefficients of calcium bicarbonate presented in Table VII; these, it may be noted, are higher than usual for salts of the unibivalent type.

TABLE VII

ACTIVITY COEFFICIENTS OF CALCIUM BICARBONATE FROM SOLUBILITY MEASUREMENTS AT $25°$

$\mu =$	0.001	0.002	0.005	0.01	0.02	
$\alpha =$	.96	.94	.91	.88	.83	
$\mu =$		.05	.08	.1	.2	0.5
In NaCl solns. $\alpha =$		.84	.70	.68	.51	.45
In CaSO$_4$ solns. $\alpha =$		.73	.66	...	...	...

In the experiments in which calcium sulfate was one of the solid phases in equilibrium with the solution, the data may be tested as to their agreement with the solubility product of calcium sulfate. Lewis and Randall[22] have compared the results obtained by Harkins and Paine[23] on the solubility of gypsum in the presence of $CuSO_4$, $MgSO_4$ and of KNO_3 by plotting against the ionic strength the ratio $1/m_\pm$ (the reciprocal of the mean molality of calcium sulfate) to γ (the activity coefficient of $MgSO_4$ at the same ionic strength). In our experiments the ionic strength varied only slightly from the average, $\mu = 0.072$ molal; at this strength we find the mean value of the ratio to be 183, as compared with 182 found by Lewis and Randall. This agreement is perhaps as close as can be expected in view of the fact that in one case the common ion is the cation, while in the other it is chiefly the anion.

[20] McCoy and Smith, THIS JOURNAL, 33, 468 (1911).
[21] Osaka, Mem. Coll. Sci. Kyoto, 5, 131 (1922).
[22] Ref. 17, p. 376.
[23] Harkins and Paine, THIS JOURNAL, 41, 1160 (1919).

The regularity of the $\log f(m)$ curve for calcite, and the agreement of the reciprocal molality–activity coefficient ratio of gypsum with the value obtained by others, may be taken as evidence that the properties of the solid phases are unaltered under the conditions investigated. As a confirmatory test of the view that solid solution and compound formation do not occur under our conditions, it is of interest to consider the effect of the partial pressure of carbon dioxide on the ratio of carbonate ion to sulfate ion in the solution as suggested by Equation 4. A more convenient expression is obtained by dividing 3 by 4, as follows

$$\frac{1}{P}\frac{(\text{Ca}^{++})(\text{HCO}_3{}^-)^2}{(\text{Ca}^{++})(\text{SO}_4{}^-)} = \frac{(K_1\gamma\lambda c)}{(K_2)}\frac{K_\text{C}}{K_\text{G}} = \varphi_0\frac{K_\text{C}}{K_\text{G}}$$

or

$$\frac{1}{P}\frac{\alpha^3[\text{Ca}^{++}][\text{HCO}_3{}^-]^2}{\beta^2[\text{Ca}^{++}][\text{SO}_4{}^-]} = \varphi_0\frac{K_\text{C}}{K_\text{G}}$$

where by canceling $[\text{Ca}^{++}]^{24}$ and rearranging, we have

$$\frac{[\text{HCO}_3{}^-]^2}{[\text{SO}_4{}^-]} = P\frac{\beta^2}{\alpha^3}\varphi_0\frac{K_\text{C}}{K_\text{G}}$$

Owing to the slight effect of P upon the ionic strength of the solutions saturated with both calcite and gypsum, α and β are practically constant; a plot of the quotient $[\text{HCO}_3{}^-]^2/[\text{SO}_4{}^-]$ against P should therefore be a smooth, almost linear curve, as it proves to be in spite of the fact that irregularities in the experimental data are accentuated by the presence of a squared term in the quotient. Any marked change in curvature would indicate some change in the solid phases; from its absence we feel justified in concluding that the stable crystalline phases, under the conditions of our measurements, are calcite and gypsum, and that no solid solution or double salt appears. It may be mentioned that there is some evidence[25] that, under similar conditions, aragonite and calcium sulfate do to some extent (apparently up to about 0.7% CaSO_4) form solid solutions, an observation which may be of considerable geological significance.

Summary

1. The solubility of calcite at $25°$ in water saturated with carbon dioxide at partial pressures ranging from 0.0003 to 1.0 atm. has been determined. The solubility product constant of calcite at $25°$, in terms of activities, proved to be 4.8×10^{-9}.

2. An apparatus is described which facilitates solubility determinations in systems in which the composition both of the liquid and the gas phase must be ascertained.

3. Measurements are presented of the solubility of calcite at $25°$ in

[24] As α and β are the mean activity coefficients of bicarbonate and sulfate, respectively, the individual ion activities being unknown, it is therefore preferable to cancel the calcium term as a concentration rather than as an activity.

[25] Adverted to earlier, and also in a previous paper, ref. 2f, pp. 508–509.

solutions of calcium sulfate and of sodium chloride under partial pressures of carbon dioxide ranging from 0.1 to 1.0 atm.; from these results the activity coefficients of calcium bicarbonate have been derived. The concentrations of calcium sulfate and carbonate in the solutions saturated with both gypsum and calcite afford no indication of any alteration in the nature of either of these solid phases under these conditions.

NEW HAVEN, CONNECTICUT

THE SOLUBILITY OF MAGNESIUM CARBONATE (NESQUEHONITE) IN WATER AT 25° AND PRESSURES OF CARBON DIOXIDE UP TO ONE ATMOSPHERE[1]

BY WALTER D. KLINE[2]

The measurements presented in this paper were made with a view to securing more reliable data than were then available[3] on the solubility of magnesium carbonate (nesquehonite, $MgCO_3 \cdot 3H_2O$) in water at 25°, for a range of partial pressures of carbon dioxide extending downward from one atmosphere, and on the limiting pressure at which magnesium hydroxide becomes the stable solid phase in equilibrium with the solution. Such data are of interest in connection with the control of the conditioning of many natural waters and the preparation of pure magnesia, and are a necessary preliminary step toward the solution of the puzzling problem of the mode of formation of dolomite.

[1] From the dissertation presented by W. D. Kline to the Graduate School of Yale University, June, 1923, in candidacy for the degree of Doctor of Philosophy.

[2] Loomis Fellow, 1921–1922; du Pont Fellow, 1922–1923.

[3] (a) Engel, *Ann. chim. phys.*, **13**, 344 (1888), determined the equilibrium between $MgCO_3 \cdot 3H_2O$, water and (1) CO_2 at pressures of 0.5–6 atm. at 12°; (2) CO_2 at 1 atm. and several temperatures up to 50°. (b) Leather and Sen, *Memoirs Dept. Agric. India* Chem. Series 3, No. 8 (1914); sundry measurements, not very reliable. (c) Mitchell, *J. Chem. Soc.*, **123**, 1887 (1923), measured the solubility at 25° at pressures of 6–21 atm. of CO_2. (d) Haehnel, *J. prakt. Chem.*, **108**, 61 (1924), made measurements at 18° and pressures 2–56 atm. of CO_2; and at 34 atm. over the temperature range 0–60°. Since, however, the solubility at 18° becomes constant at pressures exceeding 18 atm., this is evidence of a new solid phase, bicarbonate presumably; hence the temperature coefficient of solubility at 34 atm. does not apply to our solid phase. (e) Cf. also Johnston, THIS JOURNAL, **37**, 2001 (1915).

In order to compare these several results with ours, they were recalculated in terms of moles per kilo of water by assuming that (a) the solution may be regarded as all bicarbonate; (b) the temperature coefficient of specific gravity of a solution of $Na(HCO_3)$ (given for 18° in "International Critical Tables") is the same as that of water; (c) the ratio of specific gravity of equimolal solutions of $Mg(HCO_3)_2$ and $NaHCO_3$ is the same as that of equimolal solutions of $MgCl_2$ and $NaCl$. The solubility at 25° was interpolated by means of a plot of log m against $1/T$.