THE SOLUBILITY-PRODUCT CONSTANT OF CALCIUM AND MAGNESIUM CARBONATES.

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In connection with certain calculations undertaken primarily to ascertain what degree of purity of magnesium carbonate might be expected if it were deposited by evaporation at constant temperature of a solution containing both magnesium and calcium carbonates, it became necessary to determine the appropriate solubility-product constants.[1] Values of these quantities were calculated some years ago by Bodländer,[2] but these must now be revised because some of the constants employed by him are now known to be erroneous. Bodländer's calculations for calcium carbonate were revised later by Stieglitz,[3] in connection with calculations relative to the effect of a change in the amount of carbon dioxide in the atmosphere upon the proportion of calcium carbonate in gypsum deposited by the evaporation at constant temperature of solutions (*e. g.*, sea water) containing both. The available data have now all been recomputed so as to obtain really comparable values of these solubility-product constants which should be consonant with present-day knowledge of the various quantities involved in the calculations. With a knowledge of these constants one can make certain deductions which are important in relation to the question of the nature and character of the solid deposited when solutions containing both carbonates are evaporated down.

The constant cannot be obtained directly from observations on the solubility of the carbonate MCO_3 in pure water for two reasons: (1) because of the hydrolysis, the amount of which is in the first instance unknown; (2) because, as will be shown later, there cannot be true equilibrium except the solution be in contact, and have come to equilibrium, with a definite partial pressure of CO_2 which must be measured. But if the partial pressure of CO_2 is known, and the concentration of the saturated solution in contact with it (and with a definite solid phase) is determined, the solubility-product constant can readily be calculated. The equilibrium between the solid carbonate MCO_3, the solution, and an atmosphere in which the partial pressure of CO_2 is P, is determined completely by the following four equations, in all of which, and throughout this paper, symbols such as $[M]$ represent the molar concentration of the species denoted by the symbol enclosed within the brackets:

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[1] For a thorough discussion of this quantity see a series of 7 papers entitled "The Effect of Salts on the Solubility of Other Salts," by A. A. Noyes, W. C. Bray, W. D. Harkins, and others, THIS JOURNAL, **33**, 1643–86, 1807–73 (1911).

[2] Bödlander, *Z. physik. Chem.*, **35**, 23 (1900).

[3] Stieglitz, "The Relations of Equilibrium between the Carbon Dioxide of the Atmosphere and the Calcium Sulphate, 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). This paper is not so widely known as it deserves to be, probably because no one would look in such a book for a paper dealing with such a topic.

$$\text{(I).}\quad [M^{++}][CO_3^{=}] = K_M$$

$$\text{(II).}\quad [H_2CO_3] = k'[CO_2] = c'P$$

$$\text{(III).}\quad \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = k_1$$

$$\text{(IV).}\quad \frac{[H^+][CO_3^{=}]}{[HCO_3^-]} = k_2$$

(I) defines the solubility product K_M, which we wish to calculate; (II) expresses the equilibrium between the undissociated dissolved carbonic acid and the partial pressure P of the CO_2 in contact with the solution; while (III) and (IV) define, respectively, the first and second ionization constants of carbonic acid in aqueous solution. At a given temperature the values of k_1 and k_2, which are invariable, are known; the quantity c', which is a measure of the solubility of CO_2 in the solution, varies, however, with the salt concentration of the solution. We shall now proceed to evaluate these constants.

The Solubility of CO_2 in Water and Salt Solutions.

The absorption-coefficient α of a gas, as given in tables of constants, is defined as the ratio of the volume of the gas dissolved (reduced always to 0°) to the volume of the water;[1] this ratio is, in accordance with Henry's law, independent of the pressure so long as the latter is not too high. The molar concentration of the dissolved gas is then $\frac{\alpha P}{22.4}$, when P is expressed in atmospheres; for $\alpha/22.4$ we shall write c. Now if we say that the concentration of un-ionized carbonic acid $[H_2CO_3] = cP$, we make the tacit assumption that none of the CO_2 exists as such in the solution, that all of it—apart from the ions—is present as the hydrate H_2CO_3. But, strictly speaking, the H_2CO_3 (which, of course, is also in equilibrium with its ionization products) is in equilibrium with the CO_2 existing as such in solution and this in turn with the CO_2 in the gas phase; *i. e.*, if n is the proportion of the total CO_2 in solution existing as H_2CO_3, $[H_2CO_3]/[CO_2]_s = n/(1-n)$, and $[CO_2]_s = m[CO_2]$. On the other hand, as actually measured,

$$c_1 = \frac{[H_2CO_3] + [CO_2]_s}{[CO_2]} \text{ and therefore, from the above, } c_1 = \frac{[H_2CO_3]}{[CO_2]}\frac{1}{n}.$$

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[1] Some authors give the *solubility* of the gas, which is the actual volume of gas at the temperature in question absorbed by one volume of water; care must be taken to distinguish these two quantities.

The value of n is not known, but Walker and Cormack[1] from a discussion of the matter, conclude that at 18° it is almost certainly greater than 0.5. We shall therefore write

$$\text{(V).}\quad [H_2CO_3] = nk\,[CO_2] = ncP$$

where $c = \alpha/22.4$, and n, the proportion of the total CO_2 in solution existing as H_2CO_3, is greater than 0.5; we retain it, though it is unknown, in order to bring out the fact that the absolute value of certain of our constants depends upon the value assigned to n.

The absorption of CO_2 by water and aqueous solutions has been studied by several investigators with results which are satisfactorily concordant. Bohr[2] determined it in water and in two solutions of NaCl—respectively 1.17 and 3.44 N—at temperatures ranging up to about 60°; Geffcken[3] made measurements at 15° and 25° of the solubility in 0.5 and 1.0 N solutions of a few salts and common acids. The change of absorption-coefficient is nearly proportional to the salt concentration, and varies relatively little from one salt to another. It is more nearly linear, and varies less for the several salts, when it is plotted against the ion-concentration of the solutions—as indeed we should expect since the proportion of un-ionized salt is small; but the existing data are too scanty to admit of any very strict generalization of this character. In the present work it was assumed that the absorption-coefficient of CO_2 in the carbonate solutions is the same as in sodium chloride of the same *equivalent* concentration; this mode of calculation leads to practically the same result as calculation on the basis of equality of absorption in solutions of equal ion-concentration, and is simpler to carry out. The coefficients actually used are given in the appropriate place; they were read from curves drawn on the basis of values interpolated from a large scale plot of Bohr's results in water and solutions of NaCl, as follows:

VALUES OF $c = \alpha/22.4$, WHERE α IS THE ABSORPTION COEFFICIENT OF CO_2.

Temperature.	In water.	In 1.17 N solution.	In 3.44 N solution.
3.5	0.0672	0.0484	0.0270
12	0.0500	0.0367	0.0213
16	0.0441	0.0328	0.0193
25	0.0338	0.0260	0.0159
30	0.0297	0.0232	0.0142
40	0.0236	0.0185	0.0117

The next step is to obtain the value of k_1 and k_2, or more particularly of the ratio k_1/k_2, which is obtained directly from McCoy's[4] work on the carbonate-bicarbonate equilibrium.

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[1] Walker and Cormack, *J. Chem. Soc.*, **77**, 13–14 (1900); see also Walker, *Ibid.*, **83**, 182 (1903).

[2] C. Bohr, *Ann. Physik*, **68**, 500 (1899).

[3] G. Geffcken, *Z. physik. Chem.*, **49**, 257 (1904).

[4] H. N. McCoy, *Am. Chem. J.*, **29**, 437 (1903).

The Carbonate-Bicarbonate Equilibrium.

On dividing Equation III by Equation IV we obtain

$$\text{(VI).}\quad \frac{[HCO_3^-]^2}{[CO_3^=][H_2CO_3]} = \frac{k_1}{k_2} = r,$$

r being the ratio of the first to the second ionization constant of H_2CO_3; whence by combination with V

$$\text{(VII).}\quad \frac{[HCO_3^-]^2}{[CO_3^=]cP} = nr.$$

By means of Equation VII values of nr can be calculated from McCoy's data on the equilibrium at 25° between sodium bicarbonate and carbonate in aqueous solutions in contact with a measured partial pressure (P) of CO_2. Such calculations were made by McCoy; in the present calculation corrections which were indicated by McCoy, but not carried out, have been made for the change of solubility of CO_2 in salt solutions and for the degree of ionization of the salts.[1] The latter correction was made on the basis of the principle, now well established,[2] that the degree of ionization of a salt in a mixture is sensibly equal to that of a salt of the same valence type at the same total ion-concentration; this is, at the least, a more accurate procedure than the direct calculation from the conductivity of solutions of sodium carbonate or bicarbonate, on account of the complexity of the solutions and the consequent difficulty of interpreting the results.

McCoy made three series of determinations, all at 25°, the results of which are reproduced in Table I; in these three series the total concentration of sodium was, respectively, 0.1, 0.3 and 1.0 N. The values of c (the molar absorption of CO_2) and of γ_1 and γ_2 (the degrees of ionization of $NaHCO_3$ and Na_2CO_3, respectively) which were adopted follow:

	Total conc. of Na.	c.	γ_1.	γ_2.
A	0.1	0.0323	0.81	0.70
B	0.3	0.0295	0.76	0.63
C	1.0	0.0233	0.65	0.56

It will be observed that the values of nr, which are very satisfactorily concordant in each series, decrease with increasing concentration; this decrease, which is too large to be due to simple errors in the values of c and γ adopted, may be attributed to failure of the tacit assumptions that n and the activity of the water are constant.[3] However this may be, we shall adopt here the value of 5600, which is the extrapolated value at zero concentration when the three above results are plotted; in other words, $5600 = nk_1/k_2$ where k_1 and k_2 are the first and second ionization-constants of H_2CO_3.

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[1] Cf. Stieglitz, *Carnegie Inst. Publ.*, 107, 243–5 (1909).

[2] See, for instance, publications from the laboratory of A. A. Noyes.

[3] It may be noted that if we assume the relative decrease of solubility of CO_2 with increase of salt concentration to be a rough measure of the decrease in activity of the water (as has been done in attempts to estimate the extent of hydration), and calculate on this basis, the three mean values of nr become 5500, 5350 and 5000, respectively.

TABLE I.—VALUES OF $nr = \frac{[HCO_3^-]^2}{[CO_3^=]cP'}$, CALCULATED FROM MCCOY'S DATA ON THE CARBONATE-BICARBONATE EQUILIBRIUM AT 25°.

P. (Atm.)	Conc. of total bicarbonate. x.	$]HCO_3^-]$ $= \gamma_1 x$.	Conc. of total carbonate. y.	$[CO_3^=]$ $= {}^1/_2\gamma_2 y$.	nr.
		A : $x + y = 0.1$.			
0.00161	0.0682	0.0552	0.0318	0.0111	5260
0.00159	0.0690	0.0559	0.0310	0.0109	5600
0.00259	0.0760	0.0615	0.0240	0.0084	5380
0.00294	0.0775	0.0628	0.0225	0.0079	5300
0.00322	0.0781	0.0633	0.0219	0.0077	5040
0.00404	0.0818	0.0662	0.0182	0.0064	5300
0.0223	0.0951	0.0770	0.0049	0.0017	4840[1]
0.0749	0.0985	0.0798	0.0015	0.0005	5260[1]
					5300
		B : $x + y = 0.3$.			
0.00319	0.1737	0.132	0.1263	0.0398	4650
0.00583	0.2037	0.155	0.0963	0.0303	4610
0.01044	0.2307	0.176	0.0693	0.0218	4610
0.0	0.2556	0.194	0.0444	0.0140	4400
0.0	0.2664	0.203	0.0336	0.0106	4770
0.0	0.2778	0.211	0.0222	0.0070	4780
					4650
		C : $x + y = 1.0$.			
0.0436	0.758	0.492	0.242	0.0678	3510
0.0624	0.810	0.526	0.190	0.0533	3570
0.1021	0.860	0.559	0.140	0.0392	3350
0.1682	0.902	0.586	0.098	0.0274	3200
					3450

Walker and Cormack,[2] from concordant determinations of the conductivity of solutions of carbonic acid, concluded that at 18°

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3] + [CO_2]_s} = 3.04 \times 10^{-7}$$

whence

$$k_1 = \frac{3.04 \times 10^{-7}}{n} \text{ at } 18^\circ \quad \text{or} \quad \frac{3.4 \times 10^{-7}}{n} \text{ at } 25^{\circ 3}$$

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[1] Omitted in taking the mean because of the small percentage accuracy of $[CO_3^=]$ in those cases.

[2] Walker and Cormack, *J. Chem. Soc.*, 77, 8 (1900).

[3] This value is derived from that at 18° by means of the van't Hoff formula on the basis that the heat change accompanying the reaction is 2700 cal. (Lewis and Randall, THIS JOURNAL, 37, 467 (1915).)

where n, as before, is the fractional amount of the total CO_2 in solution existing in the form of H_2CO_3. Consequently

$$k_2 = \frac{k_1}{r} = \frac{3.4 \times 10^{-7}}{n} \cdot \frac{n}{5600} = 6 \times 10^{-11}$$

which is identical with the result originally computed by McCoy (6.0×10^{-11}), with that (6.4×10^{-11}) recalculated from the work of Shields[1] on the hydrolysis of sodium carbonate, and with that obtained by Auerbach and Pick[2] (6×10^{-11} at 18°) using still other methods.

The above value of nr was determined for a temperature of 25°, but it may be applied with safety at other temperatures not too far removed from 25°; in using this value for other temperatures we are tacitly assuming that nr remains constant—an assumption which, though it may well prove to be far from correct, is the best that can be done so long as the necessary data are unknown.

The Solubility-Product Constant.

On substituting in Equation VII for $[CO_3^{=}]$ its value from Equation I we obtain finally

$$[M^{++}][HCO_3^-]^2 = nrK_McP$$

or

$$\text{(VIII).} \quad nrK_M = \frac{[M^{++}][HCO_3^-]^2}{cP}.$$

Thus the solubility-product constant K_M of a carbonate can be calculated if corresponding values of the quantities on the right hand side of Equation VIII are known; the factors in the numerator can be derived from measurements of the solubility of the carbonate MCO_3 in presence of CO_2 at the pressure P by (1) correcting for the (always small and frequently negligible) amount of neutral carbonate present,[3] (2) multiplying the concentration of bicarbonate so obtained by the appropriate value of the degree of ionization, (3) inserting the appropriate values of c and P, and working out. We shall now proceed to some actual cases; but before doing so, we wish to point out that the solubility-product constant (like the solubility itself) has no significance except in relation to a definite solid phase—that this quantity is not the same for the three known forms of $CaCO_3$ (calcite, aragonite, vaterite) nor again for $MgCO_3.3H_2O$,

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[1] Shields, *Z. physik. Chem.*, **12**, 167 (1893).

[2] Auerbach and Pick, "Die Alkalität wässeriger Lösungen kohlensaurer Salze," *Arbeiten kais. Gesundheitsamt.*, **38**, 243 (1911).

[3] As will be evident later, it is not admissible to subtract (as Bodländer did in the case of $MgCO_3$) a constant quantity corresponding to the saturation concentration of the neutral carbonate as measured in pure water; the latter, moreover, is not a definite quantity, for there can be no equilibrium except in presence of a definite pressure of CO_2.

$MgCO_3.H_2O$ and $MgCO_3$ except at the transition point of one form to the other.

The Solubility-Product Constant of Calcium Carbonate (Calcite).

In this case there is no doubt as to the nature of the solid phase. Determinations of the solubility of $CaCO_3$ at 16° have been made by Schloesing[1] at partial pressures of CO_2 ranging up to 1 atm. and by Engel[2] at pressures from 1 to 6 atm. Calculations based on their results are presented in Tables II and III.

The first two columns of Table II contain the actual measurements of the partial pressure (P, in atm.) and the total concentration of calcium in the solution (expressed in mols per liter); the quantities in the other columns are derived from these, except that the values of the degree of ionization (γ) in the fourth column are those (as derived from the conductivity) of equivalent solutions of calcium acetate. In the third column are given the corrected total concentrations of bicarbonate, from which, by multiplication with the appropriate value of γ, the values of $[HCO_3^-]/2$ tabulated in the fifth column were obtained; the sixth column gives the total concentration of calcium ion, which = $^1/_2[HCO_3^-] + [CO_3^=]$, and in the last are the computed values of the constant nrK_{Ca}.

TABLE II.—CALCULATIONS ON THE BASIS OF SCHLOESING'S DATA ON THE SOLUBILITY OF CALCITE IN WATER CONTAINING cP MOLS CO_2 AT 16°; c = 0.0441.

P. (Atm.)	Total [Ca]. Mols | l.	Total $Ca(HCO_3)_2$. Mols | l.	γ.	$^1/_2[HCO_3^-]$.	$[Ca^{++}]$.	nrK_{Ca}.
0.000504	0.000746	0.000731	0.906	0.000663	0.000678	5.36×10^{-5}
0.000808	0.000850	0.000837	0.904	0.000757	0.000770	4.95
0.00333	0.001372	0.001364	0.890	0.001214	0.001222	4.99
0.01387	0.002231	0.002226	0.870	0.001940	0.001945	4.79
0.02820	0.002965	0.002961	0.856	0.002537	0.002541	5.28
0.05008	0.003600	0.003597	0.844	0.003045	0.003048	5.10
0.1422	0.005330	0.005328	0.822	0.00438	0.00438	5.36
0.2538	0.006634	0.006632	0.811	0.00538	0.00538	5.57
0.4167	0.007875	0.007874	0.798	0.00628	0.00628	5.39
0.5533	0.008855	0.008854	0.790	0.00699	0.00699	5.60
0.7297	0.00972	0.00972	0.785	0.00763	0.00763	5.52
0.9841	0.01086	0.01086	0.778	0.00845	0.00845	5.56
						5.30×10^{-5}

TABLE III.—CALCULATIONS ON THE BASIS OF ENGEL'S DATA ON THE SOLUBILITY OF CALCITE IN WATER CONTAINING cP MOLS CO_2 AT 16°.

P. (Atm.)	Total [Ca]. Mols | l.	c.	γ.	$[Ca^{++}] = {}^1/_2[HCO_3^-]$.	nrK_{Ca}.
1	0.01085	0.0439	0.778	0.00844	5.48×10^{-5}
2	0.01411	0.0438	0.756	0.01066	5.53
4	0.01834	0.0437	0.730	0.01338	5.48
6	0.02139	0.0437	0.713	0.01525	5.41
					5.47×10^{-5}

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[1] Schloesing, *Compt. rend.*, **74**, 1552; **75**, 70 (1872).

[2] Engel, *Ann. chim. phys.*, [6] **13**, 348 (1888).

A word is necessary as to the method of correcting for the neutral carbonate present—the correction namely ($= [CO_3^=]$), applied in deriving the numbers in the third column from those in the second. From Equation VII $[HCO_3^-]^2/[CO_3^=] = nrcP = 247P$ at 16°; and consequently if an approximate value of $[HCO_3^+]$ is known in advance, the concentration of $[CO_3^=]$ (which relatively is always small) can be estimated. Thus in the most dilute solution (where the correction is greatest) of Table II, the correction is $(0.00134)^2/247 \times 0.0005 = 0.000015$.[1] It can also be obtained directly as soon as a rough value of the solubility-product constant $[Ca^{++}][CO_3^=]$ is ascertained. The amount of this correction in all the solutions is evident by subtracting the figures in Column 3 (or 5) from those in Column 2 (or 6); in the stronger solutions it is obviously entirely negligible.

Table III is identical in arrangement with Table II, except that the relative absorption-coefficients of CO_2 are given in the third column; in this case the correction for neutral carbonate is entirely negligible, so that the total concentrations of bicarbonate are identical with the experimentally determined concentrations in the second column.

The constancy of the values tabulated in the last column is surprisingly good, especially in view of the fact that P ranges from 0.0005 atm. (slightly greater than the amount ordinarily present in the air) to 6 atm.; in other words, the product remains constant even when the concentration of one of the factors in the equilibrium changes as much as ten thousandfold. The mean value derived from the stronger solutions (where the experimental accuracy is greatest) is 5.50×10^{-5}, a value from which we can calculate with confidence the solubility of calcite in water at 16° saturated with CO_2 at any pressure up to that at which calcium bicarbonate would begin to appear as solid phase at this temperature. Accordingly the solubility-product constant of calcite at 16° is $[Ca^{++}][CO_3^=] = K_{Ca} = \frac{5.50 \times 10^{-5}}{5600} = 0.98 \times 10^{-8}$. It is of little use to compare this with the "solubility in pure water"[2] because, except there be no vapor phase, the latter is meaningless except in relation to a definite partial pressure of CO_2;[3] for a definite concentration of CO_2, in accordance with Equations VI and VII, can exist in equilibrium only with definite concentrations of HCO_3^- and H_2CO_3, and the latter in turn requires a definite partial pressure of CO_2.[1]

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[1] This is just about 9% of the quantity which has been considered to represent the solubility of $CaCO_3$ in pure water. From this correction the extent of hydrolysis in the several solutions can obviously be readily calculated.

[2] The most recent determinations of this quantity are by Kendall (*Phil. Mag.*, **23**, 957 (1912)), who found at 25°, 50° and 100°, respectively, 14.3, 15.0 and 17.8 mg. $CaCO_3$ per liter. There is of course no assurance that the partial pressure of CO_2 was actually the same at all temperatures, so that these values are not necessarily even comparable with one another.

[3] See Table IV., *postea*.

Determinations of the amount of $CaCO_3$ in solution in presence of CO_2 have also been made by others. Treadwell and Reuter[2] made very painstaking analyses of a series of such solutions at 15°, but—as is obvious from a perusal of their mode of working—did not secure equilibrium conditions, a fact which is borne out by the lack of constancy of the calculated solubility-product constant. Quite recently Leather and Sen[3] made series of determinations at a number of temperatures between 15° and 40°; their solutions may have attained equilibrium, but their mode of analysis is unsatisfactory.[4] This was confirmed by the calculations, which yielded very irregular results; the most that one can deduce from them is that the solubility-product constant of calcite probably decreases somewhat with the temperature, becoming apparently about 0.5×10^{-8} at 40°.

Seyler and Lloyd[5] have also made a series of determinations of the equilibrium between solid calcium carbonate and water and certain dilute salt solutions containing excess of carbon dioxide; they kept the solutions, which were shaken occasionally, for long periods in stoppered bottles completely filled with liquid, and ascertained by titration the concentration of free CO_2 and of the dissolved carbonate. Unfortunately, however, their experiments were carried out at "the temperature of the laboratory;" nevertheless despite this indefiniteness, it seemed worth while to include their results (which have been recalculated so as to conform with the others presented in this paper) because these demonstrate that the solubility-product constant of calcite is not affected by the presence in the solution of small excess amounts of added Ca^{++} (as $CaCl_2$ or $CaSO_4$) or HCO_3^- (as $NaHCO_3$). In this case $nrK_{Ca} = [Ca^{++}][HCO_3^-]^2/[H_2CO_3]$, where $[H_2CO_3]$ is the concentration of free CO_2 in solution as determined by titration; as is evident from the table its value varies about a mean, the general average being 4.80×10^{-5}. Consequently $K_{Ca} = \dfrac{4.80 \times 10^{-5}}{5600} = 0.86 \times 10^{-8}$ at the "temperature of the laboratory," whence one might deduce that this temperature was about 20°. Seyler and Lloyd also investigated the effect of the presence of a small amount of a salt ($NaCl$, Na_2SO_4, $MgSO_4$) containing no ion in common with calcium carbonate, and found an increase in the total calcium in solution, in qualitative agreement with theory; by allowing for the undissociated fraction of the several salts present one could indeed calculate the solubility-product constant in these cases too, but such calculations would have little value by reason of the paucity and uncertainty of the experimental data.

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[1] Similar remarks with respect to the equilibrium between sodium carbonate and bicarbonate were made by McCoy (*Am. Chem. J.*, **29**, 456ff. (1903)).

[2] Treadwell and Reuter, *Z. anorg. Chem.*, **17**, 170 (1898).

[3] Leather and Sen, *Memoirs Dept. Agric. India*, Chem. Series, **1**, No. 7 (1909).

[4] One obvious error is a loss of CO_2, because in some cases especially in similar work with $MgCO_3$ (see *postea*), the total CO_2 in solution, as given in their tables, is insufficient to convert all of the base present to bicarbonate. As McCoy notes (*Am. Chem. J.*, **29**, 444 (1903)) "Carbon dioxide may readily be lost from solutions rich in bicarbonate, if care be not taken to render them alkaline at once. Low results were invariably obtained when the bicarbonate solutions were measured into beakers and allowed to stand, even for four or five minutes, before adding an excess of alkali."

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

TABLE III*a*.—CALCULATIONS ON THE BASIS OF THE RESULTS OF SEYLER AND LLOYD ON THE SOLUBILITY OF CALCITE IN WATER AND DILUTE SALT SOLUTIONS CONTAINING FREE CO_2.

Free CO_2 [H_2CO_3].	[Ca] as bicarbonate.	Conc. of added salt. Mols | l.	γ_1.	γ_2.	[Ca^{++}] from bicarbonate $= 1/2[HCO_3^-]$.	[Ca^{++}] from added salt.	Total [Ca^{++}].	nrK_{Ca}.
				Without added salt.				
0.00269	0.00370	.....	0.845	...	0.00313	.....	0.00313	4.56×10^{-5}
0.00362	0.00414	.....	0.840	...	0.00348	.....	0.00348	4.66
0.0100	0.00604	.....	0.816	...	0.00492	.....	0.00492	4.76
0.0114	0.00657	.....	0.810	...	0.00532	.....	0.00532	5.28
				In presence of $CaCl_2$.				
0.00395	0.00306	0.00625	0.788	0.788	0.00242	0.00493	0.00735	4.36
				In presence of $CaSO_4$.				
0.00104	0.00244	0.00119	0.848	0.665	0.00207	0.00079	0.00286	4.71
0.00181	0.00304	0.00119	0.838	0.647	0.00255	0.00077	0.00332	4.77
0.00206	0.00316	0.00119	0.837	0.644	0.00265	0.00077	0.00342	4.66
0.00315	0.00362	0.00119	0.831	0.633	0.00301	0.00076	0.00377	4.34
0.00455	0.00441	0.00119	0.821	0.615	0.00362	0.00073	0.00435	5.01
0.00656	0.00492	0.00119	0.815	0.605	0.00401	0.00072	0.00473	4.64
0.00356	0.00350	0.00312	0.832	0.636	0.00291	0.00198	0.00489	4.65
0.00494	0.00379	0.00625	0.829	0.629	0.00314	0.00394	0.00708	5.66
				In presence of $NaHCO_3$.				
0.00475	0.00278	0.00625	0.817	0.817	0.00227	0.00511[1]	0.00965[2]	4.45
0.00406	0.00170	0.0125	0.798	0.798	0.00136	0.01000[1]	0.01272[2]	5.42
							General mean,	*4.80* $\times$ *10*$^{-5}$

A knowledge of these constants renders unnecessary experimental work such as that of Keiser and McMaster,[3] who investigated the ratio of the excess of CO_2 in solution to the amount of $CaCO_3$. And the fact of this constancy is sufficient reply to statements such as the following: "While there is some evidence which supports the view that calcium bicarbonate exists in the dissolved state, the observed facts can be regarded just as logically and more conveniently as the result of the specific solvent power of the carbon dioxide-water mixture."[4]

[1] [HCO_3^-] from added salt.

[2] Total [HCO_3^-].

[3] Keiser and McMaster, THIS JOURNAL, **30**, 1714 (1908).

[4] Cameron and Robinson, *J. Physic. Chem.*, **12**, 573 (1908).

The Solubility of Calcite in Water in Contact with the Atmosphere.

The amount of calcium carbonate which will dissolve in water in contact with the air, and the variation of this solubility with the CO_2 content of the air, are of very great importance in connection with a number of geological processes of very widespread occurrence. The saturated solution of calcite under these conditions is so dilute that the concentration of $CO_3^=$ (and even of OH^-) is not negligible in summing up the total concentration of negative ions; consequently the calculations can be carried out only by a series of approximations. One has namely to determine values of $[Ca^{++}]$, $[HCO_3^-]$, $[CO_3^=]$ and $[OH^-]$, which shall simultaneously satisfy the condition

$$[Ca^{++}] = {}^1/_2[HCO_3^-] + [CO_3^=] + {}^1/_2[OH^-]$$

and three of the following equations:[1]

$$\text{(I).}\quad [Ca^{++}][CO_3^=] = K_{Ca} = 0.98 \times 10^{-8}$$

$$\text{(VII).}\quad [HCO_3^-]^2/[CO_3^=] = nrcP = 247\ P$$

$$\text{(VIII).}\quad [Ca^{++}][HCO_3^-]^2 = nrK_{Ca}cP = 2.425 \times 10^{-6}\ P$$

$$\text{(IX).}\quad [OH^-]/[HCO_3^-] = K_w/nk_1cP = 3.730 \times 10^{-7}/P$$

$$\text{(X).}\quad [OH^-]^2/[CO_3^=] = K^2{}_w/nk_1k_2cP = 3.435 \times 10^{-11}/P$$

In order to obtain the total concentration of calcium in the solution from the ion-concentrations obtained in this way one must correct for the ionization of the $Ca(HCO_3)_2$;[2] this can be done by dividing the value of ${}^1/_2[HCO_3^-]$ by the appropriate fractional ionization (γ_1), the latter being read by inspection from a curve obtained by plotting the fractional ionization—as derived from the conductivity of solutions of calcium acetate—against the concentration of Ca^{++}. The results derived in this way for various partial pressures of CO_2 such as may occur in atmospheric air are presented in Table IV.

The amount of CO_2 in ordinary air, which is about 3 parts in 10,000, corresponds, on the basis of Table IV, to about 63 parts $CaCO_3$ per million; and, as is evident from the table, comparatively small changes in the concentration of CO_2 in the air may, in nature, easily bring about the solution or deposition of very large quantities of calcium carbonate. Its solubility would of course be slightly different in natural waters—springs, rivers or the sea; the presence of other calcium salts would make it smaller by an amount readily calculable, while salts of other radicals would of themselves make it somewhat larger. It would lead too far to discuss satisfactorily this question here, and its bearing on a number of geologic phenomena.[1] It may be affirmed, however, on the basis of analyses cited by F. W. Clarke,[2] that many natural waters are substantially saturated with calcium carbonate; while it is certain that the surface layers of the larger part of the ocean, except possibly in the Arctic and Antarctic, must in general be substantially saturated.

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[1] The numerical values refer to calcite at 16°, where $c = 0.0441$. Equation IX is obtained by combination of (III) and (V) with the relation $[H^+][OH^-] = K_W = 0.5 \times 10^{-14}$ at 18°; (X) by combination of (VII) and (IX). It may be noted that, for the purpose of these approximations, the various equations must be absolutely consistent; hence it is necessary to retain a larger number of figures than is warranted by the accuracy of the several constants, until the final result is written down.

[2] The concentrations of $CO_3^=$ and of OH^- are so small that ionization is practically complete.

TABLE IV.—THE CALCULATED SOLUBILITY OF CALCITE IN WATER AT 16° IN CONTACT WITH AIR CONTAINING THE PARTIAL PRESSURE *P* OF CO_2.

P.	$[Ca^{++}]$.	$^1/_2[HCO_3^-]$.	γ_1.	[Ca] as $Ca(HCO_3)_2$.	$[CO_3^=]$.	$[OH^-]$.	Total [Ca].	Parts $CaCO_3$ per million.
0.00020	0.000509	0.000488	0.919	0.000532	0.000019	1.82×10^{-6}	0.000552	55
0.00025	0.000546	0.000527	0.917	0.000574	0.000018	1.57	0.000593	59
0.00030	0.000579	0.000561	0.915	0.000613	0.000017	1.40	0.000631	63
0.00035	0.000608	0.000591	0.914	0.000647	0.000016	1.26	0.000664	66
0.00040	0.000635	0.000618	0.913	0.000677	0.000016	1.15	0.000694	69
0.00045	0.000659	0.000643	0.912	0.000705	0.000015	1.07	0.000721	72
0.00050	0.000682	0.000666	0.912	0.000731	0.000014	1.00	0.000746	75

The concentration of OH^-, tabulated in the seventh column of Table IV, which is a measure of the alkalinity of the solutions, increases with diminishing partial pressure of CO_2; indeed purposive variation of the proportion of CO_2 over a solution in contact with excess of calcium carbonate might, in some instances, prove a convenient method of establishing and controlling a definite alkalinity in the solution. Such an action apparently goes on on a large scale continuously in the sea, the alkalinity[3] of which corresponds closely to that of the saturated solution of $CaCO_3$ in equilibrium with air containing three parts CO_2 per 10,000.

The Solubility-Product Constant of $MgCO_3.3H_2O$ (Nesquehonite).

Determinations were made by Engel[4] of the equilibrium between $MgCO_3.3H_2O$, water, and (*a*) CO_2 at pressures ranging up to 6 atm. at 12° and (*b*) CO_2 at 1 atm. at temperatures ranging up 50°;[5] these form the basis for the figures presented in Tables V and VI. These tables are identical in arrangement with Table III, as the correction for $[CO_3^{=}]$ is absolutely negligible at the concentrations in question; the absorption-coefficient is that for solutions of sodium chloride of equivalent concentration at the particular temperature, the fractional ionization is that of an equivalent solution of magnesium chloride.[1]

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[1] This will be treated in another paper now in preparation.

[2] F. W. Clarke, "Data of Geochemistry," U. S. Geological Survey, *Bull.* 491 59ff. (1911).

[3] See Ruppin, "Die Alkalinität des Meerwassers," *Z. anorg. Chem.*, 66, 122–56 (1910), who gives numerous references.

[4] Engel, *Ann. chim. phys.*, [6] 13, 353, 354 (1888). He also gives a series of preliminary results for pressures ranging up to 9 atm. at 19.5°, with "magnesium hydrocarbonate" as solid phase, which when calculated give quite a fair constant; these have not been included because the nature of the solid phase at equilibrium is doubtful.

[5] Similar determinations have been published very recently by Leather and Sen (*Memoirs Dept. Agric. India*, Chem. Series, 3, No. 8 (1914); but—apart altogether from the circumstance that it is very questionable whether equilibrium was really attained in their experiments—their analytical results cannot be trusted, since the

TABLE V.—CALCULATIONS ON THE BASIS OF ENGEL'S DATA ON THE SOLUBILITY OF $MgCO_3.3H_2O$ IN WATER CONTAINING cP MOLS CO_2 AT 12°.

P (Atm.)	Total [Mg]. Mols | l.	c.	Ionization. γ.	$[Mg^{++}] = [HCO_3^-]/2$.	nrK_{Mg}.
0.5	0.255	0.0431	0.686	0.175	1.06
1	0.326	0.0418	0.680	0.222	1.05
1.5	0.379	0.0406	0.675	0.256	1.10
2	0.417	0.0399	0.672	0.280	1.10
2.5	0.443	0.0393	0.670	0.297	1.07
3	0.474	0.0388	0.669	0.317	1.09
4	0.519	0.0379	0.666	0.346	1.09
6	0.612	0.0362	0.662	0.404	1.19
					1.08

TABLE VI.—CALCULATIONS ON THE BASIS OF ENGEL'S DATA ON THE SOLUBILITY OF $MgCO_3.3H_2O$ IN WATER CONTAINING c MOLS CO_2 AT SEVERAL TEMPERATURES.

t.	Total [Mg]. Mols | l.	c.	γ.	$[Mg^{++}] = [HCO_3^-]/2$.	nrK_{Mg} at t.
3.5	0.422	0.0525	0.672	0.283	1.73
12	0.326	0.0418	0.680	0.222	1.05
18	0.262	0.0363	0.686	0.180	0.64
22	0.237	0.0328	0.690	0.164	0.54
30	0.187	0.0273	0.700	0.131	0.33
40	0.140	0.0223	0.715	0.100	0.18
50	0.113	0.0186	0.725	0.082	0.12

From the last column of Table V it is evident that we have a very satisfactory constant, a constancy which is the more remarkable in view of the fact that the total ion-concentration of the solution is so large—above 0.5 *M* throughout. This constancy inclines one to the belief that the solubility-product constant will, when the experimental results can be properly interpreted, be found to hold for substances, the saturated solutions of which are not extremely dilute.[2] From the mean value the

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ratio of the *total* amount of CO_2 in the solution (as given by them) to the magnesia is very irregular and in many cases is even less than 2. (Cf. footnote 4, p. 2009.) Moreover, their results when plotted directly show great inconsistencies. In accordance with this the calculated values of the product nrK_{Mg} are very irregular and show no approach to constancy.

[1] On the basis of its value at 18° in each case; but this introduces no appreciable error, since the variation in extent of ionization is very small at temperatures up to 50°. (See, for instance, Noyes and Johnston, THIS JOURNAL, **31,** 987 (1909).)

[2] It may be added that the fact of this constancy is a criterion of the substantial accuracy of the γ values chosen; for a change of 3% in the values assigned to γ suffices

product $K_{Mg} = [Mg^{++}][CO_3^{=}] = \frac{1.08}{5600} = 1.93 \times 10^{-4}$ at 12° when the solid phase is $MgCO_3.3H_2O$.[1]

From the numbers in the last column of Table VI, the values of the solubility-product constant were calculated; these are reproduced in Table VII, alongside values calculated from an equation which was derived as follows: If we integrate the well-known equation $\ln K/dT = Q/RT^2$ on the basis that Q (the heat effect of the reaction considered) is constant over the temperature range, we obtain $\ln K = (-Q/RT) + C$, which has the form $\log K = (A/T) + B$; or, in other words, when values of $\log K$ are plotted against $1/T$, the graph is a straight line. The plot of the data proved to be a straight line, the equation to which is

$$\text{(XI).} \quad \log K = (2315/T) - 11.870.$$

The agreement between the values calculated directly and those derived from Equation XI is very good, all things considered. Moreover, by comparing the above equations, we can calculate Q—namely $Q = -2315 \times 2.303\, R = -10600$ cal.; that is, the heat change corresponding to the reaction $MgCO_3.3H_2O = Mg^{++} + CO_3^{=} + 3H_2O$ is an evolution of 10600 cal.

TABLE VII.—THE SOLUBILITY-PRODUCT CONSTANT OF $MgCO_3.3H_2O$ AT VARIOUS TEMPERATURES.

t.	T.	$K_{Mg} = [Mg^{++}][CO_3^{=}]$. Derived from Table VI.	$K_{Mg} = [Mg^{++}][CO_3^{=}]$. Calc. from Equation XI.
3.5	276.5	3.09×10^{-4}	3.17×10^{-4}
12	285	1.88	1.78
18	291	1.14	1.21
22	295	0.97	0.95
30	303	0.59	0.59
40	313	0.32	0.33
50	323	0.21	0.20

The Solubility of $MgCO_3.3H_2O$ in Water in Contact with the Atmosphere, and the Question of Basic Magnesium Carbonates.—The figures in Table VII enable one to calculate, in precisely the same way as was

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to produce a pronounced trend in the values of nrK_{Mg}. Conversely, careful work of this character could be used as a means of determining the extent of ionization, which would be practically independent of the assumptions made in the usual methods of deriving this quantity. To avoid misconception, it may be remarked that the values of γ as given in the table were all chosen before any of the calculations of the value of nrK_{Mg} were made.

[1] The solubility of $MgCO_3.3H_2O$ in "pure water" is given by Auerbach (*Z. Elektrochem.*, **10,** 161 (1904)) as 0.0095 mol per liter at 15°, 0.0087 at 25°, and 0.0071 at 35°; but these results are again indefinite for the reason already pointed out (p. 2008). In this case, as it happens, the process of hydrolysis goes on quite slowly at ordinary temperatures.

done for calcite, the total solubility of $MgCO_3.3H_2O$ at temperatures up to 50° in water in contact with any partial pressure of CO_2; but in this case the sparing solubility of $Mg(OH)_2$ introduces an added complication which enters whenever the partial pressure is reduced to a definite limiting value, the magnitude of which depends upon the temperature. In order to bring out this point, which has a very important bearing on the composition of basic carbonates of magnesia, we shall make the calculations for 18° and partial pressures ranging from 0.0002 to 0.0005 atm. One has again to determine values of $[Mg^{++}]$, $[HCO_3^-]$, $[CO_3^=]$ and $[OH^-]$ which shall satisfy the condition $[Mg^{++}] = {}^1/_2[HCO_3^-] + [CO_3^=] + {}^1/_2[OH^-]$, two of the following equations:[1]

(VII). $[HCO_3^-]^2/[CO_3^=] = nrcP = 229.6\ P$

(VIII). $[Mg^{++}][HCO_3^-]^2 = nrK_{Mg}cP = 2.755 \times 10^{-2}\ P$

(IX). $[OH^-]/[HCO_3^-] = K_w/nk_1cP = 4.012 \times 10^{-7}\ P$

(X). $[OH^-]^2/[CO_3^=] = K^2_w/nk_1k_2cP = 3.694 \times 10^{-11}/P$

and *either* (I). $[Mg^{++}][CO_3^=] = K_{Mg} = 1.2 \times 10^{-4}$

or (XII). $[Mg^{++}][OH^-]^2 = 1.2 \times 10^{-11}$ [2]

The choice between (I) and (XII) is not an arbitrary one, but depends upon the value of P. For by combination of Equations I and X (or VIII and IX), one obtains the relation

$$[Mg^{++}][OH^-]^2 = \frac{K^2_w K_{Mg}}{nk_1k_2cP} = \frac{4.433 \times 10^{-15}}{P} \text{ at } 18°,$$

a value which exceeds the product XII whenever P is less than 0.000369. Consequently, when P is less than 0.000369, the solid phase *in equilibrium* with the solution at 18° is not $MgCO_3.3H_2O$, but $Mg(OH)_2$; in other words, this is a type of transition pressure, both solid phases being in equilibrium with the solution when the CO_2 pressure is exactly 0.000369 atm. This transition pressure increases rapidly with rise of temperature because K^2_w/nk_1k_2 increases rapidly while K_{Mg}/c varies little; the increase cannot, however, be calculated because the rate of increase of k_2 with temperature is not known.

From the values of the ion-concentrations computed by means of the above equations, the total amount of magnesium in solution was obtained by correcting for the ionization of $Mg(HCO_3)_2$ and $MgCO_3$ at their respective concentrations. This was done by dividing the value of (*a*) ${}^1/_2[HCO_3^-]$ (*b*) $[CO_3^=]$ by the appropriate fractional ionization (γ_1 and γ_2, respectively), which was read from a curve obtained by plotting the fractional ionization—as derived from the conductivity of solutions of (*a*)

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[1] The numerical values refer to $MgCO_3.3H_2O$ at 18°; c has been taken as 0.041. Cf. p. 2011.

[2] This value is the lower of the two given in Landolt-Börnstein-Roth Tabellen; it is due to Dupré and Bialas (*Z. angew. Chem.*, **16,** 55 (1903)).

$MgCl_2$ (*b*) $MgSO_4$—against the concentrations of Mg^{++}. The results of these calculations are presented in Table VIII.

Table VIII.—The Calculated Solubility of $MgCO_3.3H_2O$ in Water at 18° in Contact with Air Containing the Partial Pressure *P* of CO_2.

P.	$[Mg^{++}]$.	$[HCO_3^-]/2$.	$[CO_3^=]$.	$[OH^-] \times 10^{-5}$.	γ_1.	[Mg] as $Mg(HCO_3)_2$.	γ_2.	[Mg] as $MgCO_3$.	Total [Mg].
0.00020	0.01275	0.00765	0.000509	3.07	0.827	0.00925	0.505	0.01008	0.01934
0.00025	0.01454	0.00895	0.000558	2.87	0.820	0.01091	0.495	0.01126	0.02218
0.00030	0.01620	0.01017	0.000602	2.72	0.815	0.01247	0.486	0.01238	0.02486
0.00035	0.01775	0.01134	0.000640	2.60	0.810	0.01400	0.477	0.01341	0.02742
0.00040	0.01862	0.01217	0.000644	2.44	0.807	0.01506	0.473	0.01361	0.02868
0.00045	0.01906	0.01275	0.000630	2.28	0.805	0.01583	0.470	0.01340	0.02924
0.00050	0.01947	0.01330	0.000616	2.13	0.804	0.01655	0.467	0.01320	0.02976

The last column gives the total concentration of magnesium in solution at 18° at the several partial pressures, the solid phase *in equilibrium* with the solution being $MgCO_3.3H_2O$ at pressures above 0.00037, but $Mg(OH)_2$ when the pressure of CO_2 is less than 0.00037. Accordingly, if we keep the CO_2 pressure constant at *P* and evaporate off the water at 18° so slowly that equilibrium conditions are continuously attained, we shall obtain the following amounts of either $Mg(OH)_2$ or $MgCO_3.3H_2O$ from one liter of the solution:

Table IX.

P.	Total [Mg].	$Mg(OH)_2$. g.	$MgCO_3.3H_2O$. g.
0.00000	0.00015	0.0087	....
0.00020	0.01934	1.13	....
0.00025	0.02218	1.29	....
0.00030	0.02486	1.45	....
0.00035	0.02742	1.60	....
0.00040	0.02868	....	3.97
0.00045	0.02924	....	4.05
0.00050	0.02976	....	4.12

If the constant pressure were exactly the transition pressure, both solid phases would be formed; but if it is slightly above or below this limit, either carbonate or hydroxide would separate when the water is evaporated off. At higher temperatures this transition pressure is, as noted above, higher.

From the foregoing it is obvious that the ordinary methods of preparing magnesium carbonate (in which, it is safe to say, a state of equilibrium is not attained continuously) will yield a product contaminated with hydroxide, the amount of which will depend upon the mode of working generally, and upon the prevailing partial pressure of CO_2 over the liquid in particular; moreover, that this contamination can be avoided completely by working with a partial pressure *P* greater than a certain limit. This limit is readily calculable in each particular case from the equations on p. 2015; and without doubt one could easily devise a process of preparing pure $MgCO_3$ in which one atmosphere of CO_2 would suffice to prevent the precipitation of hydroxide.

The quantitative results presented above may require modification by reason of the possible inaccuracy of some of the data involved; of these the one most open to question is the solubility of magnesium hydroxide in pure water, which would tend to be found too high owing to the circumstance that the amount of magnesium present in solution in contact with magnesium hydroxide is increased more than a hundredfold when the atmosphere in contact with the solution contains as little as 2 parts CO_2 per 10,000 (see Table IX). Again the results given are subject to the limitation that the only solid phases are $MgCO_3.3H_2O$ and $Mg(OH)_2$; when conditions are such that one solid phase is $MgCO_3.H_2O$ or $MgCO_3$, the appropriate solubility-products (which at present are not known, and differ from one another, except at the mutual transition points) must be employed. Moreover, if within any temperature or pressure range a definite crystalline basic carbonate should be capable of stable existence in contact with water,[1] it would have to be taken into account in calculations relative to those conditions. In any case the general conclusions derived from these theoretical considerations are in complete accord with the established behavior of magnesium carbonate,[2] and in particular give a rational way of accounting for the well-known indefinite character of the ordinary basic carbonates of magnesia.

The Deposit from Solutions Containing both Calcium and Magnesium Carbonates.

In any solution saturated with respect to both calcite and $MgCO_3.3H_2O$ the ratio of the concentrations of Mg^{++} and Ca^{++} must have a definite value; for instance, at 16°, this ratio is

$$\frac{[Mg^{++}]}{[Ca^{++}]} = \frac{[Mg^{++}][CO_3^{=}]}{[Ca^{++}][CO_3^{=}]} = \frac{K_{Mg}}{K_{Ca}} = \frac{1.4 \times 10^{-4}}{1 \times 10^{-8}} = 14000.$$

So long as $MgCO_3.3H_2O$ is the second solid phase this value is independent of the partial pressure of CO_2, and varies relatively little with the temperature. From the foregoing it follows that if a solution containing only calcium and magnesium carbonates is evaporated down (or if the partial pressure of CO_2 is gradually reduced, or if both things happen simultaneously) at 16°, pure calcium carbonate[3] will precipitate so long as the above ratio is less than 14000, as it would normally be in natural waters, provided always that the CO_2 pressure is sufficient to prevent precipitation of magnesium hydroxide; on the other hand, the order of precipitation will be reversed if the relative concentration of magnesium ion be greater than 14000 (*e. g.*, by addition of a soluble magnesium salt). It is to be emphasized however that the foregoing deductions, which are valid only if the only solid phases separating are pure calcite and pure $MgCO_3.3H_2O$, would have to be modified if, for instance, $MgCO_3$ can occur to a slight extent in solid solution with calcite, a possibility suggested by certain geological observations.

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[1] This is equivalent to the condition that such a basic carbonate should have a definite solubility in water or water containing CO_2, it being the only solid phase present; this implies that its molar solubility must be less than $^1/_2\sqrt[3]{K_h}$, where K_h is the solubility-product constant of $Mg(OH)_2$ at the temperature in question, for otherwise $Mg(OH)_2$ would be precipitated and two solid phases would be present.

[2] See, for instance, Abegg's Handbuch, II, **2**, 66–9 (1907).

[3] Under certain circumstances this might come down as aragonite instead of calcite; but this makes no difference in principle to anything here stated, for the solubility of aragonite is apparently only about 10% greater than that of calcite. This whole question is being taken up in another paper now in preparation.

But we have another state of affairs if the partial pressure of CO_2 is such that magnesium hydroxide may precipitate; and in actual practice this case may very readily occur, since the hydroxide appears when the partial pressure of CO_2 is about 0.00037, a proportion which is somewhat greater than that normally present in outside air. This again can be readily calculated. By combination of Equations I and X we obtain the relation

$$[Ca^{++}][OH^-]^2 = [Ca^{++}][CO_3^=] \times \frac{[OH^-]^2}{[CO_3^=]} = \frac{K^2_w \cdot K_{Ca}}{nk_1k_2cP} = \frac{3.43 \times 10^{-19}}{P}$$

at 16°; consequently for values of P less than 0.00037,

$$\frac{[Mg^{++}]}{[Ca^{++}]} = \frac{[Mg^{++}][OH^-]^2}{[Ca^{++}][OH^-]^2} = \frac{1.2 \times 10^{-11}P}{3.43 \times 10^{-19}} = 3.5 \times 10^7 P,$$

a ratio which decreases steadily as P is reduced. It follows from this that calcium carbonate precipitated from a solution containing magnesium may very readily be contaminated with appreciable proportions of magnesium hydroxide, which would be removed only slowly by repeated reprecipitations. That this actually occurs in the commercial manufacture of calcium carbonate is evident from the experience of Hostetter,[1] who found it a matter of considerable difficulty to buy calcium carbonate satisfactorily free from magnesia. But this trouble may be obviated very easily, namely by conducting the operations in such a way that the liquid is always saturated with CO_2 at a pressure above a certain limiting value; this limit, which increases with the temperature, cannot at present be specified very accurately, but is in all probability not greater than 1 atm. for any conditions likely to be encountered in actual practice.

Further discussion of the deposits resulting from the concentration of solutions containing both calcium and magnesium carbonates will be deferred for the present, as it necessitates the consideration of the solubility, and proneness to supersaturation, of the several forms of calcium and magnesium carbonates, as well as of the double carbonate dolomite;

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[1] J. C. Hostetter, *J. Ind. Eng. Chem.*, **6**, 392 (1914).

and the evidence on some of these points is unsatisfactory or lacking altogether.

The Solubility-Product Constant of other Carbonates.

For the sake of completeness, the solubility-product constant of barium carbonate has also been recalculated. The data, which again are due to Schloesing, and the derived quantities are presented in Table X, which is altogether similar to Table II, except that the ionization is, in this case, that of barium acetate at the equivalent concentration. The mean value from the six last experiments is $nrK_{Ba} = 3.95 \times 10^{-5}$, whence

$$[Ba^{++}][CO_3^{=}] = 7.0 \times 10^{-9} \text{ at } 16°.$$

TABLE X.—CALCULATIONS ON THE BASIS OF SCHLOESING'S DATA ON THE SOLUBILITY OF $BaCO_3$ IN WATER CONTAINING cP MOLS CO_2 AT 16°; $c = 0.0441$.

P. (Atm.)	Total [Ba]. Mols | l.	Total $[Ba(HCO_3)_2]$. Mols | l.	γ.	$[HCO_3^-]/2$.	$[Ba^{++}]$.	nrK_{Ba}.
0.000504	0.000601	0.000589	0.930	0.000548	0.000560	3.02×10^{-5}
0.000808	0.000732	0.000722	0.924	0.000667	0.000677	3.38
0.00333	0.00117	0.00116	0.915	0.001065	0.00107	3.31
0.01387	0.00196	0.00196	0.895	0.00175	0.00175	3.51
0.0282	0.00255	0.00255	0.884	0.00225	0.00225	3.66
0.0499	0.00312	0.00312	0.875	0.00273	0.00273	3.70
0.1417	0.00464	0.00464	0.850	0.00394	0.00394	3.92
0.2529	0.00578	0.00578	0.838	0.00485	0.00485	4.09
0.4217	0.00690	0.00690	0.825	0.00570	0.00570	3.98
0.5529	0.00766	0.00766	0.818	0.00627	0.00627	4.05
0.7292	0.00843	0.00843	0.811	0.00684	0.00684	3.98
0.982	0.00941	0.00941	0.802	0.00755	0.00755	3.98
						3.95×10^{-5}

The constants of two other carbonates are known approximately;[1] namely, for silver carbonate,[2] for which it is about 10^{-12}, and for lead carbonate,[3] about 10^{-14}.

Summary.

The solubility-product constants of calcium carbonate (calcite) and of magnesium carbonate ($MgCO_3.3H_2O$), a knowledge of which is of importance in connection with several problems of geological interest, have been recomputed from the best experimental data available; the results are satisfactorily concordant. This concordance is the more remarkable in view of the fact that in the case of the data for calcium carbonate the partial pressure varies more than ten-thousandfold; while the total ion-concentration of all the magnesium carbonate solutions on which the actual solubility determinations were made, was more than 0.5 N. The recalculated results are: $[Ca^{++}][CO_3^{=}] = 0.98 \times 10^{-8}$ at 16°, when the solution is saturated with respect to calcite; $[Mg^{++}][CO_3^{=}] = 1.93 \times 10^{-4}$ at 12°, the solution being saturated with $MgCO_3.3H_2O$; $[Ba^{++}][CO_3^{=}] = 7 \times 10^{-9}$ at 16°, the solid phase being $BaCO_3$. The solubility-product constant K_{Mg} of $MgCO_3.3H_2O$ at temperatures up to 50° is given by the formula

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[1] Approximately only, because the partial pressure of CO_2 (which, however, would be small) was neither controlled nor measured.

[2] Abegg and Cox, *Z. physik. Chem.*, **46,** 11 (1903); Spencer and Le Pla, *Z. anorg. Chem.*, **65,** 14 (1910). It would be well worth while to repeat these measurements under carefully controlled conditions, especially at a series of temperatures; for a number of important deductions could be drawn from the results.

[3] Pleissner, *Arbeiten kais. Gesundheitsamt,* **26,** 30 (1907).

$$\log K_{Mg} = 2315/T - 11.870,$$

whence the heat change corresponding to the reaction

$$MgCO_3.3H_2O = Mg^{++} + CO_3^{=} + 3H_2O$$

is an evolution of 10600 cal.

With a knowledge of these constants and of the solubility-product constant of magnesium hydroxide, one can show that calcium carbonate precipitated from solutions containing magnesium is likely to be contaminated with small quantities of magnesium hydroxide which could be removed only slowly by reprecipitations as ordinarily carried out; that mixtures of magnesium carbonate and hydroxide will in general be obtained in the precipitation of magnesium by a carbonate and that the basic carbonates thus produced are merely indefinite mixtures of carbonate and hydroxide; and that both calcium and magnesium carbonates can be obtained free from contamination by keeping the partial pressure of carbon dioxide above a certain limiting value, the magnitude of which depends upon the conditions and in all probability need not be greater than 1 atm. by a suitable choice of mode of operation.

Incidentally the constant $[HCO_3^-]^2/[CO_3^{=}][H_2CO_3]$ was recalculated from McCoy's data, and found to be 5600 n at 25°, where n (which is in all likelihood greater than 0.5) is the proportion of the total CO_2 in solution which exists as H_2CO_3; whence k_2, the second ionization constant of carbonic acid, is 6×10^{-11}, identical with the accepted value of this constant. It may be pointed out, moreover, that there can be no real *equilibrium* in aqueous solutions of carbonates except in presence of a definite partial pressure of CO_2 in the atmosphere in contact with the solution—in other words, that, strictly speaking, we are dealing with a ternary system, namely, base–CO_2–H_2O; consequently any carbonate solution through which a stream of gas absolutely free from CO_2 is passed, would gradually lose its carbonate and ultimately would contain only hydroxide.

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