blowing air through the water; and the redissolving of iron by treated water has been an occasional source of trouble.[1]

These instances have been discussed at some length because they illustrate the point that by considering that there is a mobile equilibrium and applying the appropriate quantitative relations we are enabled to coördinate and account very readily for things which otherwise are isolated and inexplicable facts. The application of these principles to other specific cases may be made in the same way, though in some cases experimental work on the constants involved may be required before the complete quantitative solution of the problem can be given.

Summary.

Within any solution containing carbonate there is a readily attained equilibrium between the carbonate ion $CO_3^=$, the bicarbonate ion HCO_3^-, and the carbonic acid H_2CO_3, and in turn between the carbonic acid and the partial pressure of carbon dioxide above the solution; consequently these molecular species can coëxist only in definite proportions determined by the several equilibrium constants. An examination from this standpoint of the most commonly used titration methods for the estimation of the combined and free CO_2 in solution leads to the conclusion that many of these procedures do not yield definite results—a conclusion which is corroborated by all of the careful comparative experimental work bearing on these methods. In principle the only absolutely reliable methods are those for the total base combined with the carbonic acid and for the *total* CO_2 present in solution; in practice they yield accurate results provided that due attention is paid to the conditions discussed, or referred to, in the paper. But these two determinations suffice in general to characterize the solution with respect to either its content of free CO_2, the proportion of carbonate to bicarbonate, or the degree of alkalinity or acidity; for, since we are dealing with an equilibrium capable of fairly rapid readjustment, we are justified in applying the equilibrium constants to calculate the above quantities in the great majority of those cases in which a knowledge of them is of real importance.

WASHINGTON, D. C.

THE COMPLETE SOLUBILITY CURVE OF CALCIUM CARBONATE.

BY JOHN JOHNSTON AND E. D. WILLIAMSON.

Since the publication of a previous paper[2] dealing with the solubility-

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[1] For references see Tillmanns and Heublein, *Gesundheitsingenieur*, **35**, 609 (1912); or Tillmanns, *J. Gasbeleuchtung*, **56**, 370 (1913).

[2] Johnston, THIS JOURNAL, **37**, 2001 (1915), *q. v.*; hereinafter referred to as *Loc. cit.*

product constant of calcium and magnesium carbonates, several additional points have come up which deserve consideration. These points are, moreover, of some general importance since they apply, *mutatis mutandis*, to any carbonate (or indeed to salts of any dibasic acid); they are elucidated immediately by the consideration of the complete solubility curve of the carbonate at any temperature. We shall, therefore, discuss briefly the relation between the partial pressure of CO_2 in equilibrium with the solution and the total concentration of base in equilibrium with the stable solid phase; the latter will be hydroxide, carbonate or bicarbonate[1] according to conditions, as a carbonate is stable in presence of its aqueous solution only between certain limits of pressure of CO_2, these limits being fixed for a given base at a given temperature.

We begin by considering the equilibrium between the hydroxide $M(OH)_2$ and the aqueous solution saturated with it as affected by a progressive increase from zero of the partial pressure P of CO_2 in the atmosphere in contact with the solution. Addition of CO_2 is followed by a distribution between the vapor and liquid phases until there is equilibrium between the residual partial pressure of CO_2 and the H_2CO_3 in solution, and in turn between the latter and the several ions; the net effect of this is a definite decrease in $[OH^-]$, the concentration of hydroxide ion, which necessitates that more of the hydroxide dissolve in order to keep the solubility-product $[M^{++}][OH^-]^2$ constant. Consequently the total concentration of M^{++} increases, part of it being now associated with carbonate and bicarbonate; in other words, the apparent solubility of the base increases if the method of analysis of the solution is a determination of M, whereas it would decrease if one should determine $[OH^-]$.[2] This process continues until the product $[M^{++}][CO_3^=]$ reaches the value requisite for the precipitation of MCO_3 (on the assumption that supersaturation does not occur) which, for a given base, takes place at a definite value of P which depends only upon the temperature; this transition pressure P_1 is, at a given temperature, the highest under which solid hydroxide is stable and the lowest at which solid carbonate is stable.

At P_1 the solubility (as measured by the total $[M]$) begins to diminish,[3] because increase of P increases $[CO_3^=]$ while the product $[M^{++}][CO_3^=]$ must remain constant so long as MCO_3 is the stable solid phase; this increase of $[CO_3^=]$ continues until a definite pressure P_0 is reached, when the formation of bicarbonate in the solution becomes the predominant

[1] Throughout this paper we presume that no basic carbonate exists as a stable solid phase.

[2] Manifestly one could not determine $[OH^-]$ by an ordinary titration method, but would have to use some method which does not alter the equilibrium.

[3] This descending portion of the curve will not be realizable if the hydroxide is stable beyond a certain limiting value of P, viz., P_0 (cf. *postea*) which varies very little from one base to another.

reaction and $[CO_3^-]$ begins to decrease again. P_0 is thus a minimum in the solubility curve. With further increase beyond P_0 the concentration of both M^{++} and HCO_3^- increases steadily until the precipitation value of the product $[M^{++}][HCO_3^-]^2$ is reached at P_2, which is a transition pressure at which both carbonate and bicarbonate are present as stable solid phases. Beyond P_2 bicarbonate alone is stable, and its total solubility falls off very slowly with further increase of partial pressure of CO_2.
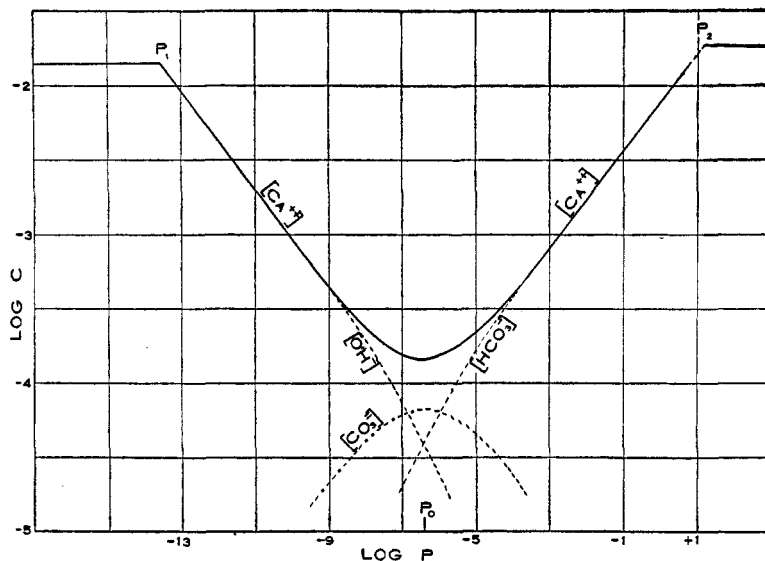

Fig. 1.—Graph of log C (C = ionic concentration) against log P (P = CO_2 pressure in atm.) for the several ions in the system CaO–H$_2$O–CO$_2$ at 16°. The stable solid phase to the left of P_1 is hydroxide, between P_1 and P_2 is carbonate, and to the right of P_2 bicarbonate. The several dotted curves are the solubility curves which would be obtained if the concentration of one or another of these ions were determined by analysis; the full curve, if correction is made for incomplete ionization, represents the solubility as ordinarily determined by estimation of calcium.

These relations are obvious from Fig. 1, which shows the variation with P of the total concentration[1] of Ca^{++} (which if it were corrected for the incomplete ionization, would be the solubility of the solid, as ordinarily measured), and also of $[OH^-]$, $[CO_3^-]$ and $[HCO_3^-]$; obviously $2[Ca^{++}] = [OH^-] + 2[CO_3^-] + [HCO_3^-]$. These curves were constructed on the basis of the equilibrium equations discussed in what follows; the only assumption made is that each solubility-product remains constant throughout the range in which the particular solid phase

[1] The scales had to be made logarithmic, as otherwise the left hand portion of the diagram up to P_0 would have been too small to be visible; for some numerical data see Table I.

is stable. The figure shows very strikingly to what different results we might be led if, instead of determining by experiment the total concentration of M, we were to analyze for one of the other three molecular species; such a course would be unlikely in the case of the carbonates but might be followed in other analogous cases, e. g., sulfites or sulfides. It may be remarked, moreover, that it is entirely possible that the range P_1P_2 within which the normal carbonate is the stable solid phase may in certain cases be very small, or even zero; the main conditions for this would be that the hydroxide be relatively insoluble and the bicarbonate not too soluble.

The Value of P_0.—The minimum solubility is realizable only if carbonate is the stable solid phase at the pressure P_0, i. e., only if P_1 is less than P_0. The equations[1] giving the necessary relations are as follows, the symbols being the same as before with the addition of m, the valence of M under these conditions, the ion-concentration of M being indicated by $[M]$:

$$[M]^{2/m} [CO_3^=] = K_C \qquad\qquad (I)$$

$$[HCO_3^-] = r[H_2CO_3] [CO_3^=] \qquad\qquad (VI)$$

$$[OH^-] = K_W^2[CO_3^=]/k_1k_2[H_2CO_3] \qquad\qquad (X')$$

These combined with the condition

$$m[M] = [HCO_3^-] + 2[CO_3^=] + [OH^-]$$

yield the expression

$$m\,[M] = \sqrt{\frac{K_C r [H_2CO_3]}{[\,/\,]^{2/m}}} + \frac{K_C}{2[M]^{2/m}} + \sqrt{\frac{K_C K_W^2}{k_1k_2[H_2CO_3][M]^{2/m}}} \qquad (XIII)$$

as the equation of the curve representing the change of solubility of the carbonate with the concentration $[H_2CO_3]$, hence with P. Whence, by differentiating and substituting, we get

$$\frac{d[M]}{d[H_2CO_3]} = \frac{m[M]\{[HCO_3^-] - [OH^-]\}}{2[H_2CO_3]\{m^2 + m[M] + 2[CO_3^=]\}} \qquad (XIV)$$

which vanishes when $[HCO_3^-] = [OH^-]$; at this point $[H_2CO_3] = K_W/k_1$, wherefore, $cP_0 = K_W/nk_1$.

The order of magnitude of P_0 is, therefore, independent of what M is, though its value is not absolutely the same for the several carbonates because the appropriate value of c (absorption coefficient of CO_2) varies slightly from one saturated solution to another. At 18°, P_0 is (for calcite) 4.0 $\times$ 10^{-7}, a pressure which therefore is easily realizable, since it is only about the one-hundredth part of the proportion normally present in the atmosphere.

The Value of P_1 and P_2.—These are obtained directly by combination of the appropriate solubility-product constants of carbonate (K_C),

[1] See *Loc. cit.*, p. 2011; Equation X' follows directly from combination of X and V.

hydroxide (K_H) and bicarbonate (K_B) with equations already given; the values follow:

$$P_1 = \frac{K_C}{K_H} \cdot \frac{K_W^2}{cnk_1k_2}$$

$$P_2 = \frac{K_B}{K_C} \cdot \frac{k_2}{cnk_1}$$

Equation XIII represents the solubility curve only between P_1 and P_2; similar equations are easily set up for the other two branches of the complete curve, *i. e.*, for the solubility of hydroxide and bicarbonate, respectively. Obviously, too, in case P_1 is greater than P_0 there will be no minimum on the solubility curve of the carbonate; this is so in the system $MgO-CO_2-H_2O$,[1] in which case P_1 is about 0.00037.

The Data for Calcium Carbonate.—In order to bring out certain points we have calculated[2] the solubility of $CaCO_3$ for a series of partial pressures extending from ordinary conditions downwards; and present the results in Table I, which supplements Table IV of the previous paper.

From the table it follows that at 16° P_0, the value of P at which there is the minimum concentration of calcium in solution, is 3.73×10^{-7} atm., corresponding to a solubility of about 16 mg. $CaCO_3$ per liter; on either side the solubility increases owing to the formation in solution of hydroxide on the one hand and of bicarbonate on the other. It is to be observed, moreover, that even at this minimum (which is the maximum concentration of $CO_3^=$) only about 46% of the Ca^{++} present is associated with carbonate, the remaining 54% being equally divided between hydroxide and bicarbonate; and that, except at pressures close to P_0, the proportion of Ca^{++} associated with $CO_3^=$ is very small. This

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[1] See *Loc. cit.*, p. 2015. In Table VIII (p. 2016) the values of $[CO_3^=]$ in the fourth column are, through a printer's error, one-tenth of what they ought to be.

[2] For the method and the values of the constants used, see *Loc. cit.*, p. 2011. Since the publication of the previous paper, we have seen in manuscript a paper by Seyler and Lloyd (which is in course of publication in the *J. Chem. Soc. London*) in which they show that Na_2CO_3 is in all probability ionized to a much smaller extent than has generally been assumed; and that on this basis recalculation of McCoy's results, as well as of a series of experiments of their own, yields a value for nk_1/k_2 of about 7100 at 25°. The adoption of this value would lower the solubility-product constant K_C in the ratio of 56 to 71, and produce a corresponding change in the other calculated values; but for the present we have preferred to retain the previous value, for the following reasons: (*a*) Auerbach and Pick, in calculating k_2 from their work, assumed a degree of ionization of Na_2CO_3 comparable to that indicated by the work of Seyler and Lloyd, and obtained the value 6×10^{-11} at 18°; whence nk_1/k_2 is 5100 at 18°, a temperature close to that we are considering (16°); (*b*) some of the other data are likewise uncertain; (*c*) in view of which, we preferred to keep the data consistent with those of the previous paper. In any case such changes will not alter the shape of the curve, but merely affect the absolute values, and to an extent which is hardly significant in the present state of accuracy of the experimental work which we are considering.

TABLE I.—THE CALCULATED ION-CONCENTRATIONS AND SOLUBILITY OF CALCITE IN WATER AT 16° IN CONTACT WITH AIR CONTAINING THE PARTIAL PRESSURE P OF CO_2.

P.[1]	$[HCO_3^-] \times 10^4$.	$[OH^-] \times 10^4$.	$[CO_3^=] \times 10^4$.	$[Ca^{++}] \times 10^4$.	Parts $CaCO_3$ per million.[2]
2.15×10^{-4}	10.0	0.0174	0.188	5.197	56
7.63×10^{-5}	7.0	0.034	0.260	3.777	40
7.62×10^{-6}	3.0	0.147	0.478	2.051	22
6.07×10^{-7}	1.0	0.614	0.666	1.473	16.0
3.85×10^{-7}	0.80	0.774	0.672	1.459	15.9
3.73×10^{-7}	0.787	0.787	0.672	1.459	15.9
2.19×10^{-7}	0.60	1.02	0.665	1.476	16.0
6.14×10^{-8}	0.30	1.82	0.593	1.654	18
9.78×10^{-9}	0.10	3.82	0.414	2.377	26
2.80×10^{-10}	0.01	13.3	0.144	6.81	74
3.16×10^{-14}	0.0000235	277.0	0.0071	138.5	2000

table enables us to define the equilibrium when $CaCO_3$ is shaken up in a closed vessel completely filled with *pure* water; for in such a case $[OH^-]$ and $[HCO_3^-]$ must be very nearly equal, the small difference between them being merely the amount of CO_2 required to bring the solution into equilibrium with a virtual pressure somewhat *less* than 3.73×10^{-7}. Under such conditions, therefore, the solubility of $CaCO_3$ would be about 16 parts per million at 16°; nor would, as a consideration of the matter shows, the result be appreciably different though 99% of the volume of the vessel were occupied by pure air. Now Kendall[3] in certain of his experiments used a method which approximately satisfies the above conditions, and found a solubility of 14 parts per million at 25°; in this connection we may remark that Kendall's results would have been very much higher if his air and water had been *completely* free from CO_2.

The transition pressure P_2 between calcium carbonate and bicarbonate has been determined by McCoy and Smith[4] to be about 15 atm. at 25°, bicarbonate being the stable solid phase above this pressure; the value of P_2 at 16° is not known, but is certainly of the same order of magnitude.

The transition pressure P_1 at which both hydroxide and carbonate

[1] From the equations it follows that $P = \dfrac{0.5b^3 + \sqrt{1.809b^3 + 3.927b^4} + 0.25b^6}{4.85 \times 10^6}$ where $b = [HCO_3^-] \times 10^4$; when b and P are fixed, the other quantities are readily calculated.

[2] Calculated on the basis that the degree of ionization is about 0.92 throughout, except for the (approximate) value in the lowest row.

[3] J. Kendall, *Phil. Mag.*, 23, 958 (1912).

[4] McCoy and Smith, THIS JOURNAL, 33, 468 (1911). This important paper was inadvertently overlooked during the preparation of the previous paper. We are obliged to Dr. McCoy for directing our attention to it. They calculate K_C to be 0.93×10^{-8} at 25°, a value which agrees very well with that given in Table II *postea*.

are stable, can be calculated if we know the solubility-product constant (K_H) of $Ca(OH)_2$. As far as one can judge from the somewhat discordant data available, the solubility of $Ca(OH)_2$ at $16°$ is about 0.021 mols per liter; whence, on the basis that its degree of ionization in the saturated solution is about 70%,
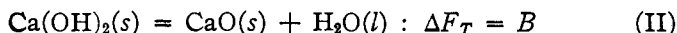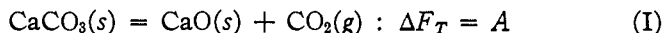
$$K_H = [Ca^{++}][OH^-]^2 = (0.015)(0.03) = 1.3 \times 10^{-5} \text{ at } 16°$$

and

$$P_1 = \frac{1.0 \times 10^{-8}}{1.3 \times 10^{-5}} \times 3.4 \times 10^{-11} = 2.6 \times 10^{-14}.$$

Consequently $Ca(OH)_2$ can be the *stable* solid phase only when the partial pressure of CO_2 is extremely small, so small that such freedom from CO_2 could be realized only by means of extraordinary precautions; this fact may be correlated with the lack of satisfactory concordance of the data on the solubility of $Ca(OH)_2$.

P_1, however, can also be calculated in a totally different way, from independent data. P_1 is the pressure of CO_2 in equilibrium with solid hydroxide and solid carbonate in the solution saturated with respect to both at the particular temperature T, and, is therefore, a measure of the free energy change C accompanying the reaction III below; but the latter quantity is the difference[1] between the corresponding quantities A and B for the reactions I and II:

$$CaCO_3(s) = CaO(s) + CO_2(g) : \Delta F_T = A \qquad (I)$$

$$Ca(OH)_2(s) = CaO(s) + H_2O(l) : \Delta F_T = B \qquad (II)$$

$$CaCO_3(s) + H_2O(l) = Ca(OH)_2(s) + CO_2(g) : \Delta F_T = C = A - B \quad (III)$$

Now it was shown in a previous paper[2] that the dissociation pressure p (expressed in mm. Hg) is reproduced over the experimental range[3] $(T = 850 - 1150)$ by the formula

$$\log p = -9340/T + 1.1 \log T - 0.0012\ T + 8.882$$

whence by extrapolation down to $289°$ abs. (*i. e.*, $16°$)

$$\log P_{289} = -23.97 \text{ (when } P \text{ is the pressure in atm.)}$$

and

$$A = \Delta F_{289} = -RT \ln P_{289} = 289 \times 4.576 \times 23.97 = 31700.$$

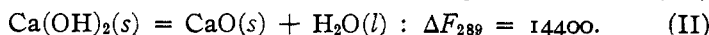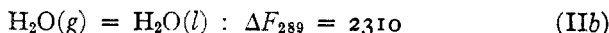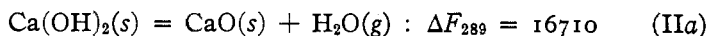In an earlier paper[4] it was shown that the free energy change of the re-

[1] We neglect here the small quantity corresponding to the difference between the vapor pressure of pure water and that of the water in the solution saturated with hydroxide and carbonate.

[2] J. Johnston, THIS JOURNAL, **32**, 938 (1910).

[3] Quite recently it was shown by Sosman, Hostetter and Merwin (*J. Wash. Acad.*, **5**, 563 (1915)) that the pressure of CO_2 in equilibrium with $CaCO_3$ at $400°$ is of the same order of magnitude (0.002 mm.) as is indicated by the formula above.

[4] J. Johnston, THIS JOURNAL, **30**, 1359 (1908).

action IIa is $\Delta F = 25870 - 31.67T$, hence $\Delta F_{289} = 16710$; while that of reaction IIb at $289°$ is $= -RT \ln 0.0178^1 = -2310$.

$$Ca(OH)_2(s) = CaO(s) + H_2O(g) : \Delta F_{289} = 16710 \qquad (IIa)$$

$$H_2O(g) = H_2O(l) : \Delta F_{289} = 2310 \qquad (IIb)$$

$$Ca(OH)_2(s) = CaO(s) + H_2O(l) : \Delta F_{289} = 14400. \qquad (II)$$

Thus we calculate that C, the free energy change of reaction III, is $31700 - 14400 = 17300$ and hence

$$\log P_1 = -\frac{17300}{289 \times 4.576} = -13.08$$

so that $P_1 = 8.3 \times 10^{-14}$.

The agreement between this value and that derived directly from the solubility data is remarkable, especially in view of the uncertainty attaching to some of the factors involved in the calculation; the large extrapolation, for example, will be accurate only when the specific heats of the several solid substances shall have been determined throughout the temperature range. From this value of P_1 we may calculate back-wards and find $K_H = \dfrac{K_C \times 3.435 \times 10^{-11}}{8.3 \times 10^{-14}} = 4 \times 10^{-6}$, as compared with 13×10^{-6} derived directly; this latter value, it may be observed, is in all probability too high, since in its derivation it was tacitly assumed that no intermediate ions are formed, that the ionization proceeds solely according to the scheme $Ca(OH)_2 \longrightarrow Ca^{++} + 2(OH^-)$. This substantial agreement between such different lines of evidence is important as a demonstration of the essential correctness of the views here discussed; it serves, moreover, either to increase confidence in the experimental data or else as a clue, by means of which errors may be more readily discovered.

TABLE II.—THE SOLUBILITY-PRODUCT CONSTANT OF CALCITE AT SEVERAL TEMPERATURES.

Temperature t.	Parts $CaCO_3$ per million. ($P = 0.00032$.)	c.	$K'_C \times 10^8$.
0	81	0.0765	1.22
5	75	0637	1.14
10	70	0535	1.06
15	65	0455	0.99
20	60	0392	0.93
25	56	0338	0.87
30	52	0297	0.81

As regards the change of solubility of calcite with temperature, Wells[2] has made a series of determinations at temperatures between $0°$ and $30°$, the solution being in contact with air containing 3.2 parts CO_2 per

[1] The vapor pressure, expressed in atm., of water at $16°$.

[2] R. C. Wells. *J. Wash. Acad. Sci.*, **5**, 617 (1915).

10,000; the results as interpolated from his curve are given in Table II, along with the appropriate values of $c(= \alpha/22.4$, where α is the absorption coefficient) and of the solubility-product calculated on the basis that nk_1/k_2 is 5600.

K'_C is given by the expression $\log K'_C = \bar{8}.087 - 0.006\ t$; whence one can, using 5600 as the value of nk_1/k_2, calculate the solubility of calcite for any partial pressure of CO_2 at any temperature up to 30°.

Summary.

The graph showing the concentration of calcium in the solution at equilibrium in the system $CaO-H_2O-CO_2$ is made up of three curves, along which the stable solid phase is hydroxide, carbonate, bicarbonate, respectively. The first extends only up to values of P, the partial pressure of CO_2, of about 10^{-14} at 16°; the second, starting from the transition point, decreases to a minimum and then rises again, as the value of P increases continuously, until P is about 15 atm.; beyond the second transition point bicarbonate is the stable solid phase. Along the whole course of the graph, all three ions OH^-, $CO_3^=$, HCO_3^- are present at relative concentrations depending upon P; so in this, as in other analogous cases, the solubility curve ascertained by experiment would have different forms according as one determined one or other of the several molecular species in solution. Thus the maximum concentration of $CO_3^=$ occurs when the solubility—as measured by the concentration of calcium in solution—is a minimum; and it is only within a restricted range of P that the base associated with $CO_3^=$ is more than a fractional proportion of the total base in solution.

The transition pressure at which both hydroxide and carbonate are stable, may be calculated either from the solubilities of hydroxide and carbonate or from their thermal dissociation pressures; these two absolutely independent methods yield results surprisingly concordant, a circumstance which demonstrates the essential correctness of the views discussed in this paper.

WASHINGTON. D. C.

SUGGESTION CONCERNING THE STATEMENT OF THE PHASE RULE.

BY THEODORE W. RICHARDS.

The most serious difficulty of the Phase Rule for beginners lies in the definition of the word "component," of which many varying definitions have been given by various authorities. Of these most are entirely legitimate, although they may lead to different choices as to the number of