sodium and potassium sulfate were mixed mechanically with sodium sulfate.

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# EQUILIBRIUM BETWEEN ALKALI-EARTH CARBONATES, CARBON DIOXIDE AND WATER.

BY HERBERT N. McCOY AND HERBERT J. SMITH.

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In view of the importance of an accurate knowledge of the state of equilibrium between calcium carbonate, carbon dioxide and water and the fact that previous experimenters[1] had not used modern physicochemical methods, nor carried the measurements to higher pressures than 6 atmospheres, we undertook a study of the system in question.

As is well known, the concentration of dissolved lime increases with increasing concentration of carbonic acid. The theory of the equilibrium has been treated by van't Hoff,[2] Bodländer[3] and Stieglitz.[4]

The following fundamental equations govern the equilibrium:

$$H \times HCO_3 = k_1 \times H_2CO_3. \tag{1}$$

$$H \times CO_3 = k_2 \times HCO_3. \tag{2}$$

$$Ca \times CO_3 = k_3, \text{ the solubility product.} \tag{3}$$

$$HCO_3 = 2Ca. \tag{4}$$

$$Ca = \alpha \times Ca(CHO_3)_2. \tag{5}$$

If $k$ is the equilibrium constant for reaction,

$$\frac{\alpha \times Ca(HCO_3)_2}{\sqrt[3]{H_2CO_3}} = \sqrt[3]{\frac{k_1k_3}{4k_2}} = k. \tag{6}$$

Bodländer showed that Schloessing's experiments gave a good equilibrium constant and calculated $k_3$, the solubility product of calcium carbonate, from the results. The value found is erroneous[5] owing to the use of an incorrect value for the secondary ionization constant of carbonic acid. Stieglitz has made a critical recalculation of the solubility product from Schloessing's experiments and other available data giving $k_1$ and $k_2$. Seyler and Lloyd[6] have also studied the problem under conditions applicable to geological problems.

In our experiments, for partial pressures of carbon dioxide, less than

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[1] Schloesing, *Compt. rend.*, 74, 1552; 75, 70 (1872); Engler, *Ann. chim. phys.*, [6] 13, 348 (1888). Seyler and Lloyd, *J. Chem. Soc.*, 95, 1347 (1909).

[2] *Z. physik. Chem.*, 1, 505 (1887).

[3] *Ibid.*, 35, 23 (1900).

[4] *Carnegie Inst. Publication*, 107, 233 (1908).

[5] Stieglitz, *Loc. cit.* McCoy, *Am. Chem. J.*, 29, 437 (1903.)

[6] *Loc. cit.*

one atmosphere, 500 cc. glass bottles were used. For higher pressures we used a 2 liter seamless, pressed steel bottle with a needle valve, capable of withstanding the pressure of liquid carbon dioxide. The inside of the bottle was effectively protected from the action of the carbonic acid by a thin coating of a mixture of beeswax and Venice turpentine, applied hot. The calcium carbonate used was made by precipitating pure calcium nitrate with ammonium carbonate at 15° and washing the precipitate free from ammonium nitrate. By working in the cold the calcite variety was obtained.

The glass bottles were charged with about 50 g. of calcium carbonate and 250 cc. of water; the steel bottle with about double these quantities. Carbon dioxide was then introduced in the desired amount. For experiments at greater than atmospheric pressure the gas was drawn from a steel cylinder of liquid carbon dioxide. The charged bottles were rotated in a thermostat at 25° + 0.02 for from 2 to 3 days, in which time equilibrium was reached. At low pressures the bottles were allowed to stand in the thermostat until the solution became clear. Portions of the latter were then removed by a pipet and analyzed. For high pressures, a brass tube, 1 × 5 cm., filled with cotton and attached to the inside of the needle valve of the steel bottle, served to filter the solution. Suitable portions of the filtered solution were drawn off into tared, evacuated, round-bottomed flasks. For the carbon dioxide analysis, the flask contained a solution of barium chloride and a known volume of standard potassium hydroxide, so that, although the carbonate solution gave off gaseous carbon dioxide as soon as the pressure was released, none of the gas was lost. The amount of solution taken for analysis was determined by weight and the excess of alkali titrated with 0.05 *N* hydrochloric acid, using phenolphthalein as indicator.[1] In the analysis for calcium the solution was run into a dry flask and although it became supersaturated with $CaCO_3$, owing to loss of $CO_2$, it remained clear for a sufficient time to prevent deposition of $CaCO_3$ in the valve or connecting tube. The solution was weighed and then titrated with $N/20$ HCl, using methyl orange as indicator.

The results of the experiments are shown in the accompanying graph, where the ordinates are molecular concentrations of $Ca(HCO_3)_2$ and the abscissas cube roots of molecular concentrations of free $H_2CO_3$, all free carbon dioxide in the solution being calculated as $H_2CO_3$. A few nearly coinciding points have been omitted. Fifteen experiments were made in glass bottles at pressures of carbon dioxide between 0.06 and 1 atmosphere. Twenty-one experiments were made in the steel bottle at pressures between 2 and 25 atmospheres. These values are not actual measured pressures but are those calculated from the solubility at atmospheric

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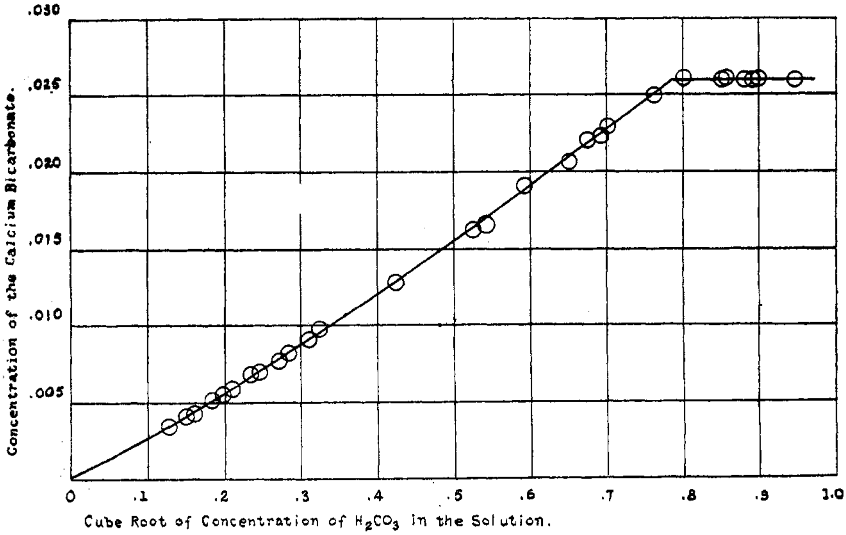
[1] Winkler's method, see Küster, *Z. anorg. Chem.*, 13, 127 (1897).

pressure[1] by Henry's law, which, however, does not apply closely for carbon dioxide as shown by Wroblewski.[2]

As shown by the graph, a maximum solubility of calcium salt is reached at a certain concentration of carbonic acid. This is 0.485 normal molecular and corresponds to a calculated carbon dioxide pressure of about



15 atmospheres. The obvious interpretation is that the solution becomes saturated with $Ca(HCO_3)_2$ at this point. This saturated solution is 0.026 molecular, equal to 0.42 g. of $Ca(HCO_3)_2$ per 100 cc. Theoretically it should be possible to convert all of the solid $CaCO_3$ present (about 100 g.) into solid bicarbonate by introducing carbon dioxide in sufficient amount at a pressure greater than 15 atmospheres. As long as any solid $CaCO_3$ remained the pressure of carbon dioxide should finally fall to 15 atmospheres. It was found, however, that pressures between 16 and 25 atmospheres remained at the end of 2 or 3 days' rotation of the steel bottle and that the solid residue was still largely, if not wholly, $CaCO_3$. This would seem to show that our interpretation is incorrect. But when we consider that about 2 days are required to dissolve the 2 g. of $CaCO_3$ necessary to saturate the solution at its maximum concentration, we could not expect to accomplish the complete conversion of the $CO_2$ and $CaCO_3$ into bicarbonate in less than 3 months. We are inclined to think, therefore, that when we can give the reaction sufficient time we shall find the facts in harmony with the hypothesis.[3] This hypothesis is also

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[1] Just, *Z. physik. Chem.*, 37, 342 (1901); Geffcken, *Ibid.*, 49, 273 (1904).

[2] *Compt. rend.*, 94, 955, 1355 (1882).

[3] This investigation had to be discontinued in Aug., 1910. We hope to resume it in the near future.

supported by the experiments of Keiser[1] who found that an unstable precipitate was formed by the action of $NH_4HCO_3$ on a cold solution of $CaCl_2$. The precipitate had the approximate composition $CaCO_3$ $1.75H_2CO_3$ and was evidently impure calcium bicarbonate. It is now easy to explain why the precipitate decomposed so readily: its decomposition pressure was much greater than 1 atmosphere.

The numerical results of 6 typical experiments of the 36 completed are given in the following table:

| Approx. pres. $CO_2$ in atmos. | 1000 $H_2CO_3$. | 1000 $Ca(HCO_3)_2$. | 100 $\alpha$. | 1000 $k$. |
|---|---|---|---|---|
| 0.1 | 3.522 | 4.116 | 86.6 | 23.4 |
| 1.1 | 37.28 | 9.734 | 81.0 | 23.6 |
| 9.9 | 332.9 | 22.36 | 72.8 | 23.5 |
| 13.2 | 444. | 24.95 | 71.3 | 23.3 |
| 16.3 | 550. | 26.00 | .... | .... |
| 25.4 | 858. | 26.03 | .... | .... |

The calculated approximate pressures are not to be considered as accurate. The concentrations of $H_2CO_3$ and $Ca(HCO_3)_2$ were found by analysis as described. In the fourth column, $\alpha$ is the assumed degree of ionization of $Ca(HCO_3)_2$, which is taken to be the same as that of calcium acetate at the same concentration, the values given having been calculated from the figures given by Kohlrausch and Holborn,[2] p. 161. The equilibrium constant, $k$, was calculated by equation 6.

$$k = \frac{\alpha \times Ca(HCO_3)_2}{\sqrt[3]{H_2CO_3}}$$

The mean value of $k$ for the 29 experiments at pressures less than 15 atmospheres, where the solutions were unsaturated with $Ca(HCO_3)_2$, was 0.0234; the maximum was 2.5 per cent. higher; the minimum was 2.5 per cent. lower; the average deviation from the mean was 1.0 per cent. The 7 experiments at pressures greater than 15 atmospheres all gave essentially identical concentrations of $Ca(HCO_3)_2$. This fact is illustrated by the last two results given in the table and is clearly shown by the graph. Naturally, these 7 experiments may not be used to calculate the equilibrium constant. Seyler and Lloyd's experiments on the solubility of $CaCO_3$ in aqueous carbonic acid were made at "room temperature." Their equilibrium constant, $F$, bears to ours the relation

$$k = 0.02\sqrt[3]{F}.$$

Their average value of $F \doteq 113$ substituted in the above equation gives $k = 0.0242$; our own experiments gave 0.0234.

In equation (6) $k_3$, the solubility product of $CaCO_3$, is expressed in terms of $k$, the equilibrium constant determined by this investigation and $k_1$

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[1] THIS JOURNAL, 30, 1711 (1908).

[2] Leitvermögen, Leipzig, 1898.

and $k_2$, the primary and secondary ionization constants of carbonic acid. Rearrangement of (6) gives

(7) $$Ca \times CO_3 = k_3 = 4k_2k^3/k_1.$$

The constant $k_1$ was determined by Walker and Carmack[1] by conductivity measurements to be $3.04 \times 10^{-7}$. The secondary constant, $k_2$, is not known with the same degree of accuracy as $k_1$. Experiments by one of us[2] on the equilibrium between $Na_2CO_3$, $NaHCO_3$, $CO_2$ and $H_2O$ give the only available data for the calculation of $k_2$. From the results with 0.1 *N* solutions, the original calculation gave the value $k_2 = 6.04 \times 10^{-11}$. The subsequent work of Geffcken[3] on the effect of salts on the solubility of carbon dioxide gave data from which Stieglitz corrected the calculation and found $k_2 = 6.20 \times 10^{-11}$. For some unknown reason, more concentrated sodium carbonate solutions gave considerably higher values: for 0.3 *N* solutions $k_2 = 7.8 \times 10^{-11}$. Normal solutions gave still higher values. Extrapolation gives $k_2 = 5.4 \times 10^{-11}$ for an infinitly dilute solution and $5.5 \times 10^{-11}$ for a solution 0.02 *N*. As the solutions of $Ca(HCO_3)_2$ were from 0.003 to 0.026 *N* we shall use in the following calculations $k_2 = 5.5 \times 10^{-11}$. Substitution of this value in equation (7) gives $k_3 = 9.3 \times 10^{-9}$. Stieglitz used $k_2 = 7 \times 10^{-11}$ and obtained from Schloessing's experiments $k_3 = 12.6 \times 10^{-9}$. If we use the same value of $k_2$, our experiments give $k_3 = 11.9 \times 10^{-9}$. We think that the lower value of $k_2$, and therefore also of $k_3$, is preferable. Seyler and Lloyd point out that $k_2$, the secondary constant for carbonic acid, decreases with decreasing concentration of the sodium carbonate solutions used in its determination by McCoy's method. For this reason they did not try to calculate the solubility product of $CaCO_3$. They have undertaken a new determination of $k_2$ but the results are apparently not yet published.

If $CaCO_3$ were not hydrolytically dissociated, the concentration of Ca (equal also to $CO_3$) in pure water, free from $CO_2$, would be $k_3 = 9.6 \times 10^{-5}$ or 9.6 mg. per liter. It is now possible to calculate the concentrations of the components of such a solution, when hydrolytic dissociation is taken into account. In addition to equations (1), (2) and (3) the following relations also exist:

(8) $$H \times OH = k_w$$

(9) $$H + 2Ca = OH + HCO_3 + 2CO_3,$$

since the solution is electrically neutral. This reduces to

(10) $$2Ca = OH + HCO_3 + 2CO_3$$

by reason of the negligibly small value of *H* compared with 2*Ca*.

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[1] *J. Chem. Soc.*, **77**, 5 (1900).

[2] McCoy, *Loc. cit.*

[3] *Loc. cit.*

Finally,

$$\text{(11)} \qquad Ca = HCO_3 + CO_3 + H_2CO_3$$

if there is no excess or deficiency of $CO_2$. The six equations give

$$\text{(12)} \qquad \frac{H^4(2H + k_1)^2}{H^2 + k_1H + k_1k_2} = \frac{k_1k_2k_w^2}{k_3}.$$

The solution of (12) gives $H = 1.09 \times 10^{-10}$, from which we then find $Ca = 1.66 \times 10^{-4}$; $CO_3 = 0.56 \times 10^{-4}$; $H_2CO_3 = 1.10 \times 10^{-4}$; $OH = 1.10 \times 10^{-4}$; $H_2CO_3 = 4.0 \times 10^{-8}$. An inspection of the figures shows that a solution formed from pure water and $CaCO_3$ would contain only 34 per cent. as much free $CO_3$ as the Ca present would represent. The remaining 66 per cent. of the $CO_3$ would have united with water to give $HCO_3$ and an equal concentration of OH. To form such a solution 16.6 mg. of $CaCO_3$ per liter of water would be required if practically complete ionization be assumed. We have calculated from the measurements of Kohlrausch[1] of the conductivity of pure water saturated with $CaCO_3$ that 12 mg. of the substance are dissolved by 1 l. of water. In so doing we have considered the hydrolysis to be 66 per cent. The agreement is only fair; the cause of the difference is not apparent.

Strontium and barium carbonates have been studied in the same way as calcium carbonate. In the case of strontium carbonate, nine experiments have been made at pressures between 0.05 and 1.1 atmospheres. The equilibrium constant $k = 1.29 \times 10^{-2}$, with an average deviation from the mean of 1.2 per cent. This value leads by equation (7) to the solubility product $Sr \times CO_3 = k_3 = 1.567 \times 10^{-9}$. With barium carbonate, eleven experiments were made at pressures between 0.2 and 30 atmospheres. The graph for $BaCO_3$ is very similar to that for $CaCO_3$; a maximum solubility, $Ba(HCO_3)_2 = 0.028$, is reached at a concentration of $H_2CO_3 = 0.727$, corresponding to a calculated $CO_2$ pressure of about 22 atmospheres. The solubility of $Ba(HCO_3)_2$ is 7.3 g. per liter or 0.73 g. in 100 cc. of water. For $BaCO_3$ the equilibrium constant was found to be $k = 2.24 \times 10^{-2}$; average deviation from mean = 0.8 per cent. The solubility product $Ba \times CO_3 = k_3 = 8.1 \times 10^{-9}$.

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[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

# EQUILIBRIUM BETWEEN SODIUM CARBONATE, SODIUM BICARBONATE AND WATER.

[SECOND PAPER.]

BY HERBERT N. MCCOY AND CHARLES D. TEST.

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Several years ago one of us made a study of the system carbonates of sodium, carbon dioxide and water,[2] for solutions of decinormal to normal

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[1] *Z. physik. Chem.*, 44, 236 (1903).

[2] McCoy, *Amer. Chem. J.*, 29, 437 (1903).