

sodium and potassium sulfate were mixed mechanically with sodium sulfate.

SHEFFIELD CHEMICAL LABORATORY, YALE UNIVERSITY,
NEW HAVEN, CONN.

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

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

BY HERBERT N. MCCOY AND HERBERT J. SMITH.

Received January 25, 1911.

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 experimenters¹ had not used modern physico-chemical 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 Bodländer³ and Stieglitz.⁴

The following fundamental equations govern the equilibrium:

- (1) $H \times HCO_3 = k_1 \times H_2CO_3.$
- (2) $H \times CO_3 = k_2 \times HCO_3.$
- (3) $Ca \times CO_3 = k_3,$ the solubility product.
- (4) $HCO_3 = 2Ca.$
- (5) $Ca = \alpha \times Ca(CHO_3)_2.$

If k is the equilibrium constant for reaction,

$$(6) \quad \frac{\alpha \times Ca(HCO_3)_2}{\sqrt[3]{H_2CO_3}} = \sqrt[3]{\frac{k_1 k_3}{4k_2}} = k.$$

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 erroneous⁵ 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 Lloyd⁶ have also studied the problem under conditions applicable to geological problems.

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

¹ Schloessing, *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.

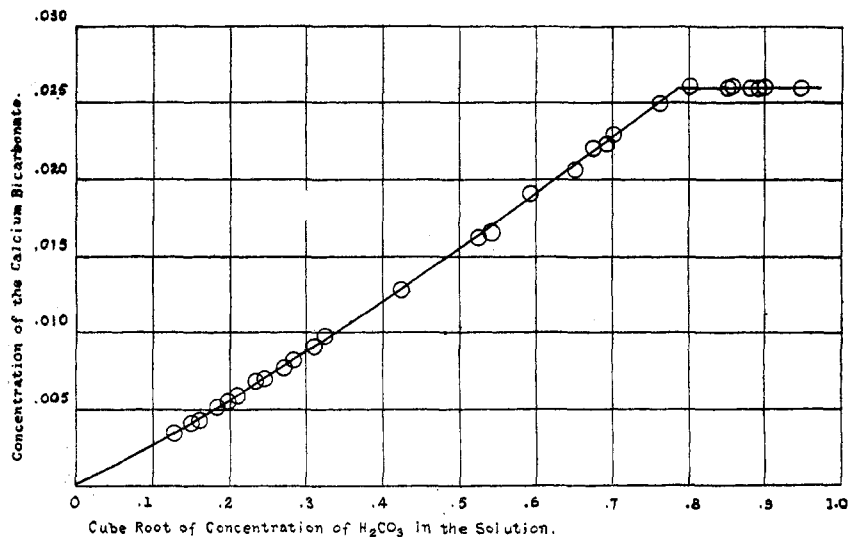
The glass bottles were charged with about 50 g. of calcium carbonate and 250 cc. of water; the steel bottle with about double these quantities. Carbon dioxide was then introduced in the desired amount. For experiments at greater than atmospheric pressure the gas was drawn from a steel cylinder of liquid carbon dioxide. The charged bottles were rotated in a thermostat at $25^{\circ} + 0.02$ 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 $\text{Ca}(\text{HCO}_3)_2$ 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

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

pressure¹ 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 $\text{Ca}(\text{HCO}_3)_2$ at this point. This saturated solution is 0.026 molecular, equal to 0.42 g. of $\text{Ca}(\text{HCO}_3)_2$ 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

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 Keiser¹ 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 $\text{CaCO}_3 \cdot 1.75\text{H}_2\text{CO}_3$ 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 $\text{Ca}(\text{HCO}_3)_2$.	100 α .	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 $\text{Ca}(\text{HCO}_3)_2$ were found by analysis as described. In the fourth column, α is the assumed degree of ionization of $\text{Ca}(\text{HCO}_3)_2$, 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.

$$k = \frac{\alpha \times \text{Ca}(\text{HCO}_3)_2}{\sqrt[3]{\text{H}_2\text{CO}_3}}$$

The mean value of k for the 29 experiments at pressures less than 15 atmospheres, where the solutions were unsaturated with $\text{Ca}(\text{HCO}_3)_2$, 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 $\text{Ca}(\text{HCO}_3)_2$. 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

$$k = 0.02^3 \sqrt{F}.$$

Their average value of $F = 113$ 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

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

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

The constant k_1 was determined by Walker and Carmack¹ by conductivity measurements to be 3.04×10^{-7} . The secondary constant, k_2 , is not known with the same degree of accuracy as k_1 . Experiments by one of us² 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 Geffcken³ 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 infinitely dilute solution and 5.5×10^{-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:

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

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

since the solution is electrically neutral. This reduces to

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

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

¹ *J. Chem. Soc.*, 77, 5 (1900).

² McCoy, *Loc. cit.*

³ *Loc. cit.*

Finally,



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

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

The solution of (12) gives $H = 1.09 \times 10^{-10}$, from which we then find $\text{Ca} = 1.66 \times 10^{-4}$; $\text{CO}_3 = 0.56 \times 10^{-4}$; $\text{H}_2\text{CO}_3 = 1.10 \times 10^{-4}$; $\text{OH} = 1.10 \times 10^{-4}$; $\text{H}_2\text{CO}_3 = 4.0 \times 10^{-8}$. 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 Kohlrausch¹ 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 $\text{Sr} \times \text{CO}_3 = k_3 = 1.567 \times 10^{-9}$. 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, $\text{Ba}(\text{HCO}_3)_2 = 0.028$, is reached at a concentration of $\text{H}_2\text{CO}_3 = 0.727$, corresponding to a calculated CO_2 pressure of about 22 atmospheres. The solubility of $\text{Ba}(\text{HCO}_3)_2$ 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 $\text{Ba} \times \text{CO}_3 = k_3 = 8.1 \times 10^{-9}$.

[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.

Received January 25, 1911.

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

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

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