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# On the Solubility of Calcium Carbonate in Water in Equilibrium with a Gaseous Phase containing Carbon Dioxide

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By

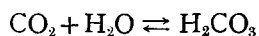
**Yukichi Osaka**

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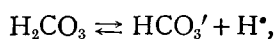
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Carbonic acid has been well known as a very weak acid, but according to recent investigations it seems to be a much stronger acid than hitherto supposed. If such be the case, the chemical equilibrium of carbonic acid must necessarily be treated in somewhat different ways. From this point of view, the author calculated the solubility product of calcium carbonate, utilizing the existing data, and then derived a formula for the calculation of the solubility of calcium carbonate in water which is in equilibrium with a gaseous phase containing carbon dioxide of a given partial pressure. The results form the present article.

When carbon dioxide is dissolved in water a portion of it forms carbonic acid :



and the carbonic acid thus formed dissociates electrolytically in two stages :



If the concentrations of the molecules and ions be denoted by enclosing their formulas within brackets and the law of mass action be applicable to this case, the following equations are obtained :

$$K_0[\text{CO}_2] = [\text{H}_2\text{CO}_3], \quad (1)$$

$$K_1[\text{H}_2\text{CO}_3] = [\text{H}^+] \times [\text{HCO}_3'], \quad (2)$$

$$K_2[\text{HCO}_3'] = [\text{H}^+] \times [\text{CO}_3''], \quad (3)$$

where  $K_0$ ,  $K_1$  and  $K_2$  are the respective equilibrium constants. The constant  $K_1$  is the first dissociation constant of carbonic acid, but it is not what is generally taken as that constant. As the concentration of carbonic acid is generally taken the sum of carbonic acid and its anhydride and the so-called first dissociation constant  $K_1'$  is defined by the following equation :

$$K_1'([\text{H}_2\text{CO}_3] + [\text{CO}_2]) = [\text{H}^+] \times [\text{HCO}_3']. \quad (4)$$

This is the apparent dissociation constant and the relation between the true dissociation constant and the apparent one is obtained from the equations (1), (2) and (4) as follows :

$$\frac{K_0 K_1}{1 + K_0} = K_1'. \quad (5)$$

As to the apparent dissociation constant, J. Walker and W. Cormack's determination,<sup>1</sup>  $3.40 \times 10^{-7}$  at  $18^\circ$ , has generally been used, but the following values given by J. Kendall<sup>2</sup> seem to be more accurate :

Temperature	$0^\circ$	$18^\circ$	$25^\circ$
$K_1' \times 10^{-7}$	2.24	3.12	3.50

Walker and Cormack expressed the opinion that the carbon dioxide dissolved in water is in combination with it to an extent of at least more than fifty per cent. If that be the case, the true dissociation constant of the acid would be of an order of  $10^{-7}$ , and carbonic acid be an acid very much weaker than acetic acid.

<sup>1</sup> J. Chem. Soc., **77**, 5 (1900).

<sup>2</sup> J. Amer. Chem. Soc., **38**, 1480 (1916).

From the behavior of aqueous carbonic acid on neutralisation, A. Thiel and R. Strohecker<sup>1</sup> came to the conclusion that in a 0.00812 molar solution at 4° only 0.67 per cent. of the total carbon dioxide dissolved in water is in combination with it. If the apparent dissociation degree may be negligible against unity, it is calculated to be 0.00608, and it follows that the true dissociation degree is 0.91. If the apparent dissociation constant at 4° be assumed to be  $3 \times 10^{-7}$ , the true constant will be  $5 \times 10^{-4}$ . Then Strohecker<sup>2</sup> reported that in a 0.008544 molar solution 0.56 per cent. of carbon dioxide is in combination with water, that the apparent dissociation constant at 4° as determined from the electrolytic conductivity is  $2.2 \times 10^{-7}$ , and that the true dissociation constant is  $4.4 \times 10^{-4}$ . Moreover L. Pusch<sup>3</sup> estimated by certain electrochemical methods the true dissociation constant of carbonic acid at 20° to be  $7.42 \times 10^{-4}$  in one case and  $7.01 \times 10^{-4}$  in the other.

As may be seen, the numerical values of the true dissociation constant found by Thiel and Strohecker on the one side and by Pusch on the other are not in good agreement, even if the difference in temperature be taken into consideration, but they show in common that the true dissociation constant is greater than  $10^{-4}$  and that carbonic acid is a much stronger acid than acetic acid.

The apparent dissociation constant of carbonic acid at 4° as interpolated from the data given by Kendall is  $2.44 \times 10^{-7}$ . If its true dissociation constant is assumed to be  $4 \times 10^{-4}$  at that temperature, from the equation (5) it follows:

$$K_0 = 0.0006.$$

If  $K_0$  be a magnitude of such an order, then it may be neglected against unity and the equation (5) may be simplified as follows:

$$K_0 K_1 = K_1'.$$

As to the second dissociation constant of carbonic acid, there are a number of data in the literature,<sup>4</sup> but the value,  $K_2 = 4.91 \times 10^{-11}$  at

<sup>1</sup> Ber. D. chem. Ges., **47**, 945 (1914).

<sup>2</sup> J. Chem. Soc. Abst., **110**, **11**, 522; from Z. Nahr Genuss., **34**, 121 (1916).

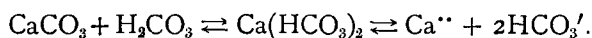
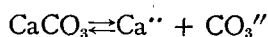
<sup>3</sup> Z. Elektrochem., **22**, 206 and 293 (1916).

<sup>4</sup> G. Bodländer, Z. physik. Chem., **35**, 23 (1900); H. N. McCoy, Amer. Chem. J., **29**, 437 (1903); J. Stieglitz, Carnegie Inst. Publ., **107**, 233 (1908), &c.

25°, determined by C. A. Seyler and P. V. Lloyd,<sup>1</sup> seems to be most reliable.

Now, taking into consideration the fact that only a small portion of the carbon dioxide dissolved in water is in combination with it, and using the data,  $K_1' = 3.50 \times 10^{-7}$  and  $K_2 = 4.91 \times 10^{-11}$ , the solubility product of calcium carbonate (calcite form) at 25° was calculated in the following way.

In a solution of calcium carbonate in water containing carbonic acid, it is electrolytically dissociated and also reacts with carbonic acid, namely :



Let  $K_3$  denote the solubility product of calcium carbonate at 25°, then

$$[\text{Ca}^{++}] \times [\text{CO}_3^{--}] = K_3. \quad (7)$$

From the equations (2), (3) and (7) the following relation is obtained :

$$\frac{[\text{Ca}^{++}] \times [\text{HCO}_3']^2}{[\text{H}_2\text{CO}_3]} = \frac{K_1' K_3}{K_2}$$

and on combining the last equation with the equations (1) and (6) we have :

$$\frac{[\text{Ca}^{++}] \times [\text{HCO}_3']^2}{[\text{CO}_2]} = \frac{K_0 K_1 K_3}{K_2} = \frac{K_1' K_3}{K_2} = K, \quad (8)$$

where  $K$  is a new constant.

H. N. McCoy and H. J. Smith<sup>2</sup> determined the amounts of free carbonic acid and calcium bicarbonate in solutions in equilibrium with carbon dioxide of different partial pressures at 25°, and gave the results of six experiments as the typical representatives of the thirty-six experiments. Omitting the two cases in which the pressure of carbon dioxide was more than 15 atmospheres and the solubility of calcium carbonate became constant independent of the pressure of carbon dioxide, their results are quoted in the following table :

<sup>1</sup> J. Chem. Soc., **111**, 138 (1917).

<sup>2</sup> J. Amer. Chem. Soc., **33**, 468 (1911).

Table 1.

Approx. press. CO <sub>2</sub> in atmos.	Free carbonic acid.	Calcium bicarbonate	Dissoc. degree. γ
0.1	0.003522	0.004116	0.866
1.1	0.03728	0.009734	0.810
9.9	0.3329	0.02236	0.726
13.2	0.444	0.02495	0.713

Here the dissociation degrees were calculated under the assumption that they were equal to those of calcium acetate of the same concentrations, which were obtained from the electrolytic conductance data given in Kohlrausch and Holborn's *Leitvermögen*. These authors calculated, in the premises, that all the carbon dioxide dissolved is in combination with water, the solubility product of calcium carbonate,  $K_3$ , by the following equation :

$$\frac{\gamma[\text{Ca}(\text{HCO}_3)_2]}{\sqrt{[\text{H}_2\text{CO}_3]}} = \sqrt[3]{\frac{K_1' K_3}{4K_2}} = K'$$

where  $[\text{Ca}(\text{HCO}_3)_2]$  denotes the total concentration of calcium bicarbonate and  $K'$  is a new constant. As the average of twenty-nine experiments they obtained  $K' = 0.0234$  and then using the data,  $K_1' = 3.04 \times 10^{-7}$  and  $K_2 = 5.5 \times 10^{-11}$ , they obtained  $K_3 = 9.3 \times 10^{-9}$ . If the other values for  $K_1'$  and  $K_2$  as adopted by the present writer, namely  $K_1' = 3.50 \times 10^{-7}$  and  $K_2 = 4.91 \times 10^{-11}$ , be used, the same equation gives  $K_3 = 5.7 \times 10^{-9}$ .

Now the solubility product of calcium carbonate is calculated, contrary to McCoy and Smith's assumption, on the understanding that the so-called free carbonic acid in the solution all exists in the state of anhydride. The following table was thus obtained from the data given by McCoy and Smith by the use of equation (8) :

Table 2.

[CO <sub>2</sub> ]	[Ca <sup>..</sup> ] + [Ca(HCO <sub>3</sub> ) <sub>2</sub> ]	γ	[Ca <sup>..</sup> ]	[HCO <sub>3</sub> ']	$K \times 10^9$
0.003525	0.004116	0.866	0.003563	0.007126	5.140
0.03728	0.009734	0.810	0.007784	0.015768	5.260
0.3329	0.02236	0.728	0.01628	0.03256	5.184
0.444	0.02495	0.713	0.01779	0.03558	5.076
					5.163

In this table and also in the following pages the symbol  $[\text{Ca}(\text{HCO}_3)_2]$ , denotes the concentration of the undissociated calcium carbonate and not the total concentration of the bicarbonate, as was the case in the equation of McCoy and Smith. From the mean value of  $K$  the solubility product of calcium carbonate at  $25^\circ$  is calculated as follows:

$$K_3 = 5.165 \times 10^{-3} \times \frac{K_2}{K_1'} = \frac{5.165 \times 4.91 \times 10^{-6}}{3.50 \times 10^{-7}} = 7.24 \times 10^{-9}.$$

Now the author proceeds to derive a formula for the calculation of the solubility of calcium carbonate in water in equilibrium with a gaseous phase containing carbon dioxide. In the calculation of the solubility product from the data of McCoy and Smith the presence of neutral calcium carbonate in the solution was not taken into consideration, but now more dilute solutions in contact with carbonic acid of much lower partial pressures are considered and it can not be neglected.

In a solution of calcium carbonate in water containing carbon dioxide there are the following equilibrium relations:

$$[\text{Ca}^{**}] \times [\text{CO}_3''] = 7.24 \times 10^{-9},$$

$$\frac{[\text{H}^*] \times [\text{HCO}_3']}{[\text{CO}_2]} = 3.50 \times 10^{-7},$$

$$[\text{H}^*] \times [\text{OH}'] = 0.82 \times 10^{-14},$$

and among the anions and cations the following relation must exist:

$$2[\text{Ca}^{**}] + [\text{H}^*] = [\text{OH}'] + [\text{HCO}_3'] + 2[\text{CO}_3'']. \quad (9)$$

According to G. Just<sup>1</sup> the solution saturated with carbon dioxide of one atmosphere at  $25^\circ$  is 0.0338 molar, and as the solubility of carbon dioxide in water follows the Henry's law, if the partial pressure of carbon dioxide in the gaseous phase be denoted by  $P$ , expressed in atmospheres, the concentration of the free carbon dioxide in the solution is

$$[\text{CO}_2] = 0.0338 P.$$

Therefore

$$[\text{H}^*] \times [\text{HCO}_3'] = 3.50 \times 10^{-7} \times 0.338P = 1.183 \times 10^{-8} P,$$

<sup>1</sup> Z. physik. Chem., **37**, 342 (1901).

and

$$[H'] = \frac{1.183 \times 10^{-8} P}{[HCO_3']},$$

$$[OH'] = \frac{0.82 \times 10^{-14}}{1.183 \times 10^{-8} P} [HCO_3'] = \frac{6.93 \times 10^{-7}}{P} [HCO_3'].$$

It is evident that  $[H']$  increases and  $[OH']$  decreases when  $P$  increases. From the experiments of McCoy and Smith it may be seen, that when  $P$  is of an order of 10,  $[HCO_3']$  and  $[Ca^{**}]$  are both of an order of  $10^{-2}$ , and in that case  $[H']$  may be neglected against  $[Ca^{**}]$  in the equation (9). Again, when  $P=0.0002$ ,  $[OH']=3.374 \times 10^{-3} [HCO_3']$  and since  $3.74 \times 10^{-3}$  may be neglected against unity without causing much error,  $[OH']$  may also be neglected in the equation (9), provided  $P$  is not extremely small.

From the above equations we have

$$\frac{[HCO_3']^2}{[CO_3'']} = \frac{1.183 \times 10^{-8} P}{4.91 \times 10^{-11}} = 241 P,$$

and since

$$[CO_3''] = \frac{7.24 \times 10^{-9}}{[Ca^{**}]},$$

we have

$$[Ca^{**}] \times [HCO_3']^2 = 7.24 \times 10^{-9} \times 241 P = 1.74 \times 10^{-6} P \quad (10)$$

and

$$[Ca^{**}] = \frac{1}{2} [HCO_3'] + \frac{7.24 \times 10^{-9}}{[Ca^{**}]} \quad (11)$$

Now from the last two equations the values of  $[Ca^{**}]$  and  $[HCO_3']$  may be obtained in the following way. For convenience the following symbols are used :

$$[Ca^{**}] = x; [HCO_3'] = y; 1.74 \times 10^{-6} P = a; 7.24 \times 10^{-9} = b; \frac{1}{2} = c;$$

then the equations (10) and (11) become

$$x^2 = cxy + b, \quad xy^2 = a.$$

On eliminating  $x$  between them we have

$$\frac{a^2}{y^4} = \frac{ac}{y} + b,$$

or

$$a^2 = acy^3 + by^4,$$

or

$$y^3(ac + by) = a^2.$$



Since  $b/a = 4.2 \times 10^{-3}/P$ ,  $c = \frac{1}{2}$  and  $y$  is considerably smaller than  $P$ ,  $by$  is much smaller than  $ac$ , it may be simplified in the following way:

It is transformed

$$y^3 ac \left(1 + \frac{b}{ac} y\right) = a^2,$$

or

$$y \sqrt[3]{ac} = \sqrt[3]{a^2} \left(1 + \frac{b}{ac} y\right)^{-\frac{1}{3}},$$

and then approximately

$$y \sqrt[3]{ac} = \sqrt[3]{a^2} \left(1 - \frac{1}{3} \frac{b}{ac} y\right),$$

or

$$y \left( \sqrt[3]{ac} + \frac{b}{3c \sqrt[3]{a}} \right) = \sqrt[3]{a^2}.$$

therefore

$$y = \frac{\sqrt[3]{a^2}}{\sqrt[3]{ac} + \frac{b}{3c \sqrt[3]{a}}},$$

or

$$y = \frac{3ac}{b + 3c \sqrt[3]{a^2 c}},$$

and hence

$$x = \frac{b^2 + 6bc \sqrt[3]{a^2 c} + 9ac^2 \sqrt[3]{ac^2}}{9ac^2}.$$

Now on substituting the proper values for the symbols we have

$$[\text{Ca}^{++}] = \frac{5.24 \times 10^{-17} + 2.49 \times 10^{-12} P^{2/3} + 2.97 \times 10^{-8} P^{4/3}}{3.91 \times 10^{-6} P}, \quad (12)$$

$$[\text{HCO}_3^-] = \frac{2.61 \times 10^{-6} P}{7.24 \times 10^{-9} + 1.72 \times 10^{-4} P^{2/3}}. \quad (13)$$

As the concentration of normal calcium carbonate is very small, it may be taken as completely dissociated, but as to the bicarbonate the dissociation must be considered as incomplete. As to the dissociation of the bicarbonate, it may be taken as the same as in the corresponding solutions of calcium acetate, as McCoy, Johnston<sup>1</sup> and others assumed. Let the degree of dissociation of the bicarbonate be denoted by  $\gamma$ , then the concentration of the undissociated part is

<sup>1</sup> J. Amer. Chem. Soc., **37**, 2001 (1915).

$$[\text{Ca}(\text{HCO}_3)_2] = \frac{1}{2}[\text{HCO}_3'] \frac{1-\gamma}{\gamma},$$

and the total concentration of the calcium in the solution is

$$C = [\text{Ca}^{++}] + \frac{1-\gamma}{2\gamma}[\text{HCO}_3']. \quad (14)$$

The values of  $\gamma$  were calculated from the data in Kohlrausch and Holborn's *Leitvermögen*, using for the migration velocities of the ions  $\frac{1}{2}\text{Ca}^{++}$  and  $\text{HCO}_3'$  the values 51.46 and 35.0 respectively. These data were all for 18°, but the values of  $\gamma$  thus calculated may be here used without bringing much error on the final result, especially when the partial pressure of carbon dioxide in the gaseous phase is low, as the author had intended. The values of  $\gamma$  calculated are given in Table 3.

Table 3.

$[\text{C}_2\text{H}_3\text{O}_2']$ or $[\text{HCO}_3']$	$\gamma$
0.0001890	0.945
0.0004665	0.933
0.000921	0.921
0.001808	0.904
0.004340	0.868
0.00831	0.831
0.01570	0.785

Any experiments at 25° which were worked with comparatively low partial pressures of carbon dioxide and might be utilized for the verification of the equations (12), (13) and (14) are not found in the literature. Thus the data at 16° published by Th. Schlösings<sup>1</sup> were taken and were compared with the calculated values for 25°. The result is represented in Table 4.

<sup>1</sup> C. R., 74, 1555 (1872).

Table 4.

<i>P</i>	[Ca <sup>++</sup> ] × 10 <sup>1</sup>	[HCO <sub>3</sub> ' ] × 10 <sup>3</sup>	γ	[Ca(HCO <sub>3</sub> ) <sub>2</sub> ] × 10 <sup>1</sup>	C	
					Calc. (25°)	Obs. (16°)
0.000504	6.12	1.20	0.91	0.59	6.7 × 10 <sup>-4</sup>	7.46 × 10 <sup>-4</sup>
0.000808	7.15	1.41	0.91	0.70	7.9	8.50
0.00333	11.4	2.26	0.89	1.40	12.8	13.72
0.01387	18.2	3.62	0.87	2.70	20.9	22.31
0.02820	23.1	4.62	0.86	3.76	26.9	29.65
0.05008	28.0	5.59	0.85	4.93	32.9	36

As there is a difference of nine degrees in temperature, no good agreement can be expected, but it may be remarked that the calculated values are somewhat smaller than the observed and that this is qualitatively in concord with the fact that the solubility of calcium carbonate in water in contact with carbon dioxide of a given partial pressure decreases as the temperature rises.<sup>1</sup>

As may be seen from Table 4, when *P* is greater than 0.02829, exactly

$$[\text{Ca}^{++}] = \frac{1}{2} [\text{HCO}_3']$$

and in that case the equation (12) and (13) may be simplified as follows:

$$[\text{Ca}^{++}] = 7.6 \times 10^{-3} P^{1/3},$$

$$[\text{HCO}_3'] = 1.52 \times 10^{-2} P^{1/3}.$$

### Summary

From the premises that carbon dioxide dissolved in water is combined with it only to a small extent and that carbonic acid is an acid much stronger than acetic acid, and using for the apparent first dissociation constant and the second dissociation constant of carbonic acid the values  $3.50 \times 10^{-7}$  and  $4.91 \times 10^{-11}$  respectively, the solubility product of calcium carbonate (calcite form) at 25° was calculated from the data given by McCoy and Smith to be  $7.24 \times 10^{-9}$ .

<sup>1</sup> Cf. Treadwell and Reuter, Z. anorg. Chem., **17**, 170 (1898).

Then the following formula was derived for the calculation of the solubility of calcium carbonate in water in contact with a gaseous phase of a given partial pressure of carbon dioxide :

$$C = [\text{Ca}^{++}] + \frac{1-\gamma}{2\gamma} [\text{HCO}_3^-],$$

where

$$[\text{Ca}^{++}] = \frac{5.24 \times 10^{-17} + 2.49 \times 10^{-12} P^{2/3} + 2.97 \times 10^{-3} P^{4/3}}{3.91 \times 10^{-6} P},$$

$$[\text{HCO}_3^-] = \frac{2.61 \times 10^{-6} P}{7.24 \times 10^{-9} + 1.72 \times 10^{-4} P^{2/3}}.$$

In this formula,  $C$  is the number of mols of calcium carbonate dissolved in one litre of water,  $P$  the partial pressure of carbon dioxide expressed in atmospheres, and  $\gamma$  the dissociation degree of calcium bicarbonate which is to be assumed to be the same as that of calcium acetate of the same concentration.

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