constant for water). Using Kendall's value for K_1 at 25° and taking K_w equal to 0.82×10^{-14}, they obtained 4.91×10^{-11} as the value of K_2 at 25°. No experimental data are known from which the variation of K_2 with temperature can be determined.

If, in Equation 10 we substitute 3.75×10^{-7} for K_1; 4.91×10^{-11} for K_2; and 4.04×10^{-3} for K, we get K_3 equal to 34.53×10^{-12}. Then if ferrous carbonate were not hydrolytically dissociated, its solubility in pure water free from carbon dioxide would be 5.8×10^{-6} gram molecules per liter.

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ON EQUILIBRIUM IN THE SYSTEM: ZINC CARBONATE, CARBON DIOXIDE AND WATER.[1]

BY HERBERT J. SMITH.

When zinc salts in solution are precipitated by alkaline carbonates, the compounds produced are apparently unstable and of variable composition. A large number of basic zinc carbonates have been described in the literature. It has been shown, however, by Mikusch[2] that there exist only 2 carbonates of zinc. One is the normal zinc carbonate, $ZnCO_3$; the other is a basic zinc carbonate whose composition is expressed by the formula $5ZnO.2CO_2.4H_2O$. All other basic zinc carbonates described in the literature are shown to be solid solutions of zinc hydroxide and neutral zinc carbonate.

It has been shown by Free[3] that the solubility of basic copper carbonate increases with the concentration of free carbon dioxide. Seyler[4] points out that Free's results exhibit regularities similar to those found for other carbonates. Seyler deduces these regularities from the principles of chemical equilibrium and shows experimentally that they apply to the solubility of basic zinc and lead carbonates. No previous experimenters have examined the equilibrium between normal zinc carbonate, carbon dioxide, and water for pressures of carbon dioxide greater than one atmosphere. In view of this fact, I have undertaken a study of this system under high pressures.

The theory of this equilibrium from the standpoint of the law of mass action and the ionic theory is similar to that deduced for the system: ferrous carbonate, carbon dioxide and water. This is given in the preceding paper. Since the valence of zinc ion is the same as that of the fer-

[1] From a dissertation submitted to the Faculty of the Ogden Graduate School of Science of the University of Chicago in candidacy for the Degree of Doctor of Philosophy.

[1] Z. Phys. Chem., 56, 367 (1906).

[3] THIS JOURNAL, 30, 1366 (1908).

[4] Analyst, 33, 756 (1908).

rous ion, an equation similar to (9) of that paper should hold for the zinc equilibrium.

The zinc carbonate used in these experiments was prepared from the purest commercially obtainable zinc carbonate by washing repeatedly with large quantities of boiling water. The basic zinc carbonate thus obtained was placed with water in a steel bottle and carbon dioxide was added until a pressure of 30 atmospheres was reached. The steel bottle was rotated in a thermostat at 25° for several days.

About 50 g. of the zinc carbonate thus prepared was placed in a steel bottle. The bottle was then nearly filled with water and closed with a plug carrying a needle valve, through which it was charged with carbon dioxide from a cylinder of the liquefied gas. The inside of the bottle was protected from the action of the carbonic acid by a coating of beeswax applied hot. The cylinder and bottle were then rotated in a thermostat for several days until equilibrium had been reached. Preliminary experiments showed that about one week's rotation was necessary for this.

The solution was then analyzed for dissolved zinc salt and carbon dioxide. In this case the zinc was determined by adding to a weighed portion of the solution an excess of 0.05 N hydrochloric acid, boiling to remove all carbon dioxide, cooling, adding one drop of methyl orange, and titrating the excess of acid with 0.05 N barium hydroxide. This method of analysis is described by Kantor and Benedikt.[1] Preliminary experiments carried out with known weights of zinc showed it to be accurate. The carbon dioxide was determined as described in the accompanying paper on ferrous carbonate.

In Table I are given the results of experiments carried out at 25°. Table II gives results at a temperature of 30°. Col. 1 gives concentration of free carbonic acid in gram molecules per liter. Col. 2 the concentrations of zinc bicarbonate in gram molecules per liter. Col. 3 gives the degrees of ionization of the zinc bicarbonate. It is assumed that the bicarbonate is ionized to the same extent as zinc chloride solutions of equivalent concentrations. The ionization of the zinc chloride solutions are calculated from the data given in Kohlrausch's *Leitervermögen der Elektrolyte*, 1st Edition, p. 160 (1898). Col. 4 gives the values of the equilibrium constant calculated from the equation

$$\frac{\alpha \times [Zn(HCO_3)_2]^2}{\sqrt[3]{[H_2CO]}} = \sqrt[3]{\frac{K_1K_3}{4K_2}} = K.$$

In the fifth column are given the pressures of the carbon dioxide. These pressures were not actually measured, but were calculated on the assumption that Henry's law holds for high pressures of the gas. The solubility of the gas in pure water at 25° under one atmosphere is given by Geffcken[2]

[1] *Z. angew. Chem.*, 1888, p. 236.

[2] Geffcken, *Z. phys. Chem.*, 49, 273 (1904).

as 0.03374 gram molecules per liter.   However, these calculated pressures are lower than the actual pressures, as it is well known that Henry's law does not apply under these high pressures.

TABLE I.—SOLUBILITY OF ZINC CARBONATE IN CARBONATED WATER AT 25°.

1. $[H_2CO_3]$.	2. $[Zn(HCO_3)_2]$.	3. α.	4. $K \times 10^3$.	5. Atmospheres pressure.
0.1390	0.00194	0.909	3.40	4.12
0.1797	0.00211	0.905	3.39	5.33
0.2579	0.00242	0.899	3.41	7.64
0.3580	0.00270	0.894	3.40	10.61
0.4103	0.00278	0.894	3.35	12.16
0.4480	0.00291	0.892	3.39	13.29
0.6657	0.00317	0.888	3.22	19.73
0.6969	0.00319	0.888	3.20	20.65
0.7610	0.00343	0.885	3.33	22.56
1.3701	0.00445	0.871	3.48	40.61

Av., 3.36

TABLE II.—SOLUBILITY OF ZINC CARBONATE IN CARBONATED WATER AT 30°.

1. $[H_2CO_3]$.	2. $[Zn(HCO_3)_2]$.	3. α.	4. $K \times 10^3$.
0.1838	0.00215	0.904	3.42
0.3838	0.00277	0.894	3.41
0.4038	0.00286	0.892	3.41
0.4601	0.00308	0.889	3.55
0.6064	0.00324	0.888	3.40
0.6257	0.00337	0.886	3.49
0.7470	0.00352	0.884	3.43
0.8351	0.00376	0.880	3.51
1.0840	0.00339	0.878	3.41
1.1275	0.00429	0.874	3.60

Av., 3.47

Since $$K = \sqrt[3]{\frac{K_1 K_3}{4K_2}} \quad \text{or} \quad K_3 = \frac{K^3 . K_{42}}{K_1}$$

it is possible to calculate K_3, the solubility product constant of zinc carbonate.   Substituting $K = 3.36 \times 10^{-3}$, $K_1 = 3.50 \times 10^{-7}$ and $K_2 = 4.91 \times 10^{-11}$, we find $K_3 = 21 \times 10^{-12}$ at 25°.

If zinc carbonate were not hydrolytically dissociated, its solubility in pure water at 25° would be 4.58×10^{-6} gram molecules per liter.

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