

ditions. When the solution becomes very slightly alkaline the absorption band which is characteristic of the acid solution broadens abruptly, extending further into the green towards the red end of the spectrum, but leaving some of the green region still visible. The indications are very marked, so that rosolic acid lends itself well to this spectroscopic method. The neutral point as indicated by the spectroscope is the same as that found without its aid, so that the divergence of indications by rosolic acid from those by other indicators is not eliminated by the use of this new method.

Litmus and Hematoxylin have been examined only as to their suitability for use with the spectroscope in a very cursory manner, but the probabilities appear to be in their favor. Litmus must be used in considerably larger quantity than usual, as in the case of cochineal and methyl orange. When alkaline, it shows a well marked band. Hematoxylin gives a sharply defined edge to the absorption band seen in alkaline solution only when a considerable amount of it is present.

Summary.

1. The spectroscope is an efficient means of distinguishing the exact neutral point in many acidimetric titrations.
2. It can be used for this purpose in cases where the unaided eye would fail.
3. The necessary concentration of most indicators is greater when they are to be used in connection with the spectroscope.
4. The best conditions under which some of the commonest indicators can be used in connection with the spectroscope have been established.

OTTAWA, CANADA.

ON EQUILIBRIUM IN THE SYSTEM: FERROUS CARBONATE, CARBON DIOXIDE AND WATER.¹

By HERBERT J. SMITH.

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It has long been known that ferrous carbonate is more soluble in water containing carbon dioxide than in pure water.² The increase in solubility is due to the formation of the more soluble ferrous bicarbonate, which has, however, never been obtained in the solid state. It is shown in this paper that the solid salt, at a temperature of 25°, would have a decomposition tension of carbon dioxide greater than 25 atmospheres.

If we study the system: ferrous carbonate, carbon dioxide and water

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.

² Wagner, *Z. anal. Chem.*, 6, 171 (1867); Hauer, *J. prakt. Chem.*, 81, 381 (1860).

from the standpoint of the ionic theory and the law of mass action, we find that a certain quantitative relation must exist between the concentration of the dissolved ferrous salt and concentration of the carbon dioxide in solution.

The following 5 equations govern the equilibrium:

$$[\text{H}^+] \times [\text{HCO}_3^-] = K_1 \times [\text{H}_2\text{CO}_3] \quad (1)$$

$$[\text{H}^+] \times [\text{CO}_3^{--}] = K_2 \times [\text{HCO}_3^-] \quad (2)$$

$$[\text{Fe}^{++}] \times [\text{CO}_3^{--}] = K_3 \text{ (The solubility product constant)} \quad (3)$$

$$[\text{HCO}_3^-] = 2[\text{Fe}^{++}] \quad (4)$$

$$\alpha \times [\text{Fe}(\text{HCO}_3)_2] = [\text{Fe}^{++}] \quad (5)$$

where α is the degree of ionization of the ferrous bicarbonates.

Dividing Equations 1 by 2 we get

$$\frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{--}]} = \frac{K_1}{K_2} \times [\text{H}_2\text{CO}_3]. \quad (6)$$

Multiplying (6) by (3) we have

$$[\text{HCO}_3^-]^2 \times [\text{Fe}^{++}] = \frac{K_1 K_3}{K_2} [\text{H}_2\text{CO}_3]. \quad (7)$$

But since from (4) $2[\text{Fe}^{++}] = [\text{HCO}_3^-]$ we have

$$\frac{[\text{Fe}^{++}]}{\sqrt[3]{[\text{H}_2\text{CO}_3]}} = \sqrt[3]{\frac{K_1 K_3}{4K_2}} \text{ and since } [\text{Fe}^{++}] = \alpha \times [\text{Fe}(\text{HCO}_3)_2], \quad (8)$$

we have finally

$$\frac{\alpha \times [\text{Fe}(\text{HCO}_3)_2]}{\sqrt[3]{[\text{H}_2\text{CO}_3]}} = \sqrt[3]{\frac{K_1 K_3}{4K_2}} = K \quad (9)$$

where K is the equilibrium constant for the system.

No quantitative data can be found in the literature for testing the applicability of Equation 9. However, Stieglitz¹ and McCoy and Smith² have applied a similar expression to measurements on the solubility of calcium carbonate in carbonated waters, and have shown that a good equilibrium constant is thereby obtained.

In Table I are given the results of some experiments which I have carried out on equilibrium in the system: ferrous carbonate, carbon dioxide and water.

The ferrous carbonate used was prepared according to the following method: Equimolecular quantities of solid ferrous sulfate and sodium bicarbonate were placed in a steel bottle. The air was displaced from the bottle by a stream of carbon dioxide. Water previously saturated with carbon dioxide was added. The bottle was then closed by a plug carrying a needle valve and carbon dioxide was added from a cylinder of compressed gas until a pressure of 400 pounds had been attained in

¹ *Carnegie Inst. Publication*, 107, 233 (1909).

² *THIS JOURNAL*, 33, 468 (1911).

the bottle. The valve was then closed, and the bottle kept at a temperature of 100° for several days. The ferrous carbonate obtained in this way is pure white.

The precipitate was filtered in an atmosphere of carbon dioxide and washed with water previously saturated with the gas. The precipitate is much more easily filtered and washed than one obtained by precipitation in open vessels. According to Senarmont¹ the crystals obtained by the above procedure are isomorphous with calcite and similar to the mineral siderite.

From 50 to 100 g. of the ferrous carbonate were placed in the steel bottle described by McCoy and Smith.² One liter of water was added, and carbon dioxide admitted through the needle valve from a cylinder of the liquefied gas. A pressure gauge afforded a means for determining the approximate pressure of the gas within the bottle. The bottle was rotated in a thermostat at 30° for several days until a state of equilibrium had been reached. Preliminary experiments showed that one week's rotation was sufficient for this.

When equilibrium had been finally attained within the bottle, the concentrations of the dissolved ferrous salt and of the carbon dioxide in solution were determined. The portion of the solution used for the analysis was withdrawn from the bottle through a brass tube packed with cotton. This tube was attached to the valve on the inside of the bottle. For the carbon dioxide determination the filtered portion was received in a tared and evacuated flask containing a few cc. of conc. sulfuric acid. The gas was removed from the flask by a stream of carbon dioxide-free air, and dried by passing through conc. sulfuric acid and over phosphorus pentoxide. It was finally absorbed in weighed Fleming towers filled with soda-lime and phosphorus pentoxide. It will be noted that in this way all of the carbon dioxide, both free and combined, is evolved. Since the iron exists in solution as the bicarbonate, the free carbon dioxide is easily obtained by subtracting from the total twice the concentration of the iron. All concentrations must be expressed, of course, in gram molecules per liter. The portion used for the iron analysis was boiled with nitric acid to oxidize the iron. The iron was next precipitated as ferric hydroxide, the precipitate washed with boiling water and redissolved in dil. sulfuric acid. The iron was then reduced to the ferrous state, using amalgamated zinc. Finally, the iron was determined by titration with seventieth normal potassium permanganate.

In the first column of Table I are given the concentrations of free carbonic acid in gram molecules per liter. The second column gives the corresponding concentrations of the ferrous bicarbonate in gram

¹ *Compt. rend.*, 28, 693 (1849).

² *THIS JOURNAL*, 33, 468 (1911).

molecules per liter. The third column gives the assumed degrees of ionizations of the ferrous bicarbonate. These ionizations I have assumed to be the same as for barium nitrate solutions of equivalent concentrations. The ionization values for barium nitrate are those given by Noyes and Melcher.¹ In the fourth column are given values for K , the equilibrium constant for the system. These values are obtained from Equation 9, using the data in Cols. 1, 2 and 3 of the table.

TABLE I.—SOLUBILITY OF FERROUS BICARBONATE IN CARBONATED WATER AT 30°.

1. (H ₂ CO ₃).	2. Fe(HCO ₃) ₂ .	3. α .	4. $K \times 10^3$.
0.1868	0.00245	0.912	3.91
0.1985	0.00256	0.909	3.99
0.2168	0.00262	0.908	3.96
0.2327	0.00274	0.907	4.04
0.2960	0.00303	0.902	4.10
0.3116	0.00304	0.902	4.04
0.3153	0.00318	0.898	4.19
0.3294	0.00311	0.900	4.05
0.3745	0.00315	0.898	3.93
0.4046	0.00332	0.896	4.02
0.4750	0.00348	0.893	3.98
0.6600	0.00402	0.884	4.08
0.7154	0.00418	0.880	4.11
0.7600	0.00434	0.878	4.18

Av., 4.04

Rearrangement of Equation 9 gives

$$[\text{Fe}^{++}] \times [\text{CO}_3^{--}] = K_3 = \frac{4K_2K^3}{K_1}. \quad (10)$$

We see that, given the values of K_1 and K_2 , we can calculate the value of K_3 , since K is now known.

The value of K_1 , the first ionization constant of carbonic acid, was first accurately determined by Walker and Carmack.² They found K_1 to equal 3.04×10^{-7} at 18°. A more recent, and perhaps a slightly more accurate, value has been obtained by Kendall.³ He found K_1 to equal 3.12×10^{-7} at 18°. Kendall also determined values for K_1 at 0° and at 25°. Assuming that the value increases at the same rate between 25 and 30° as it does between 0 and 25°, we get a value for K_1 of 3.75×10^{-7} at 30°.

The best value for K_2 , the second ionization constant for carbonic acid, has been obtained by Seyler and Lloyd.⁴ The calculation of K_2 from their experimental data involves a knowledge of K_1 and of K_w (ion product

¹ Carnegie Inst. Publication, 63, 108 (1907).

² J. Chem. Soc., 77, 8 (1900).

³ THIS JOURNAL, 38, 1480 (1916).

⁴ J. Chem. Soc., III, 138 (1917).

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

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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 Mikusch² 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 $5ZnO \cdot 2CO_2 \cdot 4H_2O$. 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 Free³ that the solubility of basic copper carbonate increases with the concentration of free carbon dioxide. Seyler⁴ 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.

² *Z. Phys. Chem.*, **56**, 367 (1906).

³ *THIS JOURNAL*, **30**, 1366 (1908).

⁴ *Analyst*, **33**, 756 (1908).