[Contribution from the Department of Chemical Engineering, Massachusetts Institute of Technology]

THE SOLUBILITY OF FERROUS HYDROXIDE AND ITS EFFECT UPON CORROSION

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I. The Solubility of Ferrous Hydroxide

It has been pointed out[1] that the effect of protective films in the corrosion of iron may be largely regulated by the solubility of ferrous hydroxide. The present investigation was undertaken to determine the solubility of ferrous hydroxide in pure water and also in salt solutions, with the hope of further explaining the effect of various salts upon the rate of corrosion.

Bineau[2] seems to be the only one who attempted to determine directly the solubility of ferrous hydroxide in water. He prepared a solution of ferrous hydroxide by means of iron and pure water, slightly aerated and found that it contained about one part of ferrous hydroxide in 150,000, or 7.5×10^{-5} moles per liter. Müller,[3] from data on the ferric-ferro potential, calculated the solubility product of ferrous hydroxide to be $(\mathrm{Fe})(\mathrm{OH})^2 = 1.69 \times 10^{-14}$. Likewise, Krassa,[4] from data on the ferrous-ion concentration in 20% potassium hydroxide solution, calculated the solubility product to be $(\mathrm{Fe})(\mathrm{OH})^2 = 8.7 \times 10^{-14}$. Shipley and McHaffie,[5] working on the rate of corrosion of iron in the absence of oxygen, calculated the solubility product to be $(\mathrm{Fe})(\mathrm{OH})^2 = 3.9 \times 10^{-15}$. By using the above figures and *assuming complete ionization*, the solubility of ferrous hydroxide was calculated in each case to be 1.6×10^{-5}, 2.8×10^{-5} and 1×10^{-5}, respectively. Lamb[6] determined the ferrous-ion concentration in a saturated solution of ferrous hydroxide by conductivity methods to be 1.35×10^{-5}. All the methods (excepting Bineau's) would give low values for the *total* solubility if the ferrous hydroxide were not 100% dissociated. No work could be found relating to the solubility of ferrous hydroxide in salt solutions.

In the present investigation, solutions of ferrous hydroxide were prepared by adding pure iron powder to the deoxygenated solution in which the solubility of ferrous hydroxide was to be determined. The solutions were then allowed to stand until saturated with ferrous hydroxide and

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[1] Whitman, Russell and Altieri, *Ind. Eng. Chem.*, **16**, 665 (1924).

[2] Bineau, *Compt. rend.*, **41**, 509 (1855).

[3] Müller, *Z. Elektrochem.*, **14**, 77 (1908).

[4] Krassa, *ibid.*, **15**, 491 (1909).

[5] Shipley and McHaffie, *Can. Chem. Met.*, **8**, 5, 121 (1924).

[6] Lamb, This Journal, **32**, 1214 (1910).

after they were filtered under hydrogen, the filtrates were analyzed for iron by a colorimetric method.

Experimental Part.—The apparatus used for preparing saturated solutions of ferrous hydroxide consisted of a 300cc. Florence flask closed with a rubber stopper (sealed in place) and equipped with two glass tubes. One of these tubes reached to the bottom of the flask while the other passed just through the stopper. The upper ends of the tubes were connected with rubber tubing which could be closed by screw clamps.

The solution in which the solubility of ferrous hydroxide was to be determined was first introduced into the flask. This solution was then deoxygenated by alternate evacuation and flushing with hydrogen. Iron powder which had been freshly reduced in a stream of hydrogen was next emptied into the flask and the solution was allowed to stand at 40° for 18 hours and then cooled to 25°.

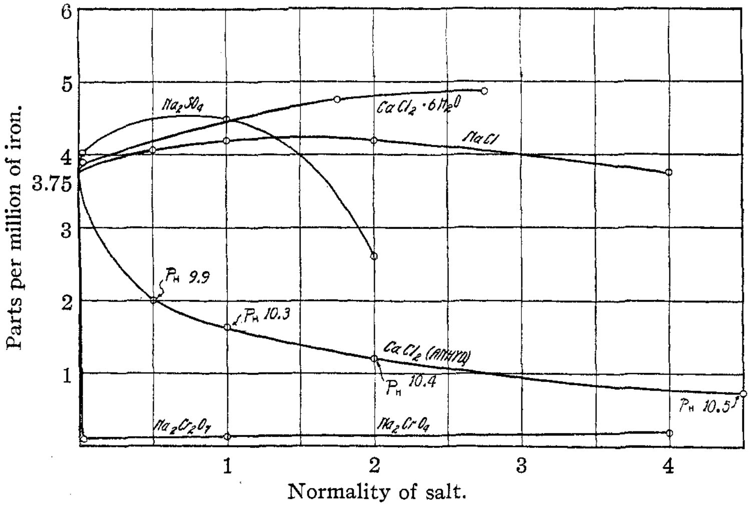

Fig. 1.—Solubility of ferrous hydroxide.

The solutions were filtered through an alundum crucible in a suction filter kept in an atmosphere of hydrogen. The filtrate was analyzed for iron by the method of Stokes and Cain,[7] which consists in oxidizing the iron to the ferric state and then precipitating it as the hydroxide together with manganese hydroxide which holds it on the filter. This residue was subsequently dissolved in a solution of thiocyanic acid saturated with mercuric thiocyanate, the color being extracted with a mixture of amyl alcohol and ether and then compared with that obtained from a standard solution of ferric alum.

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[7] Stokes and Cain, THIS JOURNAL, **29**, 409 (1907).

Blank determinations for iron were made on all the salts used in preparing the solutions.

Results.—The total solubility of ferrous hydroxide in conductivity water, prepared by redistilling water from alkaline potassium permanganate, was found to be 3.75 parts of iron per million, or 6.7×10^{-5} moles per liter. The Sörensen value (P_H) of this solution was 9.6.

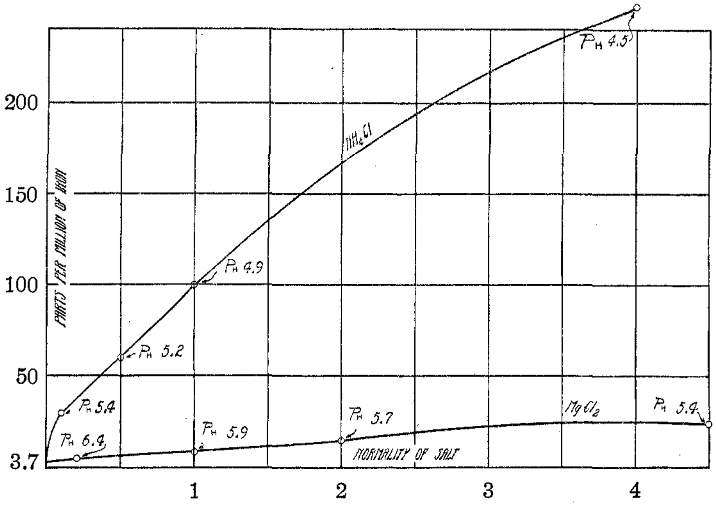

Fig. 2.—Solubility of ferrous hydroxide.

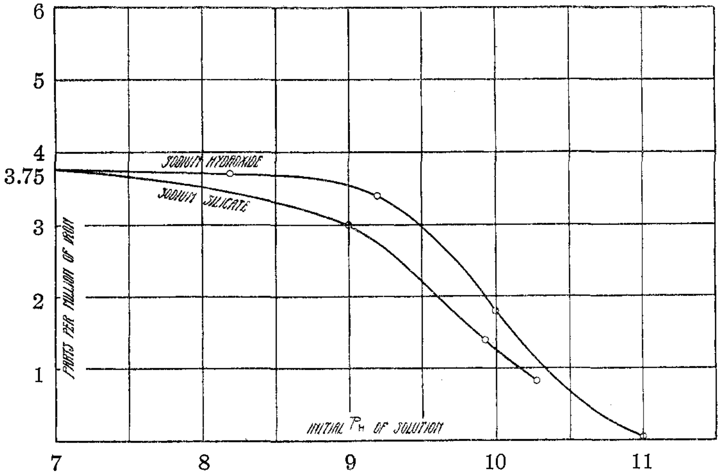

Fig. 3.—Solubility of ferrous hydroxide.

The results obtained in salt solutions of various concentrations are given in Figs. 1, 2 and 3.

As it was feared that the results showing the solubility of iron in sodium dichromate might not give the true solubility owing to the passivifying nature of these salts, another experiment was carried out in which the chromate was added to a saturated solution of ferrous hydroxide in water. The amount of iron remaining in solution was found to be less than 0.2 parts per million, which is the same that was obtained by adding the iron to the chromate solution in the normal procedure.

Discussion.—The accuracy of the analysis for iron is about 0.1 p. p. m. on the average. In the determinations with chromate and dichromate the iron may have been in the ferric rather than the ferrous state—the results should therefore be interpreted merely as showing that iron hydroxide is practically insoluble in these solutions above 0.01 *N*.

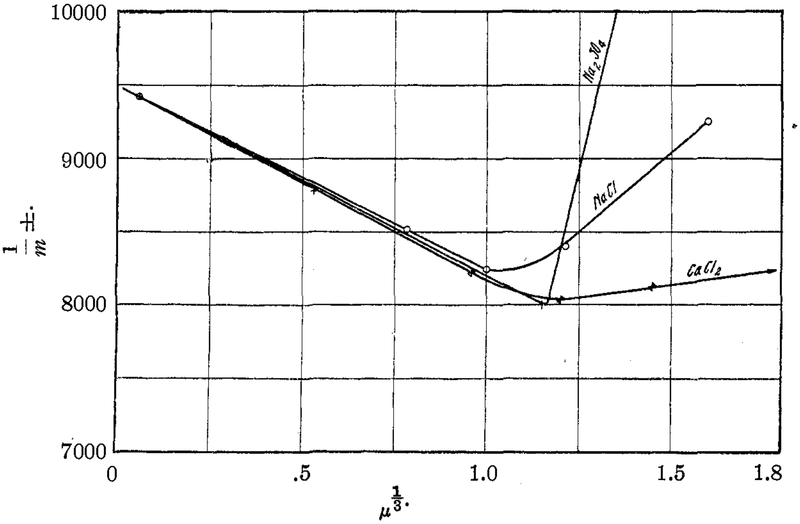

Fig. 4.

The difference in the solubility of ferrous hydroxide in anhydrous and hexahydrated calcium chloride as shown in Fig. 1 is due to the fact that the anhydrous salt contains a small amount of calcium oxide, as indicated by the *P*H values shown in the figure.

According to Lewis and Randall,[8] the activity of a substance is the same in all solutions of the same ionic strength. Using their method of calculation, Fig. 4 shows the plot of the reciprocal of the mean molality ($m\pm$) against the cube root of the ionic strength (μ), where

$$m\pm = \sqrt[3]{(\mathrm{Fe})(\mathrm{OH})^2};\ \mu = \frac{1}{2}\,[(\mathrm{Fe})\,4 + (\mathrm{OH}) + (\mathrm{A})\,V_A^2 + (\mathrm{B})\,V_B^2 \ldots]$$

V_A being the valence of A, and V_B the valence of B. The fact that the curves plotted in Fig. 4 check closely indicates that the ferrous hydroxide

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[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923.

present was in true solution and that the colloidal form, if present at any time, did not enter into the final analysis. As a result, Fig. 4 may be used to calculate the solubility of ferrous hydroxide in non-oxidizing solutions of any ionic strength up to 1.

From the data for the solubility in sodium hydroxide the percentage dissociation of ferrous hydroxide may be calculated where the hydrogen-ion concentration of the sodium hydroxide and of the sodium hydroxide solution of ferrous hydroxide is known.

First, calculating from the solubility in pure water, we find 6.7×10^{-5} mole of ferrous hydroxide (dissociated plus undissociated), in solution and that it has a P_H of 9.6, or an hydroxyl-ion concentration of 4×10^{-5}. From this it is seen that the ferrous-ion concentration is 2×10^{-5} (thus checking the values of Müller,[3] Krassa[4] and Lamb[6]) and that the percentage ionization is $Fe^{++}/Fe(OH)_2 = 2 \times 10^{-5}/6.7 \times 10^{-5} = 30\%$. The dissociation constant is $(Fe^{++})(OH^-)^2/(Fe(OH)_2) = (2 \times 10^{-5})(4 \times 10^{-5})^2/(4.7 \times 10^{-5}) = 6.8 \times 10^{-10}$.

Calculating from the solubility in sodium hydroxide of an initial P_H of 8.2, the ionization is 29% and the dissociation constant is 6.0×10^{-10}. Likewise, in sodium hydroxide of an initial P_H of 9.2, the ionization is 24% and the dissociation constant 1.15×10^{-10}. These three values may be considered good checks, as a very small error in determining the Sörensen value would make a large difference in the calculated dissociation, especially in the last case.

By using the above data on the solubility of ferrous hydroxide together with the specific electrode potentials, the free energy of the formation of ferrous hydroxide from the elements at 25° may be calculated. Thus using Thomsen's rule, $E = E_a + E_k - (I/N_a + I/N_k) \times 0.0591 \log K$, we get $E = 0.441 + 0.3976 - 1.5 \times 0.0591 \times (-4.4)$; $E = 1.239$; and $-\Delta F = 2 \times 23{,}074 \times 1.239$; $\Delta F = -57{,}200$ calories.

II. Comparison with Corrosion Data

Earlier data on the rate of corrosion of iron in solutions of electrolytes have been obtained mainly from "beaker" tests, where the solution is exposed to the air. It is now well recognized that such tests are affected not only by the absorption of impurities from the air and by the change in oxygen solubility, but also by the change in specific rate of absorption of gaseous oxygen due to the presence of the dissolved material. These factors make it difficult to interpret the results of "beaker" tests in terms of the specific effect of the electrolyte on the rate of corrosion.

The corrosion results reported in this paper are the first of a series on the effect of electrolytes in corrosion and have been obtained in apparatus similar to that introduced by Speller and Kendall.[9] The method con-

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[9] Speller and Kendall, *Ind. Eng. Chem.*, **15**, 134 (1923).

sists in circulating the solution through 60 meters of 12mm. steel pipe and measuring the decrease in concentration of dissolved oxygen. The method of calculating the data into the form of specific corrosion rates has been described in several papers.[1] In most of the experiments it was necessary to recirculate the solution to avoid excessive waste of chemicals, meanwhile aerating to renew the oxygen supply and filtering to remove rust. With all the different solutions the initial corrosion rate was the same and it generally required from one to two weeks for the rate to drop off to a constant value, thus indicating the building up of a protective film against

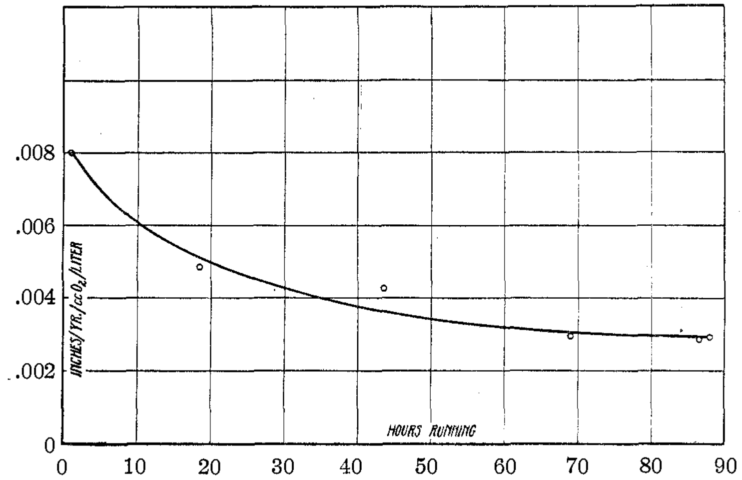

Fig. 5.—Corrosion in 0.125 *N* Na_2SO_4 solution *vs.* time.

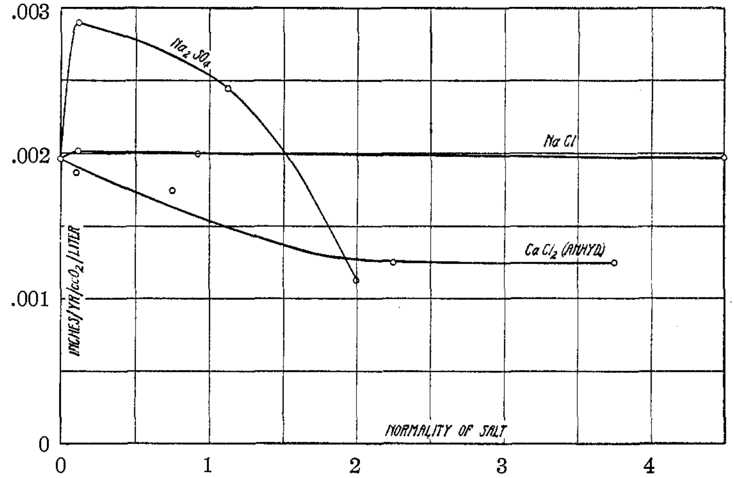

Fig. 6.—Corrosion in salt solutions.

the surface of the metal. Fig. 5 shows how the rate of corrosion varied with time in the case of the action of sodium sulfate upon freshly cleaned iron pipe.

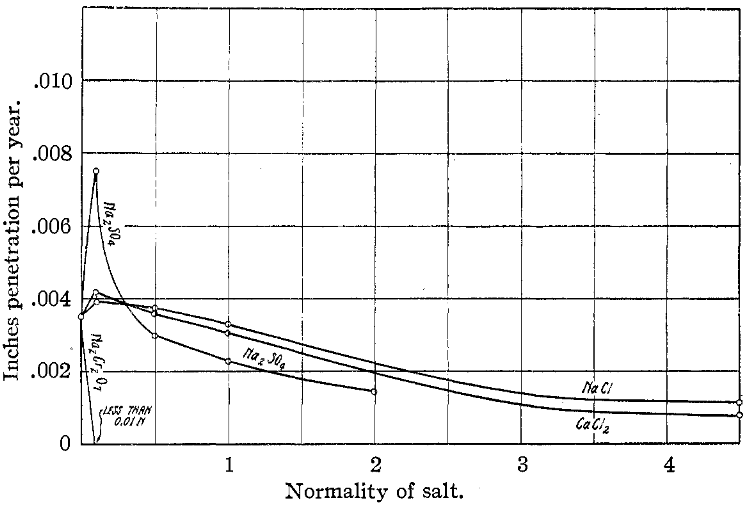

Fig. 7.—Beaker tests on corrosion in salt solutions.

The corrosion results obtained with sodium sulfate, sodium chloride and calcium chloride are shown in Fig. 6, where the specific rate of corrosion

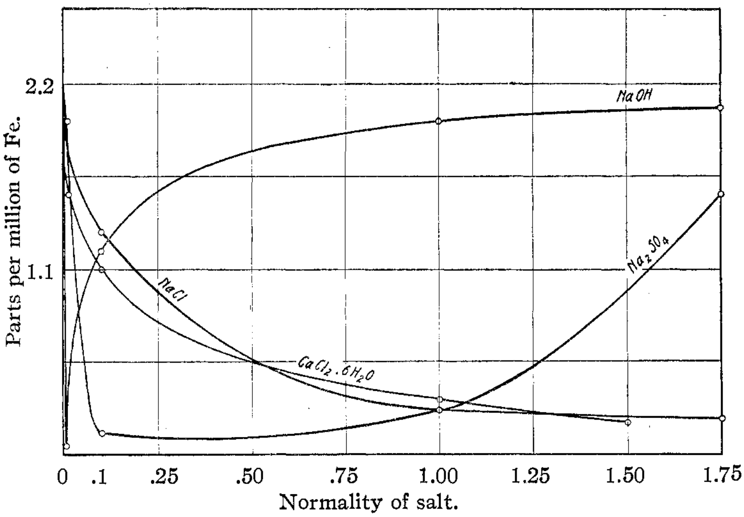

Fig. 8.—Stability of colloidal $Fe(OH)_3$ in salt solutions.

(inches of penetration per year when the dissolved oxygen content is 1 cc. per liter) is plotted against normality. Fig. 7 shows the results of various beaker tests with the same salts and with sodium dichromate expressed as inches of penetration per year.

Friend[10] has claimed that colloidal ferric hydroxide acts as a catalyst in corrosion, and that the decreased corrosion in more concentrated solutions is largely due to the precipitation of this colloidal catalyst. It seemed advisable, therefore, to determine by experiment the effect of the various solutions in precipitating colloidal ferric hydroxide.

These experiments consisted in preparing a colloidal solution of ferric hydroxide by boiling iron in aerated water and then filtering through an alundum crucible. The filtrate was a colloidal solution containing by analysis about 4.4 parts per million of ferric iron (no ferrous present). Equal quantities of this and of standard salt solutions were then mixed and allowed to stand for five hours. Then they were filtered as above and analyzed for iron. The results of these tests are shown in Fig. 8.

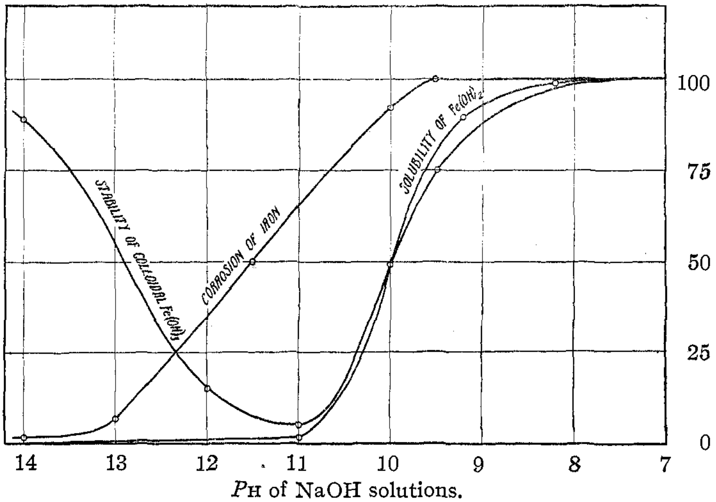

Fig. 9.—Relation between corrosion, the solubility of $Fe(OH)_2$ and the stability of colloidal $Fe(OH)_3$ in NaOH solutions. Corrosion: 100 = 0.002 in. per g. per cc. of O_2 per liter. Colloidal $Fe(OH)_3$: 100 = 2.2 parts per million Fe. Solubility of $Fe(OH)_2$: 100 = 3.75 parts per million Fe.

Discussion.—A comparison of Figs. 1 and 6 and 7 shows the general similarity between the effects of three salts on corrosion and on the solubility of ferrous hydroxide. Furthermore, although the corrosion data with chromates were obtained only in beaker tests, the salt greatly reduces both the rate of corrosion and the solubility even in concentrations below 0.01 *N*. It is, of course, logical that the acidic salts, such as ammonium chloride and magnesium chloride, should increase both the solu-

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[10] Friend, *Carnegie Scholarship Mem.*, **11** (1922).

bility of ferrous hydroxide and the rate of corrosion, although no specific data on the latter point are given in this paper.

Fig. 9 brings out the effects of sodium hydroxide on corrosion, solubility and precipitation of colloid. The concentration of sodium hydroxide is expressed on a logarithmic scale as Sörensen (P_{H}) value. While the corrosion and solubility curves do not coincide, they have the same shape and indicate that a relationship exists between solubility and corrosion. It seems probable that the corrosion rate is greater than would be predicted from the solubility of ferrous rust because the rust film is subject to erosion by the moving water. This would permit relatively rapid corrosion of the exposed metal because the solution is highly conducting. This conclusion is checked by the fact that a plot of corrosion rates obtained in quiet sodium hydroxide solutions[1] more nearly coincides with the curve of solubility of ferrous hydroxide.

A logical explanation of the relation between corrosion and solubility of ferrous hydroxide is that the solubility determines the degree of film protection. On this basis, a low solubility means high protectivity, since the ferrous ions formed by corrosion will be quickly precipitated on the metal as hydroxide and will build up a dense, adherent film. Any increase in solubility, by giving the ferrous ions greater freedom to get away from the metal, would decrease the protectivity of this film.

A comparison of the data for sodium chloride and sodium sulfate in Figs. 6 and 8, shows that the effects of the salts in precipitating colloidal ferric hydroxide do not parallel their effects upon corrosion and that corrosion is not at a minimum at the point of maximum precipitation. This is well brought out for the case of sodium hydroxide in Fig. 9. The value of Friend's hypothesis that decreased corrosion in salt solutions is largely determined by precipitation of colloid seems doubtful on the basis of these data.

This line of attack suggests interesting possibilities for a study of passivity. The experiments with chromates and dichromates reported in the first part of this paper show that in these solutions which passivify iron, iron hydroxides are practically insoluble. Certain writers have attributed the decreased corrosion in alkalies to passivity. The results given here indicate that the decreased corrosion is due to decreased solubility of the ferrous hydroxide. The possible relationship between passivity and the solubility of the corrosion products appears to justify further investigation.

This work was done under the Corrosion Fellowship established at this Laboratory by the National Tube Company.

Summary

1. The solubility of ferrous hydroxide has been determined in water (6.7×10^{-5} mole per liter) and in solutions of various concentrations of

the following salts: sodium sulfate, calcium chloride, sodium chloride, ammonium chloride, magnesium chloride, sodium dichromate, sodium chromate, sodium silicate and sodium hydroxide.

2. Data are given whereby the solubility of ferrous hydroxide may be calculated in non-oxidizing salt solutions in which the ionic strength does not exceed unity.

3. From the data on the solubility of ferrous hydroxide and the hydrogen-ion concentration of its saturated solution the dissociation constant is calculated as 6×10^{-10}, and the ionization in saturated water solution as 30% at 25°.

4. The free energy of formation of ferrous hydroxide has been calculated from the specific electrode potentials and the solubility to be —57,200 calories.

5. It has been shown that the precipitation of colloidal ferric hydroxide in salt solution has apparently no direct connection with the rate of corrosion.

6. The rate of corrosion in salt solutions parallels the solubility of ferrous hydroxide in these solutions. It is suggested that this is due to changes in film protectivity with the solubility of the ferrous rust.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTION OF ULTRAVIOLET LIGHT UPON CARBON DIOXIDE AND WATER

BY C. W. PORTER AND H. C. RAMSPERGER

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As early as 1870 Baeyer[1] suggested that the first step in the photosynthesis of sugars and starches in plants might be the formation of formaldehyde from carbon dioxide and water. At an earlier date Butlerow[2] had observed that reducing sugars are formed by the action of dilute aqueous alkali upon formaldehyde. Emil Fischer[3] isolated from the mixture of sugars thus produced some of the well-known hexoses that occur in nature.

To confirm the Baeyer theory many investigators have tried to reduce carbon dioxide to formaldehyde by water under the influence of visible and ultraviolet light. Among those who have reported successful attempts are Usher and Priestley,[4] Moore and Webster,[5] Baly, Heilbron and Barker.[6]

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[1] Baeyer, *Ber.*, **3**, 63 (1870).

[2] Butlerow, *Ann.*, **120**, 295 (1861).

[3] Fischer, *Ber.*, **21**, 989 (1888).

[4] Usher and Priestley, *Proc. Roy. Soc.*, **84B**, 101 (1911).

[5] Moore and Webster, *ibid.*, **90B**, 168 (1918).

[6] Baly, Heilbron and Barker, *J. Chem. Soc.*, **119**, 1025 (1921).