S 34. *The Passivity of Metals. Part IX. The Solubility Product of Freshly Precipitated Ferric Hydroxide.*

By U. R. Evans and M. J. Pryor.

The solubility product of the freshly precipitated " gelatinous " ferric hydroxide has been determined by an electrometric method. A value of $10^{-35 \cdot 5}$ has been obtained, at 20°, which agrees well with the value determined by Kriukov and Awsejewitsch under similar conditions.

The solubility product of ferric hydroxide is of interest in the study of certain corrosion reactions. The gelatinous product formed by the action of alkali on ferric salts is a metastable phase, which only slowly ages, passing into a more compact and less soluble condition. In this respect, it is similar to the hydroxides and basic salts of zinc studied by Feitknecht (*Métaux et Corrosion*, 1947, **22**, 192), which often separate from solution in a metastable condition in preference to the less soluble, more stable forms.

The solubility product of the metastable hydroxide is particularly important in connection with the use of alkaline inhibitors. If an inhibitor is added in insufficient quantity, a loose membrane of ferric hydroxide is formed over the susceptible points where corrosion is proceeding, and prevents the inhibitor from reaching just those points where its presence is necessary for the prevention of attack. The combination of large cathode and small anode then leads to intense localised attack or pitting. Thus, if the inhibitor is to be effective, it must be added in such a proportion that, should any precipitation occur at all, it occurs in physical contact with the metallic surface, and not as a loose membrane. Consequently the main factor determining the concentration needed to avoid pitting is the solubility product of the hydroxide.

Most values of solubility products recorded in the literature refer to stable phases, although in the case of hydroxides, some experimenters have studied metastable forms. Values referring to stable forms which only appear slowly are, however, of limited use in studying the phenomena of corrosion and passivity.

The structure of the gelatinous ferric hydroxide is admittedly undefined. The precipitate formed by the interaction of ferric chloride and alkali was found, however, in the *X*-ray researches of Böhm (*Z. anorg. Chem.*, 1925, **149**, 203) to be amorphous. Fordham and Tyson (*J.*, 1937, 483) studied, by means of electron diffraction, the membranous form of ferric hydroxide, obtained from the interaction of ferric chloride and sodium hydroxide. They obtained a well-defined ring pattern characteristic of a face-centred cubic structure with $a = 5{\cdot}70$ A., quite different from the hydroxide, goethite, Fe_2O_3,H_2O, examined by de Jong (*Natuurwetensch. Tijds.*, 1930, **12**, 69). It is by no means certain, however, that the compound investigated by Fordham and Tyson is the same as that of Böhm, for they prepared the hydroxide membrane by electrolysis, between platinum electrodes, with the two solutions separated by a collodion membrane. It seems likely that the product under examination in this paper is similar to the one investigated by Böhm.

Previous Work.—The divergent values for the solubility product of ferric hydroxide found in the literature may be due, not only to the variable forms of precipitate but also to the tendency to form colloidal solutions. Britton (*J.*, 1925, 2148), by an electrometric titration of an acid solution of ferric chloride with sodium hydroxide, found the solubility product to be $10^{-37\cdot7}$ at pH 2·3. At this pH, however, the hydroxide was largely colloidal and was not coagulated until the pH had been further raised to 6·6. Jellinek and Gordon (*Z. physikal. Chem.*, 1924, **112**, 207) measured the hydrion concentrations, with a hydrogen electrode, of solutions of ferric chloride in potassium chloride, to which sodium hydroxide had been added; the concentration of ferric ions in solution was measured colorimetrically with thiocyanate. They obtained a value of $10^{-37\cdot9}$ but their method is open to criticism, since the introduction of thiocyanate would probably alter the concentration of ferric ions in equilibrium with the hydroxide. Ruff and Hirsch (*Z. anorg. Chem.*, 1925, **146**, 338), by a fractional precipitation method, determined a value of $10^{-35\cdot96}$, while Kriukov and Awsejewitsch (*Z. Elektrochem.*, 1933, **39**, 884) measured the variation of solubility product with pH, by an electrometric titration of an acid solution of ferric sulphate with sodium hydroxide. They found a variation between $0{\cdot}1 \times 10^{-36}$ at pH 2·32 and $3{\cdot}45 \times 10^{-35}$ at pH 3·45. A calculation based on the redox potential of the ferrous–ferric equilibrium gave a value of $10^{-36\cdot5}$.

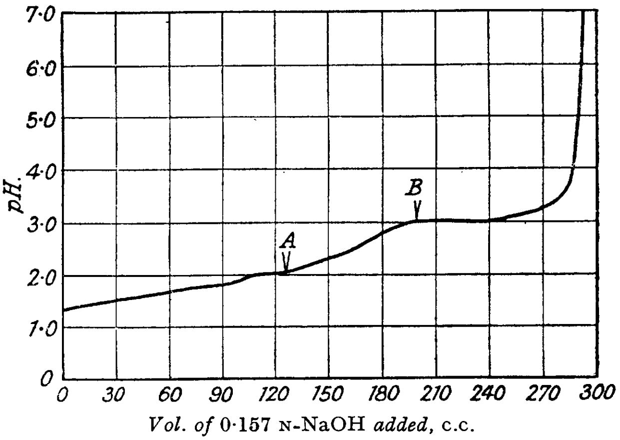
Cooper (*Proc. Roy. Soc.*, 1937, *B*, **124**, 299) recalculated the results of Kriukov and Awsejewitsch, using the concept of activities, arbitrarily assuming a value of 0·2 for the activity coefficient of ferric ions. He thus obtained values between $10^{-37\cdot7}$ and $10^{-39\cdot2}$.

EXPERIMENTAL.

The solubility product of the gelatinous hydroxide was determined by electrometric titration. The ferric alum employed was free from $Cr^{\cdot\cdot\cdot}$, $Mn^{\cdot}$, $Ni^{\cdot\cdot}$, NO_3', Br', and I'; there was a barely detectable trace of Cl', but as this ion has a lower flocculating power than SO_4'' its presence may be neglected. Ferrous ions—the presence of which might have affected the results—could not be detected by the sensitive $\alpha\alpha'$-dipyridyl test.

In a typical experiment an acid ferric alum solution (0·05M-H_2SO_4 and 0·02M-ferric ammonium sulphate) was titrated with sodium hydroxide (0·157M). The calculated volume of alkali required to neutralise the acid was 127·0 c.c. and that required to precipitate the hydroxide completely was 153·2 c.c., making a total of 280·2 c.c.

During the titration the hydrogen-ion activity was measured by means of a glass electrode in conjunction with a calomel half-cell; the temperature was maintained at 20° ± 0·25° by means of a water-bath. The solution was vigorously stirred, by mechanical means, so that the pH soon became steady after each addition of alkali. Special care was taken to decide the exact pH at which precipitation first occurred. The relation between pH and the volume of alkali added is shown in the Figure.



The free acid was neutralised at point *A* after the addition of 127 c.c. of 0·157N-sodium hydroxide. The further addition of alkali gave rise to formation of a colloidal solution of ferric hydroxide, whose colour changed from pale yellow to deep red between pH 2·0 and 3·0. After 200 c.c. of sodium hydroxide had been added and the pH of the solution had risen to 3·00 gelatinous ferric hydroxide was observed to be precipitated at the point *B*. Its formation was further characterised by a marked flattening of the titration curve.

If the assumption was then made that the quantity of " free " ferric ions still in solution at *B* was equivalent to the additional volume of sodium hydroxide that had to be added to complete the precipitation of the hydroxide, the value of the solubility product could be calculated. Chemical examination of the solution in equilibrium with the gelatinous hydroxide justified this assumption.

Thus, the free ferric ion content of the solution at *B*, where gelatinous ferric hydroxide is first precipitated

$$\equiv 280{\cdot}2 - 200 = 80{\cdot}2 \text{ c.c. of } 0{\cdot}157\text{N-NaOH},$$

i.e., the concentration of ferric ions in solution at *B*

$$\equiv \frac{80{\cdot}2}{400} \times 0{\cdot}157 \times \frac{1}{3} = 1{\cdot}05 \times 10^{-2} \text{ g.-ion/litre.}$$

Precipitation of gelatinous ferric hydroxide first occurs at pH 3·00. Since K_w at 20° is $10^{-14{\cdot}20}$, [OH]′ must be $10^{-14{\cdot}20+3{\cdot}00}$, that is $10^{-11{\cdot}20}$. Consequently, the solubility product of ferric hydroxide

$$K = [\mathrm{Fe}^{+++}][\mathrm{OH}']^3 = 1{\cdot}05 \times 10^{-2} \times 10^{-33{\cdot}60} = 10^{-35{\cdot}58} \text{ at } 20°.$$

Results.—In all, six determinations were made at four different concentrations of reagents, one of the experiments being performed in triplicate. The results are shown in the table.

Expt.	Concn. of acid, N.	Concn. of alkali, N.	Concn. of ferric alum, M.	Solubility product.	Expt.	Concn. of acid, N.	Concn. of alkali, N.	Concn. of ferric alum, M.	Solubility product.
I	0·1000	0·1570	0·0200	$10^{-35{\cdot}58}$	IV(*a*)	0·1000	0·2295	0·0191	$10^{-35{\cdot}47}$
II	0·1330	0·4590	0·0191	$10^{-35{\cdot}42}$	IV(*b*)	0·1000	0·2295	0·0191	$10^{-35{\cdot}44}$
III	0·0500	0·1836	0·0091	$10^{-35{\cdot}57}$	IV(*c*)	0·1000	0·2295	0·0191	$10^{-35{\cdot}47}$

In all the experiments the gelatinous ferric hydroxide was first precipitated within a pH range of 3·00—3·05. Despite the fact that the initial pH of precipitation varied slightly, and that different effective concentrations of reagents were used, the solubility product appeared to be constant within the limits of experimental error. This indicates that the number is a true solubility constant; previously, owing to the colloidal nature of the system, uncertainty had been felt as to whether this would be the case. Thus the solubility product of gelatinous ferric hydroxide appears to be $10^{-35{\cdot}5}$ at 20°.

DISCUSSION.

The value of $10^{-35{\cdot}5}$ is higher than those generally quoted for the solubility product of ferric hydroxide. In the freshly precipitated, gelatinous, state the hydroxide is, however, more soluble than in the aged or colloidal condition, and so the difference in solubility product is not surprising. Kriukov and Awsejewitsch (*loc. cit.*) found the solubility product of ferric hydroxide, at pH 2·98, to be $0{\cdot}7 \times 10^{-36}$, at 18°, which is in reasonable accord with the authors' result, since the solubility product will be likely to increase rapidly with a rise in temperature.

This value of solubility product may be useful in predicting the conditions under which ferric hydroxide will be formed in certain corrosion reactions.

One of the authors (M. J. P.) wishes to thank the Department of Scientific and Industrial Research for financial support.

DEPARTMENT OF METALLURGY, CAMBRIDGE UNIVERSITY. [*Received, July 28th,* 1948.]