179. *The Solubility Products of Ferrous and Ferrosic Hydroxides.*

By T. V. ARDEN.

Values of $2{\cdot}4 \times 10^{-14}$ and $6{\cdot}4 \times 10^{-18}$ for the solubility products of ferrous hydroxide and freshly precipitated green ferrosic hydroxide have been obtained by potentiometric titration with sodium hydroxide in sulphate solution, using a glass electrode.

THE precipitation of ferrous hydroxide has been widely studied, and the solubility product determined by a variety of methods. The highest value recorded, 7×10^{-13}, was obtained by Schrager (*Coll. Czech. Chem. Comm.*, 1929, **1**, 275), while the lowest, $2{\cdot}5 \times 10^{-21}$, was given by Bödlander (*Z. Elektrochem.*, 1900, **8**, 840). The latter value was confirmed by Britton (*J.*, 1925, **127**, 2110), by potentiometric titration of ferrous sulphate with sodium hydroxide, using a hydrogen electrode. The same method was used by Elder (*Trans. Amer. Electrochem. Soc.*, 1930, 57) who obtained a figure of $4{\cdot}8 \times 10^{-16}$. Conductivity measurements of saturated ferrous hydroxide solutions were used by Lamb (*J. Amer. Chem. Soc.*, 1910, **32**, 1214), and by Murata (*J. Soc. Chem. Ind. Japan*, 1932, **35**, 523), to calculate values of $9{\cdot}9 \times 10^{-15}$ and $2{\cdot}9 \times 10^{-15}$ respectively. Shipley and McHaffie (*Canadian Chem. Met.*, 1924, **8**, 5, 121) determined the solubility product of ferrous hydroxide as $3{\cdot}9 \times 10^{-15}$, from observations of the rate of corrosion of metallic iron in oxygen-free water. The solubilities of metallic iron in pure water, and in potassium hydroxide solution, were shown by Bineau (*Compt. rend.*, 1879, **41**, 509) and Krassa (*Z. Elektrochem.*, 1909, **15**, 491) to be $7{\cdot}5 \times 10^{-5}$ and $2{\cdot}8 \times 10^{-5}$ respectively, giving solubility products of $2{\cdot}0 \times 10^{-13}$ and $8{\cdot}7 \times 10^{-14}$, assuming complete ionisation. Whitman, Russell, and Davis (*J. Amer. Chem. Soc.*, 1925, **47**, 70) showed that ferrous hydroxide is only 30% ionised in saturated solution, the undissociated molecules being in true solution. The solubility of metallic iron in pure water at 25° was found to be $6{\cdot}7 \times 10^{-5}$, in agreement with the results of Bineau; but the solubility product, calculated from determinations of the pH of the saturated solution, was $3{\cdot}2 \times 10^{-14}$. A recalculation of Bineau's and Krassa's results, with allowance for the degree of ionisation of ferrous hydroxide, gives values of $4{\cdot}1 \times 10^{-14}$ and $2{\cdot}6 \times 10^{-14}$, respectively, for the solubility product.

The product of the reaction of pure ferrous sulphate solution with alkali is a white gelatinous precipitate, which becomes green in the presence of traces of ferric salts, owing to the presence of ferrosic hydroxide. The green compound is formed at a pH (6·4 in 0·05M-solution) considerably lower than that of pure ferrous hydroxide (8·1 in 0·05M-solution); and it is therefore necessary, in studying the precipitation of ferrous hydroxide, to eliminate both ferric iron and free oxygen from the system. It is extremely difficult to remove all traces of Fe^{+++}, and in a titrimetric procedure failure to prevent oxidation would result in low values for the solubility product. In the case of Britton's experiments, it was stated that air was not completely excluded. In methods based upon determinations of the solubility of iron in water (Bineau, Krassa, Lamb, Murata, and Whitman) the effect of traces of oxygen would be to raise the apparent solubility product; but the resulting errors would be small, since the solutions produced by this method are sufficiently alkaline to render the solubility of ferric iron negligible. The true solubility product of ferrous hydroxide therefore appears to be of the order of 10^{-14}, and results which are considerably lower than this figure are likely to have been influenced by oxidation.

The object of this work has been to determine $K_{\mathrm{Fe(OH)}_2}$ from measurements of the changes in pH during a titration of ferrous sulphate with sodium hydroxide, in the complete absence of ferric iron or oxygen. In addition, the precipitation of ferrosic hydroxide has been studied, by titrations of mixtures of ferric and ferrous sulphates, in varying ratios. Titrations have also been carried out in the presence of atmospheric oxygen, to demonstrate the large errors which are caused in these conditions.

EXPERIMENTAL.

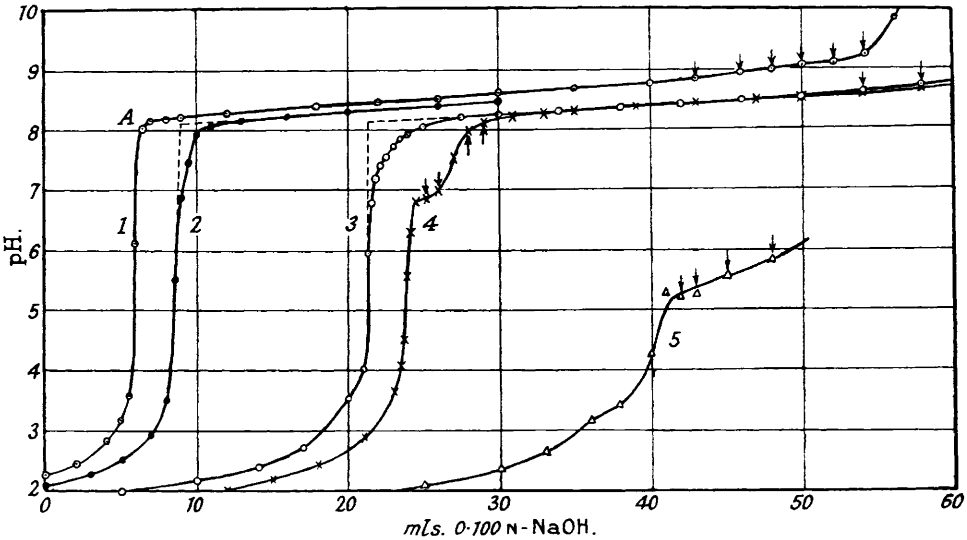
Ferrous Sulphate Solution.—A stock solution of 0·05M-ferrous sulphate, containing 0·05M-H_2SO_4, was prepared from pure metallic iron, and AnalaR sulphuric acid. It was impossible to maintain this solution in a fully reduced condition, and a further reduction was therefore carried out immediately before each titration, by boiling a measured portion of the solution with metallic iron or magnesium in the sealed titration vessel. The experiment was then carried out under an atmosphere of hydrogen, the passage of which also served to agitate the solution. When iron was used for the reduction, the total ferrous content of the solution was determined at the end of the experiment; when magnesium was used, no interference with the titration was caused, since the step in the titration curve caused by the precipitation of magnesium hydroxide occurred at pH 10·5, after the completion of the ferrous reaction.

Ferric Sulphate Solution.—A solution containing 0·033M-ferric sulphate and 0·05M-H_2SO_4 was prepared by dissolving metallic iron in sulphuric acid, and oxidising with AnalaR hydrogen peroxide. The excess of peroxide was removed by prolonged boiling, and the solution was de-aerated immediately before each use by the prolonged passage of hydrogen.

Sodium Hydroxide Solution.—A solution (0·100N.) of sodium hydroxide was de-aerated by the prolonged passage of hydrogen immediately before each experiment.

Ferrous Hydroxide Precipitation.—A portion of the stock ferrous solution, initially at pH 1·5, was reduced and titrated with sodium hydroxide at 20°, the pH being determined by means of a glass electrode and a dip-type calomel half-cell. The electrode system was standardised before and after each experiment at pH 3·97 and 9·18, no results being accepted unless the four standardisation readings agreed within pH 0·05. After each addition of alkali, the pH was allowed to reach equilibrium. In the early stages of the titration, this process took place rapidly, but during the final stages of precipitation the pH dropped slowly to the values shown. (The direction and magnitude of changes of pH with time are indicated by arrows touching the curves.) In the complete absence of ferric iron, sharp inflexions occurred at the point corresponding to the first permanent white precipitate (*A*, Fig. 1, Curve 1). In the presence of small traces of Fe^{+++}, the inflexions were less clearly defined (Fig. 1, Curves 2 and 3), and the formation of ferrous hydroxide was preceded by formation of traces of green ferrosic hydroxide. The true pH of first precipitation could nevertheless be determined by extrapolation of the horizontal and vertical portions of the curves. When sufficient ferric iron was present to give a definite green colour to the precipitate, the resultant curves were considerably distorted (Fig. 1, Curve 4) and were not used for the calculation of results. In a typical experiment, 50 ml. of 0·0500M-ferrous sulphate solution were reduced with magnesium, and titrated with 0·100N-sodium hydroxide. The point of first precipitation (*A*, Fig. 1, Curve 1) occurred after the addition of 6·1 ml. of alkali, when the total volume was 56·1 ml. The concentration of ferrous iron, $[Fe^{++}]$, is $0·05 \times 50/56·1 = 4·48 \times 10^{-2}$. The pH was then 8·10, and since K_w at 20° is $10^{-14·18}$, $[OH']$ is $10^{-6·08}$.

FIG. 1.



Then $K = [Fe^{++}] \times [OH']^2 = 4·48 \times 10^{-2} \times 10^{-12·16} = 3·1 \times 10^{-14}$, where K is the apparent solubility product, assuming complete dissociation of ferrous sulphate, and neglecting activity corrections.

The following results are calculated from curves in which the distortion is less than in curve 3 (Fig. 1)

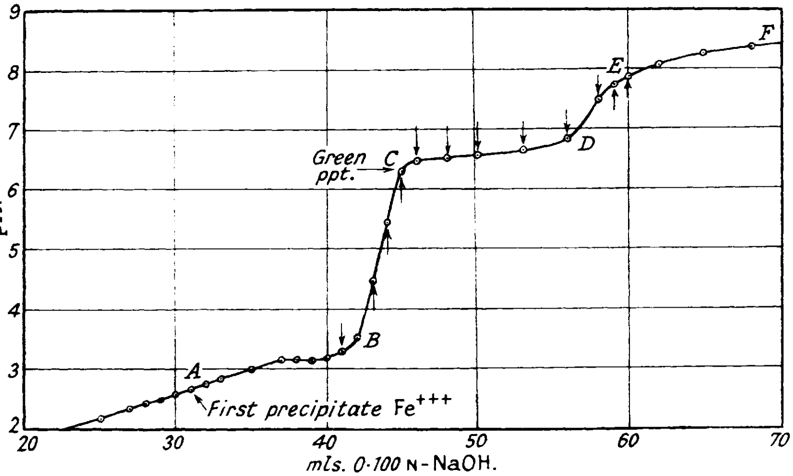
Expt.	$[Fe^{++}]$ at *A*.	pH.	$[OH']$.	Solubility product.
1	$4·48 \times 10^{-2}$	8·10	$10^{-6·08}$	$3·1 \times 10^{-14}$
2	$3·24 \times 10^{-2}$	8·15	$10^{-6·03}$	$2·8 \times 10^{-14}$
3	$4·23 \times 10^{-2}$	8·00	$10^{-6·18}$	$1·9 \times 10^{-14}$
4	$3·5 \times 10^{-2}$	8·10	$10^{-6·08}$	$2·4 \times 10^{-14}$
5	$8·10 \times 10^{-3}$	8·44	$10^{-5·74}$	$3·0 \times 10^{-14}$
6	$8·10 \times 10^{-3}$	8·40	$10^{-5·78}$	$2·2 \times 10^{-14}$
7	$3·96 \times 10^{-3}$	8·5	$10^{-5·7}$	$1·6 \times 10^{-14}$

The agreement between experiments at different concentrations is good, and gives a mean value $K = 2{\cdot}4 \times 10^{-14}$.

Titration in the Presence of Air.—A titration carried out in a closed vessel containing some air gave a precipitate, largely composed of ferric hydroxide, with some ferrosic hydroxide, at pH 5·25. The resultant curve (Curve 5, Fig. 1) resembles that obtained by Britton, and the apparent solubility product calculated from it is $5{\cdot}3 \times 10^{-20}$.

Ferrosic Hydroxide Precipitation.—The procedure described for ferrous hydroxide was used, with the addition of a measured quantity of 0·033M-ferric sulphate solution after reduction of the ferrous solution. In a typical experiment (Fig. 2), 15 ml. of 0·033M-Fe^{+++} and 50 ml. of 0·05M-Fe^{++} were titrated with 0·100M-NaOH. Basic ferric sulphate was first precipitated between pH 2·5 and 3·5, the curve (*A*—*B*) being of the characteristic type observed by Evans and Prior (*J.*, 1949, S 157). The complete precipitation of ferric iron was followed by further reaction of the precipitate with sodium hydroxide to form $Fe(OH)_3$, the pH rising rapidly during this process (*B*—*C*). At *C*, the formation of dark olive-green ferrosic hydroxide was accompanied by a sharp inflexion in the curve, and in the region *C*–*D*, the pH readings dropped slowly after each addition of alkali, to the values shown. If the normally accepted formula for ferrosic hydroxide is assumed, the reaction in the region *C*–*D* is

FIG. 2.



$$2Fe(OH)_3 + Fe^{++} + 2OH' = Fe_3(OH)_8$$

and the solubility product of $Fe_3(OH)_8$ is therefore $K' = [Fe^{++}] \times [OH']^2$. The end point of this reaction was marked by an inflexion at *D*, after which the pH readings rose rapidly on to a curve *E*—*F* similar to those obtained with pure ferrous iron solutions.

Results were as follows :

Expt.	$[Fe^{++}]$ at *C*.	pH.	$[OH']$.	*K*.
1	$2{\cdot}38 \times 10^{-2}$	6·35	$10^{-7{\cdot}83}$	$5{\cdot}2 \times 10^{-18}$
2	$3{\cdot}20 \times 10^{-2}$	6·40	$10^{-7{\cdot}78}$	$8{\cdot}9 \times 10^{-18}$
3	$2{\cdot}35 \times 10^{-2}$	6·35	$10^{-7{\cdot}83}$	$5{\cdot}1 \times 10^{-18}$
			Mean	$6{\cdot}4 \times 10^{-18}$

DISCUSSION.

Ferrous Hydroxide.—The value $2{\cdot}4 \times 10^{-14}$ for the solubility product is in good agreement with the results obtained by Bineau and by Whitman, from solubility determinations, and by Müller from the Fe^{+++}/Fe^{++} potential. The titration curves are variable in length, the molecular ratio of sodium hydroxide required to give complete precipitation being between 1·7 and 1·9. This is in agreement with the findings of Pickering (*J.*, 1907, **91**, 1981), who considered the precipitate to be $10FeO,SO_3$. The formation of such a compound is normally accompanied, however, by a clear inflexion at the end of precipitation, as in the case of $4CuO,SO_3$, or $5ZnO,SO_3$. In the case of ferrous iron the final inflexions are ill-defined, and in the last stages of the curve, the pH readings fall slowly when the solution is kept. This effect could result from the occlusion of ferrous sulphate on a precipitate of ferrous hydroxide, and the formation of a basic ferrous sulphate cannot therefore be inferred from this work.

Ferrosic Hydroxide.—The term " ferrosic hydroxide " has been applied to compounds with widely differing properties, and the value $6{\cdot}4 \times 10^{-18}$ for the solubility product applies only to the compound produced from mixed ferric and ferrous solutions under conditions of rising pH.

The addition of excess of alkali causes the formation of a black compound, insoluble in mineral acids, which has not been studied in detail. The rate of fall of pH in the later stages of the curve *C–D* was so slow that equilibrium was not always attained, and the length *C–D* has been found variable. In all cases, however, the length of this curve was considerably greater than that required for $Fe_3(OH)_8$, and corresponds with the formation of $Fe_4(OH)_{10}$ [in Fig. 2, Found : 11 ml., $Fe_3(OH)_8$ requires 5·0 ml. $Fe_4(OH)_{10}$ requires 10·0 ml.]. A compound corresponding to this formula was prepared by Baudisch and Merzer (*Biochem. Z.*, 1920, **37**, 107) who considered it to be $HO{\cdot}Fe{\cdot}O{\cdot}Fe(OH)_2$. It appears that this compound is formed under the conditions of these experiments, by further reaction of $Fe_3(OH)_8$ in the presence of excess of ferrous iron.

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