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On the Solubility Product of Precipitated Iron(III) Hydroxide

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The solubility equilibrium of precipitated iron(III) hydroxide was investigated at 25 °C by determining the $[Fe^{3+}]$ and $[H^+]$ of solutions in contact with the solid phase. $[Fe^{3+}]$ and $[H^+]$ were measured using the cells

$$- \text{ CE} \mid \text{solution S} \mid \text{Pt} + \qquad (A)$$

$$- \text{ Glass electrode} \mid \text{solution S} \mid \text{CE} + \qquad (B)$$

CE denotes the half-cell

$$\mid NaClO_4\text{: 3 M} \mid NaCl\text{: 0.010 M, } NaClO_4\text{: 2.990 M} \mid AgCl, Ag$$

and solution S had the general composition

$$[Fe(III)] = B_3 \text{ M, } [Fe(II)] = B_2 \text{ M, } [H^+] = H \text{ M, } [Na^+] = (3.000 - 3B_3 - 2B_2 - H) \text{ M, } [ClO_4^-] = 3.000 \text{ M,}$$

where H is the hydrogen ion concentration assuming no hydrolysis or precipitation. B_3 was varied from 0.001 to 0.100 M and h, the actual hydrogen ion concentration of the solutions measured with cell (B), ranged from 2×10^{-2} to 2×10^{-3} M.

The precipitation reaction attains a steady state after about 200 h shown by the fact that after this period no further systematic change in $[Fe^{3+}]$ and $[H^+]$ could be detected; see Fig. 1.

The data for precipitates older than 200 h could be explained by assuming the reaction

$$Fe^{3+} + 2\ H_2O \rightleftharpoons FeOOH\ (s) + 3\ H^+$$

with $\log K = -3.96 \pm 0.10$. Since in 3 M $NaClO_4$ $\log K_{H_2O} = \log [H^+] + \log (OH^-] = -14.22$ [15],

$$\log K_s = \log ([Fe^{3+}]\ [OH^-]^3) = -38.7 \pm 0.2.$$

On the basis of Hedström's measurements [9] and the data obtained in this work, the experimental conditions for obtaining supersaturated solutions have been discussed.

A number of investigations have been devoted to the determination of the solubility product of precipitated iron(III) hydroxide. Previous work is summarized in Table 1.

Table 1.

Author	t °C	pK_s	anion present	method
Jellinek and Gordon [1] (1924)	14	37.9	Cl^-	$E(H_2)$, Fe(III) analytically
Britton [2] (1925)	18	37.7	Cl^-	$E(O_2)$
Elder [3] (1930)	?	35.4–37.5	Cl^-	$E(gl, H_2)$
Kriukow and Awsejevitsch[4] (1933)	18	36.5	SO_4^{2-}	E(gl, Fe [2,3] redox)
Bézier [5] (1945)	18	36.9–38.2	ClO_4^-	E(gl)
Evans and Pryor [6] (1949)	20	35.5	SO_4^{2-}	E(gl)
Aksel'rud and Fialkov [7] (1950)	18	37.5	SO_4^{2-}	$E(Sb, Sb_2O_3)$, Fe(III) analytically

$E(H_2)$: hydrogen electrode, $E(O_2)$: oxygen electrode, E(gl): glass electrode, E(Fe [2,3]) : Fe^{2+} – Fe^{3+} redox electrode, $E(Sb, Sb_2O_3)$: Sb, Sb_2O_3 electrode.

All of these authors, with the exception of Aksel'rud and Fialkov, employed the same approach; a potentiometric titration was made by adding NaOH to a solution containing Fe(III) until a considerable part of the iron was precipitated. The majority of the investigators [2,3,5,6] determined the pH of the solutions in contact with the solid phase; the solubility product was calculated by making the assumptions that all iron(III) in the solution is present as Fe^{3+} and that the precipitate has the composition $Fe(OH)_3$. Jellinek and Gordon [1] supplemented the pH measurements with the colorimetric or gravimetric determination of the total iron(III) content of the solution. Kriukow and Awsejewitsch [4] utilized both pH and redox potential measurements. Aksel'rud and Fialkov's pK_s value [7] is based on the determination of the pH and of the total iron concentration of $Fe_2(SO_4)_3$ solutions in contact with iron(III) hydroxide.

Gayer and Woontner have studied recently [8] the total solubility of FeOOH in $HClO_4$ and NaOH solutions at 25 °C. For solutions of $pH > 5$ the data could be explained by assuming the equilibrium

$$FeOOH(s) + H_2O \rightleftharpoons Fe(OH)_3 \text{ (dissolved)}$$

with p$K = 6.5$. For more acidic solutions the interpretation of the solubility data proved to be difficult because of the simultaneous presence of a series of hydrolysis products. In the pH range 1 to 3 the predominant part of the dissolved iron was found to exist as $Fe(OH)_2^+$.

The wide discrepancies among the reported results show that the experimental conditions were not chosen adequately to provide a reliable value of the solubility product.

Though it has been recognised very early [1] that the rate of precipitation is slow at room temperature and that freshly precipitated iron(III) hydroxide is far from being in equilibrium, no evidence has been given in any work that equilibrium was established under the described experimental conditions.

Precipitation with OH^- often yields a basic salt of a composition depending on the anion present in the solution and the temperature. Thus it cannot be assumed *a priori* that FeOOH is formed, but a method must be found to ascertain the composition of the solid phase.

Since Fe^{3+} is an acid of considerable strength [9], calculations made from pH measurements without taking into account the hydrolysis constants cannot give a correct value of the solubility product.

It is desirable to study the solubility equilibrium in a broad range of hydrogen and iron concentrations in order to test the validity of the assumptions made in computing the solubility product. Using solutions of varying ionic strengths the evaluation of the emf measurements is very difficult, since no method is available to estimate accurately the activity factors in mixed electrolytes containing a number of ions of various charges at appreciable concentrations.

The present work was undertaken to determine the solubility product of precipitated iron hydroxide by emf measurements in the constant ionic medium $[ClO_4^-] = 3$ M. The method of investigation was rather similar to that worked out in this laboratory to study the hydrolysis equilibria of metal ions. Though the results are applicable only in this ionic medium, the general approach might be of some value also under other experimental conditions.

Symbols used in the text

b = concentration of Fe^{3+}.
B_2 = total concentration of iron(II).
B_3 = total concentration of iron(III).
E_{0A} = a constant, defined by eqn. 1.
E_{0B} = a constant, defined by eqn. 2.
E_j = $-16.7\ h$ mV = liquid junction potential.
h = actual hydrogen ion concentration in the test solution.
H = hydrogen ion concentration, assuming no hydrolysis or precipitation.
K = equilibrium constant defined by eqn. 3.
K_s = equilibrium constant defined by eqn. 6.
M = moles/liter.

METHOD

To study this solubility equilibrium a series of test solutions were prepared. The iron(III) concentration of the test solutions was varied between 0.001 and 0.1 M, and in each of these the hydrogen ion concentration was adjusted so that a visible precipitate was slowly formed. The $[H^+]$ and $[Fe^{3+}]$ of the test solutions were periodically examined by emf measurements, and these were extended until no further systematic concentration change could be detected.

All test solutions (S) investigated had the general composition

$[Fe(III)] : B_3$ M, $[Fe(II)] : B_2$ M, $[H^+] : H$ M, $[Na^+] : (3.000 - 3\,B_3 - 2B_2 - H)$ M, $[ClO_4^-] : 3.000$ M where B_3 denotes the total concentration of Fe(III), B_2 that of Fe(II), and H is the hydrogen ion concentration assuming no hydrolysis and precipitation. The test solutions were prepared by mixing an Fe(III)—Fe(II) stock solution and a $NaHCO_3$ solution (both containing 3 M ClO_4^-) in such a ratio that a visible precipitate was formed within a few days. $NaHCO_3$ has been used as the base, since preliminary experiments have shown, in accordance with Hedström [9], that NaOH causes an irreversible precipitation. The hydrolysis of CO_2 could be neglected since the pH of the test solutions never exceeded 3. Moreover a strong stream of N_2 was led through the solutions; thus the CO_2 concentration was always very low.

The $[H^+]$ and $[Fe^{3+}]$ of the test solutions were determined by measuring the emfs of the cells

$$- \text{ CE} \mid \text{solution S} \mid \text{Pt} + \qquad \text{(A)}$$

and

$$- \text{ Glass electrode} \mid \text{solution S} \mid \text{CE} + \qquad \text{(B)}$$

CE denotes the half-cell

Ag, AgCl | 0.010 M NaCl, 2.990 M $NaClO_4$ | 3.000 M $NaClO_4$ |

The emfs of the cells (A) and (B) can be written at 25 °C

$$E_A = E_{0A} + 59.16 \log (b / [Fe^{2+}]) + E_j \qquad (1)$$

and

$$E_B = E_{0B} - 59.16 \log h - E_j \qquad (2)$$

where E_{0A} and E_{0B} are constants, b and h are the actual $[Fe^{3+}]$ and $[H^+]$ of the test solutions, and E_j denotes the liquid junction potential at the junction 3 M $NaClO_4$ | solution S. E_j was calculated with the equation $E_j = -16.7\ h$ mV determined previously [10]. The acidity constant of Fe^{2+} is so low [11] that in the pH range studied the $[Fe^{2+}]$ could be set equal to B_2. The activity factors of the reacting species were assumed to be constants; this is certainly a good approximation since the solutions were rather dilute in Fe(III), Fe(II) and H^+.

E_{0A} and E_{0B} were determined by measuring E_A and E_B with solutions of so high an acidity that the hydrolysis of Fe^{3+} could be neglected. Each time before a test solution was measured, E_{0A} and E_{0B} were checked. The constancy of these quantities for a long period was an indication that the cell equipment functioned satisfactorily.

A few series of measurements were made as potentiometric titrations with the technique usually employed in this laboratory in order to study the degree of supersaturation attained under these experimental conditions. B_3 and B_2 were kept constant in each series while the $[H^+]$ was decreased stepwise by the addition of $NaHCO_3$ until a solid phase became visible.

MATERIALS AND ANALYSIS

Iron (III) perchlorate solutions were made from $Fe(NO_3)_3 \cdot 9\ H_2O$ "Baker's Analyzed" by adding 72 % $HClO_4$ in excess and expelling the HNO_3 and a large part of the excess $HClO_4$ by heating with an infra-red lamp. In the stock solution containing about 1 M Fe(III) no NO_3^-, Cl^- and SO_4^{2-} could be detected.

Iron (III) was determined potentiometrically according to the method described by Berecki-Biedermann[12], the accuracy was ± 0.1 %. The $Na_2S_2O_3$ solution was standardized against twice recrystallized KIO_3.

Iron (II) perchlorate solution was prepared from a portion of the iron(III) perchlorate stock solution by electrolytic reduction. The iron(II) concentration was determined by potentiometric titration using $K_2Cr_2O_7$. The $K_2Cr_2O_7$ preparation was purified by recrystallisation and made water-free by melting at 400 °C. The same result was found within 0.1 % when this $K_2Cr_2O_7$ or the KIO_3 was used to standardize the thiosulfate solution.

The total iron concentration of the iron(II) perchlorate stock solution was determined by oxidizing Fe^{2+} with H_2O_2 solution. The excess peroxide was expelled by boiling, and in the cooled solution Fe(III) was titrated by the same method[12] as above.

The excess hydrogen ion concentration, H, of the Fe(III) and Fe(II) stock solutions was determined using the ion exchange resin "Duolite C3" in the hydrogen form. The hydrogen ion concentration of the eluate which is equal to the $[ClO_4^-]$ was determined with standard NaOH. H was calculated according to the equation

$$[ClO_4^-] = H + 3\ B_3 + 2\ B_2$$

$HClO_4$, NaOH, $NaHCO_3$, $NaClO_4$, and NaCl solutions were prepared and analyzed as described previously[13].

Nitrogen taken from a cylinder was freed of oxygen by passing it through hot activated copper. Acid and basic impurities were absorbed in NaOH and H_2SO_4 solutions, and finally the gas was led through water and 3 M $NaClO_4$ to obtain the right vapor pressure.

Experimental details of the emf measurements

E_A was measured with a recently certified Leeds and Northrup potentiometer of type K2, which could be read to 0.01 mV. E_B was determined with a valve potentiometer "Radiometer PHM3" Copenhagen. The sensitivity of this instrument is ± 0.2 mV.

Ag, AgCl electrodes were prepared as usual in this laboratory[13]. Redox potentials were measured with bright Pt-foils. When two electrodes were simultaneously employed they always agreed within 0.05 mV.

The glass electrodes were prepared by Dr. E. Blomgren, Uppsala. They came to equilibrium within 10—15 min and have given constant and reproducible potentials within ± 0.2 mV.

All measurements were carried out in a paraffin oil thermostat at 25.0 ± 0.1 °C.

SURVEY OF MEASUREMENTS

Procedure. Test solutions with the following B_3 values were studied: 1.000×10^{-3}, 5.00×10^{-3}, 1.000×10^{-2}, 2.50×10^{-2} and 1.000×10^{-1} M. B_2 was always chosen to be approximately equal to B_3. With lower values of B_3 than 1 mM no satisfactory results could be obtained; this may be explained by the slow rate of precipitation and the low redox- and pH-buffer capacity of such dilute solutions. In order to avoid complications due to the variation of the activity factors, the higher limit of B_3 was set at 0.1 M.

O_2 and CO_2 were expelled from the test solutions by passing a strong stream of N_2 through them for about half an hour. The vessels were then closed with well fitting rubber stoppers, which were coated with paraffin and finally they were placed in the thermostat.

Though Fe^{2+} is rather slowly oxidized by air in $HClO_4$ solutions, it was important to check to what extent oxidation might have occurred during the long periods of measurement (10—20 days). For this purpose a number of solutions were transferred immediately after preparation to glass bottles, made

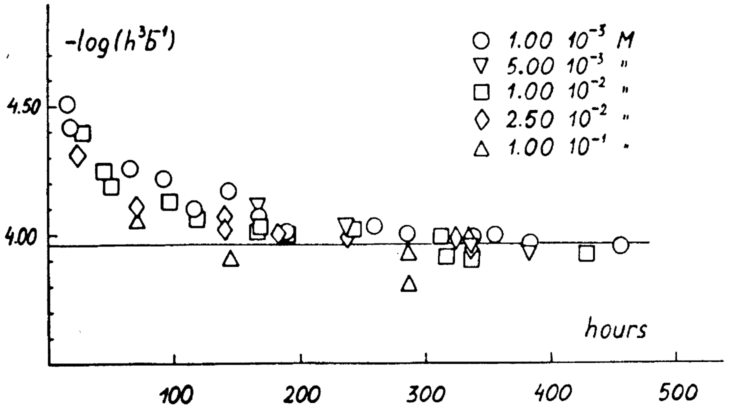

Fig. 1. Attainment of the steady state. $\log(h^3b^{-1})$ as a function of time. The horizontal line represents the solubility product $\log K = -3.96$ calculated by the plot given in Fig. 2.

free from O_2 and CO_2 by bubbling through N_2, and then the bottles were sealed and placed in the thermostat. After two weeks $\log h$ and $\log b$ were measured and found to agree within 0.01 units with the $\log h$ and $\log b$ values of solutions of the same composition, which were kept in the normal way and examined frequently. Thus no appreciable error could have been introduced by oxidation.

In the first week $\log h$ and $\log b$ varied rapidly and E_A and E_B were measured each day; later on measurements were generally made every second day.

Attainment of the steady state. The progress of the precipitation is illustrated in Fig. 1 which shows $\log(h^3b^{-1})$ as a function of the age of the test solution. The starting point of the reaction was taken when the solution was immersed in the thermostat. All test solutions were studied at least for 10 days; the majority of them were examined for a period of two weeks.

In the first 200 h the plot $\log(h^3b^{-1})^{-1}$ *versus* time is seen to give a gradually falling curve of monotonically decreasing slope; this type of time dependence indicates that the precipitation reaction is approaching to a steady state where the rate of reaction becomes negligible. This final state seems to be attained in about 200 h. As Fig. 1 shows, no further systematic variation of $\log(h^3b^{-1})$ can be detected within the limits of experimental error for test solutions older than 200 h, and all points, except one for $B_3 = 1 \times 10^{-1}$, are seen to lie in the interval —3.85 to —4.05. The uncertainty of the $\log(h^3b^{-1})$ values in the steady state may be estimated to be ± 0.05 on the basis of measurements made in solutions of the same B_3 value.

Composition of the precipitate. A chemical analysis of the precipitate could not be made, because no method was found to wash it free from the mother liquid. When the solid phase separated by centrifugation was washed with water, a colloidal solution was formed which could not be made to coagulate by centrifugation. Addition of SO_4^{2-} broke the sol very rapidly but the introduction of sulfate is of course not desirable.

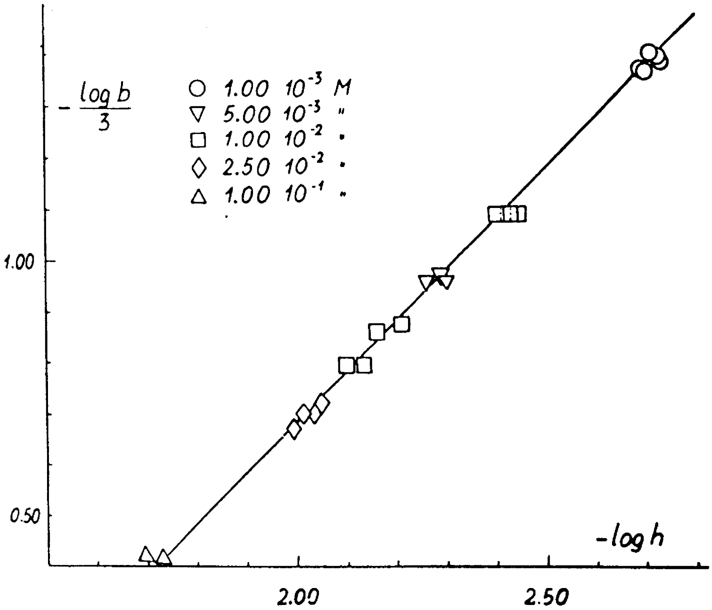

Fig. 2. Determination of log K. $\frac{\log b}{3}$ as a function of log h for test solutions older than 200 h. The line represents the equation $\frac{\log b}{3} = \log h + 1.32$.

There is, however, indirect evidence that no basic salt has been formed. Fig. 2 shows $\frac{\log b}{3}$ as a function of log h for all test solutions older than 200 h. The experimental points are seen to lie reasonably well on a straight line of unit slope. This indicates that these data may be explained by the reaction

$$\mathrm{Fe^{3+} + 2\ H_2O \rightleftharpoons FeOOH(s) + 3\ H^+} \quad K = h^3 b^{-1} \tag{3}$$

i. e. three hydrogen ions are set free when one Fe^{3+} is precipitated. By this type of argument it cannot be decided whether the precipitate contains OH groups ($Fe(OH)_3$), O atoms (Fe_2O_3), or both (FeOOH), because the water concentration was kept constant in all experiments. The precipitate may also contain H_2O and $NaClO_4$ but their presence cannot be ascertained because of similar reasons.

The compositions of aged precipitates formed from acidic iron(III) solutions were investigated with X-ray analyses by Weiser and Milligan [14]. They have found that, when no basic salt is formed, the solid phase always consists of FeOOH. Since there is strong evidence that no basic salt is formed from the solutions studied in this work, the precipitate has most likely the composition FeOOH. This was the reason for writing eqn. (3) in the form given.

An attempt was made to identify the fresh precipitate by X-ray diffraction using a Guinier camera with Cu$K\alpha$ radiation. All the lines in the X-ray photograph could be ascribed to $NaClO_4$ except two very weak ones having $10^4 \sin^2\Theta$ values 1 952 and 2 548. Thus by this method no definite conclusion could be made concerning the composition of the precipitate.

CALCULATION OF THE SOLUBILITY PRODUCT

Log K of eqn. (3) may be conveniently calculated by the plot $\log b^{\frac{1}{3}}$ ($\log h$), Fig. 2. A line of unit slope was drawn through all experimental points, the intercept of which gives according to (3) $\frac{-\log K}{3}$. It was found

$$\log K = -3.96 \pm 0.10 \tag{4}$$

According to measurements made in this laboratory [15], the ionic product of water in 3 M $NaClO_4$ at 25 °C

$$\log K_{H_2O} = -14.22 \pm 0.10 \tag{5}$$

thus the solubility product expressed with OH^-, $\log K_s$, will be

$$\log K_s = 3 \log K_{H_2O} - \log K = -38.7 \pm 0.2 \tag{6}$$

This $\log K_s$ value is considerably lower than any one reported previously; see Table 1. The discrepancy may be explained, besides other reasons, by the fact that previous work was done with quite fresh precipitates, far from being in equilibrium; see Fig. 1.

The data presented in this work give no evidence that the $\log K_s$ or the $\log K$ value calculated refers to a real equilibrium. In order to show that the steady state corresponds to a true equilibrium experiments are required which would show that the same state is attained from the reversed direction, *i. e.* by dissolving a part of the precipitate with the addition of hydrogen ions. A few experiments were made for this purpose but without success. It was found that the dissolution of the precipitate is a very slow process, and at about pH 2 no appreciable dissolution could be detected within two weeks.

Though it cannot be claimed that real equilibrium was attained in our experiments the data clearly indicate that when reaction (3) proceeds with the *formation* of the solid phase, a steady state is reached relatively rapidly which may be well described with the constant (4) or (6).

ON SUPERSATURATED SOLUTIONS

The solubility and hydrolysis equilibria of the Fe^{3+} ion are visualized in Fig. 3 where $\log(B_3/b)$ is plotted as a function of $\log h$ for the B_3 values 0.05, 0.010, 0.001 and 0.0001 M. The straight lines illustrate the solubility equilibrium (3), calculated with the constant (4) and the full-drawn curves represent the hydrolysis equilibria

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$$

$$Fe^{3+} + 2\ H_2O \rightleftharpoons Fe(OH)_2^+ + 2\ H^+$$

$$2\ Fe^{3+} + 2\ H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2\ H^+$$

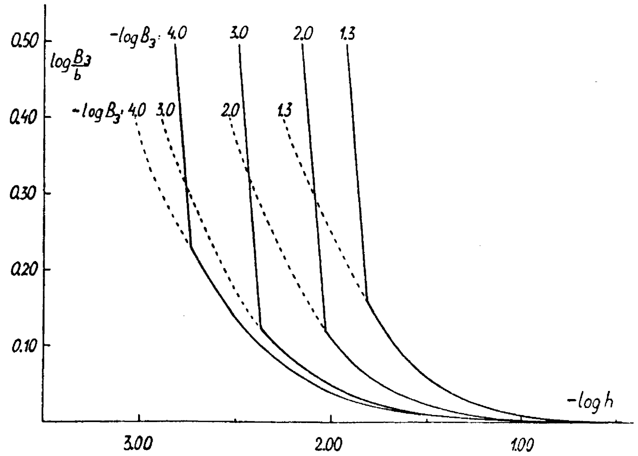

Fig. 3. The solubility and hydrolysis equilibria of the Fe^{3+} ion. log $\frac{B_3}{b}$ as a function of log h for the log B_3 values -4, -3, -2 and -1.3. The straight lines illustrate the solubility equilibrium calculated with log $K = -3.96$; the full drawn curves represent the hydrolysis equilibria calculated with the constants given by Hedström [9]; the broken curves show Hedström's data obtained in supersaturated solutions.

calculated with the constants given by Hedström [9]. The broken curves show Hedström's experimental data obtained in supersaturated solutions with a potentiometric titration technique. He started from a practically unhydrolyzed solution and increased the pH stepwise by adding small amounts of a $NaHCO_3$ solution and a Fe^{3+} solution containing H^+ in excess. Hedström found that steady and reproducible redox and glass electrode potentials can be obtained until log (B_3/b) attains about 0.4; however above this value the potentials became unstable indicating a slow precipitation.

In order to study the conditions for obtaining supersaturated solutions a number of potentiometric titrations were made. Following carefully Hedström's technique his results could be wholly confirmed. A few series of measurements were made in a somewhat different manner. Starting from an unhydrolysed solution the pH was increased in big steps by adding each time a large amount of a $NaHCO_3$ solution and a Fe^{3+} solution containing H^+ in excess. In this case practically no supersaturation could be achieved. At the pH value where according to (4) a precipitate should be formed the potentials began to drift because of the formation of the solid phase, and no steady value was reached in one or two days.

For example when a single addition of $NaHCO_3$ solution was sufficient to cause a slight excess over the solubility product, precipitation started immediately, whereas if the same pH was attained in about ten steps no precipitation could be detected for 2—3 h.

The absence of supersaturation under these experimental conditions may be explained by the fact that, despite the vigorous agitation, a local excess of

HCO_3^- is very difficult to avoid when a relatively large amount of the base is added at once. In those regions of the solution where for a short period the pH is increased, crystal nuclei of FeOOH may be formed; when the acidity is so high that the solid phase is not stable these dissolve rapidly after the local concentration differences disappeared. In the stability region of the FeOOH (s), however, the presence of the nuclei assures that the solid phase will be formed with a high rate.

A considerable part of Hedström's measurements was made in supersaturated solutions, but this fact does not invalidate any of his conclusions concerning the hydrolysis equilibria, since under the experimental conditions chosen by him the rate of precipitation is negligible compared with that of the hydrolysis. By the study of supersaturated solutions the useful pH range could be much extended, and this has been of great help to provide a complete picture of the hydrolysis process.

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