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Studies on the Hydrolysis of Metal Ions

Part 57. The Hydrolysis of the Iron(III) Ion and the Solubility Product of $Fe(OH)_{2.70}Cl_{0.30}$ in 0.5 M $(Na^+)Cl^-$ Medium

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The hydrolysis equilibria of the iron(III) species prevailing in 0.5 M $(Na^+)Cl^-$ medium have been investigated at 25°C by measuring with emf methods the concentration of unhydrolyzed iron(III) ions (= $[Fe^{3+}]$) and that of hydrogen ions in solutions of accurately determined analytical composition. This study includes the [Fe(III)] range 0.001 to 0.025 M.

The hydrolysis proved to be a slow process involving the formation of a precipitate. In sufficiently alkalified solutions a stationary state was attained after three weeks. The emf data obtained in the stationary state could be explained by assuming the reaction

$$Fe^{3+} + 2.70\ H_2O + 0.30\ Cl^- \rightarrow Fe(OH)_{2.70}Cl_{0.30}(s) + 2.70\ H^+$$

with a value of -3.04 ± 0.05 for the logarithm of the solubility product = $2.70 \log [H^+] - \log [Fe^{3+}]$.

In the stationary state no evidence was found for the presence of appreciable amounts of soluble hydrolysis products.

The X-ray powder pattern of the precipitates of the composition $Fe(OH)_{2.70}Cl_{0.30}$ was found to agree with that ascribed by previous investigators [17–19] to "β-FeOOH".

The instability of dilute iron(III) chloride solutions has attracted the curiosity of successive generations of investigators. When such solutions are left to stand at room temperature they become gradually turbid, and finally, under certain conditions only after a period of years, they yield a crystalline yellow precipitate.

In 1861 Th. Graham [1] demonstrated on the basis of dialysis experiments that iron(III) chloride solutions alkalified with $(NH_4)_2CO_3$ contain particles of colloidal size in considerable concentration. The first quantitative investigation on the hydrolysis of Fe(III) was made in 1878 by Wiedemann [2] who determined by susceptibility measurements the amount of colloidal and solid hydrolysis products in a series of solutions at various temperatures. This method proved to be very sensitive since Wiedemann could show that the ratio between the susceptibilities of the hydrolysis products and of the dissolved iron species does not exceed 0.2.

In 1896 Goodwin [3] discovered that the conductivity of iron(III) chloride solutions increases with time. He explained this behaviour by assuming that the equilibrium $Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+$ is established instantaneously, whereas the reactions leading to the formation of solid iron(III) hydroxide occur very slowly. Goodwin, combining conductivity and freezing point depression data, was able to calculate the $[FeOH^{2+}]$ of his freshly prepared test solutions. In 1907 Bjerrum [4] reinterpreted Goodwin's conductivity data by introducing more plausible assumptions concerning the equivalent conductivities of the reacting species, and he estimated the value of 2.5×10^{-3} M for the equilibrium constant of the reaction

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

In the early years of this century interest shifted from the study of equilibria to the colloid chemical aspects of hydrolysis, and in the first three decades problems such as the mechanism of the coagulation and the size, shape and charge of the hydrolysis products of colloidal dimensions were studied in great detail. The results of this research activity up to 1934 form the subject of a series of exhaustive and critical reviews published in Abeggs Handbuch der Anorganischen Chemie [5] and need not be discussed here. The more recent work of Lamb and Jacques [6] contains also much valuable, although mainly qualitative, information on the rate and mechanism of the precipitation.

In 1935 Jander and Jahr,[7] who studied for the first time iron(III) chloride solutions of controlled acidities, came to the conclusion that reproducible data on hydrolyzed solutions can only be obtained after the period required for the formation of the solid phase had come to an end. These authors found that the molar diffusion coefficient of the dissolved iron(III) species remains unchanged as increasing amounts of precipitate are formed by alkalification from an initially acid solution. Jander and Jahr explained this result by the absence of soluble polynuclear hydrolysis products.

Symbols often used in the text

h = concentration of hydrogen ions
H = $[Cl^-]-3[Fe(III)]-2[Fe(II)]-[Na^+]$ = proton excess assuming no hydrolysis
B = total concentration of iron(III) species
b = $[Fe^{3+}]$ = concentration of unhydrolyzed iron(III) ions
P = $(h-H)\,(B-b)^{-1}$ = value of the ratio OH groups/Fe(III) atoms in the hydrolysis products

THE METHOD OF INVESTIGATION

In the present work the hydrolysis equilibria were studied at 25°C by determining with emf measurements the concentration of the H^+ and of the Fe^{3+} ions in a series of iron(III) chloride solutions of varying acidity. The total molarity of the test solutions was maintained at the 0.5 M level by adding NaCl, thus they were prepared so as to have the general composition B M Fe(III), B_2 M Fe(II), H M H^+, $(0.5-3\,B-2\,B_2-H)$ M Na^+, 0.5 M Cl^- where

B denotes the total concentration of the iron(III) ions and B_2 that of the Fe(II) ions. All the test solutions were initially clear, but in those where an appreciable hydrolysis could be detected a precipitate was found to be formed slowly, and when the hydrolysis attained the stationary state a considerable part of the iron(III) ions was present in the solid phase.

The symbol H denotes the proton excess assuming no hydrolysis. H can, of course, take positive as well as negative values. Iron(II) ions had to be added for enabling us to employ the Fe^{3+}—Fe^{2+} couple, the ratio BB_2^{-1} was varied between 0.3 and 3.

In order to avoid appreciable variations in the activity factors of the reacting species the sum $3\ B + 2\ B_2 + H$ was always kept below 0.125 M. The standard state was chosen so that the activity factors of the reacting species tend to unity as the composition of the solutions approaches 0.5 M NaCl.

This study covers the B range 0.001 to 0.025 M. The upper limit was set by the requirement not to exceed the concentration interval where the variation of the activity factors is negligible, whereas the lower limit was imposed by experimental difficulties. In hydrolyzed solutions more dilute for B than 1 mM the $[Fe^{3+}]$ proved to be diminished to below 1 μM, and owing to the slowness of the electrode reactions and to the interference of impurities we have not been able to attain reversible redox potentials at such low $[Fe^{3+}]$ values.

The concentration of the hydrogen ions and of the unhydrolyzed iron(III) ions were determined by measuring the emfs of the cells

$$-\text{SE} \mid \text{test solution} \mid \text{GE} + \qquad \text{(G)}$$

and

$$-\text{SE} \mid \text{test solution} \mid \text{Pt} + \qquad \text{(R)}$$

where GE denotes a glass electrode half-cell and SE the reference half-cell of the composition

Ag, AgCl(s) | 0.5 M NaCl saturated with AgCl | 0.5 M NaCl |

The emfs of these cells can be written at 25°C

$$E_G = E_{G,0} + 59.15 \log h - E_j \qquad (1)$$

and

$$E_R = E_{R,0} + 59.15 \log \frac{[Fe^{3+}]}{[Fe^{2+}]} - E_j \qquad (2)$$

In eqns. (1) and (2) $E_{G,0}$ and $E_{R,0}$ denote constants, h is the symbol for the hydrogen ion concentration and E_j represents the liquid junction potential arising between the test solution and 0.5 M NaCl. The symbols $[Fe^{3+}]$ and $[Fe^{2+}]$ denote the concentrations of the unhydrolyzed iron(III) and iron(II) ions.

The Fe^{3+} and Fe^{2+} ions have been shown [8a,8b] by several independent methods to form a series of mononuclear complex species with Cl^-, and therefore $[Fe^{3+}]$ and $[Fe^{2+}]$ denote in reality the sums

[free iron(III) ion] $(1 + \sum\beta_n [Cl^-]^n)$ and [free iron(II) ion] $(1 + \sum\beta_m [Cl^-]^m)$,

where β_n and β_m stand for the formation constants of the chloride complexes. We can estimate on the basis of Olerup's results [8a] (which have

been confirmed by subsequent investigators [8b]) that at $[Cl^-]_{total} = 0.5$ M and for the B and B_2 values in question the predominating complex species have the composition $FeCl^{2+}$, $FeCl_2^+$ and $FeCl^+$. Because $([Fe(III)]+[Fe(II)]) \times [Cl^-]^{-1}_{total}$ never exceeded 0.07 the $[Cl^-]$ remained essentially constant in our test solutions, and consequently the $[Fe^{3+}]$ and $[Fe^{2+}]$ values are proportional to the concentrations of the free iron(III) and iron(II) ions. For the sake of brevity we now introduce the symbol

$$b = [Fe^{3+}]$$

The liquid junction potential, E_j, was determined by measuring the emf of the cell

$$- \overset{(Pt),H_2}{GE} \mid h \text{ M } H^+, (0.5-h) \text{ M } Na^+, 0.5 \text{ M } Cl^- \mid \text{SE} + \qquad \text{(H)}$$

as a function of h in the range 0.001 to 0.1 M. The emf data were found to be explained with an uncertainty of ± 0.05 mV by assuming for the liquid junction potential the equation

$$E_j = 59.15 \log (1 + 4.78\, h) \text{ mV}$$

Previously one of us (G.B.) determined, using a hydrogen and a silver electrode, the liquid junction potential of the junction;

$$h \text{ M } H^+, (0.5-h) \text{ M } Na^+, 0.5 \text{ M } ClO_4^- \mid 0.5 \text{ M } NaClO_4$$

and up to $h = 0.150$ M the data could be described with the equation

$$E_j = 59.15 \log (1 + 5.4\, h) \text{ mV}$$

Thus the magnitudes of the liquid junction potentials in these two media differ but little; this is a reasonable result since the difference between the mobilities of the Cl^- and the ClO_4^- ions is small.

Data obtained with cell (H) have shown moreover that the emf of a cell consisting of a glass electrode and a hydrogen half-cell remains constant to within ± 0.1 mV as Na^+ is replaced by H^+, consequently eqn. (1) may be regarded as a close approximation.

Each time when a series of hydrolyzed solutions was examined the measurements were extended to acidities exceeding 20 mM in order to ascertain the actual values of $E_{G,0}$ and $E_{R,0}$. For every B level investigated the quantities $E_G - 59.15 \log H + E_j(H)$ and $E_R - 59.15 \log (B/B_2) + E_j(H)$ proved to remain constants at $H \geq 20$ mM. These constants were accepted as the pertinent $E_{G,0}$ and $E_{R,0}$ values, and they were employed to calculate h and b of the hydrolyzed solutions.

In order to see whether any correction is needed to be introduced on account of the hydrolysis of Fe^{2+}, the hydrogen ion concentration of a series of solutions of the composition: 0.1 M Fe(II), H M H^+, $(0.3-H)$ M Na^+, 0.5 M Cl^- was measured with cell (G). Two methods were employed to vary H. In the first a solution of $H = 5 \times 10^{-3}$ M was chosen and its acidity was stepwise decreased by constant current coulometry until $Fe(OH)_2$ precipitated. In the second method we started with a 0.1 M Fe(II) solution saturated with $Fe(OH)_2$ and increased H by adding portionwise another solution containing

besides 0.1 M Fe(II) also 0.01 M H^+ and 0.5 M Cl^-. In both the acidification and the alkalification experiments $E_G - 59.15 \log H + E_j(H) = E_{G,0}$ was found to be constant indicating that for $B_2 \leq 0.1$ M and $\log h \geq -6$ no appreciable hydrolysis occurs. We could thus set $[Fe^{2+}] = B_2$ and thereby calculate b on the basis of the E_R measurements.

THE METHOD OF FOLLOWING THE ATTAINMENT OF THE STATIONARY STATE

A few series of emf measurements, which were carried out as potentiometric titrations, with optically clear solutions have convinced us that at 25°C the hydrolysis process as well as the uptake of protons by the hydrolyzed species occurs so slowly that at least several days are required to reach equilibrium. Since when alkalifying a transient precipitate could always be observed, we first believed, recalling our experience [9] with iron(III) perchlorate solutions, that the rate determining step is the redissolution. We tried, therefore, to perform the alkalification as mildly as possible. The test solution was stirred vigorously and either a dilute $NaHCO_3$ solution was added dropwise or a slow stream of ozone (see the next section) was introduced. However, we have not been able to influence the rate of hydrolysis by varying the conditions of alkalification.

We were thus forced to prepare a series of test solutions and measure periodically $\log h$ and $\log b$ until no further systematic change in these quantities could be detected. As the hydrolysis proceeded each of the test solutions became gradually turbid and finally (often only after a couple of weeks) a precipitate has been formed.

The test solutions were preserved under a slight overpressure of pure argon in a room kept at 25.0 ± 0.2°C. Precautions were taken to minimize contact with air during the manipulations required for the emf measurements. Control experiments (*cf.* the next section) have shown the oxidation of Fe^{2+} by air to proceed so slowly that during the few seconds, while the solution remained unprotected, no appreciable oxidation could have taken place.

Before and after a set of hydrolyzed solutions was examined, $E_{G,0}$ and $E_{R,0}$ were checked with highly acidified reference solutions. The difference between the $E_{G,0}$ values measured prior and after the experiment never exceeded 0.2 mV, while the difference between the $E_{R,0}$ values was always less than 0.1 mV. We found about the same reproducibilities for the E_G and E_R determinations in hydrolyzed solutions. Consequently, the uncertainty of the $\log h$ values can be estimated to amount to ± 0.01 units and that of the $\log b$ values to ± 0.005 units. The set of $\log h(B,H)$ and $\log b(B,H)$ values will serve as the starting point for ascertainment of the composition of the hydrolysis products.

EXPERIMENTAL DETAILS

All the iron solutions employed in this research were prepared from $Fe(NO_3)_3(H_2O)_9$ of *p.a.* quality supplied by Merck Co. This commercial product was purified by double recrystallization from freshly distilled 12 M HNO_3. The crystals were dried at 120°C.

Then they were heated gradually to 400°C and kept at this temperature until no more evolution of nitrogen oxides could be observed. Finally the iron oxide thus formed was converted to Fe_2O_3 by ignition at 850°C. The resulting product was found not to contain detectable amounts of NO_3^- and NO_2^- ions, and its content of copper, manganese, and chromium proved to be less than 0.01 %. These metals are active impurities since in the presence of their ions the accuracy of the redox potential measurement is impaired.

Iron(III) chloride stock solutions were prepared by two methods.

1) Finely divided Fe_2O_3 was added in small excess to 1 M HCl and the mixture was refluxed for 12 h. The excess of Fe_2O_3 could easily be removed by filtration through spongy platinum. The chloride concentration of the filtrate was determined by precipitating AgCl, the analyses were carried out following closely Winkler's procedure [10] which is especially adapted to iron solutions. The [Fe(III)] was measured by iodometric titration with amperometric end-point determination. The method developed by Berecki-Biedermann [11] has yielded results accurate to within 0.1 % down to millimolar concentrations. In each case the $[Cl^-]$ equalled 3 [Fe(III)] to within 0.1 %. We have not been able to prepare solutions with $H < 0$ by prolonging the period of reflux.

In a solution of such low acidity ($H \approx 0$) considerable hydrolysis occurs, and in the course of a few weeks a precipitate appears. With the idea to see whether the mode of preparation of the test solutions influences the log h and log b data, stock solutions of $H = 0.1$ M were also made where the hydrolysis is quite negligible. Then test solutions of identical analytical composition were prepared from the unhydrolyzed and the hydrolyzed stock. Both test solutions attained the stationary state in nearly the same period (three weeks), and the log h and log b values agreed to within 0.01 units.

A similar comparison was made among solutions alkalified with NaOH, $NaHCO_3$ and by ozonisation. In all such experiments closely agreeing log h and log b values were obtained. We can thus conclude that the composition of a solution which has reached the stationary state is determined only by H, B and the formation constants of the hydrolysis products.

2) In a later stage of this work a more convenient method was found to prepare iron(III) chloride solutions of low acidity. The method is based on the reactions

$$Fe(s) + 2\,H^+ \rightarrow Fe^{2+} + H_2$$

and

$$2\,Fe^{2+} + O_3 + 2\,H^+ \rightarrow 2\,Fe^{3+} + H_2O + O_2$$

Iron(III) oxide, prepared as described above, was reduced by hydrogen at 500°C in a quartz apparatus and a weighed amount of the resulting porous iron was dissolved in a measured volume of standardized hydrochloric acid. Iron reduced at such a low temperature dissolves, without heating, rapidly in excess of hydrochloric acid.

At $\log h > -3$ Fe^{2+} is oxidized so slowly by air that the iron(II) stock solutions could be preserved unchanged under argon for several weeks. About 5 % of the Fe^{2+} was found to be oxidized when a vigorous stream of oxygen was passed through a stock solution for 24 h.

On the other hand, ozone oxidizes Fe^{2+} instantaneously at $\log h > -4$, whereas the rate of oxidation of Cl^- by O_3 becomes appreciable only at $\log h > -1$.

A slow stream of ozone was introduced into the acid Fe^{2+} solution and the progress of oxidation (as well as of alkalification) was followed by taking samples and determining their $[Fe^{2+}]$ by titration with a $K_2Cr_2O_7$ solution. Ozonization was stopped when the value of $[Fe^{2+}]$ indicated that the required acidity was approached, and finally oxygen and ozone were expelled by passing argon through the solution.

Such amounts of iron and hydrochloric acid were weighed in that, when the desired H value was attained, the ratio [Fe(II)]/[Fe(III)] was not less than 0.5. Therefore, after having added NaCl and diluting, the solution could be used directly for redox potential measurements.

The main advantage of the ozonization method is, besides its simplicity, that solutions containing hydrolyzed species in high concentration can be prepared without adding an alkaline solution. These, when conventionally prepared, always contain considerable amounts of impurities such as substances dissolved from glass or plastics surfaces.

Iron(II) chloride solutions were made as described above. The $[Fe^{2+}]$ was checked by potentiometric titration with a $K_2Cr_2O_7$ solution prepared from a $K_2Cr_2O_7$ sample

of at least 99.99 % purity. To determine the $[Cl^-]$ first Fe^{2+} was converted to Fe^{3+} by an excess of H_2O_2, and then AgCl was precipitated. The results of the analyses always agreed within 0.1 % with the $[Fe^{2+}]$ and $[Cl^-]$ values calculated on the basis of the weighings and the dilution.

Iron(II) chloride solutions saturated with $Fe(OH)_2$, which were used to study the hydrolysis of Fe^{2+}, were made by adding iron in excess to a hydrochloric acid solution. Within a few hours the iron crystals became covered by a layer of pale green $Fe(OH)_2$ and the dissolution ceased. To attain saturation the solution was stirred for 12 to 24 h, and then the iron(II) hydroxide and the iron were removed by filtration through platinum. Saturation and filtration was carried out using the apparatus shown earlier.[12]

White iron(II) hydroxide may be prepared by starting with an acid iron(II) chloride solution. This is freed from oxygen by passing through it pure argon for 8 to 10 h, and then the solution is alkalified with oxygen-free NaOH prepared *in situ* by coulometry from a slightly acidified NaCl solution. The apparatus described in Ref. 13 was employed for this preparation. Glass electrode data have indicated a small difference (less than 0.1 logarithmic unit) between the solubility products of white and pale green iron(II) hydroxide.

Hydrochloric acid solutions were prepared from 11 M HCl of *p.a.* quality; Fe(III) and Cl_2 were removed from the commercial acid by distillation. The stock solutions were standardized against purified samples of Tl_2CO_3 and $KHCO_3$. The results with these standard substances agreed to within 0.1 %.

Sodium chloride p.a. was purified by preparing a 5 M NaCl solution containing 0.1 M HCl. The solution was filtered through platinum to remove dust and the filtrate was evaporated at 120°C. The crystals thus formed were dried at 360°C. A 3 M NaCl solution prepared from the purified crystals was found by the potentiometric method of Ciavatta [14] to contain 18 μM weak protolytes.

Sodium hydrogencarbonate solutions were made from a commercial product of *p.a.* quality which had been purified by recrystallization from distilled water saturated with CO_2. The NaOH and $NaHCO_3$ solutions were standardized *via* a HCl solution against $KHCO_3$.

Argon was taken from a cylinder and it first was led through active copper kept at 180°C and then through three washing bottles containing in succession 0.5 M KOH, H_2O and 0.5 M NaCl.

The emf measurements were carried out in a paraffin oil thermostat kept at 25.00 ± 0.01°C. The E_R values were measured with a Leeds & Northrup K_3 type potentiometer and the E_G values with a radiometer PHM 4 type valve potentiometer. This instrument had to be calibrated frequently against the K_3 potentiometer.

The cell arrangement was similar to that described by Forsling, Hietanen and Sillén.[15] The Ag,AgCl electrode and the 0.5 M NaCl solution saturated with AgCl had to be often replaced because the half-cell becomes slowly contaminated with silicon grease and then it shows irregular potentials.

The redox potentials were measured by immersing at least two bright platinum foils into the test solution. As long as solutions with log $[Fe^{3+}]$ values exceeding -5 were studied, these electrodes attained in half-an hour a value for the redox potential which remained constant within a few hundredths of a mV for several hours and they never differed more than 0.05 mV. At less than micromolar iron(III) concentrations, however, we have not been able to find a method for obtaining reversible potentials. The value of E_R kept drifting at a rate of a few tenths of a mV per hour in the direction corresponding to a decrease in $[Fe^{3+}]\,[Fe^{2+}]^{-1}$ as long as we cared to measure. A number of methods were tried to clean the surface of the platinum electrodes but none brought any significant improvement. Probably the failure is due to some contamination present in the solution.

E_G was measured with Beckman glass electrodes of the type 40498. These were chosen because of their excellent reproducibility. Rinsing a glass elctrode with water, drying and reinserting it into a test solution seldom caused a change of as much as 0.2 mV in E_G.

RESULTS

The attainment of the stationary state. Altogether more than sixty test solutions were prepared covering the B range 1 to 25 mM. At each level of B the analytical excess of hydrogen ions was decreased in equidistant steps from a value where the hydrolysis is negligible to $H = -2B$. At a still greater proton deficiency b was found in the course of a few days to drop to such a low value ($\sim$1 μM) that it could not be measured reliably. Every solution was studied by emf measurements, at five to ten days intervals, for at least six weeks.

The rate of the hydrolysis proved to be determined primarily by the degree of alkalification. For each iron concentration studied a certain value, H_{max}, was found for the analytical hydrogen ion concentration so that in solutions of $-2B < H < H_{max}$ both log h and log b attained after three weeks values which did not show further systematic change; this indicates the establishment of a stationary state. A considerable amount of precipitate has appeared within a few days in these strongly alkalified solutions, and after a week the number of OH groups bound per iron atom in the hydrolysis products, $= P$, was found to exceed the value of 2.5. In the following two to three weeks P slowly increased further by about 0.2 units. A typical example for the attainment of the stationary state is given in Table 1.

Table 1. An example for the attainment of the stationary state. $B = 0.0100$ M, $H = -7.92 \times 10^{-4}$ M.

Days	$-\log h$ M	$-\log[Fe^{3+}]$ M	$P = (h-H)/(B-b)$
0.05	2.61_6	2.19_5	0.89
6	2.03_8	2.21_4	2.56
15	1.99_7	2.23_6	2.58
30	1.96_7	2.24_9	2.65
40	1.95_0	2.26_1	2.66
54	1.95_4	2.26_0	2.65

We have assumed that the stationary state corresponds to the minimum of the thermodynamic potential and applied the law of mass action to the final log $h(B,H)$ and log $b(B,H)$ data. This will form the subject of the next section.

Anticipating the results of that section we can summarize all our observations concerning the rate of hydrolysis in a concise way. In solutions where on the basis of the equilibrium constant of eqn. (4) the average number of hydrogen ions set free per ion(III) atom, $Z = (h-H)B^{-1}$, is calculated to exceed unity, a stationary state is reached in three to four weeks. For $0.5 < Z < 1$ the attainment of the stationary state requires more than two months. In this Z range after 5—6 weeks coagulation occurs and P attains a value around 2.7 but both log b and log h are still changing at the end of

a two months period. At lower Z values the rate is almost unappreciable within two months and in such optically clear solutions P has a value near to unity.

We have arbitrarily decided not to follow any test solution longer than two months, thus from the present study the range $Z < 1$ is excluded.

Unsuccessful attempts were made to investigate the suppression of the hydrolysis by acidifying test solutions which had attained the stationary state and which contained a large amount of precipitate. No significant increase in log b could be observed in the course of two months except in solutions containing so much added HCl that H became finally equal to 0.1 M, where $[Fe^{3+}] = [Fe(III)]$. Similar difficulties were encountered earlier when the solubility equilibria of FeOOH(s) were investigated.[9]

Since we could not find suitable experimental conditions for studying the suppression of hydrolysis, we cannot claim that the solutions where log h and log b attained constant levels have reached equilibrium, but only a stationary state.

In the light of the present experiments the difficulties of the previous investigators who were working with acidified or slightly alkalified dilute iron solutions become understandable. Under such conditions the hydrolysis proceeds extremely slowly indeed.

Our experiments were not designed to yield detailed information on the mechanism of the hydrolysis. Nevertheless, the few data available on the time dependence of b and h suggest that in the initial stage of hydrolysis soluble species containing one OH group per iron atom are formed. This (or these) species appears to be converted to the final product, which has a very low solubility, the more rapidly the greater is the difference $h_{\text{stationary}} - H$, which is the measure of the degree of the initial supersaturation.

The composition of the precipitate. The set of log b(log h) data obtained in the stationary state, where we have assumed conditions to prevail which justify the application of the law of mass action, will serve to ascertain the composition of the solid phase. A plot of log b *versus* log h has revealed that the points can be well approximated by a straight line having a slope of around 2.7 and an intercept of 3.0. This result implies that in the entire log h range studied the solid phase has a constant composition and the reaction leading to the formation of the precipitate can be written as

$$Fe^{3+} + p\,H_2O + (3-p)\,Cl^- \rightarrow Fe(OH)_p\,Cl_{(3-p)}\,(s) + p\,H^+ \qquad (3)$$

with $p = 2.7$, and the logarithm of the solubility product, $\log K_{2.7} = 2.7 \log h - \log b = -3.0$. As usual, the species belonging to the solvent, (H_2O and Cl^-) have been left out from the expression for the solubility product since their concentrations are constants. The most probable values of p and K_p and as well as the magnitudes of their uncertainties were estimated by applying to the log b(log h) data the principle of least squares. The calculations were made with an electronic computer using Ingri's and Sillén's [16] Letagrop program. This treatment yielded the results

$$p = 2.70 \pm 0.02 \text{ and } \log K_{2.70} = -3.04 \pm 0.05 \qquad (4)$$

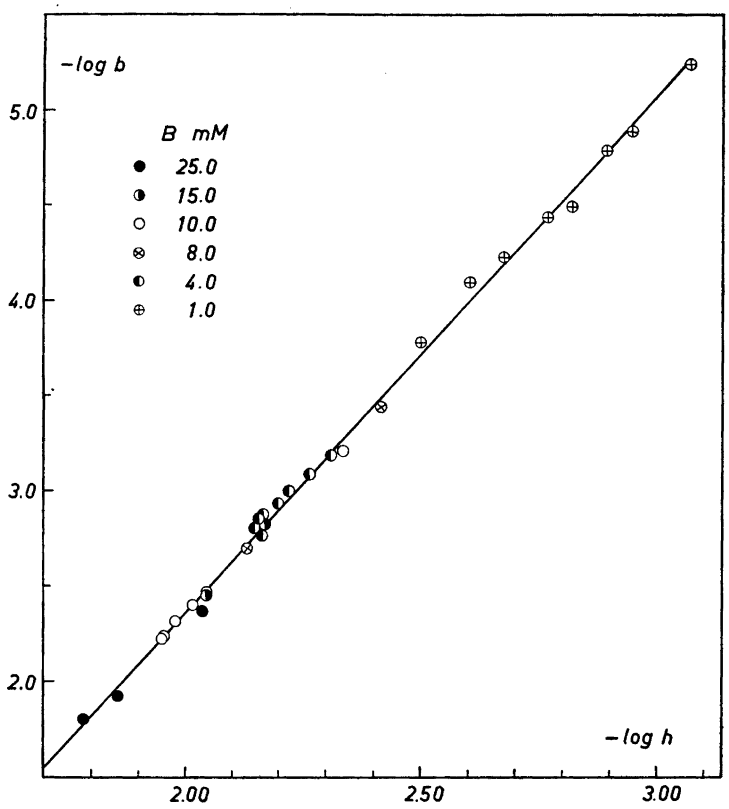

Fig. 1. log b as a function of log h in the stationary state. The line represents the equation $\log b = 3.04 + 2.70 \log h$.

The agreement between the experimental points and the equation $\log b = 2.70 \log h + 3.04$ is illustrated in Fig. 1. Of the 30 experimental data considered, for 14 the difference $\log b_{\text{measured}} - \log b_{\text{calculated}}$ proved to be positive, and for 16 negative. The average positive deviation amounts to 0.04 and the average negative to 0.03 units. Neither the magnitude nor the sign of the deviations shows any appreciable trend with log h. The magnitude of the uncertainty for log $K_{2.70}$, given in (4), does not significantly exceed the value estimated on the basis of the uncertainties of the log h and log b measurements ($\Delta \log h = \pm 0.01$ and $\Delta \log b = \pm 0.005$).

Since the concentration of species belonging to the ionic medium is kept constant throughout, their presence cannot be detected in the reaction products. Thus the precipitate may contain also water and NaCl, and the formula given in (3) is to be regarded as a convenient abbreviation for $FeO(OH)_{0.7}Cl_{0.3}(NaCl)_x(H_2O)_y$ where x and y denote unknowns. The emf data indicate only that when one mole of Fe^{3+} is precipitated 2.70 moles of hydrogen ions are set free.

At last we may emphasize that closely agreeing log b and log h values were found in solutions where B was kept constant while [Fe^{2+}] varied from 3 B to 0.3 B. Consequently no appreciable amounts of iron(II) ions can be present in the solid phase.

Interpretation of the h(B,H) and b(B,H) data. To acquire further information on the composition of the hydrolysis products we combined the emf and the analytical data, and we calculated for each experimental point obtained in the stationary state the quantity $(h-H)\ (B-b)^{-1} = P$ which is equal to the ratio OH groups/iron(III) ions in the hydrolyzed species. The results of these calculations, illustrated in Fig. 2, afford evidence that in the entire log h range studied P remains constant within $2.6_9 \pm 0.10$. For most of the experimental points both $h-H$ and $B-b$ represents a small difference between two large numbers and therefore the 4 % uncertainty in P is understandable.

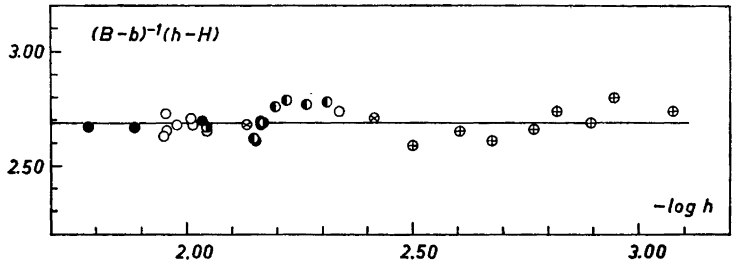

Fig. 2. P, the number of OH groups bound per iron(III) ion in the hydrolysis products, as a function of log h. The horizontal line represents the average value of P which is equal to 2.69. The symbols are the same as in Fig. 1.

Since the average value of P was found to coincide with the OH/Fe(III) ratio in the solid phase, p, we can conclude that all, soluble and insoluble, hydrolysis products contain on the average 2.7 OH groups per Fe(III).

Determination of the concentration of the iron(III) species present in solution. To find out whether soluble hydrolysis products are also present in the stationary state, efforts were made to develop a technique for the accurate determination of the total concentration of the iron(III) ions in the test solutions.

The finely divided precipitate was separated by centrifugation and the supernatant was removed with great care by suction. The turbidity of the removed solution was compared with that of an acidified iron(III) chloride solution of approximately the same [Fe(III)]. In case any difference could be detected between the intensities of the light scattered, the test solution was again centrifuged or if repeated centrifugation did not reduce further the turbidity, the solution was rejected. Of the fifteen solutions examined eight proved to be optically clear, and these were, after acidification, analyzed for [Fe(III)] using the method described in Ref. 11.

The results of these analyses, which cover the B range 4 to 25 mM, are summarized in Table 2 which shows also the corresponding Fe^{3+} concentrations determined by emf measurements. The absence of any systematic deviation between the analytically and potentiometrically determined iron(III) concentrations furnishes evidence that no appreciable amounts of soluble hydrolysis products are formed. Thus the emf and analysis data of the present accuracy can be explained by assuming exclusively reaction (3).

Table 2. Comparison of $[Fe^{3+}]$ with [Fe(III)].

B mM	$[Fe^{3+}]$ mM from E_R measurements	[Fe(III)] mM from analysis	$\frac{[Fe(III)]-[Fe^{3+}]}{[Fe(III)]}$ 100
25.00	21.79	21.52	−1.2
25.00	15.70	15.46	−1.6
10.00	6.90	6.97	+1.0
10.00	5.49	5.58	+1.6
4.00	1.82	1.78	−2.2
4.00	1.70	1.67	−1.8
4.00	1.55	1.59	+2.5
4.00	1.40	1.44	+2.8

It would be desirable to amplify the validity of this conclusion by a greater number of analyses of higher accuracy. We hope to provide such data when studying the hydrolysis at elevated temperatures. On the other hand we have no reason to doubt that the analyzed solutions are representative.

Attempts to analyze the precipitate separated by centrifugation failed. When we tried to wash it free from the mother liquid, peptization occurred. Equilibrium analysis seems to be at present the most reliable method to determine the composition of finely divided precipitates.

The X-ray powder patterns of the precipitates which had attained the stationary state were examined with a Guinier camera employing Cu$K\alpha$ radiation. Some of the precipitates yielded patterns with strong, sharp lines whereas on the patterns of the others only a few faint and broad lines could be detected. Using the diagrams with the sharpest lines the interplanar spacings were calculated and found to agree with the data reported by earlier investigators [17–19] who, following Weiser and Milligan,[17] called the solid phase formed from hydrolyzed iron(III) chloride solutions "β-FeOOH".

The X-ray and electron diffraction patterns of our precipitates were examined in detail by Rune Söderquist and the main results of his study are summarized in a short communication in this volume.[20]

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