

78. *The Hydrolysis of Ferric Iron in Sulphate Solution.*

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Ferric sulphate hydrolyses in three stages, to FeOH^{++} , $\text{Fe}(\text{OH})_2^+$, and a precipitate whose composition varies according to the dilution. The reaction constants for the formation of FeOH^{++} and $\text{Fe}(\text{OH})_2^+$ have been found from pH measurements to be $K_1 = 1.25 \times 10^{-3}$ $K_2 = 4.2 \times 10^{-4}$ at 25°. There is evidence for the presence in solution of an acid complex, which may be ferrisulphuric acid, $(\text{FeOH})(\text{HSO}_4)_2$.

The immediate reaction of sodium hydroxide with ferric sulphate solution gives an unstable solution containing high concentrations of the basic ions. When the ratio $\text{NaOH} : \text{Fe}$ exceeds 0.5 : 1, a precipitate of $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ is formed, precipitation being complete when the ratio is 2.5 : 1. The addition of more sodium hydroxide causes the conversion of this precipitate into ferric hydroxide. On storage, solutions having a ratio of less than 0.5 : 1 deposit ferric oxy-pentasulphate [ferric (2 : 5) sulphate], $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3$, which is stable for long periods. The precipitate of $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ [ferric (2 : 1) sulphate] is slowly dehydrated, and then hydrolyses further during several months to give ferric octaoxysulphate [(3 : 1) sulphate], $3\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$. The ferric hydroxide precipitate is stable for an indefinite period at less than pH 7.0. In the presence of excess of sodium hydroxide, it is slowly dehydrated, to form goethite, $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The effect of concentration on the titration results are discussed.

THE formation of ferric hydroxide as a result of the action of alkali hydroxides on ferric salts has been studied by many workers, and values for the solubility product varying from 10^{-38} to 10^{-39} have been found. These values have usually been calculated on the assumption that ferric hydroxide is formed by the direct combination of ferric and hydroxyl ions, the solubility product therefore being given by $K = [\text{Fe}^{+++}][\text{OH}^-]^3$. Kriekov and Awzsjewitsch (*Z. Elektrochem.*, 1933, **39**, 884), by potentiometric titration of ferric sulphate with sodium hydroxide, found that the value for K varied throughout the titration; but Evans and Prior (*J.*, 1949, S157), by a similar method using ferric ammonium sulphate, obtained values which were independent of concentration. Both these groups of workers found that the first precipitation occurred late in the titration, after more sodium hydroxide had been added than was required to neutralise the free sulphuric acid present. The same observation was made by Britton (*J.*, 1925, **127**, 2148), from experiments in chloride solution. The significance of this observation does not appear to have been generally realised. For example, in the work of Evans and Prior (*loc. cit.*), the concentration of ferric ions, $[\text{Fe}^{+++}]$, was assumed to be equal to the ferric-iron concentration at the point of precipitation. Since this point represented the addition of approximately 1.2 molecules of sodium hydroxide for each atom of iron, after the removal of free acid, this assumption cannot be justified. The direct reaction between ferric and hydroxyl ions would lead to precipitation of ferric hydroxide as soon as free acid had been removed (Point A, Fig. 1). The formation of clear solutions after the addition of sodium hydroxide beyond this point can be explained only by the presence of soluble ions, a colloidal hydroxide or a basic salt. In each of these cases, the concentration of ferric ions would be considerably less than the total iron concentration, and the calculated value for $K_{\text{Fe}(\text{OH})_3}$ would be correspondingly in error.

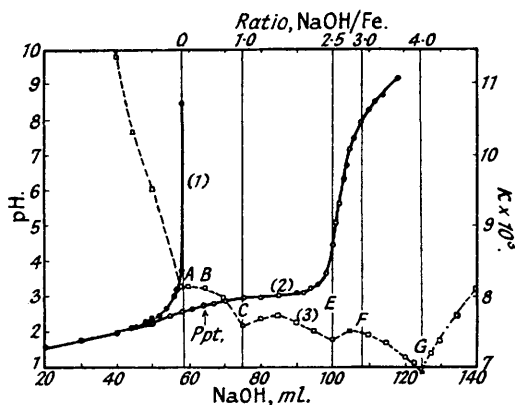
It was found by the author (unpublished work at the Chemical Research Laboratory, 1948) that the action of sodium hydroxide on ferric sulphate solutions results in the formation of a series of basic ions, followed by the precipitation of ferric penta-oxysulphate [(2 : 1) sulphate], $[\text{Fe}_2(\text{OH})_6]_2\text{SO}_4$. The formation of this compound was complete at pH 3.0, in M/60-solution, the further addition of sodium hydroxide causing its conversion into ferric hydroxide in the pH range 3.0—8.0. Ferric hydroxide was thus not in equilibrium with Fe^{+++} and OH^- ions, and the concept of a solubility product for it was therefore considered to be without meaning. A repetition of the work of Evans and Prior, using both potentiometric and conductimetric titrations, showed that the same reaction mechanism occurred under the conditions of their experiments.

EXPERIMENTAL.

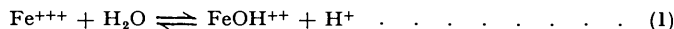
In a typical experiment, a solution of ferric ammonium sulphate was prepared from "AnalaR" ferric alum, together with a known quantity of free sulphuric acid. The solution was 1.0017M/30 with

respect to Fe^{+++} , 0.339M/10 with respect to NH_4^+ , and 1.116M/20 with respect to free sulphuric acid. The calculated quantities of 0.1000N/10-sodium hydroxide for the titration with 50 ml. of this solution were: 58.3 ml. for neutralisation of free acid, 50.1 ml. for formation of $\text{Fe}(\text{OH})_3$ (total 108.4 ml.), and 16.7 ml. for the formation of NH_4OH (overall total, 125.1 ml.). Two titrations were carried out simultaneously, at $25.0^\circ \pm 0.02^\circ$, the pH being measured by means of a glass electrode in conjunction with a saturated calomel half-cell in one case, and, in the other case, the conductivity being measured by means of a dip-type electrode system with a Mullard universal measuring bridge at 1000 cycles. A titration of 50 ml. of 1.116M/20-sulphuric acid was also carried out, with measurement of pH only. In Fig. 1, the pH curve for the ferric sulphate titration (2) falls below that for the sulphuric acid solution (1) before all free acid is removed, indicating that extensive hydrolysis takes place even in the presence of free acid. The neutralisation of free acid at *A* is not accompanied by any inflexion in the pH curve, although its position is defined by a break in the conductivity curve (3). In the region *AC* the pH rises slowly, with a corresponding reduction in conductivity, this process ending at *C*, where 75.0 ml. of sodium hydroxide solution have been added, representing a $\text{NaOH} : \text{Fe}$ ratio of 1 : 1. The precipitation point, which has been found to vary according to the rate of titration, occurred in this case at *B*. From *C*, the pH and conductivity remain almost constant, to *E* (100.0 ml. of NaOH), where the pH rises and a conductivity minimum occurs. Chemical determinations show that precipitation of iron is complete at this point, which represents the addition of 2.49 mols. of NaOH per atom of Fe . The precipitate at this point is therefore ferric pentaoxysulphate, $[\text{Fe}_2(\text{OH})_5]_2\text{SO}_4$ or $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$. From this point, the conductivity of the solution rises, in spite of the reduction in hydrogen-ion concentration, owing to the conversion of the precipitate into $\text{Fe}(\text{OH})_3$, and the consequent liberation of sulphate ions. This process is complete at about *F*, where an ill-defined conductivity maximum is followed by decreasing conductivity in the region *FG*, as ammonium sulphate is converted into ammonium hydroxide. The minimum at *G* (125 ml. of NaOH) agrees with the calculated end-point for the overall reaction, the subsequent sharp rise in conductivity being due to the addition of excess of sodium hydroxide.

FIG. 1.



It is inferred from this preliminary experiment that the formation of ferric hydroxide occurs in at least three stages. The first involves the formation of a soluble complex containing one hydroxyl group for each iron atom, and may be written



This reaction was first proposed by Goodwin (*Z. physikal. Chem.*, 1896, **21**, 1), and has been studied by Lamb and Jacques (*J. Amer. Chem. Soc.*, 1938, **60**, 1215) and by Bray and Hershey (*ibid.*, 1934, **56**, 1899), who found the reaction constant to be 2.5×10^{-3} and 4.9×10^{-3} , respectively.

The second stage is the precipitation of ferric pentaoxysulphate, $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$. No reaction is given for this process at this point, since it will be shown that a further hydrolysis stage occurs before the formation of the precipitate. The final process, the conversion of ferric pentaoxysulphate into ferric hydroxide, is not complete until the pH has been raised above 7.0. Since the presence of ammonium sulphate in solution complicates the interpretation of the pH and conductivity curves in the region *EG*, the use of ferric alum was discontinued, and pure ferric sulphate solutions used. The hydrolysis of ferric sulphate was studied by the measurement of the pH of solutions, containing no free acid, at concentrations varying from 2×10^{-2} to 1×10^{-3} g.-atom of Fe/l .

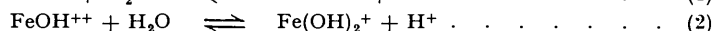
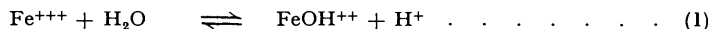
The Hydrolysis of Ferric Sulphate.—Attempts to prepare pure ferric sulphate by repeated recrystallisations did not result in complete removal of free sulphuric acid. Accordingly, a solution was prepared from spectrographically pure metallic iron, and a measured quantity of *N*-sulphuric acid ("AnalaR"). The solution was oxidised with a small excess of 100-vol. "AnalaR" hydrogen peroxide, which was first adjusted to pH 7.0. The excess of peroxide was removed by prolonged boiling, and the solution was then aged for 10 days in order to establish equilibrium between all the ions present. A small quantity of iron was deposited as a film on the glass during the boiling process. This was redissolved in hydrochloric acid, the quantity determined, and subtracted from the total weight of iron used. The stock iron solution thus prepared was 0.994M/30 with respect to iron, and 0.459M/20 with

respect to free sulphuric acid. Thus 25 ml. of this solution required 10.9 ml. of 0.1054*N*-sodium hydroxide for neutralisation of free acid, and the concentration of the resulting solution was 2.29×10^{-2} g.-atom of Fe/l. The pH of this solution was measured at 25.0°, and a series of dilutions was carried out, freshly boiled conductivity water having a pH of 6.2 being used. The presence of sodium sulphate in the ferric sulphate solution is a disadvantage of this procedure, but the method is the only one which has been found to ensure a precise knowledge of the composition of the solution. The results are shown in Table I.

TABLE I.

C.	pH.	[H ⁺].	[H ⁺]/C.	Remarks.
2.29 × 10 ⁻²	2.30	5.01 × 10 ⁻³	0.219	
1.145	2.45	3.54 "	0.308	
5.725 × 10 ⁻³	2.61	2.45 "	0.429	
2.863	2.78	1.66 "	0.579	
1.432	2.96	1.10 "	0.770	
7.16 × 10 ⁻⁴	3.14	0.72 "	1.01	Faint cloud
3.58	3.35	4.46 × 10 ⁻⁴	1.25	Precipitate
1.79	3.48	3.30 "	1.85	
8.95 × 10 ⁻⁵	3.73	1.86 "	2.07	
4.47	4.04	9.10 × 10 ⁻⁵	2.04	
2.24	4.32	4.78 "	2.13	
1.12	4.63	2.36 "	2.12	

The value [H⁺]/C representing the number of hydrogen ions produced by 1 atom of iron, approaches a maximum value of approximately 2.1 at zero concentration. Since this experiment was carried out very rapidly, in order to minimise the effect of the precipitation stage of hydrolysis, the results would suggest the formation of Fe(OH)₂⁺ as the last soluble product of hydrolysis. The possible single-stage hydrolysis processes, which could occur before the point of precipitation, include the direct formation from Fe⁺⁺⁺ ions of FeOH⁺⁺, Fe(OH)₂⁺, Fe₂O⁴⁺, or Fe₂(OH)₃³⁺. The reaction constant of each of these processes was calculated, and found in each case to vary in a regular manner with pH. None of these processes, therefore, can represent the mechanism of hydrolysis. The simplest two-stage process which can be postulated is



The relation between hydrogen-ion concentration and total iron concentration can be calculated from the following equations, activity coefficients being neglected :

$$K_1 = [\text{FeOH}^{++}][\text{H}^+]/[\text{Fe}^{+++}]$$

$$K_2 = [\text{Fe(OH)}_2^+][\text{H}^+]/[\text{FeOH}^{++}]$$

$$[\text{Fe}^{+++}] + [\text{FeOH}^{++}] + [\text{Fe(OH)}_2^+] = C \text{ (total iron)}$$

and $3[\text{Fe}^{+++}] + 2[\text{FeOH}^{++}] + [\text{Fe(OH)}_2^+] + [\text{H}^+] = 3C$ (electrical neutrality)

Elimination of [Fe⁺⁺⁺], [FeOH⁺⁺], and [Fe(OH)₂⁺] gives

$$K_1(C[\text{H}^+] - [\text{H}^+]^2) + K_1K_2(2C - [\text{H}^+]) = [\text{H}^+]^3 \quad (3)$$

The results of Table I have been used to calculate values for K_1 and K_2 , with the results given in Table II.

TABLE II.

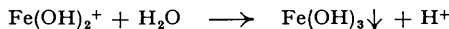
C × 10 ³ .	K ₁ × 10 ³ .	K ₂ × 10 ⁴ .
22.9		
11.45	1.15	5.20
5.725	1.32	3.68
2.863	1.28	3.68
1.432		
Mean	1.25	4.2

Equation (3) can be rearranged as follows :

$$C = \frac{[\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+]}{K_1[\text{H}^+] + 2K_1K_2}$$

By substituting the values calculated for K_1 and K_2 , a theoretical dilution curve has been calculated, and is given as the upper continuous line in Fig. 2. The observed values from Table I have been plotted as circles, which fall on the theoretical curve well beyond the region which was used for the calculation of K_1 and K_2 . These values fall below the calculated curve only when the hydrolysis mechanism has been changed by the formation of a solid phase.

The effect of this third stage of hydrolysis was investigated by measuring the pH at each concentration over a period of several days. The resultant curves, which are shown in Fig. 2, are remarkable in assuming a sigmoid form, the significance of which will be discussed in conjunction with the titration results of Fig. 4. Considering at present only the upper portions of each curve, it is seen that with increasing time, the curves tend to approach the lower continuous curve at an increasingly high concentration. If the third stage of hydrolysis in dilute solution is given by the equation



then

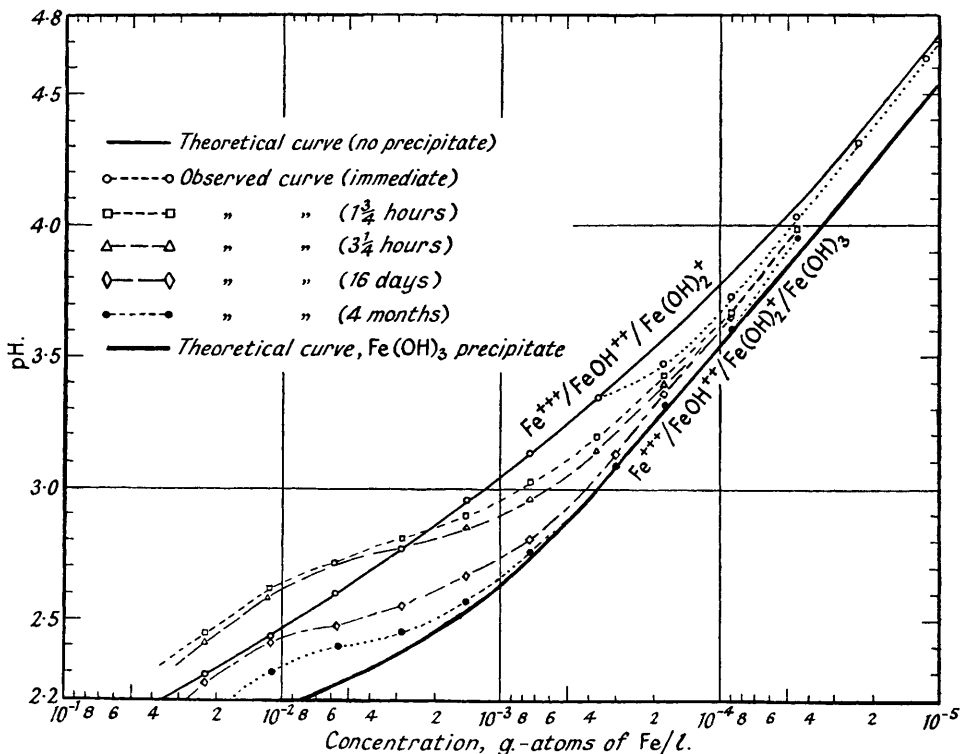
$$K_3 = [\text{H}^+]/[\text{Fe(OH)}_2^+]$$

By a reasoning similar to that used for equation (3), it can be shown that

$$K_1K_2K_3(3C - [\text{H}^+]) = 3[\text{H}^+]^3 + 2K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] \quad (4)$$

On substituting the values previously determined for K_1 and K_2 , and the single value $\text{pH} = 3.09$ when

FIG. 2.



$C = 3.575 \times 10^{-4}$, taken from the final observed curve of Fig. 2, K_3 is found to be 95. Equation (4) then becomes

$$5.0 \times 10^{-5}(3C - [\text{H}^+]) = 3[\text{H}^+]^3 + 2.5 \times 10^{-3}[\text{H}^+]^2 + 5.25 \times 10^{-7}[\text{H}^+] \quad (5)$$

The lower continuous line in Fig. 2 is a curve calculated from equation (5). The agreement with the observed curves is good in solutions more dilute than 10⁻³ g.-atom of Fe/l. In more concentrated solutions, the observed pH values fell above the calculated curve. It is shown below, in the consideration of titration results, that this phenomenon is due to the formation of a basic sulphate, ferric oxy-penta-sulphate [(2 : 5)sulphate], 2Fe₂O₃.5SO₃, as the solid product of hydrolysis at concentrations higher than 10⁻³ g.-atom of Fe/l.

The results of these dilution tests demonstrate that the complete hydrolysis of ferric sulphate is a slow process, and pH measurements vary according to the moment of determination. A study of the reactions of ferric sulphate must therefore include the effect of time, and a normal titration technique, even if carried out at a known rate, must lead to false conclusions, since the observations are made progressively later as the titration proceeds, and the solutions are in correspondingly different equilibrium states.

To overcome this difficulty, the technique of the static titration was used, separate flasks each containing 25 ml. of ferric sulphate solution being treated with quantities of 0.1054N-sodium

FIG. 3A.
Quantity of iron precipitated.

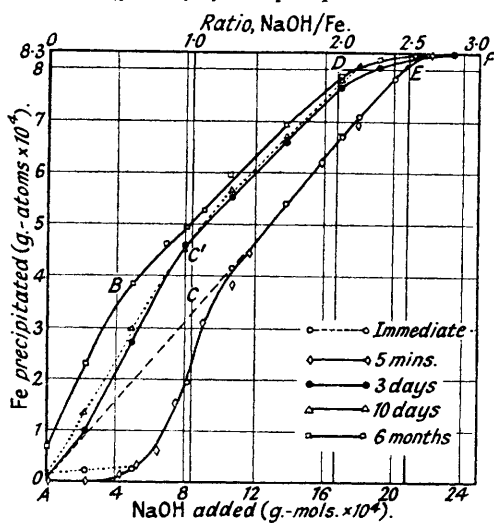


FIG. 3B.
Ratio SO_4/Fe .

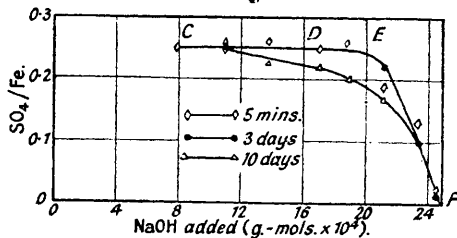
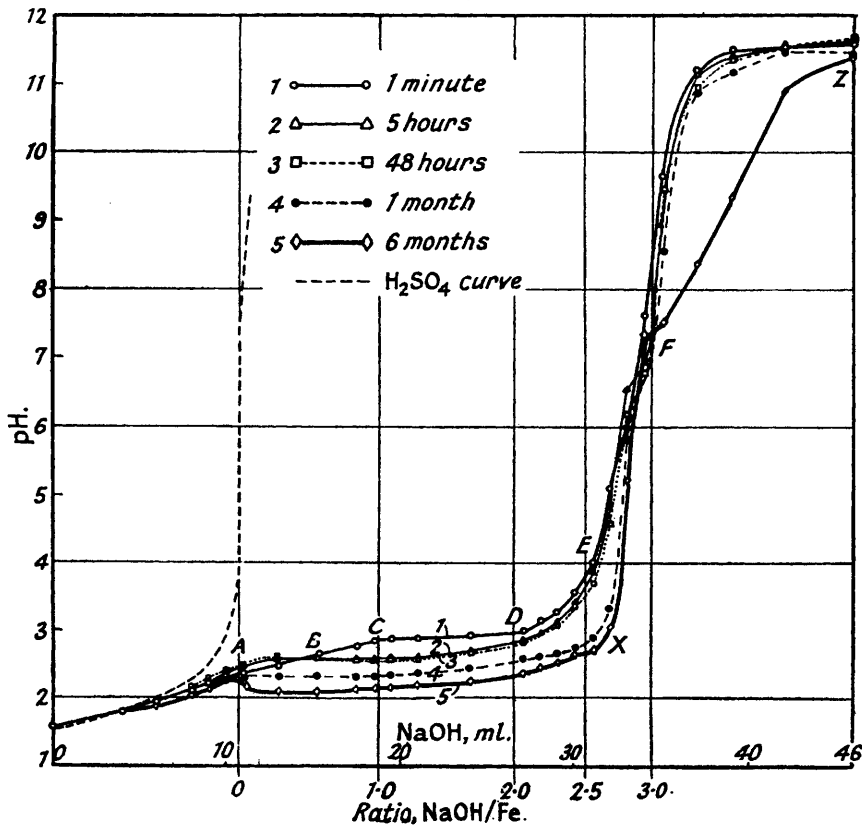


FIG. 4.

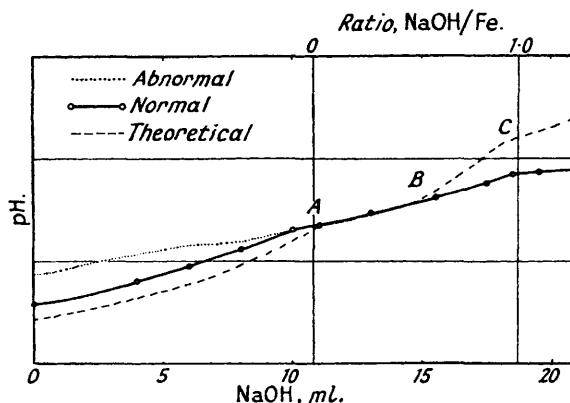


hydroxide solution varying from 0 to 46.0 ml. The titration was carried out in 26 steps, six identical series being prepared. Two were used for measurements of pH and conductivity, severally, over a period of 6 months, and the other four were centrifuged after different time intervals, for the determination of the quantity of the iron precipitated, and the analysis of the precipitates. For convenience in reference, Figs. 3—9, giving the results of these titrations, have all been lettered in the same manner. The start of the titration is represented by point *O*, where no sodium hydroxide is added. Point *A*, at 10.9 ml., represents the calculated end of free acid; *B* = 14.8 ml. (NaOH/Fe = 0.5); *C* = 18.8 ml. (NaOH/Fe = 1.0); *D* = 26.6 ml. (NaOH/Fe = 2.0); *E* = 30.6 ml. (NaOH/Fe = 2.5); and *F*, at 34.5 ml. (NaOH/Fe = 3.0), represents the calculated complete formation of ferric hydroxide or oxide.

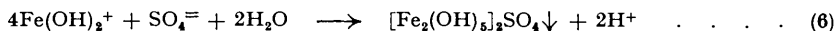
A study of the precipitation curves (Fig. 3), the pH curves (Fig. 4), and the conductivity curves (Fig. 6) shows that the reaction of sodium hydroxide with ferric sulphate takes place in three periods of time, which have been termed the initial, intermediate, and final equilibrium stages. The initial stage is of some minutes' duration, after which a steady change takes place in all parts of the titration, to establish the intermediate stage after about 24 hours. The stability of this stage is shown by the precipitation curves (Fig. 3) which, after a considerable change from the early results, are almost unchanged between 3 and 10 days, by the pH curves, which are identical at 5 and at 48 hours, and by the conductivity curves, which preserve a constant form between 5 and 48 hours, although a small overall increase occurs in this time. The final stage, reached in 4—6 months, is characterised by further modifications in the curves of Figs. 3, 4, and 6. Each of these equilibrium stages is also characterised by clearly-defined changes in the physical form and chemical reactivity of the precipitates and solutions.

Initial Equilibrium Stage (1—5 Minutes).—The initial curves in Figs. 3, 4, and 6 were plotted from measurements made one minute after mixing each of the solutions. The liquors in the region *AB* contained small traces of solids which formed round the drops of the sodium hydroxide solution and

FIG. 5.



redissolved during the first five minutes to give clear, deep red solutions. In Fig. 3, the total quantity of iron precipitated (in g.-atoms) has been plotted against the quantity of sodium hydroxide added (in g.-mols.). The precipitation of ferric hydroxide from the start of the titration would result in a straight line *AF*, of slope 0.333. The curves observed after 1 and 5 minutes show that the delay in precipitation occurring in the region *AB*, owing to the formation of FeOH^{++} and $\text{Fe}(\text{OH})_2^+$ ions, is followed between *B* and *C* by a rapid increase in the quantity of iron deposited. From *C* to *E* the quantity of precipitate, which at this stage is brown and gelatinous, increases proportionally to the amount of sodium hydroxide added, along a curve which, if produced in the direction *EC*, passes through the origin. The slope of the straight line *CE* is 0.405, or 2.02/5, indicating that 2 atoms of iron are precipitated by 5 molecules of sodium hydroxide. It is thus evident that the overall process resulting immediately from the addition of sodium hydroxide solution to ferric sulphate solution consists of, first, the production of an unstable solution containing an abnormally high proportion of the basic ions FeOH^{++} and $\text{Fe}(\text{OH})_2^+$, and secondly, the breakdown of this solution by the addition of more sodium hydroxide, to form ferric pentaoxysulphate, by a reaction of the type



This process is complete at *E*, when the NaOH/Fe ratio is 2.5. No iron can then be detected in solution.

The analyses of the precipitates at points in the titration between *C* and *F* (Fig. 3, *B*) give some confirmation of this mechanism. Analytical results must be treated with caution, since the process of filtration and washing can, if prolonged, lead to considerable hydrolysis of the precipitate, with the loss of sulphate. Nevertheless, the results shown in Fig. 3*B* indicate that the ratio SO_4 :Fe in the precipitate approximates to 0.25 throughout the region *CE*, after which it falls to zero at *F*. This agrees with the postulate of an initial precipitate of ferric pentaoxysulphate, $[\text{Fe}_2(\text{OH})_5]_2\text{SO}_4$, which is converted into ferric hydroxide in the region *EF*, by the action of more sodium hydroxide. It is noticeable that the precipitate becomes darker, as sulphate is removed, until in the region *FZ* it is in the dark red-brown form which is observed in the analytical precipitation of ferric hydroxide.

pH Changes in the Initial Equilibrium Stage.—Measurements of pH were made by means of a glass electrode in conjunction with a dip-type calomel half-cell. The electrode system was standardised before and after each set of readings at pH 3.97 and 9.18, freshly prepared phthalate and borate buffers being used. The agreement between the four standardisation readings was always within pH 0.05, and usually within pH 0.02. Curve 1 of Fig. 4, measured after 1 minute, is similar to those recorded by Britton, and by Evans and Prior, and is characterised by three distinct sections: *OAC*, where little precipitation occurs, and the pH rises steadily, *CD*, where the pH remains constant, and *DEF*, in which the curve again rises rapidly. In the region *OAB*, before precipitation occurs, the pH-volume relationship is governed by the first two hydrolysis stages of the ferric ion, for, from the equations for K_1 , K_2 , and C (p. 352) and

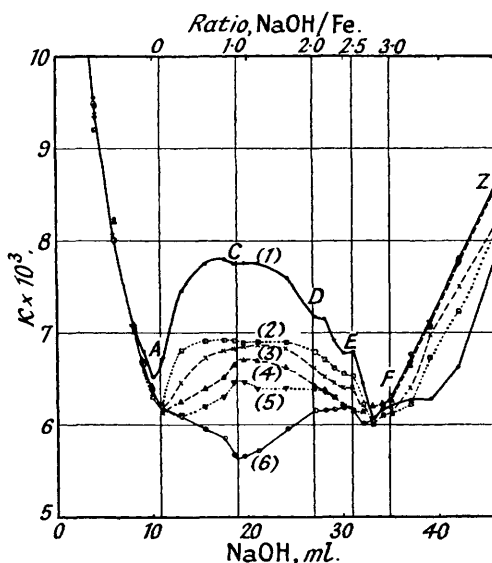
$$[H^+] = [FeOH^{++}] + 2[Fe(OH)_2^+] - [B]$$

where $[B]$ represents the concentration of added alkali, we have

$$C = \frac{([H^+] + [B])([H^+]^2 + K_1[H^+] + K_1K_2)}{K_1([H^+] + 2K_2)} \quad \dots \quad (7)$$

Equation (7) is of general application; in the particular case of this titration, with the values of K_1 and K_2 in Table II we have $C = 0.0329 \times 25/(25 + v)$, where v = the volume of sodium hydroxide added.

FIG. 6.



(1) 6 months.
(4) 48 hours.

(2) 2 months.
(5) 5 hours.

(3) 13 days.
(6) 1 minute.

Moreover, since $[B] = 0$ when $v = 10.9$, $[B] = 0.1054(v - 10.9)/(25 + v)$. These values being substituted in equation (7), it can be shown that

$$[H^+]^3(25 + v) + [H^+]^2(0.107v - 1.11) + [H^+](1.31v - 24.3) \times 10^{-4} + 5.25 \times 10^{-7}(0.1054v - 2.78) = 0 \quad \dots \quad (8)$$

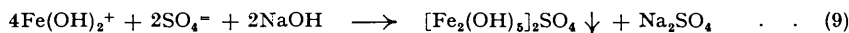
Equation (8) has been used to calculate a theoretical titration curve, which is shown together with the observed initial curve in Fig. 5. The agreement between the two curves is good in the region *AB*, but the calculated results are too low in the presence of free acid. The effects of activity and of the presence of HSO_4^- ions, both of which would tend to raise the observed pH, have not been considered in arriving at equation (8), and might account for this difference. There is also some evidence for the formation of an acid complex of ferric sulphate, whose presence would also tend to raise the observed pH.

Ferrisulphuric Acid.—The ferric sulphate solution used for the titration shown in Fig. 4 was aged for some days before use. It has been found that similar titrations carried out on identical freshly prepared solutions frequently give higher pH values in the region *OA*. The elevation is variable, according to the age and manner of preparation of the solution, and the effect normally disappears after one or two days. The maximum elevation of this type which has been observed is recorded in Fig. 5 (dotted line). The pH values in the presence of free acid are higher than those given by the same concentration of sulphuric acid in the absence of iron, and indicate the removal of sulphuric acid from the solution by the formation of an acid ferric sulphate. No evidence for the composition of such a compound can be

deduced from this work. The existence of the compound, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3$, in the solid state is, however, well known. It occurs as the mineral rhomboclase, $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, and its presence as a solid phase in contact with acid solutions of ferric sulphate has been demonstrated by Applebey and Wilkes (*J.*, 1922, **121**, 337) and others by phase-rule studies. Recoura (*Compt. rend.*, 1911, **153**, 1223) considered it to be ferrisulphuric acid, $\text{Fe}(\text{OH})(\text{HSO}_4)_2$, and prepared the ethyl and other esters. It is suggested that this compound may be formed to an undefined extent in acid solutions of ferric sulphate. The presence of such an acid salt would raise the pH in the region *OA*, and give a further reason for the variation between observed and calculated pH values.

The Mechanism of Precipitation.—The initial pH curve (Fig. 4) is divided into 4 sections, *AC*, *CD*, *DE*, and *EF*, the positions of *A*, *C*, *D*, and *E* being confirmed by inflexions on the corresponding conductivity curve (Fig. 6). The most obvious explanation of these inflexions would be the formation of $\text{Fe}(\text{OH})\text{SO}_4$ in the region *AC*, followed by its conversion into $[\text{Fe}(\text{OH})_2]_2\text{SO}_4$ and $[\text{Fe}_2(\text{OH})_6]_2\text{SO}_4$ in the regions *CD* and *DE*. This process would, however, involve the complete removal of iron from solution at *C*. Moreover, a calculation of the acid produced during the further hydrolysis to the final state (Fig. 4) shows that this value is much less than would occur were the precipitate $\text{Fe}(\text{OH})\text{SO}_4$ or $[\text{Fe}(\text{OH})_2]_2\text{SO}_4$, but agrees well with the initial formation of $[\text{Fe}_2(\text{OH})_6]_2\text{SO}_4$ at all points in the titration.

The titration results can be explained by a consideration of the processes in solution leading up to precipitation. In the region *AD*, the primary process has been shown to be the production of increasing quantities of the basic ions $\text{Fe}(\text{OH})^{++}$ and $\text{Fe}(\text{OH})_2^+$, followed by the formation of a precipitate. The inflexion in the pH curve at *C* is caused by the rapid increase in the total quantity of precipitate occurring at this point (cf. Fig. 3), while the horizontal section *CD* agrees with the concept that hydrolysis in solution is taking place simultaneously with precipitation. If the precipitation reaction were the only one occurring, the pH curve would rise at a rate governed by the solubility product of the precipitate. In the region *DE*, the mechanism changes. In the absence of a precipitate, the whole of the iron present at *D* would be converted into $\text{Fe}(\text{OH})_2^+$; thus the precipitate may be considered as being formed from a solution of uniform ionic type, by the reaction



In this region, therefore, the pH is governed by the solubility product of ferric pentaoxysulphate, $K = [\text{Fe}(\text{OH})_2^+]^4[\text{SO}_4^{--}][\text{OH}^-]^2$, and thus rises rapidly as $[\text{Fe}(\text{OH})_2^+]$ is reduced to zero at *E*. The overall process of precipitation in the initial equilibrium stage may thus be considered as (i) hydrolysis in solution from *A* to *C*, with formation of FeOH^{++} and $\text{Fe}(\text{OH})_2^+$, and a corresponding rise in pH, (ii) further hydrolysis, together with precipitation from *C* to *D*, at constant pH, (iii) precipitation from a completely hydrolysed solution from *D* to *E*, with rapidly rising pH, (iv) conversion of the basic sulphate into ferric hydroxide from *E* to *F*, the rate of rise of pH increasing. This mechanism represents an oversimplified picture of the process, in which the reactions of each section are in practice somewhat modified by the preceding and succeeding sections.

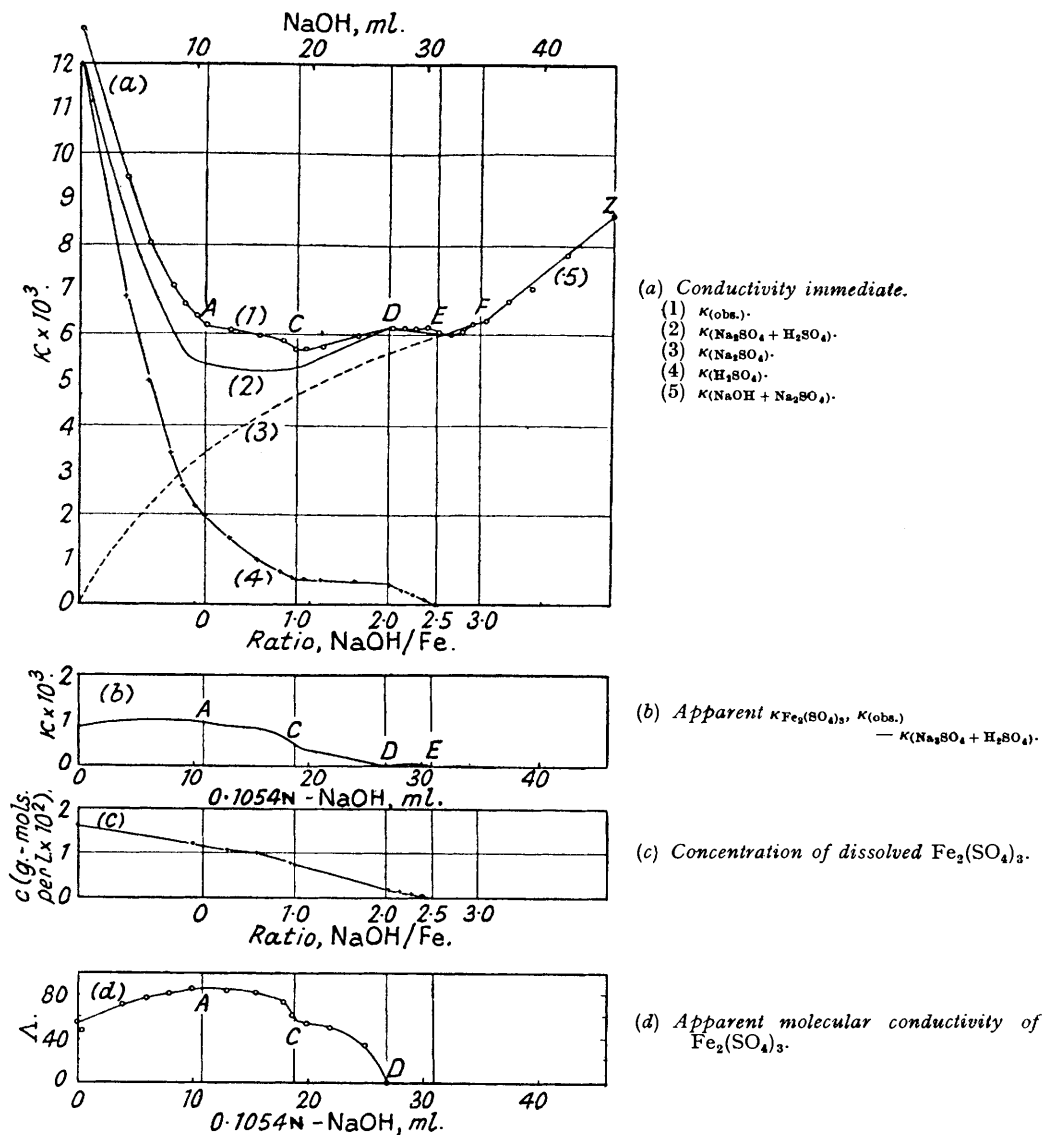
Conductivity Changes in the Initial Equilibrium Stage.—Conductivities were measured 1 minute after the solutions had been mixed, a dip-type electrode system being used in conjunction with a Mullard universal measuring bridge. The initial conductivity curve (Fig. 6) is notably different from those measured later, the conductivities in the region *AF* being very low, with a minimum at *C*. The conductivity curves have been analysed, by the calculation of the conductivities of all the ions present other than those of iron and its associated sulphate. The conductivity of the sodium sulphate formed at each stage of the titration was measured by a series of conductimetric titrations, each of 25 ml. of sulphuric acid, of varied concentration, with 0.1054*N*-sodium hydroxide. The minima of these titrations were plotted against the volumes of sodium hydroxide added at the minimum points. In the last of these titrations, this volume was 34.6 ml., and in this case the alkaline portion of the curve gave the total conductivity of sodium hydroxide and sodium sulphate in the region *FZ*. The curves for $\kappa_{\text{Na}_2\text{SO}_4}$ and for $\kappa_{(\text{NaOH} + \text{Na}_2\text{SO}_4)}$, which are common to all periods, have been plotted in Figs. 7—9 as broken and continuous lines respectively. The total conductivity of the sulphuric acid present at any point, including both the free acid and that formed by hydrolysis, has been calculated by assuming (i) $\text{pH} = \log a_{\text{H}^+}$, (ii) $\kappa = 0.430a_{\text{H}} (\Lambda_{\infty, \text{H}_2\text{SO}_4} = 430 \text{ at } 25^\circ)$. These assumptions give reasonably accurate results in the region *AF*, where $[\text{H}^+]$ is low, but the results in solutions containing high concentrations of free acid are of little value. The continuous curves in Figs. 7a—9a give the total conductivity of all ions other than those of ferric sulphate, *i.e.*, $\kappa_{(\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4)}$ in the region *OAF*, and $\kappa_{(\text{Na}_2\text{SO}_4 + \text{NaOH})}$ in the region *FZ*. These curves therefore represent the "salt line" of the titration. The differences between them and the observed curves give the variation of the apparent specific conductivities of the ferric sulphate solutions (Figs. 7b—9b). By comparison with the measured concentration of the ferric sulphate remaining in solution (Figs. 7c—9c), the apparent molar conductivities of the ferric sulphate remaining in solution have been calculated by the expression $\Lambda = \kappa/c \times 1000$. These values are undoubtedly affected to some extent by the occlusion of sodium sulphate on to the precipitates; nevertheless, the curves yield valuable information on the changes taking place in solution.

Fig. 7 gives the analysis of the initial curve of Fig. 6. The observed conductivity curve has been correlated at all stages with the changes in conductivity due to the sulphuric acid and sodium sulphate present. The apparent molecular conductivity (Fig. 7d) of the ferric sulphate remaining in solution is at a maximum at *A*, decreasing rapidly to zero at *D*, along a curve which is inflected at *C*. This observation is in accordance with the concept of hydrolysis in solution in two stages, to give increasing quantities of poorly-conducting basic ions. The apparent value of zero at *D* would indicate that the $\text{Fe}(\text{OH})_2^+$ ion is non-conducting, but it is probable that the observed conductivity has been reduced by the occlusion of soluble salts by the precipitate. Nevertheless, the rapid decrease in the molar conductivity from *C* to *D* shows that the true molar conductivity of the basic ion is low. From *D*, the

observed specific conductivity of the solution (Fig. 7a) follows the salt line closely, little change in conductivity resulting from the conversion of $\text{Fe}(\text{OH})_3^+$ ions into insoluble ferric pentaoxysulphate, while from E to F, the observed conductivity rises with the salt line, as sulphate is extracted from the precipitate. In the presence of excess of alkali, the observed curve follows the $\text{NaOH}-\text{Na}_2\text{SO}_4$ curve, showing that, apart from a small degree of occlusion of soluble salts on the precipitate, no further action takes place in alkaline solution.

The Intermediate Equilibrium Stage.—During the first 4–5 hours after mixing, marked changes

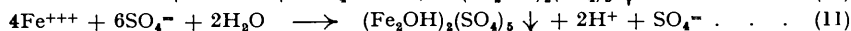
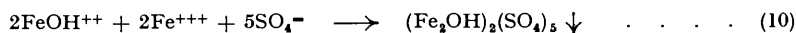
Fig. 7.



occur in all the solutions forming the titration. The changes are largely complete after 24 hours, and the appearance of the precipitates, together with the pH and conductivity curves which demonstrate the reactions in solution, then show little further change for some days. This intermediate condition then breaks down gradually, during some months, to the final stage. The intermediate stage is characterised by a large increase in the quantity of precipitate occurring throughout the titration (Fig. 3a), together with fundamental changes in the appearances and characteristics of the precipitates. In the region AB, the deep red clear solutions become cloudy after 5–10 minutes, and then slowly deposit precipitates which after 24–30 hours assume a characteristic bright orange, flocculent condition which is observed

nowhere else in the titration. The supernatant liquors simultaneously lose their colour, until after 24 hours they are only a pale amber. This process is accompanied by a rise in pH similar to that observed during the hydrolysis experiment (Fig. 2). The conductivity also rises in this region, in spite of the reduction in hydrogen-ion concentration, and the loss of iron by precipitation. From *B* to *E*, the original gelatinous red-brown precipitate changes to a yellow powder, with an increase in the total quantity of precipitate, together with corresponding increases in hydrogen-ion concentration and conductivity. In the region *EF*, the original dark brown gelatinous precipitates are unchanged, and little difference is observed from the original pH and conductivity curves. From *F* to *Z*, where excess of alkali is present, the precipitates gradually change in form during several days, to give a drab yellow powder. This process is increasingly rapid with increasing concentration of free sodium hydroxide, and is complete after 5 days in all solutions whose pH is greater than 8.0.

The Region AB (NaOH/Fe = 0—0.50).—The rise in pH in this region (Fig. 4), in spite of the formation of a precipitate, constitutes a reversal of the normal process of hydrolysis. The explanation for it is found in the nature of the precipitate, which is clearly distinguishable from that occurring in the region *BE*. The mineral copiapite, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 18\text{H}_2\text{O}$, is known to be produced by hydrolysis of slightly acid solutions of ferric sulphate; and Scharizer (*Z. Krist.*, 1913, **52**, 384) considered that its formation was due to the condensation of four molecules of ferrisulphuric acid. Wirth and Bakke (*Z. anorg. Chem.*, 1914, **87**, 21), in a phase-rule study of the system $\text{Fe}_2\text{O}_3\text{—SO}_3\text{—H}_2\text{O}$, showed that a similar material existed in contact with solutions in which the $\text{SO}_3 : \text{Fe}_2\text{O}_3$ ratio was approximately 3 : 1. The region of formation of this compound has been defined more clearly in this work, since it has been found to occur only in those solutions characterised by rising pH values, *i.e.*, between 9.0 and 13.8 ml. of NaOH, where the $\text{SO}_3 : \text{Fe}_2\text{O}_3$ ratio is 3.2—2.5 : 1. The end of formation of this compound at *B* (NaOH/Fe = 0.5) points clearly to the structure $(\text{Fe}_2\text{OH})_2(\text{SO}_4)_5$, or $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3$, in agreement with the results of earlier workers. Analyses have given variable results, owing to the effects of hydrolysis during filtration and washing. The formation of this compound can be explained by either of the following reactions :



The first of these processes, by partly removing the less basic ions from solution, would result in a reversal of the hydrolysis of the $\text{Fe}(\text{OH})_3^+$ ions, and a corresponding rise in pH. This reversal of hydrolysis would account also for the decrease in the colour of the solutions, by the decrease in the concentration of the highly coloured basic ions. Moreover, the establishment of new equilibrium conditions, with a higher proportion of the less basic ions, would account for the rise in the molecular conductivity in this region. Rabinowitch and Stockmeyer (*J. Amer. Chem. Soc.*, 1942, **64**, 335), in a study of the absorption spectra of ferric perchlorate, isolated the spectra of Fe^{+++} and FeOH^{++} , and found deviations from Beer's law which could be explained by the formation of $\text{Fe}_2\text{OH}^{5+}$. In the consideration of the final equilibrium stage, it will be shown that increases in the quantity of ferric oxypentasulphate over a period of 6 months are accompanied by a reduction in pH. During this stage, therefore, the attainment of equilibrium by reaction (10) must be followed by a slow further hydrolysis by reaction (11).

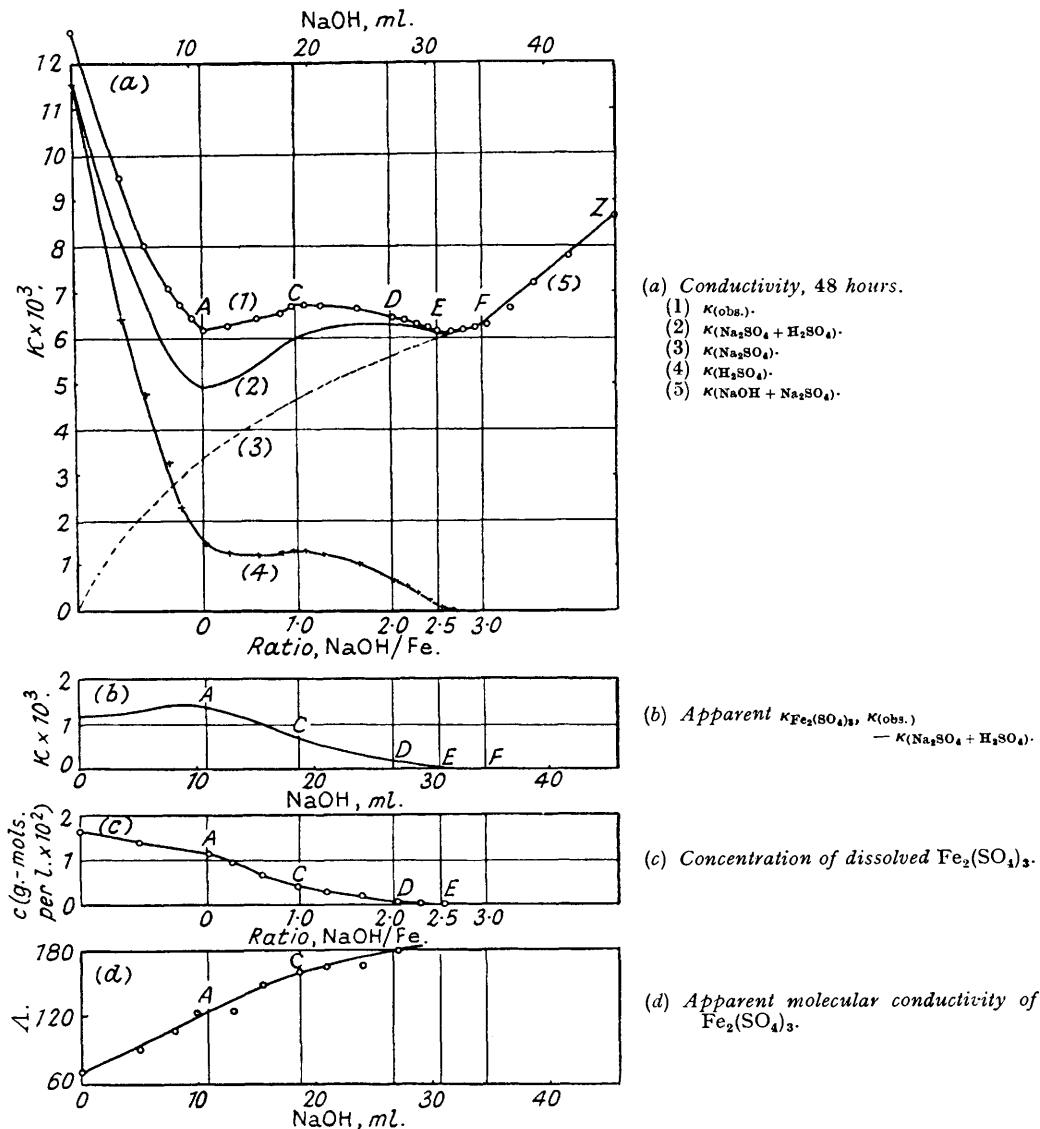
Reactions (10) and (11) can also explain the series of sigmoid curves observed during the dilution experiment (Fig. 2). It has already been shown that the precipitate formed in dilute solution (less than 10^{-3} g.-atom of Fe/l.) is ferric oxide or hydroxide. It is now apparent that in solutions more concentrated than 3×10^{-3} g.-atom of Fe/l., the precipitate is largely ferric oxypentasulphate, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3$. The dilution curves therefore consist of two distinct sections, each associated with one of these compounds, while the sigmoid portion represents the transition between them. There is no conclusive evidence to show whether this transition is a single process, or whether the sulphates of the ions FeOH^{++} and $\text{Fe}(\text{OH})_3^+$ occur as intermediate steps; but the sharp changes in the dilution curve make the former mechanism more probable. It is shown below that in the titration with sodium hydroxide, the transition from ferric oxypentasulphate to ferric pentaoxysulphate is almost certainly direct.

The Region BE (NaOH/Fe = 0.50—2.50).—The slimy yellow precipitate in this region can be seen to exist in three forms, light yellow, dull yellow, and dull orange, the boundaries between them being at *C* and *D*. The first of these deposits dissolves fairly readily in dilute mineral acids, whereas the second and the third are increasingly difficult to dissolve. These three deposits are associated with three approximately linear sections *AC*, *CD*, and *DE* of the precipitation curves observed after 3 and 10 days (Fig. 3), the ratio (Fe precipitated)/(NaOH added) decreasing from section to section. Point *C* is also marked by inflexions in the pH and conductivity curves (Figs. 4 and 6); but *D* is less clearly defined in these curves. The increase in hydrogen-ion concentration in the region *BE*, during the first 24 hours, is of the order to be expected from the increase in quantity of the precipitate, assuming that its composition is unchanged, and allowing for the partial reversal of hydrolysis of the basic ions remaining in solution, caused by the decrease in pH. The precipitates occurring after *E* are all coloured dark brown by the presence in them of the increasing quantities of $\text{Fe}(\text{OH})_3$. It is therefore considered that the precipitates in the region *BE*, in the intermediate equilibrium stage, consist of ferric pentaoxysulphate, in three different physical forms, which are probably in decreasing states of hydration. The analyses of the precipitates (Fig. 3*B*) tend to confirm this view, since the $\text{SO}_4 : \text{Fe}$ ratio after 3 days, as in the initial stage, is 0.25 in the region *CE*, and is then reduced to zero by the addition of sodium hydroxide in section *EF*. After 10 days, the loss of some sulphate is apparent towards the end of the region. Further confirmation of the chemical nature of the precipitate is given by a consideration of the processes leading to the final equilibrium stage (see p. 361).

Conductivity Changes in the Intermediate Stage (Fig. 6).—The increase in conductivity occurring in the first 5 hours is accompanied by a change in the form of the conductivity curve from *A* to *E*. The

minimum at *C* disappears, to be replaced by a maximum, while a second maximum appears at *D*. The curves remain constant in type for several days, although the overall level rises steadily. An analysis of the 48-hour curve from Fig. 6 is given in Fig. 8, which demonstrates that the observed inflexions can be correlated with the changes in pH and sodium sulphate concentration. The molar conductivity of the ferric sulphate remaining in solution (Fig. 8*d*), after correction for the effect of all the other ions in solution, has increased throughout the region *AE*. Moreover, this value increases in the direction *AE*, i.e., with decreasing concentration of the remaining iron, instead of decreasing rapidly as was observed

FIG. 8.



in the initial stage. It is obvious that the process occurring in solution during the intermediate equilibrium stage is one of simplification. The solutions formed in the first stage, containing large proportions of the basic ferric ions, are unstable, and break down to form ferric pentaoxysulphate, together with a corresponding quantity of hydrogen ions. The increase in hydrogen-ion concentration displaces the hydrolysis equilibria in solution in the direction of formation of the less basic ions, and the molar conductivity of the iron remaining in solution is thus increased. The specific conductivity of the ferric sulphate (Fig. 8*b*) becomes zero at *E*, where precipitation is complete, and the specific conductivity of the solution (Fig. 8*a*) then rises along the salt line, owing to the formation of sodium sulphate by the

action of sodium hydroxide on the precipitate. This process is complete at *F*, after which the observed curve is identical with the salt line representing the addition of excess alkali.

The Effect of Excess of Alkali.—The changes in the appearance of the ferric hydroxide precipitate in the region *FZ* are not accompanied by any change in pH or conductivity, and thus cannot be explained by a reaction between ferric hydroxide and excess of sodium hydroxide. This was confirmed by centrifuging off the precipitate after 5 days, and determining the free sodium hydroxide in the solution. In all cases the quantity found was equal to the calculated excess. By *X*-ray crystallographic measurements, the precipitate was shown to be goethite, $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The formation of this compound by the ageing of ferric hydroxide precipitate has been recorded by Krause and Niklewski (*Ber.*, 1938, 71, 423). The effect of pH upon the rate of formation of this compound, and the complete stability of $\text{Fe}(\text{OH})_3$ at pH values less than 8.0, do not appear to have been previously reported.

The Final Equilibrium Stage.—From about 5 days to 6 months after the preparation of the solutions, a gradual change takes place over the whole of the region from just before *A*, to *F*, the end of ferric hydroxide formation. Traces of ferric oxy-pentasulphate appear before *A*, until after 6 months all those solutions which were characterised by a rise in pH between the initial and intermediate equilibrium states, contain small quantities of this material. Solutions to which less than 9 ml. of sodium hydroxide solution have been added ($\text{SO}_3/\text{Fe}_2\text{O}_3 > 3.2$) remain clear, with no measurable changes in pH or conductivity. The final precipitation curve (Fig. 8*a*, curve 5) is different in type from the intermediate-stage curves. An increase in the quantity of iron precipitated in the early portion of the curve results in the disappearance of the inflexion at *C*, and its replacement by one at *B*. The pH curve (Fig. 4) has a maximum just before *A*, where the pH is little changed from its original value. The existence in this region of a salt less basic than in the rest of the titration is suggested by this observation, while the unchanged appearance of the precipitate, together with the small changes in the pH and conductivities, indicate that the original precipitate of ferric oxy-pentasulphate remains stable, in the region around *A*. The height of the pH maximum over the produced portion of the final curve *DC* is of the order to be expected from the presence of copiapite at *A*.

In the succeeding portions of the curve, the pH has fallen considerably from the values measured at 48 hours, although the total quantity of the precipitate remains almost unchanged in the region *CE*. The final pH curve gives no indication of the inflexion at *C* which characterised the intermediate-stage curves. The fall in pH is accompanied by a change in the appearance of all the precipitates in the region *BE*, to a uniform drab yellow material, the limits of occurrence of which are in the clearly-defined region *BX*. The plateau on the pH curve has similarly lengthened, the inflexion at *E* being replaced by one at *X*. It is evident that the precipitate of ferric penta-oxy-sulphate, which existed during the initial and intermediate stages, has hydrolysed further in the solid state, forming a more basic compound, with liberation of sulphuric acid. The composition of this compound is given by the position of *X* (32.8 ml.), where its formation is complete, and the $\text{NaOH} : \text{Fe}$ ratio is 8 : 3. This value corresponds with the formation of ferric octa-oxy-sulphate [(3 : 1) sulphate], $3\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot x\text{H}_2\text{O}$, which is considered to be the final product of hydrolysis in ferric sulphate solutions in which the $\text{SO}_3 : \text{Fe}_2\text{O}_3$ ratio is between 2.50 and 0.33. A small error in the position of *X* would lead to a considerable difference in the formula deduced for this compound, but the same value has been found in three series of tests, and is confirmed by conductivity measurements.

Conductivity Changes in the Final Equilibrium Stage.—The final curve of Fig. 6 has been analysed in Fig. 9. The observed curve is very similar to the salt line throughout the titration, the calculated inflexions at *A*, *E*, *X*, and *F* in the salt line being reproduced exactly by inflexions in the observed curve. Unfortunately, some adsorption of soluble salts has taken place on long standing, with the result that the observed conductivity is below the calculated curve during part of the titration. Consequently, it is not possible to calculate the molar conductivity of the iron remaining in solution. Nevertheless, the conductivity curve is valuable in confirming the deductions made from pH observations. The pronounced conductivity minimum at *A* confirms the pH maximum observed at this point, and substantiates the presence of ferric oxy-pentasulphate in this region. The coincidence of the observed curve with the $\kappa_{\text{Na}_2\text{SO}_4}$ curve, which previously occurred at *E*, now appears at *X* (32.8 ml.), in confirmation of the pH results, and the rising section *EF* is correspondingly shortened to *XF*. These observations give added confirmation of the composition $3\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ for the final compound.

By assuming this composition, it is possible to calculate the composition of the compounds occurring in the region *BE* during the intermediate equilibrium stage, by a method independent of those previously used. For example, at *D* :

pH change from 48 hours to 6 months = 2.99—2.34.

Whence, total production of hydrogen ions in 51.6 ml. = 1.82×10^{-4} g.-ion.

Total iron precipitated in 48 hours = 7.64×10^{-4} g.-atom.

Increase in precipitate from 48 hours to 6 months = 0.27×10^{-4} g.-atom.

Production of hydrogen associated with this increase = 0.72×10^{-4} g.-ion.

Therefore, quantity of hydrogen ions produced by the hydrolysis of the original precipitate = $(1.82 - 0.72) \times 10^{-4} = 1.10 \times 10^{-4}$.

Calculated H^+ production, assuming the original precipitate to be $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$, $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$, and $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 = 12.7 \times 10^{-4}$, 5.1×10^{-4} , and 1.27×10^{-4} g.-ion, respectively.

It follows that the original precipitate at *D* is $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$, in agreement with previous calculations. Similar results are obtained at other points in the titration.

Reactions in the Presence of Excess of Sodium Hydroxide.—The formation of goethite in the intermediate equilibrium stage is followed by the slow absorption of sodium hydroxide by the precipitate, as

shown by the decreases in the pH and conductivity readings in the region *FZ*. The adsorption of zinc, cobalt, and nickel salts on aged ferric oxides was studied by Kolthoff and Overholzer (*J. Physical Chem.*, 1939, **43**, 767), who considered the effect to be due to the formation of ferrites. It seems very probable that the same process occurs in these experiments. The horizontal portion of the final conductivity curve (Figs. 6 and 9) extends from *F* to about 42 ml. of NaOH, after which the conductivity rises rapidly. Since *F* is at 34.5 ml., the equivalent of 7.5 ml. of 0.1054*N*-NaOH has been absorbed by the precipitate from 25 ml. of 0.0166*M*- $\text{Fe}_2(\text{SO}_4)_3$. Thus 0.95 mol. of NaOH is absorbed by 1 mol. of $\text{Fe}(\text{OH})_3$, suggesting the formation of sodium metaferrite, NaFeO_2 . The slow reactions of hydrated ferric oxide in alkaline solution are the subject of a more detailed study, which will be communicated later.

FIG. 9.
Conductivity after 6 months.

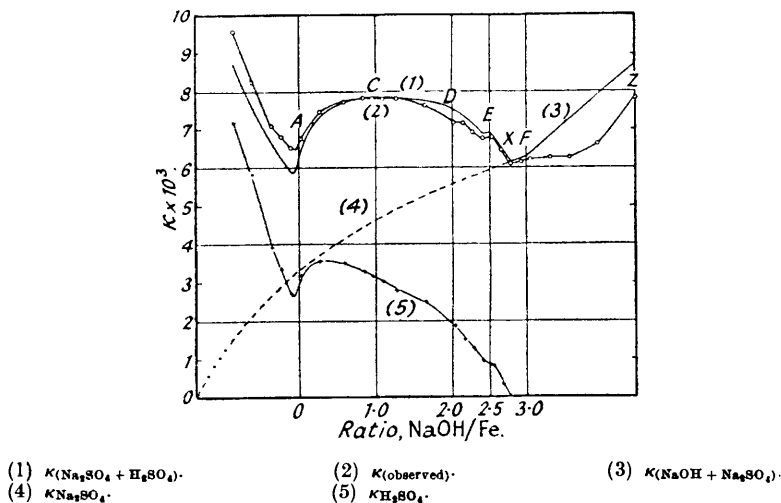
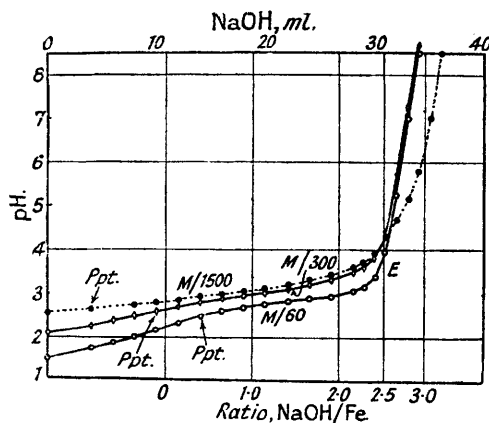


FIG. 10.



The Effect of Concentration on Titration Results.—The differences which occur in the hydrolysis mechanism of ferric sulphate with increasing dilution suggest that the form of the titration curves should change when the iron concentration is reduced below $m/300$. Three titrations were carried out, simultaneously, at 25°. In the first, 25 ml. of $m/60$ -ferric sulphate solution were titrated with 0.1054*N*-sodium hydroxide, while in the second and third, the same quantity of solution was diluted to 125 ml. ($m/300$) and 625 ml. ($m/1500$) before titration with the same alkali. The point of first precipitation (Fig. 10) becomes progressively earlier at increasing dilution, owing to the increasing effect of hydrolysis. Moreover, while the first two curves are similar in type, the third is markedly different. The general level is little above the second, in spite of the decrease in concentration. If the same three titrations are carried out rather more slowly, the third curve is slightly below the second. This effect is due to the marked increase in the rate of precipitation which occurs in the upper portion of the pH-dilution curve

(Fig 2), and suggests that at low concentrations the condition which has been called the "initial equilibrium stage" is of only momentary duration. It is noticeable that the precipitate formed in the region *AE*, at $m/1500$ -concentration, is a yellow powder resembling the product of the intermediate equilibrium stage, rather than the gelatinous compound initially formed in $m/60$ -solutions. The inflexion observed at *E* in curves 1 and 2 is almost indiscernible in curve 3, showing that the transformation of the basic salt into the hydroxide is a much less clearly-defined process at lower concentrations.

DISCUSSION.

The Basic Sulphates.—The evidence of this work indicates the formation, according to the conditions, of three basic sulphates: ferric oxypentasulphate, $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot x\text{H}_2\text{O}$, corresponding to the mineral copiapite; ferric pentaoxysulphate, $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot x\text{H}_2\text{O}$, equivalent to the minerals glockerite and hydroglockerite; and ferric octaoxysulphate, $3\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot x\text{H}_2\text{O}$, which has not previously been reported. The postulation of the ions FeOH^{++} and $\text{Fe}(\text{OH})_2^+$ suggests that the corresponding basic sulphates $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ and $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ may occur as intermediate stages in the hydrolysis and titration processes. It is known that ferric oxydisulphate, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$, occurs as a series of minerals in various states of hydration between those of butlerite ($2\text{H}_2\text{O}$) and fibroferrite ($10\text{H}_2\text{O}$). Similarly, ferric dioxysulphate [(1:1)sulphate], $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$, exists as borgstromite (anhydrous) and planoferrite ($15\text{H}_2\text{O}$), together with intermediate compounds. Posnjak and Merwin (*J. Amer. Chem. Soc.*, 1922, **44**, 1983), in phase-rule studies at 75 – 200° , showed that $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$ occurred as a solid phase at all temperatures, the hydration varying according to the temperature. The results of this work do not indicate the presence of either ferric dioxysulphate or ferric oxydisulphate for any finite period of time at 25° . One observation exists, however, to suggest their momentary formation during the initial equilibrium stage. It has been shown that in the intermediate equilibrium stage, ferric pentaoxysulphate occurs in three forms which can be distinguished visually, the boundaries between them coinciding with inflexions in pH and conductivity curves at *C* and *D*. Since the state of the solution at the intermediate stage is little changed throughout the titration, the difference in the form of the precipitate must result from some difference in the mechanism of precipitation in the regions *AC*, *CD*, and *DE*. A possible process would be the initial formation of $\text{Fe}(\text{OH})\text{SO}_4$, $[\text{Fe}(\text{OH})_2]_2\text{SO}_4$, and $[\text{Fe}_2(\text{OH})_5]_2\text{SO}_4$ in these regions, followed immediately by their conversion into three forms of $[\text{Fe}_2(\text{OH})_5]_2\text{SO}_4$, which lose water during the second equilibrium stage, to give three different hydrates of $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$.

Basic Ions.—The hydrolysis of ferric sulphate solutions can be explained quantitatively by the postulation of the ions Fe^{+++} , FeOH^{++} , and $\text{Fe}(\text{OH})_2^+$ as the only ones present in solution. The presence of FeO^+ ions in solutions obtained from the ultra-filtration of ferric hydroxide sols has been demonstrated by Krestinskaya and Khavimov (*J. Gen. Chem. U.S.S.R.*, 1944, **14**, 70), and evidence for the existence of FeOH^{++} has been given by the absorption-spectra studies of Rabinowitch and Stockmeyer (*loc. cit.*). The formation of ferric oxypentasulphate and ferric pentaoxysulphate, which can be considered as the sulphates of $\text{Fe}_2\text{OH}^{5+}$ and $\text{Fe}_2(\text{OH})_5^+$, suggests the possibility that the hydrolysis process may occur through the medium of diatomic ions. In this case, equilibria would occur between Fe^{3+} , Fe_2^{6+} , $\text{Fe}_2\text{OH}^{5+}$, $\text{Fe}_2(\text{OH})_2^{4+}$, $\text{Fe}_2(\text{OH})_4^{2+}$, and $\text{Fe}_2(\text{OH})_5^+$. No evidence has been found for an ion of the type $\text{Fe}_2(\text{OH})_3^{3+}$. The postulation of the diatomic process involves some difficulties, since the increase in pH in the region *AB* during the intermediate equilibrium stage is less easy to explain if the ion $\text{Fe}_2\text{OH}^{5+}$ is considered to be present from the beginning. The monatomic hydrolysis process is preferred, as giving the simplest mechanism reconcilable with all observations.

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