[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Slow Hydrolysis of Ferric Chloride in Dilute Solution. I. The Change in Conductance, Color and Chloride Ion Concentration

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It has long been recognized that ferric chloride when dissolved in water is not only subject to the usual instantaneous hydrolysis characteristic of the salt of a strong acid and a weak base, but also, except in concentrated solution, undergoes a further relatively slow hydrolysis which, depending upon the circumstances, may require an interval varying from a few moments to a month or more for its completion. This slow hydrolysis is attended not only by a progressive increase in the conductivity and acidity of the solution, but also by the formation of a yellow-orange colloidal solution from which ferric hydroxide ultimately precipitates.

This surprisingly slow hydrolysis of a highly ionized inorganic salt, accompanied by so striking a color change, has been the object of a great number of investigations during the past fifty years. Three excellent digests of these investigations have recently appeared,[1] so that it is unnecessary to review them here. It suffices to point out that in spite of the number and variety of these investigations there are still important discrepancies in the experimental findings and a wide divergence in the explanations put forward by even the most recent of the investigators; moreover, and still more noteworthy, none of the explanations attempts any *quantitative* correlation of the experimental data.

We have therefore undertaken a further study of this slow hydrolysis. We have repeated and extended the earlier measurements of the increase in conductance of these solutions, using certain improved experimental arrangements, and we have followed the phenomenon by means of colorimetric and electrometric measurements. We have also studied the effect of temperature and of added acids upon the slow hydrolysis and upon the colloidal solutions which result therefrom.

I. Conductance Measurements

After a number of exploratory studies of the phenomenon by earlier investigators, Goodwin and later Goodwin and Grover[2] followed the progressive hydrolysis of dilute solutions of ferric chloride by extensive measurements of their electrical conductance.

In spite of the evident care and skill with which these measurements were executed the one pair of duplicate experiments recorded are in disagreement and the later comparable measurements of Goodwin and Grover in most instances differ greatly from the earlier ones of Goodwin. Goodwin and Grover suggest that the differences may have been due to the different "stock" solutions from which the dilute solution whose hydrolysis was studied, were prepared. Later investigators[3] experienced similar difficulties and concluded that the rate of hydrolysis was extremely sensitive to traces of impurities and even to minute differences in the method by which the dilute solutions were prepared.

Our earlier measurements by the same method were equally unsatisfactory. A simple expedient sufficed, however, to eliminate the greater part of the irregularities. Instead of preparing our definitive solutions by the rapid dilution of a concentrated stock solution, we prepared them by the addition of a small, weighed portion of the pure anhydrous salt to pure water. This assured a constant and reproducible starting material and, since it dissolved almost instantaneously, the moment of addition afforded a precise zero-point for the measurement of time. After this procedure was adopted, our velocity measurements became definite and reproducible.

Experimental Details

Materials.—The ferric chloride was either Kahlbaum pre-war sublimed anhydrous ferric chloride, or else anhydrous salt which we prepared by passing dry chlorine over heated iron wire of known high purity. In either case the product was further purified by resublimation in dry air.

The ferric nitrate was a Kahlbaum sample of the salt $Fe(NO_3)_3 \cdot 9H_2O$, occurring in the form of pale violet crys-

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(1) (a) Gmelin, "Handbuch der anorganischen Chemie," 8th Edition, Iron Part B, Verlag Chemie, Berlin, 1929, pp. 272–278. (b) Abegg, "Handbuch der anorganischen Chemie," Vol. IV, Iron and its Compounds, Part B, S. Hirzel, Leipzig, 1930, pp. 187–192. (c) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XIX, Longmans, Green and Co., New York, N. Y., 1935, pp. 59–65.

(2) H. M. Goodwin, *Z. physik. Chem.*, **21**, 1 (1896); also *Technology Quarterly*, **9**, 254 (1896); H. M. Goodwin and F. W. Grover, *Phys. Rev.*, [1] **11**, 195 (1900); also *Technology Quarterly*, **13**, 327 (1900).

(3) B. E. Moore, *Phys. Rev.*, **12**, 164 (1901); L. Michel, *Compt. rend.*, **147**, 1288 (1907).

tals, faintly moist with dilute nitric acid. Only small. clear crystals were chosen. These were blotted with hardened filter paper, powdered in a dry atmosphere, and exposed for several hours in a desiccator over sodium hydroxide. The product seemed dry and poured freely.

Other materials used were prepared from the best available commercial materials and were further purified by recrystallization, or, in the case of acids, by redistillation.

The potassium chloride used in standardizing the conductance cells was thrice precipitated with hydrogen chloride and fused in platinum. A 0.002000 N solution was prepared according to the method of Kohlrausch. Its specific conductance was taken as 2.765×10^{-3} at 25°, and 3.312×10^{-3} mhos at 35°.(4)

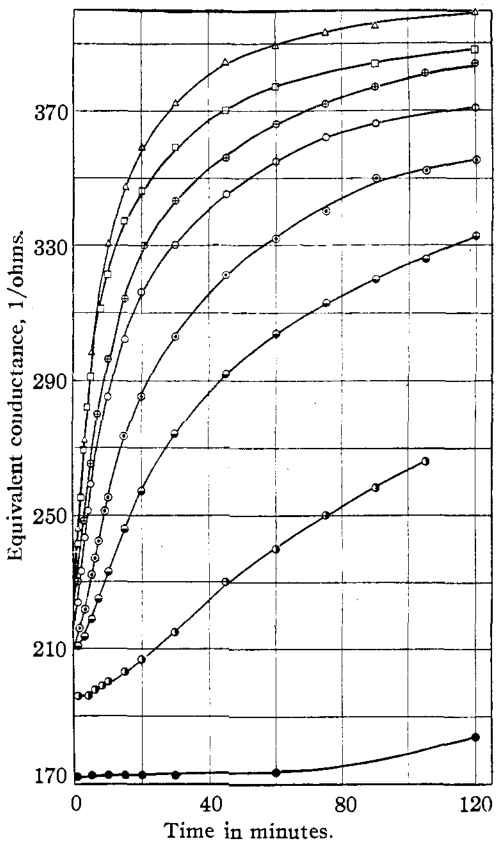

Fig. 1.—Change of the conductance of ferric chloride solutions with time at 25°: ●, 0.01000 N; ◑, 0.00400 N; ⊖, 0.00200 N; ⊙, 0.001333 N; ○, 0.001000 N; ⊕, 0.000800 N; □, 0.000667 N; △, 0.000500 N.

All solutions were made up in conductivity water prepared either by redistillation from permanganate and barium hydroxide, or from Nessler's reagent according to the advice of Kendall.(5)

Apparatus.—Since the conductances to be measured were in general, changing, frequently quite rapidly, extreme precision was out of the question and an elaborate apparatus and technique were not required. A General Radio Microphone Hummer (1000 cycles) was used as a source of current and an air condenser of the same manufacture was used to eliminate capacitance effects. The cells consisted of a number of "dip" electrodes held in a central position by rubber stoppers in 2-liter, round-bottomed, long-necked Pyrex flasks. At 75° the measurements were made in a quartz cell previously described.(6) Two thermostats filled with water maintained temperatures of 25 ± 0.005 and 35 ± 0.05°, respectively; a third filled with glycerol maintained a temperature of 75 ± 0.1°.

The average error of a bridge setting was 0.03%; the calibration error of the comparison resistances was under ±0.05%. A large number of measurements of the cell constant were made at frequent intervals during the course of the investigation and their average deviation from the mean was ±0.05%.

Procedure.—The preparation of solutions of exactly known concentration was the only difficult part of the procedure. The requisite amount (0.05–1.0 g.) of ferric chloride was weighed to the nearest 0.1 mg. by means of small weighing bottles ground to fit interchangeably onto the curved male delivery tube of a larger stock bottle. This avoided any exposure of the extremely hygroscopic salt to the external air. The requisite weight of water was then placed in the 2-liter flask and brought to the precise temperature of the thermostat. After a small amount of this water had been withdrawn, the salt, at a predetermined moment, was shaken into the main body of water, the weighing bottle rinsed quickly several times with the withdrawn water and finally the flask was shaken vigorously for fifteen seconds and returned to the thermostat. The already connected dip electrode was inserted, plunged up and down several times and a bridge setting made. This usually could be accomplished within one minute after the start.

With ferric sulfate this improved procedure could not be adopted because of the slow rate of solution even of the finely ground sample. A stock solution was therefore prepared which on analysis was found to be 1.846 N, and all solutions studied were prepared by diluting this solution.

Results

Precision and Reproducibility.—The errors involved in the conductance measurements themselves, *i. e.*, in the setting of the bridge, the calibration of the resistances and the cells, the constancy of temperature, etc., individually affected the final values by only a few hundredths of a per cent. The uncertainty in the zero time could have been hardly more than ± ten seconds and this would have had no significant effect on the conductivity except in the first few measurements in the most rapidly changing solutions. The most serious source of error was the uncertainty as to the weight of the salt taken, which may have been as great as ±0.2 mg., corresponding to an error in the conductance of from 0.02 to 0.4%. The over-all error of the conductance measure-

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(4) Kohlrausch: see Landolt-Börnstein, Ed. 5, Vol. II, Berlin, 1923, p. 1098.

(5) Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

(6) Lamb and Fairhall, *ibid.*, **45**, 381 (1923).

ments may then be estimated as no greater than about ±0.5%.

This estimate is confirmed by the fact that duplicate conductance measurements made upon independently prepared solutions over a period of several years and with independently assembled apparatus showed an average deviation of the individual measurements from the mean of exactly this magnitude.

Our measurements made at 35° and particularly at 75° were less precise, chiefly because of the greater rapidity of the hydrolysis. The precision of the measurements with ferric sulfate, in which a "stock" solution rather than the anhydrous salt had to be used, was also distinctly less.

Ferric Chloride.—Our results for this substance at 25° are shown graphically[7] in Figs. 1 and 2.

The marked inverse effect of the concentration upon the speed of the progressive hydrolysis is apparent from these results. The conductance reaches about 90% of its final value at 0.0004 N in one hour; at 0.0010 N in five hours; at 0.0040 N in one hundred thirty hours and at 0.0100 N in four hundred hours. The previously recognized induction period is apparent at concentrations of 0.0013 N and higher. Here the progress of the hydrolysis is at first barely perceptible; gradually, however, it increases and then finally decreases as hydrolysis becomes nearly complete. The results are in qualitative agreement with the measurements of Goodwin and of Goodwin and Grover.

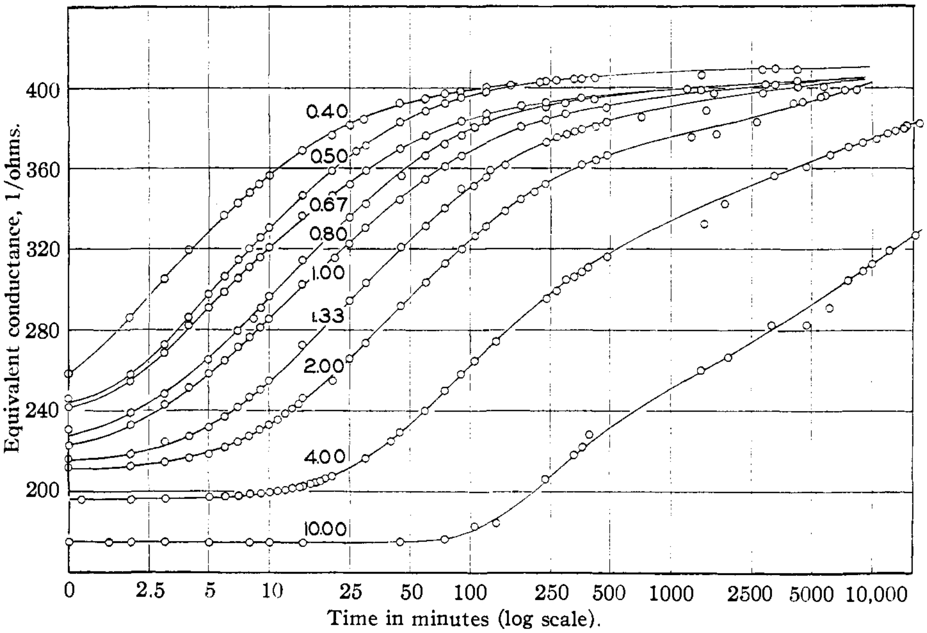

Fig. 2.—Change of the conductance of ferric chloride solutions with time at 25°: symbols represent milliequivalent normal.

The results with ferric chloride solutions at 35° are shown graphically[7] in Fig. 3. The great increase in the speed of hydrolysis at 35° as compared with 25° is obvious and confirms the observations of Goodwin and others. The general shape of the curves remains unaltered, although it is evident that the initial lag is much less marked and is displaced toward higher concentrations.

At 75° the speed of hydrolysis is so great that with solutions less than 0.004 N no change in conductance could be observed; *i. e.*, the change was complete before the first measurement (at 1 minute). Only the readings at two minutes, sixty minutes and the end are therefore given in Table I.

TABLE I

EQUIVALENT CONDUCTANCE OF FERRIC CHLORIDE SOLUTIONS AT 75°

Time, min.	Concentration, $N \times 10^3$ 40.00 1/ohm	10.00 1/ohm	4.00 1/ohm	2.00 1/ohm	1.00 1/ohm
2	459	620	653	693	695
60	562	654	669	693	695
Final	589	664	675	693	696

Ferric Nitrate.—Corresponding measurements of the changing conductance of ferric nitrate solutions have not, so far as we are aware, been made. Our summarized results[7] for these solutions, given in Fig. 4, show that they behave almost exactly like the chloride solutions except that their conductances are in general slightly smaller, corresponding to the lesser mobility of the nitrate as compared with the chloride ion.

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(7) The numerical data on which these figures are based are available in American Documentation Institute Document No. 1060, American Documentation Institute, 2101 Constitution Ave., Washington, D. C. (microfilm, 30¢; photocopies, $1.10). Complete numerical data for all the measurements are available in the Thesis by Dr. Alfred G. Jacques entitled "The Hydrolysis of Ferric Salt Solutions," 1931, Harvard University, Cambridge, Mass.

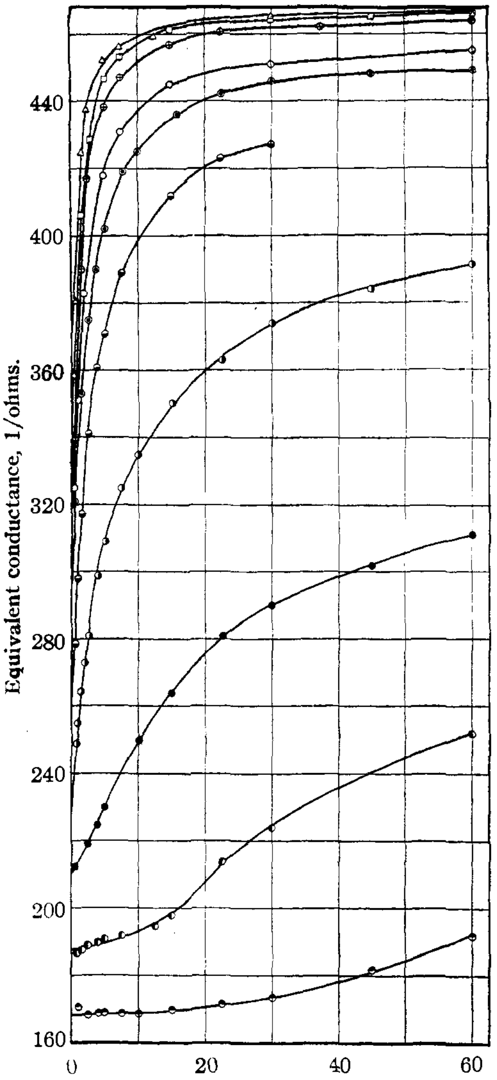

Fig. 3.—Change of the conductance of ferric chloride solutions with time at 35°: ◓, 0.0400 *N*; ◐, 0.0200 *N*; ●, 0.0100 *N*; ◑, 0.00400 *N*; ◒, 0.00200 *N*; ⊙, 0.001333 *N*; ○, 0.001000 *N*; ⊕, 0.000800 *N*; □, 0.000667 *N*; △, 0.000500 *N*.

Ferric Sulfate.—There appear to be no previous measurements of the changing conductivity of dilute solutions of this substance, although measurements on concentrated solutions of ferric sulfate and of ferric ammonium sulfate have been made, respectively, by Wells[8] and by Wagner.[9] Our results are shown graphically[7] in Fig. 5.

These curves show that the initial rate of change is at first faster, but after a few minutes is considerably slower, than in the corresponding chloride and nitrate solutions.[10] It should be noted that none of these sulfate solutions exhibits any suggestion of an induction period. This may, however, be only a matter of degree, since Wells[8] did find such a "lag" at considerably higher concentrations.

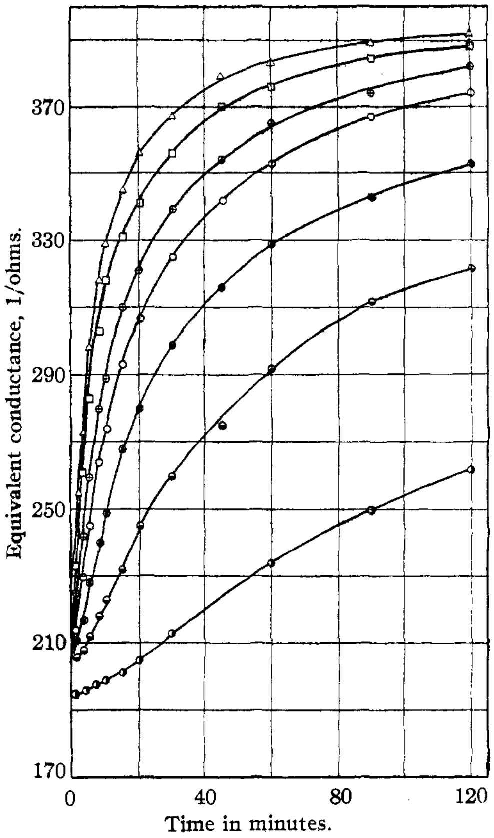

Fig. 4.—Change of the conductance of ferric nitrate solutions with time at 25°: ◑, 0.00400 *N*; ◒, 0.00200 *N*; ⊙, 0.001333 *N*; ○, 0.001000 *N*; ⊕, 0.000800 *N*; □, 0.000667 *N*; △, 0.000500 *N*.

Moreover, the external appearance of the ferric sulfate solutions on slow hydrolysis is decidedly different from that of the chloride and nitrate solutions. The latter flush to an orange color which deepens with time, and only in the most concentrated solutions studied at 25° is there any appreciable turbidity. The sulfate solutions, on the other hand, quickly develop a pale yellow color and in a short time become decidedly turbid. In twenty-four hours all of the sulfate solutions studied deposited a reddish-yellow precipitate, which on long standing changed into a sandy, less flocculent form, doubtless in part due to dehydration.

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(8) Wells, This Journal, **31**, 1027 (1909).

(9) Wagner, *Monatsh.*, **34**, 1129 (1913); **35**, 931 (1913); *Kolloid-Z.*, **14**, 149 (1914).

(10) It should be remarked that the concordance of the individual measurements with smooth curves is less satisfactory, as might be expected from the method used in preparing the solutions.

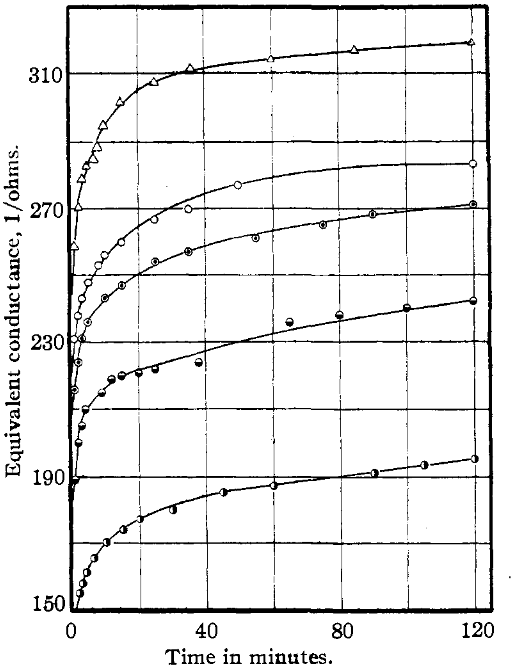

Fig. 5.—Change of the conductance of ferric sulfate solutions with time at 25°: ◑, 0.00400 *N*; ◒, 0.00200 *N*; ⊙, 0.00133 *N*; ○, 0.00100 *N*; △, 0.00050 *N*.

Effect of Gelatin on the Slow Hydrolysis.—Wagner[9] found that gelatin and agar-agar greatly decreased the rate of the slow hydrolysis and accentuated the induction period. Since there was the possibility that this effect might have been caused by minute acidic impurities in the gelatin, we have made similar conductimetric experiments using a sample of "iso-electric ash-free" gelatin as supplied by the Eastman Kodak Company. Our results shown graphically[7] in Fig. 6 confirm the findings of Wagner; indeed they show that the rate of hydrolysis is markedly lessened by as little as 0.002% of gelatin. At higher concentrations of gelatin not shown in the figure still longer induction periods were observed. A point of interest not reported by Wagner is that in all the ferric chloride solutions more concentrated than 0.021 *N* to which gelatin in the above amounts was added, cloudiness always developed before the end of twenty-four hours.

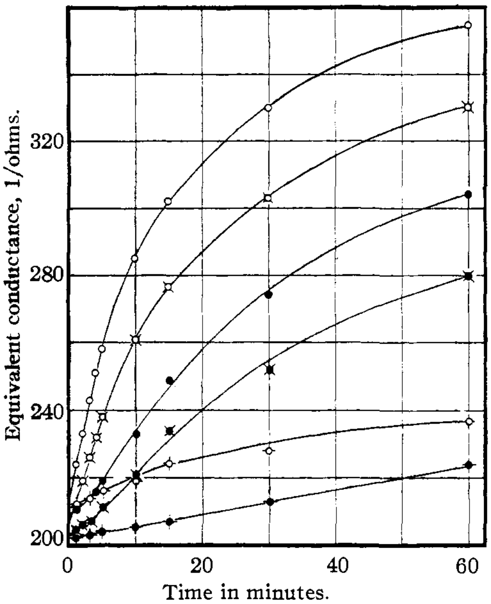

Fig. 6.—Effect of gelatin on the change in conductance of ferric chloride solutions at 25°: -○-, 0.02% gelatin in 0.001 *N*; ⟩○⟨, 0.002% gelatin in 0.001 *N*; ○, no gelatin in 0.001 *N*; -●-, 0.02% gelatin in 0.002 *N*; ⟩●⟨, 0.002% gelatin in 0.002 *N*; ●, no gelatin in 0.002 *N*.

Initial and Final Conductances.—These were obtained by graphical extrapolation and are given in Table II. The extrapolation to zero time was reasonably certain in the case of the solutions more concentrated than 0.001 *N* and at 25°, as they changed but slowly; it was progressively less certain in the more dilute solutions and at higher temperatures. Conversely, the extrapolation to the final state while reasonably certain in the more dilute solutions was less certain in the concentrated solutions where the duration of an experiment was excessively long; indeed in the most concentrated solutions a slight change was still taking

TABLE II

INITIAL AND FINAL CONDUCTANCES OF FERRIC CHLORIDE SOLUTIONS

				25°					
Concentration, m*N*[a]	10.0	4.0	2.0	1.33	1.00	0.80	0.667	0.50	0.40
Initial, mhos	174.5	195.2	209	210	218	221.3	226.5	228	232.5
Final, mhos	347	388	399	402	405	406	406	410	407
				35°					
Initial, mhos	211	240	254	265	278	...	305	...	...
Final, mhos	420	450	460	464	469	469	470	470	...

[a] m*N* = milli-equivalent normal.

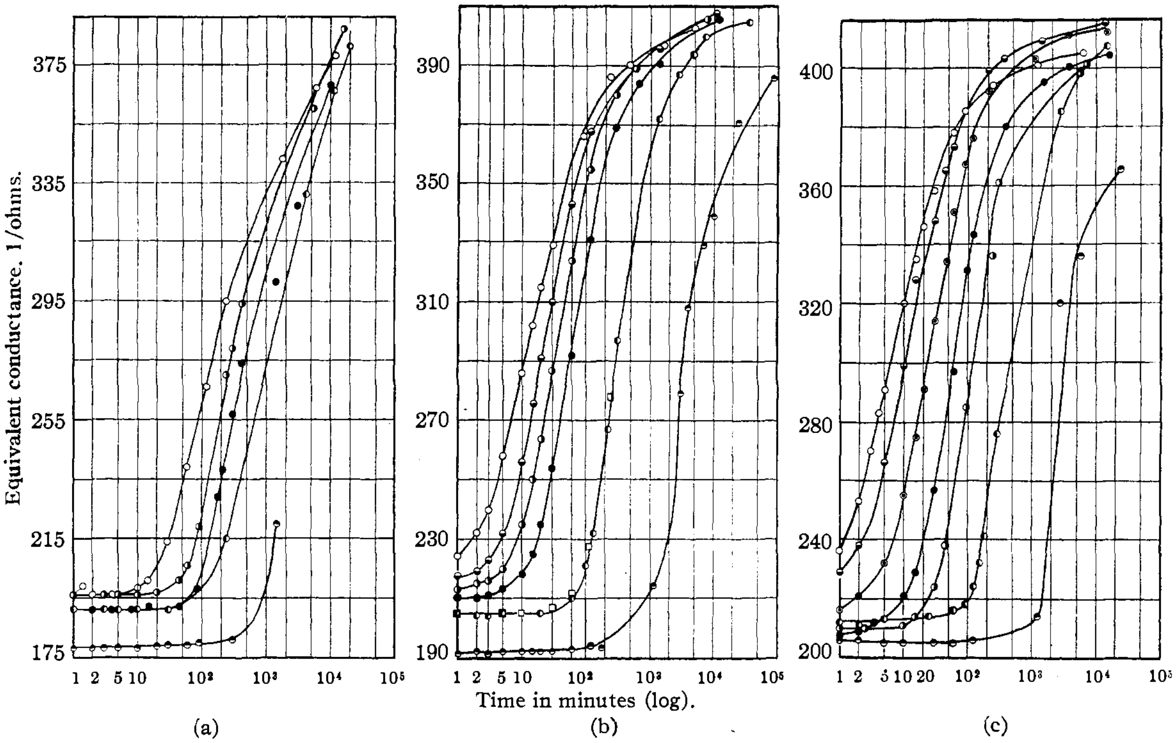

Fig. 7a.—Effect of acid on the change of conductance of 0.00400 N ferric chloride at 25°: ⊖, 0.00105 N HCl; ◐, 0.000417 N; ●, 0.000222 N; ◑, 0.000115 N; ○, no acid.

Fig. 7b.—Effect of acid on the change of conductance of 0.00100 N ferric chloride at 25°: ⊖, 0.00104 N HCl; ◐, 0.000402 N HCl; ●, 0.000223 N HCl; ◑, 0.000102 N HCl; ◒, 0.000051 N HCl; □, 0.00390 N HNO_3; ○, no acid.

Fig. 7c.—Effect of acid on the change of conductance of 0.000667 N ferric chloride at 25°: ⊖, 0.00070 N HCl; ◐, 0.00040 N; ◑, 0.000263 N; ●, 0.000197 N; ⊙, 0.000106 N; ◒, 0.0000434 N; ○, no acid.

place after two months at 25°. The initial and final values thus obtained are greater the lower the concentration, as would be expected because of the increase both in apparent ionization and in hydrolysis.

Effect of Prior Addition of Acid.—It has been shown by Goodwin and others and especially by Malfitano and Michel[11] that acids retard the slow hydrolysis of ferric salts; that hydrochloric and nitric acids are particularly active, the effect being primarily that of the hydrogen ions although the anions, too, may exert a specific action; and that acids also tend to give rise to an induction period or to prolong one already present. Malfitano and Michel, however, found that while *minute* amounts of hydrochloric acid retard the hydrolysis at the start, they later accelerate it.

Finding that our modified procedure gave reproducible and trustworthy results in acidified as well as in pure aqueous solutions, we have reëxamined the effect of hydrochloric, nitric and sulfuric acids on the hydrolysis of ferric chloride over a wide range of concentrations both of the acid and the salt.

Solutions of the acids of known strength were prepared by dilution of standard solutions. Their conductances were measured, the requisite amount of ferric chloride added at a prearranged moment, as usual, and the conductance measurements continued at intervals. The *apparent* specific conductances of the pure ferric chloride solutions were obtained by subtracting the observed specific conductance of the acid solution from that of the mixture. From these the *apparent* equivalent conductances of the ferric chloride solutions were computed.

1. **Hydrochloric and Nitric Acids.**—Our data for these acids are shown in graphical[7] form in Fig. 7a, b, and c.

These data confirm unequivocally the retarding effect of these acids and their ability to establish or to prolong a previously established induction period as found by Goodwin and others. Contrary to the findings of Malfitano and Michel they show that even the smallest concentration

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[11] Malfitano and Michel, *Compt. rend.*, **145**, 185 (1907); **146**, 338 (1908); **147**, 804 (1908).

of hydrochloric acid (0.000016 *M*) added at the start will cause a perceptible retardation that persists throughout the whole course of the hydrolysis.

It was found that nitric acid at the same concentration had the same effect as hydrochloric on the rate of hydrolysis.

To compare the final extent of conversion with and without the addition of acid, we have corrected the final apparent conductances for repression of ionization on the assumption that the equivalent conductance of the additional hydrochloric acid in the final solution is the same as in a pure solution of the same total equivalent concentration. The resulting corrected final equivalent conductances of the acidified 0.001 and 0.000667 *N* ferric chloride solutions average 408.3 ± 1 and 411.0 ± 3, respectively, as compared with 405 and 406 1/ohms for these solutions when no acid was initially present. These slightly larger values cannot be ascribed to a greater hydrolysis, since added acid could not produce such a result directly. They probably reflect a decreased adsorption of ferric chloride and hydrochloric acid by the colloidal ferric hydroxide due to the coarser micelle formed during the slow hydrolysis in the more acid media. This is in accord with other evidence to be presented later.

2. **Sulfuric Acid.**—The results obtained with sulfuric acid are shown in Fig. 8,[7] where for the sake of comparison two experiments with hydrochloric acid are included. The effect of sulfuric acid differs considerably from that of hydrochloric and nitric acids. In the most dilute solutions (up to 0.0001 *N*) it actually accelerates the initial hydrolysis. In agreement with this, only the most concentrated solution (H_2SO_4 = 0.000965 *N*) shows any induction effect, whereas some induction effect is evident with hydrochloric acid at a concentration ten times smaller. A continuing retarding effect comparable with that shown by the hydrochloric and nitric acid is, however, superposed on this initial accelerating effect. The immediate inference from these results is that the initial accelerating effect is due to the sulfate ion while the continuing, retarding effect is to be ascribed to the hydrogen ion.

Effect of Subsequent Addition of Acid.—Malfitano and Michel found that acid added *after* the slow hydrolysis had started was less effective than acid added previously. Thus they found that while 0.01 *N* acid added to a 0.1 *N* solution of ferric chloride before the start prevented the hydrolysis; if added after the hydrolysis had progressed to some extent, it produced no retardation or reversal.

We have investigated this in the more dilute solutions with which we are concerned by dropping into separate portions of a 0.001 *N* ferric chloride solution thin-walled Pyrex-glass ampoules containing enough of a 0.1 *N* hydrochloric acid solution to give a 0.0002 *N* final solution, breaking the ampoules quickly, at 2, 3, 4, 15 and 60 minute intervals after the start, stirring thoroughly and comparing the consequent rate of change of the conductivity with that of a similar solution containing at the start the same concentration of added acid.

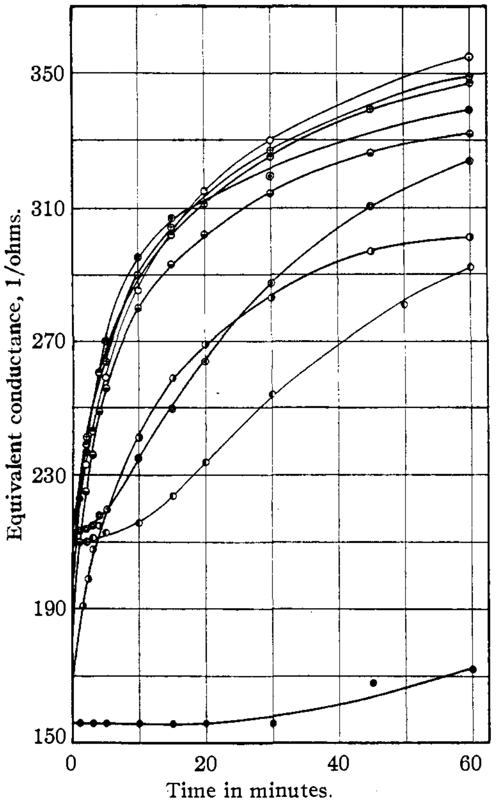

Fig. 8.—Change of conductance of 0.001 *N* ferric chloride solution in the presence of sulfuric acid at 25°: ●, 0.000965 *N*; ◑, 0.000402 *N*; ◒, 0.000198 *N*; ⊙, 0.0000971 *N*; ◓, 0.0000205 *N*; ⊕, 0.0000145 *N*; ○, none; ◐, 0.000223 *N* HCl; ⦿, 0.000102 *N* HCl.

It can be seen from Fig. 9 where the resulting data[7] are presented that, contrary to the findings of Malfitano and Michel, the subsequent additions like previous ones slow down the hydrolysis

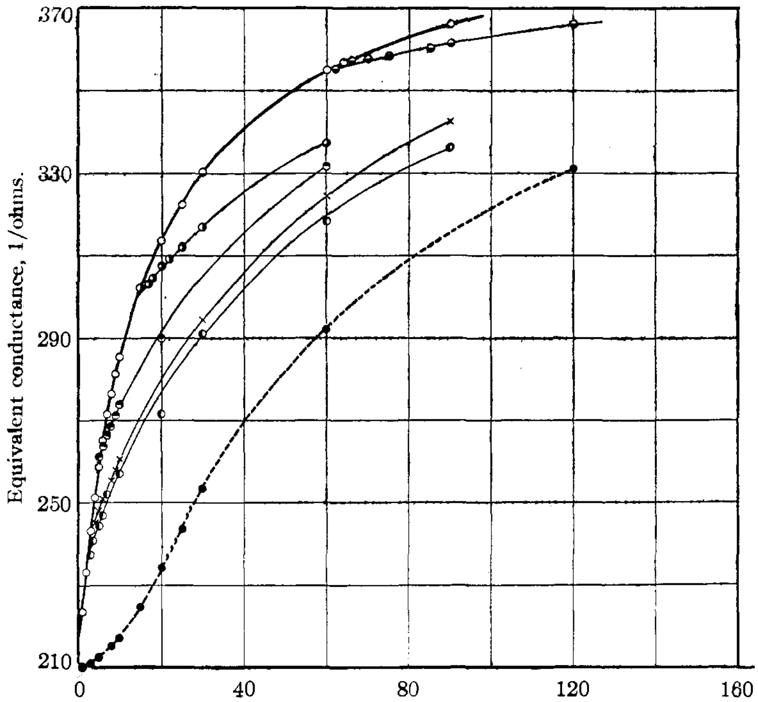

Fig. 9.—Effect of subsequent addition of acid on the change of conductance of 0.00100 N ferric chloride: ●, at start; ◐, after two minutes; ×, after three minutes; ⊖, after four minutes; ◑, after fifteen minutes; ◒, after sixty minutes; ○, no acid.

markedly. The later additions, to be sure, produce somewhat less marked retardations than the earlier ones, for much acid has of course been liberated meanwhile by the hydrolysis itself, but the slope of the curves after each subsequent addition is always nearly identical at the same equivalent conductivity with that of the curve obtained when the same amount of acid is added at the start. In other words, the retarding effect of acid at the same total concentration of acid is the same irrespective of the time at which the acid is added.

The Extent of the Final Conversion.—It has long been recognized from measurements of a variety of properties of the final definitive colloidal solutions, namely, their magnetism,[12a] color,[12b,c] conductivity,[12d] the velocity of their decomposition of diazoacetic ester,[12e] chloride ion activity[12f] and finally their composition after ultrafiltration,[12g] that the conversion to ferric hydroxide and free acid is by no means complete even on prolonged standing, although it approaches completion in the very dilute solutions. The numerical data obtained by the earlier investigators are discordant and are uncertain for several reasons. Of the more recent data only those obtained by Heymann on a single solution appear reliable; those of Quartaroli are somewhat doubtful since his solutions, except perhaps the most dilute ones, were not adequately aged.

Conductance measurements can be used to compute the extent of the final conversion provided the assumption is made that the hydrochloric acid formed and the residual ferric chloride unhydrolyzed exert their conductance unaffected by the presence of the non-conducting, colloidal ferric hydroxide. This is equivalent to the assumption that there is no significant adsorption of chloride upon the colloid in these dilute solutions, or, if adsorbed, the chloride communicates its conductance undiminished to the colloid. On this assumption, which later evidence will show to be justified, we have computed the extent of the final conversion from our conductance data by dividing the observed increase in conductance over unhydrolyzed ferric chloride by the calculated increase for complete conversion. Since the conductance of unhydrolyzed ferric chloride is not accurately known, we have used that of lanthanum chloride,[13] after careful measurements by E. B. Damon with the glass electrode had shown that it is not perceptibly hydrolyzed under these conditions at 25°.[14]

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[12] (a) G. Wiedmann, *Wied. Ann.*, **5**, 51 (1878); (b) T. Ewan, *Proc. Roy. Soc.* (London), **56**, 286 (1894); **57**, 142 (1895); (c) Antony and Giglio, *Gazz. chim. ital.*, **25**, II, 1 (1895); (d) Wagner, *Monatsh.*, **34**, 95, 931 (1913); (e) Quartaroli, *Gazz. chim. ital.*, **45**, I, 139 (1915); (f) F. L. Browne, THIS JOURNAL, **45**, 302 (1923); (g) E. Heymann, *Z. anorg. chem.*, **171**, 22 and 27 (1928); *Kolloid-Z.*, **47**, 48 (1929).

[13] Jones and Bickford, THIS JOURNAL, **56**, 602 (1934).

[14] In these measurements a MacInnes-Belcher [Duncan A. MacInnes and Donald Belcher, *Ind. Eng. Chem., Anal. Ed.*, **5**, 199 (1930)] glass electrode was used, filled with a 0.001 M solution which had been prepared from conductivity water and specially purified lanthanum chloride kindly furnished us by Dr. W. A. Ray and swept free from carbon dioxide with purified air. Preliminary measurements with this solution and with a similarly prepared solution of potassium chloride indicated no appreciable difference in the hydrogen-ion concentration of the two solutions.

These measurements in such feebly buffered solutions are, however, subject to two errors, first acidity due to the absorption of carbon dioxide from the air during the measurements, and, second, alkalinity due to the solubility of the Corning 015 glass spiral. In the final measurements the first error was eliminated by using a closed system protected by soda-lime tubes, the second by a double extrapolation of the observed potential readings to the moment of contact with the glass spiral.

This double extrapolation was accomplished by making two series

TABLE III

EXTENT OF CONVERSION IN FERRIC CHLORIDE SOLUTIONS

Concn. $FeCl_3$, $N \times 10^3$	25° Equivalent conductance, mhos HCl	25° Equivalent conductance, mhos $LaCl_3$	25° Equivalent conductance, mhos Obsd.	25° Conversion, %	35° Equivalent conductance, mhos Obsd.	35° Equivalent conductance, mhos Corr. to 25°	35° Conversion, %	75° Equivalent conductance, mhos Obsd.	75° Equivalent conductance, mhos Corr. to 25°	75° Conversion, %
10.000	411.0	121.7	347	77.9	420	363.3	83.5	664	392	93.4
4.000	416.2	129.1	388	90.2	450	389.3	90.6	675	398	93.7
2.000	419.3	133.3	399	93.3	460	397.9	92.5	693	409	96.4
1.333	420.6	135.8	402	93.5	464	401.4	93.3	...	...	..
1.000	421.4	137.1	405	94.1	469	405.7	94.5	695	410	96.0
0.800	422.0	137.9	406	94.4	469	405.7	94.3	...	...	..
.667	422.4	138.6	406	94.0	470	406.6	94.4	...	...	..
.500	423.0	139.7	410	95.2	470	406.8	94.3	...	...	..

The percentages of conversion thus obtained are listed in the fifth column of Table III and are shown graphically in Fig. 10, along with the data of Quartaroli and the single datum of Heymann referred to previously. It can be seen from this figure that our values at 25° lie on a smooth curve and are in good agreement with the previous data in those solutions where a comparison can be made.

The agreement with Heymann's value is particularly significant because this value was based on analytical determinations of ferric ion in the ultrafiltrate and involved no assumption as to adsorption on the colloidal ferric hydroxide. The agreement therefore lends reciprocal support to our underlying assumption that this adsorption was small and negligible in this connection.

The percentage conversions at 35 and 75° also have been computed from the observed values of the conductance at these temperatures after correction to 25° by multiplication by the factors 0.865 and 0.590 obtained from known data[15] for hydrochloric acid on the assumption that the temperature coefficient for the conductance of the final solution is substantially that of pure hydrochloric acid at these concentrations. These percentage conversions are listed in the eighth and eleventh columns of Table III. It can be seen that at 35° these are very slightly, at 75° definitely, greater than those at 25°. This is what would be expected from the known effect of increasing temperature on the hydrolysis of salts in homogeneous solutions.

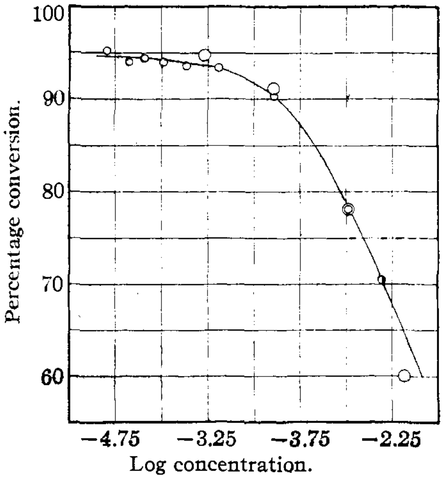

Fig. 10.—Extent of conversion of ferric chloride solutions at various concentrations: ○, Lamb and Jacques; ○, Quartaroli; ◑, Heymann.

The question next arose as to whether the solutions which had attained the greater percentage conversion at 75° on cooling to 35 and 25° would revert precisely to the lesser conversions obtained directly at these temperatures; *i. e.*, whether ferric chloride would be re-formed at these temperatures from the colloidal ferric hydroxide and hydrochloric acid to yield the same equilibrium mixture. It had already been observed[16] that a freshly prepared unhydrolyzed solution and a second portion of the same solution extensively hydrolyzed by heating, if kept at ordinary temperatures, approach the same de-

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of observations. In the first series, fresh samples of solution were introduced at seven-minute intervals and readings taken at about thirty-second intervals. The readings extrapolated to zero time gave for 8 successive runs a mean value of *p*H 7.329 with an average deviation from the mean of ±0.009. These extrapolated values are, however, too large due to the solution which takes place during the constant intervals between each run. A second series was therefore run at three-minute intervals. This, as was to be expected, gave smaller extrapolated values, the average of six successive runs being *p*H = 7.190 ± 0.007. Extrapolating these mean values linearly to a zero interval gave as a final, doubly extrapolated value, *p*H = 7.08.

The calculated value of *p*H for a 0.001 *M* solution of lanthanum chloride if there is no hydrolysis, taking Bjerrum's [N. Bjerrum, *Z. physik. Chem.*, **59**, 350 (1907)] value of 13.99 for *p*H at 25° and assuming the limiting law of Debye-Hückel for solutions of higher ionic strength, is *p*H = 7.035. The close agreement of our slightly higher observed value of *p*H with this calculated value indicates that lanthanum chloride is not appreciably hydrolyzed under these conditions.

(15) "International Critical Tables," Vol. VI, 1929, p. 242, and Noyes and others, THIS JOURNAL, **30**, 335 (1908).

(16) Foussereau, *Ann. chim. phys.*, [6] **11**, 393 (1887); Malfitano, *ibid.*, [8] **25**, 169 (1912).

gree of hydrolysis from opposite directions. Heymann[12g] had already found that a 0.015 *N* solution of ferric chloride kept at 80° until a stationary state has been reached, at which a 100% conversion to colloidal ferric hydroxide is observed, on cooling to 37°, reverted to 80% colloidal ferric hydroxide, which is the percentage conversion ultimately attained by the same ferric chloride solution kept at this temperature. He found, however, that the colloidal hydroxide formed at 80° never adsorbed as much chloride as that formed isothermally at lower temperatures.

In order to secure further evidence on this question we have measured the conductance of several solutions of ferric chloride at 75° in a quartz cell, and after a stationary state was attained have transferred them to the 35° thermostat, cooling them rapidly to this temperature, adding the water required to correct for the contraction and, as soon as thermal equilibrium was established, have again measured the conductance. With two of the solutions the experiment was repeated, except that they were chilled to 25° instead of 35°. The equivalent conductances thus obtained together with the corresponding equivalent conductances as previously observed after prolonged maintenance at the respective temperatures are given in Table IV. In this table columns are also included with the heading "Calcd." giving the equivalent conductances which the respective solutions would have exhibited had no reversion to ferric chloride taken place, based on the known temperature coefficient of conductance of hydrochloric acid.

TABLE IV

EFFECT OF SUDDEN CHILLING

Concn., m. equiv.	Final equivalent conductance 1/ohm						
		35°			25°		
	75°	Calcd.	Chilled from 75°	Direct isothermal	Calcd.	Chilled from 75°	Direct isothermal
10	664	455	442	420	392	...	...
4	675	462	458[a]	450	398	...	...
2	693	475	468	460	409	406	398
1	695	476	470	469	410	404	406

[a] After twenty-four hours at 35°, 450.

It can be seen from Table IV that in the most dilute solution cooled from 75 to 35° where the rate of change was greatest and in one of the more concentrated solutions which after cooling stood twenty-four hours at 35°, the values found in the prolonged isothermal, direct, reaction were precisely attained. In every case at least some reversion to ferric chloride took place even in the short time required for chilling, and it is reasonable to suppose that in time a precise adjustment always would have taken place. It thus appears that a reversible equilibrium is indeed established in these heterogeneous systems, at least in the case of these dilute solutions.

The general conclusions to be drawn from these experiments on the extent of conversion are then as follows. The conversion is more nearly complete the higher the temperature and the lower the initial concentration of the ferric chloride The final, stationary state is a heterogeneous equilibrium which adjusts itself in both directions, although at low temperatures this adjustment is very slow. The amount of adsorption of hydrochloric acid and of ferric chloride on the colloidal ferric hydroxide is slight and in most respects negligible, although the slightly greater conversions in acidified solutions indicate that some adsorption does take place.

II. Colorimetric Measurements

We have also followed the progress of the slow hydrolysis by measurements of the intensity of the yellow color which develops in the originally nearly colorless solutions of ferric chloride concurrently with the increase in conductivity. Extensive studies have been made of the color of ferric salt solutions prior to the onset of the slow hydrolysis[17] and Ewan[12b] has used colorimetric measurements to ascertain the extent of the conversion of ferric chloride solution on long standing, into colloidal ferric hydroxide. Goodwin[2] has suggested such measurements as a means for determining the rate of the hydrolysis, but they appear never to have been used before for this purpose. The colorimetric, as compared with the conductimetric method, has the advantages of rapidity and simplicity. Our procedure was to prepare solutions of the ferric salt employing the same technique as with the conductimetric measurements and then at measured intervals to compare the developed color with that of suitable standards.

Our colorimeter was of the Duboscq type with 110-mm. cups. It was contained in an air thermostat consisting of an inner compartment completely surrounded by an air jacket. A fan operating in an opening of the inner compartment and a heater contained in the jacket and utilizing the heater-regulator circuit described by Clark[18] main-

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[17] Gmelins "Handbuch der anorganischen Chemie," 8th Edition, Iron Part B, Verlag Chemie, Berlin, 1929, pp. 259-261.

[18] Clark, "Determination of Hydrogen Ions," 3rd Ed., Williams and Wilkins Co., Baltimore, Md., 1928, p. 363.

tained a temperature of 25.0 ± 0.1° throughout the thermostat over long periods of time. The light from a "Palo Daylight Lamp" was admitted to the inner compartment through a doubly glazed window with a 2-cm. air space between the glasses.

Solutions of various dyes were tried as color standards but were discarded because of fading. Ultimately a 0.0012 *N* solution of ferric chloride aged for two months at 25° was employed as a primary standard. This was supplemented by a similarly aged solution of half its concentration for use with solutions less than 0.001 *N*. Eye fatigue was avoided by use of a disk of light blue glass.

The solutions, after preparation, were instantly transferred to the colorimeter cup, the plunger set at a definite point and the solution of the standard brought to a precise match. At first, when the solutions were changing rapidly, only a single reading was made at each prearranged moment; later several readings were made and the results averaged. Duplicate runs were made at each concentration and the results given in the curves are based on the averages of these duplicates. Except at the beginning, when the change was very rapid, and in certain of the more deeply colored solutions, the average deviation of these duplicate runs was usually about 1% of the color of the standard.

The averaged readings were brought to a comparable basis by dividing them by the corresponding concentration and multiplying by 0.0012, the concentration of the standard solution, and have then been designated "specific colors."

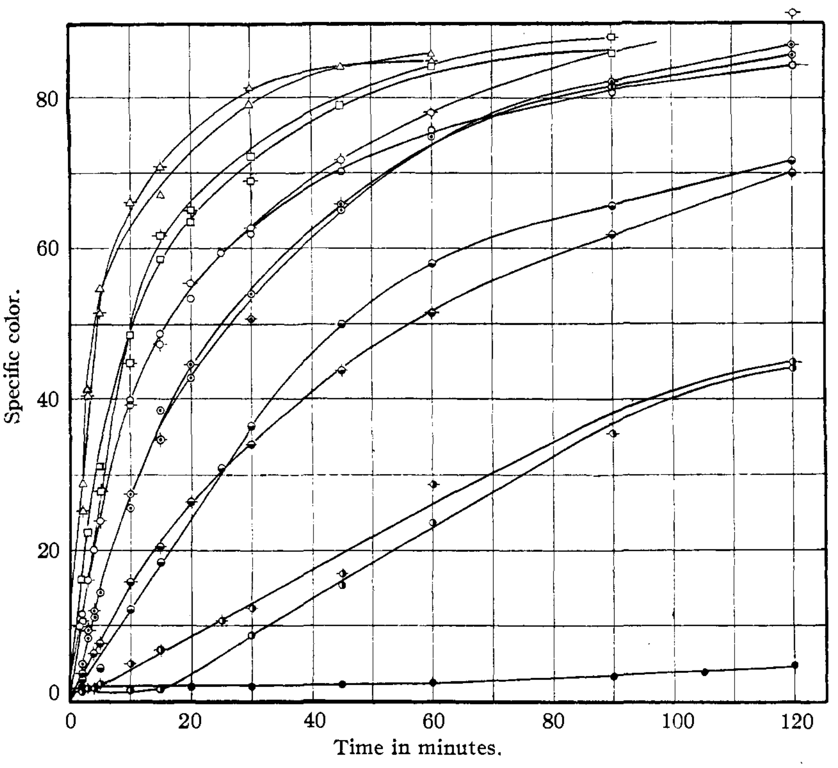

Fig. 11.—Color change during the hydrolysis of ferric chloride and nitrate solutions at 25°: Ferric chloride: ●, 0.0100 *N*; ◑, 0.00400 *N*; ◒, 0.00200 *N*; ⊙, 0.00133 *N*; ○, 0.00100 *N*; □, 0.00067 *N*; △, 0.00050 *N*. Ferric nitrate: -◑-, 0.00400 *N*; -◒-, 0.00200 *N*; -⊙-, 0.00133 *N*; -○-, 0.00100 *N*; -□-, 0.00067 *N*; -△-, 0.00050 *N*.

Results

The specific colors for ferric chloride, ferric nitrate and for ferric chloride solutions containing acid are shown as functions of time in Figs. 11 and 12.

These curves closely parallel the corresponding curves for the change of the conductance with the time as can be shown by plotting the curve (Fig. 1) for the change in the conductance of the 0.001 *N* solution of ferric chloride in Fig. 11 where the corresponding curve for the change in specific color is shown. This close parallelism indicates that the substance responsible for the color is formed commensurately with the acid liberated throughout the course of the slow hydrolysis. This substance can be nothing other than ferric hydroxide and not the various complicated basic salts postulated by many previous investigators.

Final Color.—The specific colors in the final equilibrium state were obtained by extrapolation, as in the case of the final conductances, and are collected in Tables V and VI.

Since the specific colors are only relative values they do not permit an independent calculation of the percentage conversion of the final solutions, but by taking as a standard the percentage conversion of the 0.001 *N* solution without the addition of acid, as obtained from the conductance measurements, corresponding values for the percentage conversion of the other solutions can be calculated. These are given for the ferric chloride solutions in the final row of Table V. It can be seen that the values for the more dilute solutions agree reasonably well with the corresponding values obtained from the conductance measurements (Table III). In the more concentrated solutions, however, the values for the percentage conversion become progressively greater. A similar excessive increase in the specific colors with increasing acid concentration is seen in Table VI.

TABLE V

SPECIFIC COLORS AND PERCENTAGE CONVERSION IN FINAL SOLUTIONS AT 25°

Concentration, $N \times 10^3$	10.00	4.00	2.00	1.33	1.00	0.80	0.67	0.50
Specific colors $FeCl_3$	109	118	106	104	97	99	101	93
Specific colors $Fe(NO)_3$	...	115	112	108	105	104	110	99
% conversion $FeCl_3$	105	114	102	100	[93.9]	96	97	89

TABLE VI

SPECIFIC COLORS AT EQUILIBRIUM IN FERRIC CHLORIDE SOLUTIONS WITH ADDED HYDROCHLORIC ACID AT 25°

Concn. $FeCl_3$, N	0.00100	0.000667	0.00040	0.00020	0.00010	0.00005	0.00002
0.004000	...	...	170	168	147	125	125
.001000	384[a]	...	130	121	116	110	107
.000667	...	185	138	117	113	109	109

[a] Very turbid.

A real increase of the percentage conversion with increasing concentration is out of the question and the observed effect must then be due to an increase in the specific absorption of the ferric hydroxide in the more concentrated solutions. Such an increase would result from a greater particle size in these solutions and a consequent increase in the light lost by scattered radiation (Tyndall beam).[19] A similar inference was drawn with regard to the acidified solutions in connection with the measurements of their final conductances. This inference is also supported by the macroscopic, optical properties of the solution. All the solutions hydrolyzed at 25° showed Tyndall cones when light from a 500-watt arc lamp was focused within them, but in solutions up to a concentration of 0.002 N the cones were scarcely brighter than those observed in ordinary conductivity water that had not been specially treated to remove dust. The 0.004 N solution gave a distinctly brighter cone and the 0.01 N solution a still brighter one. Indeed, the latter solution was slightly turbid to the unaided eye. Solutions of greater concentration having a yellow rather than the characteristic red-orange color of ferric hydroxide solutions were markedly turbid, exhibited strong Tyndall cones and usually deposited yellow, sandy precipitates long before equilibrium was attained.

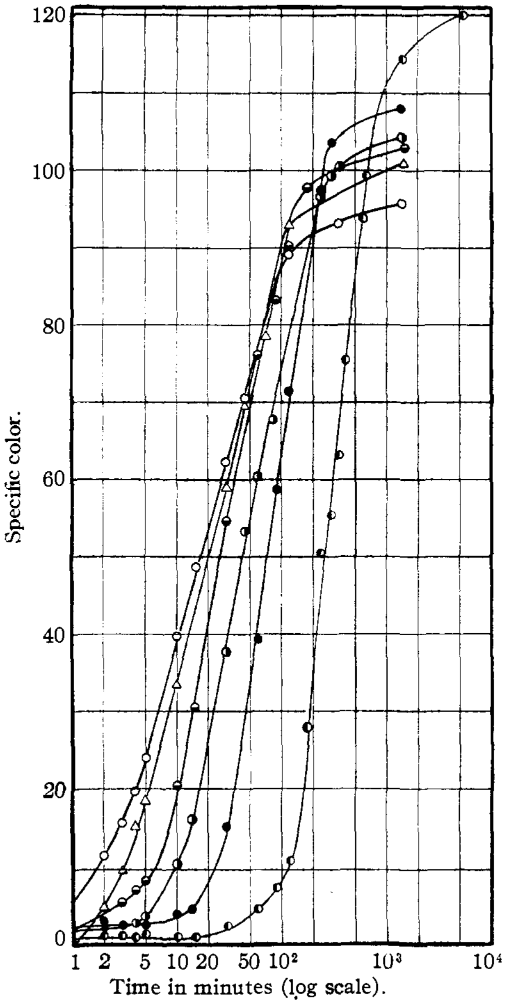

Fig. 12.—Color change of 0.00100 N ferric chloride solution in the presence of added acid: ◐, 0.00400 N; ●, 0.00200 N; ◑, 0.00100 N; ◒, 0.00050 N; Δ, 0.00020 N; ○, no acid.

Solutions hydrolyzed at 35° were all somewhat less turbid than corresponding solutions hydrolyzed at 25°. Only the 0.02 and 0.04 N solutions gave cones brighter than those in conductivity water and only the latter solution was faintly turbid. Both of these solutions, however, had the characteristic red-orange rather than yellow color of coarsely divided ferric hydroxide. The unduly intense specific color of the more concentrated and the acidified solutions can, therefore, be reasonably explained as due to the greater coarseness of the

[19] Garnett, *Phil. Trans.*, **A203**, 385 (1904); **A205**, 237 (1906); Svedberg, "Die Entstehung der Moleküle," Leipzig, 1912, p. 29.

colloidal particles of ferric hydroxide that they contain.

The colorimetric evidence, therefore, not only indicates that ferric hydroxide is formed throughout the course of the slow hydrolysis rather than a basic chloride, but it is also in accord with the conclusion drawn from the conductance measurements that in the dilute solutions only a slight and in most respects a negligible amount of chloride is adsorbed on the colloidal ferric hydroxide. They also indicate that the colloid particles of ferric hydroxide are coarser in the acidified and the more concentrated solutions.

III. The Chloride-Ion Concentration

Some information is already available in the literature as to the amount of chlorine present in or adsorbed upon the colloid in equilibrium with the hydrolyzed solution of ferric chloride, at least in the case of the more concentrated solutions. Browne,[20] from measurements with the calomel electrode in ferric chloride solutions "which had reached hydrolytic equilibrium," calculated the amounts of ferric chloride and hydrochloric acid present therein. From his results it follows that, while in 0.004 N solution *no* adsorption takes place, in more concentrated solutions adsorption does take place, becoming progressively greater as the concentration increases, until in 0.257 N solution the colloidal ferric hydroxide would appear to contain 9 atoms of chlorine per atom of iron! More credible and unequivocal evidence was obtained by Heymann[12g] who, at intervals during the slow hydrolysis of a 0.015 N solution of ferric chloride, withdrew samples of the intermicellar liquid by ultrafiltration and analyzed them for chloride. Simultaneously the amount of colloid formed up to that time was ascertained. From these data it followed that the colloid formed during the first stages of the slow hydrolysis contained as much as 0.3 atom of chlorine per atom of iron; later the content of chlorine diminished rapidly to 0.15 atom of chlorine per atom of iron and remained constant at that value indefinitely thereafter.

In order to obtain further evidence as to the concentration of chloride ion in these solutions during slow hydrolysis and hence the amount of chlorine held by the ferric hydroxide colloid, particularly in the dilute solutions with which we are here concerned, we have measured the potential of the silver–silver chloride electrode in a 0.001 and a 0.004 N solution of ferric chloride at intervals during the course of the slow hydrolysis.

The electrodes were prepared according to the directions of MacInnes and Parker[21] and two agreeing to within 1 mv. were selected. A saturated ammonium nitrate solution was used as a salt-bridge and measurements were made by means of a sensitive potentiometer, a Compton electrometer being used partly as a null and partly as a measuring instrument. A 0.1 N solution of hydrochloric acid served as the known solution and a temperature of 25.00 ± 0.01° was maintained.

The rapidity and accuracy of adjustment of potentials on these electrodes were demonstrated by removing a pair of electrodes from the 0.1 N hydrochlorc acid solution in which they were regularly kept immersing one of them in standard 0.1 N, the other in standard 0.001 N hydrochloric acid connected by a salt-bridge and observing at intervals the potential. After 0.5, 1, 2, 3 and 4 minutes this was 0.1098, 0.1112, 0.1132, 0.1138 and 0.1138 v., respectively. On replacing the salt-bridge by a fresh one the final constant value changed to 0.1144 v. Allowing for the constant difference of 0.7 mv. shown between these two electrodes in the same solution before and after the measurements, the constant final potentials were 0.1131 and 0.1137 v. The potential calculated from the known activities of the two solutions is 0.1135 v.[22] These results show that the definitive potential is reached after two minutes to within a millivolt and after three minutes to within a few tenths of a millivolt, and that this definitive potential is very nearly the potential calculated from the known activities.

To make a measurement the two silver chloride electrodes were removed from the 0.1 N solution of hydrochloric acid in which they were regularly kept, washed thoroughly with conductivity water, dried with filter paper and then allowed to dry further in the air for about five minutes. Meanwhile the solution of ferric chloride was prepared at a prearranged moment, employing the same technique as had been followed in the conductivity measurements, and a sample was placed in one arm containing a 0.101 N solution of hydrochloric acid. The salt-bridge was then inserted and a measurement made.

Results

The observed potentials corrected for slight differences in the individual electrodes are listed in Table VII. From them, after subtraction of the above 0.1137 v. in order to refer them to the definitive 0.001 N solution of hydrochloric acid whose activity was taken as 0.000965 on the basis of the computations of Randall and Young,[23] the activities listed in the second column of Table VII were computed.

These activities were in turn converted into concentrations by a semi-empirical method, de-

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(20) Browne, THIS JOURNAL, **45**, 292 (1923).

(21) MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

(22) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 336.

(23) Randall and Young, THIS JOURNAL, **50**, 989 (1928).

pending upon the fact that very little chloride could have been removed from the solution by adsorption upon it or by the formation of any insoluble basic chloride. The observed potentials in the initial solution were therefore used to establish empirically the activity coefficient of chloride ion in them and this coefficient was then applied to the subsequent measurements in proportion to the concentration of residual ferric salt. Additive corrections for the effect of the hydrochloric acid corresponding to the colloid formed were also applied, based on the activity coefficients as given by Randall and Young.

TABLE VII

CONCENTRATION OF CHLORIDE DURING SLOW HYDROLYSIS

TEMPERATURE 25°

Time, min.	E. m. f. obsd., v.	Activity chloride $M \times 10^3$	% colloid	Concn. chloride $M \times 10^3$
		0.000333 M $FeCl_3$		
3	0.1155	0.900	16	1.01
4	.1155	.900	16	1.01
5	.1155	.900	21	1.00
10	.1156	.897	36	0.98
15	.1164	.869	43	.95
20	.1158	.890	49	.97
30	.1159	.886	57	.96
45	.1156	.897	63	.96
60	.1158	.890	66	.95
90	.1149	.921	70	.98
120	.1146	.932	74	.99
150	.1143	.943	76	1.00
180	.1142	.946	78	1.00
24 hrs.	.1141	.950	86	1.00
6 wks.	.1143	.943	(90)	0.98
		0.001333 M $FeCl_3$		
3	0.0810	3.70	1.7	4.00
4	.0810	3.70	2.7	4.00
5	.0810	3.70	5.0	4.00
6	.0807	3.73	6.0	4.03
9	.0813	3.65	8.0	3.94
15	.0814	3.64	11.0	3.92
30	.0808	3.72	16.0	3.99
60	.0814	3.64	26.0	3.88
90	.0812	3.64	30.0	3.87
120	.0811	3.68	34.0	3.90
180	.0807	3.73	42.0	3.93
240	.0809	3.71	49.0	3.89
6 wks.	.0808	3.72	(70.0)	3.85

The broad inference from these results is that throughout the slow hydrolysis there is at most only a small change in the potential of the chloride electrode or in the activities and concentrations computed from them. The observed potentials exhibit irregular variations of about ±0.4 mv. and a slight downward trend of about this same numerical magnitude. The resultant irregular variation in the activities and concentrations is about 2%. No definite trend in the concentrations can be seen in the case of the 0.001 *N* solution, but in the case of the 0.004 *N* solution the final concentrations are about 3% smaller than the initial ones.

Since any such deficit in the final solutions is doubtless due to adsorption of chloride on the colloid, our results in the case of the 0.004 *N* solution indicate that only about 0.16 atom of chlorine is present in the colloid per atom of iron. In the case of the 0.001 *N* solution our results show that this ratio must be much smaller, certainly no greater than 0.07 atom of chlorine for every atom of iron. These ratios are in general agreement with the observations of Heymann[12g] above mentioned.

A later communication will present additional information as to this slow hydrolysis derived from measurements with the glass electrode.

Summary

1. By using solutions freshly prepared from the anhydrous salt, reproducible values of the changing conductance of ferric salt solutions during their characteristic slow hydrolysis have been obtained over a considerable range of concentration and temperature, with and without the addition of acids. The previously observed marked increase in the speed of the hydrolysis with increasing dilution and temperature and the induction period in the most concentrated solutions have been confirmed. The previously observed pronounced decelerating effect of acids such as hydrochloric and nitric upon the hydrolysis has also been confirmed, but, contrary to certain prior findings, this effect is found to prevail even at extreme dilution and after subsequent as well as prior addition of acid to the system. Sulfuric acid exerts a duplex effect: a continuing deceleration characteristic of acids in general, and an initial acceleration due apparently to the marked adsorption of the sulfate ion by the colloidal ferric hydroxide.

2. From these measurements the extent of the final conversion to hydrochloric acid and colloidal ferric hydroxide has been computed over a considerable range of concentrations and temperatures. The conversion is more nearly complete the higher the temperature and the lower the initial concentration of the ferric chloride. The final, stationary state is a heterogeneous equilibrium which adjusts itself in both directions, al-

though at low temperature this adjustment is relatively slow. The amount of adsorption of hydrochloric acid and of ferric chloride on the colloidal ferric hydroxide also is slight and in most respects negligible, although the slightly greater conversion in acidified solution indicates that some adsorption does take place.

3. The progress of the slow hydrolysis of ferric chloride and nitrate has also been followed by measurements of the color which develops in these solutions. The curves thus obtained have been found to parallel closely the corresponding curves obtained from the conductance measurements, indicating that a single colored substance, ferric hydroxide, is formed commensurately with the liberated hydrochloric acid responsible for the increase in conductance.

4. The potential of the silver–silver chloride electrode has been measured in dilute solutions of ferric chloride at intervals during the slow hydrolysis. In 1.3 millimolar solution a barely measurable while in a 0.3 millimolar solution no change in concentration of chloride ion is observed. This confirms the inferences from the conductance measurements as to a negligible adsorption of chloride on the colloidal ferric hydroxide in dilute solution.

CAMBRIDGE, MASS. RECEIVED JANUARY 12, 1938

NOTES

Rapid Exchange between Deutero-ammonia and Hydrazine

BY PAUL C. CROSS AND PHILIP A. LEIGHTON

Measurements of the photochemical decomposition of ND_3–N_2H_4 mixtures were undertaken recently in this Laboratory for the purpose of obtaining additional experimental data upon which to base a study of the mechanisms of the photodecompositions of ammonia, hydrazine, and ammonia–hydrazine mixtures.[1] Unfortunately, as far as the original intentions were concerned, the experiments showed that the exchange equilibrium was established by a rapid thermal exchange under all the experimental conditions employed, thus nullifying the value of the deuterium as an indicator.

Estimates of the rate of this exchange were obtained by the analysis, using a quartz fiber manometer, of the hydrogen–deuterium mixture from the thermal decomposition products of both the ammonia and the hydrazine of a mixture which had been separated by distillation at the temperature of an alcohol–carbon dioxide bath. The hydrogen and deuterium were separated from the nitrogen by diffusion through a palladium thimble under conditions which allowed the diffusion equilibrium to be established quickly, thus avoiding uncertainties due to diffusion-fractionation. The thermal decomposition was carried out on the heater of the palladium thimble. Contamination from previous samples was minimized by thorough outgassing of the compartments on both sides of the thimble with the latter at a temperature considerably higher than that used for the separation. The probable error of the analyses is of the order of 3 to 5%.

To quote a typical experiment, approximately 10 mm. of each ND_3 and N_2H_4 were mixed and in contact for about thirty seconds at 26.5° before the hydrazine was frozen down. The ammonia then analyzed 39% deutero-, and the hydrazine 45% deutero-. Mixtures from which the hydrazine was frozen down within a few seconds after mixing showed similar analyses. There was even evidence of an exchange between solid N_2H_4 and gaseous ND_3 at temperatures as low as $-70°$, as demonstrated by the following results: 10 mm. of N_2H_4 was frozen down and an equal amount of ND_3 introduced. A sample of ammonia taken at once analyzed 101% deutero-. After twenty-five minutes the ammonia analyzed 96% deutero-, and after six hours, 86%. The trend is unmistakable, and is definitely larger than the likely error in the analyses. At the conclusion of this run the hydrazine was evaporated with the remaining ammonia and immediately frozen down again, after which the ammonia analyzed 40% deutero-.

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(1) E. O. Wiig, THIS JOURNAL, **59**, 827 (1937); H. J. Welge and A. O. Beckman, *ibid.*, **58**, 2462 (1936); R. A. Ogg, Jr., P. A. Leighton and F. W. Bergstrom, *ibid.*, **56**, 318 (1934); E. O. Wiig and G. B. Kistiakowsky, *ibid.*, **54**, 1806 (1932); A. Farkas and P. Harteck, *Z. physik. Chem.*, **B25**, 257 (1934).