the intermediate reactions. The exact mechanism of this secondary catalysis is not yet clear.

Summary

1. A small amount of copper salt greatly accelerates the decomposition of hydrogen peroxide by iron salts in acid solution. Other metallic salts do not appear to have this "promoter effect."

2. For a given concentration of iron salt, either sulfate or chloride, there is a maximum rate of reaction with about 1 millimole per liter of added copper salt. This maximum effective concentration of copper appears to be independent of the concentration of iron salt.

3. The extent of promotion (measured by the "promotion factor," which is the ratio of the maximum rate to the normal rate for the iron alone) is independent of the acid concentration and temperature.

4. The extent of promotion is much greater for ferric sulfate than for ferric chloride, although the maximum rate obtained in each case is the same. The promotion factors for the two systems approach each other as the concentration of iron approaches zero.

5. The facts are best explained by the following assumptions regarding the mechanism of promotion. (a) The iron salt is the primary catalyst, by virtue of its ability to form an intermediate compound. (b) The copper salt is a secondary catalyst, accelerating both the formation and subsequent decomposition of the intermediate product. The effect of the secondary catalyst is dependent upon its concentration only for very small quantities, a maximum effective concentration being noticeable. The mechanism of this secondary catalysis has not yet been completely explained.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY, No. 420]

FERRIC SALT AS THE "SOLUTION LINK" IN THE STABILITY OF FERRIC OXIDE HYDROSOL[1]

BY ARTHUR W. THOMAS AND ALEXANDER FRIEDEN

RECEIVED JUNE 13, 1923

Ferric oxide hydrosol was first prepared by Arnold Maus.[2] It was regarded as a chemical compound[3] until the introduction of the process of dialysis. Péan de St. Gilles[4] and Thomas Graham[5] looked upon it as

---

[1] This work was completed in February, 1922, and is adapted from the dissertation submitted by Alexander Frieden in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1922.

[2] Maus, *Ann. Phys. Chem.*, 11, 75 (1827).

[3] Souberain, *Ann. chim. phys.*, **44**, 325 (1830). Rose, *Ann. Phys. Chem.*, **24**, 301 (1832). Schönbein, *ibid.*, **39**, 141 (1836). Scherer, *ibid.*, **44**, 453 (1838). Berzelius, "Lehrbuch der Chemie," **1845**, vol. III, p. 555.

[4] Péan de St. Gilles, *J. prakt. Chem.*, [1] 66, 137 (1855).

[5] Graham, *Phil. Trans.*, 161, 183 (1861).

a soluble form of ferric hydroxide containing "impurities" but it soon became apparent[6] that at least some of the impurities associated with this modification of hydrated ferric oxide were necessary for its stability in solution, as was found in the case of diverse colloidal dispersions, resulting in the evolution of the complex theory of colloids.[7]

Numerous attempts have been made to determine the relationship of the adsorbed electrolyte to the adsorbent, ferric oxide.[8] Of these, the work of Linder and Picton,[9] Malfitano,[10] and Nicolardot[11] are important, though of little quantitative significance in the light of improved methods of investigation available at the present time. Interesting quantitative relationships have been obtained by Neidle,[12] by Pauli and Matula[13] and, since the completion of this work, by Mathews and Browne,[14] and by Browne.[15]

The object of this research was to obtain quantitative relationships between the substances that make up the colloidal particles and to determine the amount of electrolyte required to keep the particles dispersed.

Method

Preparation of the Hydrosols.—(1) About 14 *M* ammonium hydroxide solution was delivered drop by drop from a buret into a 3 *M* solution of ferric chloride, which was continually and vigorously agitated by a motor stirrer. The addition of ammonium hydroxide solution was continued until the resultant precipitate was peptized with great difficulty.

(2) Ammonium hydroxide was added as above until a permanent precipitate was just formed; 0.33 *M* ferric chloride solution was then added, and the mixture stirred until the precipitate dispersed.

(3) To a hydrosol prepared by Method 1 ferric chloride solution was added until the entire sol precipitated, and the resulting precipitate was dispersed in distilled water.

(4) Fifty cc. of *M* hydrochloric acid was added to a freshly prepared and washed precipitate of ferric hydroxide prepared from 250 cc. of 3 *M* ferric chloride solution. The mixture was allowed to stand until the precipitate was peptized.

---

[6] Kastner, *Ann. chim. phys.*, [3] **57**, 231 (1859). Debray, *Compt. rend.*, **59**, 174 (1864). Magnier de la Source, *ibid.*, **90**, 1352 (1880). Wiedemann, *Ann. Phys. Chem.*, [3] **5**, 45 (1878). Wagner, *Kolloid Z.*, **14**, 149 (1914). Wyrouboff, *Ann. chim. phys.*, **7**, 449 (1905). Hantz and Desch, *Ann. Chem.*, **323**, 38 (1902). Ruer, *Z. anorg. allgem. Chem.*, **43**, 85 (1905).

[7] von Weimarn, "Zur Lehre der Zustande der Materie," Theodor Steinkopff, Leipzig, **1914**, vol. 1, p. 60. Beans and Eastlack, THIS JOURNAL, **37**, 2667 (1915).

[8] Krecke, *J. prakt. Chem.*, [2] **3**, 286 (1871).

[9] Linder and Picton, *J. Chem. Soc.*, **87**, 1919 (1905).

[10] Malfitano, *Compt. rend.*, **139**, 1221 (1904); **140**, 1245 (1905); **141**, 660, 680 (1905); **143**, 172, 1141 (1906); *Z. physik. Chem.*, **68**, 232 (1909).

[11] Nicolardot, *Ann. chim. phys.*, **6**, 334 (1905); *Compt. rend.*, **140**, 310 (1905).

[12] Neidle, THIS JOURNAL, **39**, 2334 (1917).

[13] Pauli and Matula, *Kolloid Z.*, **21**, 49 (1917).

[14] Mathews and Browne, THIS JOURNAL, **43**, 2336 (1921).

[15] Browne, *ibid.*, **45**, 297 (1923).

The hydrosols prepared by the first two methods were blood-red and perfectly clear to reflected and transmitted light. Those prepared by the third method were clear to transmitted, but slightly turbid to reflected light, while the sols prepared by the last method were decidedly turbid to reflected, although clear to transmitted light.

Dialysis.—Cups[16] of very fine, unglazed porcelain were first tried as dialyzers. It was found, however, that these were permeable to ferric ions for only a short time. After a few days of dialysis, there was but a slight amount of ferric ion in the diffusate, though the hydrosol in the cup contained a large amount of ferric chloride. Evidently the membrane of ferric oxide formed within the walls of the cup is impermeable to ferric ion.

Unglazed porcelain cups could not, therefore, be used at this stage of dialysis. In subsequent dialysis experiments, in which all of the unadsorbed ferric chloride had left the solution and further dialysis was merely a slow hydrolysis, porcelain cups of smaller size and thinner wall were employed. These were permeable to chloride and hydrogen ions.

For the preliminary dialysis, collodion bags were employed. These bags were prepared in a 2-liter Florence flask and were changed as soon as a coating of ferric oxide had been formed on the walls of the membrane, in order to speed up the process of dialysis. Some of these sols were dialyzed at room temperature and others at 60°. The diffusate was changed every 24 hours, distilled water being used throughout. The preliminary dialysis was considered complete when the diffusate of 24 hours, usually 1 liter in volume, acidified and evaporated to 10 cc., showed no color upon addition of 5 cc. of *M* ammonium thiocyanate solution. In view of the high delicacy of this test for the ferric ion, its concentration in the hydrosol is negligible at this point. (The ratio[17] of the concentration in moles of ferric oxide to that of ferric chloride, $Fe_2O_3/FeCl_3$, was about ten at this point.) The test for the ferric ion as given by ammonium thiocyanate applied to the sol directly was negative long before this ratio was reached. The ammonium chloride formed in the preparation of the sol disappeared within a comparatively short time.

The length of time required for the completion of dialysis varied from 2 to 5 months, depending upon the concentration of the sol and the temperature at which the dialysis was performed. Excessive dilution of the dialyzing hydrosol was avoided by having the level of the water in the outer vessel much lower than that of the hydrosol inside.

---

[16] Obtained from Coors Porcelain Company, Golden, Colorado.

[17] The values given throughout this paper were obtained as follows. The chlorine found by analysis was calculated to ferric chloride; the ferric chloride computed to ferric oxide which was subtracted from the total ferric oxide (from total iron found by analysis), giving the values of ferric oxide cited.

Analyses

Iron.—The solution was evaporated with sulfuric acid until fumes of sulfur trioxide formed and was then reduced in a Jones reductor and was determined by titration with potassium permanganate.

Chlorine.—To a definite volume of the hydrosol, nitric acid was added to make the final concentration about 3 *M*. The covered beaker was allowed to stand in the dark until all of the ferric oxide had dissolved, which usually required a week or 10 days. Approximately 0.1 *M* silver nitrate was then added in excess of the amount necessary to precipitate all the chloride. A slight variation in the procedure was to add the silver nitrate before the addition of nitric acid. Separate experiments on pure potassium chloride showed that the procedures could be used interchangeably, and that there was no danger of loss of chloride by oxidation. The chloride concentration was determined either gravimetrically or by the method of Volhard.

Experimental Part

At the beginning of this investigation, measurements of the conductivity of ferric oxide hydrosol during dialysis were made in the hope of getting quantitative indication of an end-point in the purification. The measurements showed, as anticipated, that the conductivity gradually decreases as dialysis proceeds, but after a certain time the hydrosol showed a conductivity lower than that of the distilled water against which it was being dialyzed. The conductivity of ferric oxide hydrosol has been reported by several investigators,[10,13,18] but the results differ widely because of the variable quantities of peptizing electrolyte present and are obviously of no value.

Due to the failure of the conductivity method, the measurement of the depression of the freezing point was tried, and since this also failed to serve our purpose (see later), the observation of beginning of precipitation was adopted as end-point in dialysis. The incipience of precipitation does not mean the coagulation of the hydrosol, since thereafter precipitation proceeds gradually, the system assuming a turbid appearance which increases with continued dialysis until finally the entire sol becomes a gel.

Two and one-half liters of a sol (Fe_2O_3, 9.3105; $FeCl_3$ 0.7143 g./liter; ratio, 13) was dialyzed for 4 weeks at room temperature against a volume of 1 liter of distilled water, the outside water being changed several times each day for the first week and once a day thereafter. Samples were withdrawn for analysis at frequent intervals until precipitation began. At this point the hydrosol contained 3.2653 g./liter of ferric oxide and 0.1539 g./liter of ferric chloride, that is, a molar ratio, $Fe_2O_3/FeCl_3$, of

---

[18] Duclaux, *Compt. rend.*, **140,** 1468 (1905); *Kolloid Z.*, **3,** 126 (1908). Goodwin and Graver, *Phys. Rev.*, **9,** 251 (1896); **11,** 193 (1900). Dumanski, *Z. physik. Chem.*, **60,** 553 (1907).

21.5. The dialysis was continued for 10 weeks, until all of the sol was converted to a gel in which the molar ratio of ferric oxide to ferric chloride was 48.

A sol was dialyzed at 60° for 10 weeks. At the end of this time, the 24-hour diffusate when evaporated to 10 cc. gave no test for ferric ion. The sol then contained 8.1017 g./liter of ferric oxide and 0.8397 g./liter of ferric chloride. When precipitation began (after 18 days) the hydrosol contained 1.1961 g./liter of oxide and 0.0593 g./liter of chloride thus showing a molar ratio of 20.5.

This would seem to indicate that dilution has no marked effect on the point at which precipitation begins.[19] To verify this, two sols of molar ratios 11.7 and 12.9 were made up to various dilutions and dialyzed in collodion bags to the first appearance of a precipitate. The two series showed identical results, the first of which is described in Table I.

TABLE I

EFFECT OF DILUTION ON END-POINT

Dilution	none	1.87	3.04	7.75	13.80
Fe_2O_3, g./l.	4.1838	2.3144	1.3711	0.5396	0.3019
$FeCl_3$, g./l.	0.3637	0.1118	0.0650	.0266	.0149
Ratio of Fe_2O_3 to $FeCl_3$	12[a]	21	22	21	21

[a] Original sol. not dialyzed to incipience of precipitation.

It was deemed probable that the gradual precipitation, which sets in after the initial appearance of precipitate, might be due to excessive hydrolysis and dialysis near the walls of the collodion bags. If so, this would affect the limiting ratio. To test this probability, a series of sols was dialyzed in small, unglazed porcelain cups. The solutions were stirred throughout the entire period by a current of nitrogen, kept at a temperature of 50–60°, and analyzed when a turbidity became perceptible.

The data in Table II are taken from one of two series of different sols which gave identical results. The sol used in Table II contained 5.867 g./liter, of ferric oxide and 0.3743 g./liter, of ferric chloride; ratio = 16.

TABLE II

EFFECT OF DILUTION ON END-POINT

Dilution	none	1.33	2.00	2.66	4.00
Fe_2O_3, g./l.	4.9186	3.6492	2.3434	1.6119	1.4292
$FeCl_3$, g./l.	0.2453	0.1829	0.1160	0.0934	0.0669
Ratio of Fe_2O_3 to $FeCl_3$	20	20	21	20	22

Following the incipience of precipitation, gradual flocculation was observed in all cases. Analyses of samples of such sols showed that their molar ratios of ferric oxide to ferric chloride gradually increased as dialysis

---

[19] The value at which incipience of precipitation is found and the fact that dilution of the sol does not affect it are not in agreement with the experience of Neidle, Ref. 12.

continued to final complete precipitation. These analyses were not very accurate because it was impossible to free the hydrosol entirely from precipitated particles that were held in suspension. Centrifuging at about 1000 "times gravity" for the purpose of removing these suspended particles frequently resulted in the breaking out of the entire dispersed phase from dispersion in the form of a fairly continuous jelly phase. This is rather significant in that it suggests a jelly-like structure of this hydrosol. Due to the inaccuracies of the analyses the results are not reported, but it is of interest to recall that Duclaux[20] claimed that ferric oxide hydrosol could be dialyzed to a limiting value of 170 $Fe_2O_3 . 1FeCl_3$.

Since the dispersed phases of hydrosols, prepared as just described, migrate to the cathode when subjected to the action of an electrical current, the particles are said to be positively charged due to the ferric chloride of the complex, the ferric ions thereof remaining in contact with the ferric oxide while the chloride ions are located in the water phase directly bathing the particles. Since like charged bodies repel one another, the electrical charges of the particles are supposed to overcome the mutual attractive forces of the particles, a rather commonly accepted explanation for the stability of inorganic colloidal particles.

According to this explanation, the limiting ratio of ferric chloride to ferric oxide should increase with increased concentration of the particles, since the mutual attractive force varies inversely as some power of the distance between the particles. The more closely the particles are packed, the greater should be the charge required to keep them repelling one another.

Examination of the data reveals no such tendency. Apparently the electrical charge is not the predominating factor for the stability.[21] The

---

[20] Duclaux, *Compt. rend.*, **143**, 296 (1906).

[21] In connection with this statement it is timely to quote the criticism of the electrical charge theory of stability recently made by Porter and Hedges [*Phil. Mag.*, **44**, 641 (1922)]: "If the particles really contained charges all of one sign only they would tend to move toward the boundary. This is the equivalent of the fundamental electrical fact that statical charges reside close to the surface of conductors. When we are dealing with large particles instead of electrons, there is no doubt that they would occupy a larger region, instead of a thin superficial area, but still there would be an accumulation at the boundary. This is the opposite to what is observed." "But the charges in the solution are not only of one sign. The solution, as a whole, is uncharged; consequently an equal opposite charge is to be looked for. This opposite charge is the second member of the double layer close to the surface of each particle. When the existence of this double layer is recognized, the electric forces between the particles become zero, except insofar as relative displacement takes place by induction between two members of a layer so as to give it an electrical movement. In this case the force between two such doublets in the equilibrium state will, on the average, be an *attraction* and not a repulsion."

In his famous paper on the "Mathematical Theory of the Kinetics of the Coagulation of Colloidal Solutions," M. v. Smoluchowski [*Z. physik. Chem.*, **92**, 129 (1917)] arrives at conclusions identical with the statements of Professor Porter quoted above.

fact that the limiting ratio, that is, the point corresponding to incipience of precipitation, is always nearly the same[22] indicates that regardless of the concentration of the sol, 1 mole of ferric chloride is required to keep about 21 moles of ferric oxide dispersed in the colloidal condition.[23] Any amount of ferric chloride in excess of this ratio might be regarded as impurity. The stability of the ferric oxide hydrosol must then be due not to the electrical charge of the particles but to the solution forces (solubility) of the adsorbed ferric chloride. The high solution forces of the ferric chloride molecules pull the ferric oxide particles with which they are combined by secondary valence or "adsorption forces" into semisolution. Upon removal of the ferric chloride by hydrolysis the insoluble particles of ferric oxide, having lost their "solution-link," precipitate.

According to the "solution-link" hypothesis this hydrosol should be soluble in any liquid in which ferric chloride dissolves. It was found that dilution of the hydrosol with an unlimited amount of alcohol had no effect upon its appearance, nor did the addition of ether to this alcosol precipitate it, provided a large excess was not added.

An iron oxide hydrosol stabilized by ferric sulfate should be precipitated by alcohol according to the hypothesis. Such a sol was prepared resembling the Péan de St. Gilles sol in appearance. Addition of alcohol precipitated it instantly.

Hydrogen-Ion Concentration.—Pauli and Matula[18] attempted to measure the hydrogen-ion concentration of ferric oxide hydrosols. Good results were obtained by them when using sols which had "aged" for 6 months or which were heated for a few hours at 80°, this being equivalent to aging, that is, hydrolyzing excess ferric chloride. Their measurements had to be made quickly and their platinum electrodes were saturated with hydrogen before coming in contact with the hydrosol to be measured. The results indicated that the hydrosols were neutral,[24] that is, had a hydrogen-ion concentration of the order of 10^{-7}.

Measurements of hydrogen-ion concentration would be impossible in the presence of ferric ion for obvious reasons. Using well dialyzed sols in which the concentration of ferric ions was supposedly nil, we found no evidence of a reducing potential but could not get what is considered to be an absolutely satisfactory equilibrium reading due to the deposition of ferric oxide gel upon the platinized electrode. However, taking the mean of a series of readings which were not widely divergent, a hydrogen-

[22] The slight deviations from the value of 21 may be ascribed as due to errors in the determination of the end-point of dialysis by means of the observation of the beginning of precipitation.

[23] This is the "purity" at which Browne (Ref. 15) found the heat of coagulation of ferric oxide hydrosol to be practically zero.

[24] Very recently, Browne (Ref. 15) using a similar method also reports that ferric oxide hydrosols are neutral.

ion concentration of $10^{-4.9}$ was indicated. This was the same for a series of our "pure" hydrosols of various concentrations and consequently the hydrogen-ion concentration does not appear to depend upon the concentration of the dispersed phase, at least over the range which we studied. We should say that our "pure" ferric oxide hydrosols showed a hydrogen-ion concentration of 10^{-5}.

An acid reaction is to be expected, since upon dialysis of sols from which the free ferric chloride has been removed only hydrogen and chloride ions are found in the diffusate across the collodion membrane. Consequently, the ferric chloride of the dispersed phase is in equilibrium with the ions of hydrochloric acid in the dispersion medium, which in the case of our "pure" sols is of the order of 0.00001 *M*.

Behavior upon Freezing.—As previously mentioned, freezing-point depression was tried as a quantitative method for following purification, but it was found that a well dialyzed sol gives a depression of the freezing point within the range of experimental error of measurement with the Beckmann thermometer.

Péan de St. Gilles was inclined to regard his hydrosols as true solutions because they froze in a "normal" manner. In 1889, Ljubawin[25] froze, among other colloidal substances, ferric oxide hydrosol and found that as the liquid cooled, particles of ferric oxide concentrated in the center while the periferous layers of the ice became colorless. When the mass was melted again, all of the iron oxide particles redispersed. Lottermoser[26] found that only those sols which are deficient in electrolyte were precipitated on freezing. Sols rich in electrolyte were not affected even upon continued freezing.

Our experiments showed that when a pure ferric oxide hydrosol is only partially frozen, ice crystals are formed which upon melting leave the sol as homogeneous in appearance as it was before the operation. But when cooling is continued until freezing is complete, some precipitation is noted when the mass melts. The longer the sol has been cooled, the greater will be the amount of gel formed. The precipitate is in the form of short, amorphous, shiny, needle-like particles. When the sol is allowed to remain in contact with the ice-salt mixture for some length of time, the entire solution turns to a dark red, solid mass. When cooling is continued separation of the water begins as a layer of colorless ice near the walls of the test-tube, and such layers continue inward until, in the center, there are deposited the red brown particles above described. These particles are arranged in a string-like formation throughout the height of the tube. When the ice is melted they do not redisperse. The water obtained by melting the ice shows a barely perceptible test for chloride ion and none

---

[25] Ljubawin, *Z. physik. Chem.*, **4**, 486 (1889).

[26] Lottermoser, *Ber.*, 41, 3976 (1908).

for ferric ion. The gel particles are practically insoluble in dil. nitric acid, but readily soluble in concentrated acid. Analysis showed that about 80% of the ferric chloride of the original hydrosol particles was retained in this gel. This behavior is quite different from that of Bredig gold hydrosols upon freezing, since Beans and Beaver[27] find that all of the stabilizing electrolyte is removed from the gold particles through the congelation.

These observations support the conclusion that the stability of these hydrosols is due to the solution forces of the adsorbed ferric chloride rather than to the electrical charge of the particles.

The ferric chloride in the congelation gel from the pure sols must be dispersed throughout the compact solid mass, for although there is sufficient ferric chloride present to redisperse the particles, at least partially, such redispersion does not take place; but when an impure sol is frozen, that is, one to which some ferric chloride has been added, the gel particles redisperse upon melting; this is like the experience of Gutbier and Flury[28] with selenium oxide sols.

Relationship Between Graham's Hydrosol and the So-Called "Meta-iron" Hydrosol of Péan de St. Gilles. Water of Hydration.—The hydrosol that Péan de St. Gilles prepared by heating and boiling solutions of the acetate differed slightly in properties from Graham's in that it was not so clear and that a precipitate formed on continued heating which was insoluble in concd. acids but soluble in dil. acids and water. Graham, in analogy to the two modifications of tin oxide sol, called it the "meta-iron" oxide hydrosol, an appellation that is still used.

In the course of this investigation, it was found that this conception of two modifications of ferric oxide hydrosol is not justifiable, the main difference between the two being water of hydration of the particles, as suggested by others.[29,30]

This was demonstrated as follows. A hydrosol prepared by Method 3 was dialyzed at room temperature until it showed the molar ratio, $Fe_2O_3/FeCl_3 = 18$. A portion of this sol was then dialyzed in a porcelain cup at about 60° while it was continuously stirred with nitrogen and was analyzed (a), after 5 days of dialysis, and then again (b) after 9 days. In (a) incipience of precipitation was not evident while in (b) a decided precipitation had started. The ratios of $Fe_2O_3/FeCl_3$ were (a) 20 and (b) 26. Another hydrosol prepared by peptizing ferric hydroxide gel with a small amount of hydrochloric acid was dialyzed as described above. This initially turbid sol increased in turbidity as dialysis was continued so that

---

[27] D. J. Beaver, *Dissertation*, Columbia University, 1921.

[28] Gutbier and Flury, *Kolloid Z.*, **29**, 161 (1921).

[29] Roscoe and Schorlemmer, "Treatise on Chemistry," D. Appleton and Co., 1900, vol. 2, p. 998.

[30] Bancroft, *J. Phys. Chem.*, 19, 232 (1915).

the beginning of precipitation could not be determined accurately. When the end-point was presumed to have been reached, it showed upon analysis a ratio, $Fe_2O_3/FeCl_3 = 23$.

It is thus seen that the limiting value for these "meta-iron oxide," or Péan de St. Gilles' sols is of the same magnitude as that of the Graham sol. This would indicate that the turbidity of this sol is due to dehydration rather than to the presence of larger ferric oxide aggregates.

Since, according to Einstein,[31] the viscosity of a colloidal dispersion is expressed by the formula $\eta' = \eta(1 + kf)$, where η' is the viscosity of the system, η the viscosity of the dispersion medium, and f the ratio of the total volume of the dispersed phase over the total volume of the system, which means as Wo. Ostwald[32] and others have shown that the viscosity of a colloidal solution increases with the amount of the dispersion medium taken up by the dispersed phase, the Péan de St. Gilles sol should have a lower viscosity than the Graham sol of the same concentration if our supposition is correct.

To determine whether this is the case, 10cc. portions of a Graham hydrosol were treated with various amounts of 2 *N* ferric chloride solution until the turbidity which first appeared gradually changed to a coarse bright yellow dispersion[33] and the viscosities were measured.

The measurements were made by means of an Ostwald viscometer, in a constant temperature bath at 25 ± 0.01°. Table III shows the results. The figures signify the time in seconds for outflow.

Table III

Viscosity of Graham Hydrosol, No. 15

FeCl$_3$ added Expt.	Cc.	Time. Sec.	Comparative data	Time Sec.
2	0.1	73	Pure hydrosol (Expt. 1)	81
3	0.2	73	Distilled water	71
4	0.3	74	10 cc. dist. water + 2 cc. of 2 *N* FeCl$_3$	80
5	0.5	75	10 cc. dist. water + 10 cc. of 2 *N* FeCl$_3$	137
6	1.0	78		
7	2.0	99		

No. 1 was perfectly clear; Nos. 2, 3, 4 and 5 were clear to transmitted, but turbid to reflected light. They resembled the Péan de St. Gilles sol in all respects. The turbidity gradually increased with increasing amounts of ferric chloride. No. 6 was decidedly brown while No. 7 was yellow. After three hours, the viscosities were again measured and found to be unchanged.

From these results it is seen that the addition of ferric chloride first decreases the viscosity and then increases it. The decrease in viscosity

---

[31] Hatschek, *Kolloid Z.*, **7**, 301 (1910); **8**, 34 (1911).

[32] Wo. Ostwald, *Trans. Faraday Soc.*, **9**, 34 (1913).

[33] A sol so treated is identical in appearance with the "meta-iron oxide" modification.

indicates a diminution in size of the particles which could only have been caused by a loss of water of hydration by the dispersed phase. The increase in viscosity observed upon the addition of larger amounts of ferric chloride is due to the coalescence of the particles preliminary to precipitation.

As to the mechanism of the dehydration of the sol by ferric chloride, we can only venture to say that it is possibly due to the high hydration of the electrolyte added, thus causing a partial dehydration of the dispersed Fe_2O_3–$FeCl_3$–H_2O phase, or in view of the fact that this sol migrates in an electrical field showing that the adsorbed and peptizing electrolyte is ionized, even though the degree be extremely small, then the Donnan effect of the added ferric chloride would result in a decrease in swelling (hydration) of the dispersed phase as in the case of the addition of hydrochloric acid or a neutral salt to gelatin jelly swollen in a solution of hydrochloric acid. Both suggested mechanisms may operate at the same time.

Summary

Evidence is submitted which indicates that the stability of ferric oxide sol, stabilized by ferric chloride, is due to the solubility (or solution forces) of the adsorbed ferric chloride in the dispersion medium, rather than to the mutual repulsive forces of the particles presumed to reside in their electrical charges of like sign. The so-called "meta-iron" sol of Péan de St. Gilles is one in which the particles of the dispersed phase are less hydrated than in the Graham ferric oxide hydrosol.

New York, N. Y.

[Contribution from the Chemical Laboratories, Columbia University, No. 421]

THE MECHANISM OF THE MUTUAL PRECIPITATION OF CERTAIN HYDROSOLS[1]

By Arthur W. Thomas and Lucille Johnson

Received June 13, 1923

The literature[2] concerning the mutual precipitation of hydrosols treats this phenomenon as an electrical one by which the positively charged particles of one hydrosol neutralize the negatively charged particles of the

---

[1] Adapted from the dissertation submitted by Lucille Johnson in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, New York City, May, 1923.

[2] Linder and Picton, *J. Chem. Soc.*, 71, 586 (1897). Lottermoser, "Anorg. Kolloide," Stuttgart, 1901, p. 77; through Zsigmondy-Spear, "Chemistry of Colloids," Wiley and Sons, New York, 1917, p. 56. Bechhold, *Z. physik. Chem.*, 48, 385 (1904). Neisser and Friedman, *Münch. Med. Wochschr.*, **51**, 465, 827 (1904). Henri, *Compt. rend. soc. biol.*, **55**, 1666 (1903). Teague and Buxton, *Z. physik. Chem.*, **60**, 489 (1907). Spring, *Bull. acad. roy. Belg.* (Sciences), **1900**, p. 483. Biltz, *Ber.*, **37**, 1095 (1904). Billitzer, *Z. physik. Chem.*, **51**, 129 (1905).