HYDROUS OXIDES. I

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Hydrous Ferric Oxide

In a recent communication on adsorption by hydrous ferric oxide,[1] prepared by the method of Péan de St. Gilles, attention was called to some interesting and important properties of the precipitated oxide that will now be considered in detail.

HISTORICAL

Preparation of Colloidal Ferric Oxide

The Péan de St. Gilles Colloid.—Péan de St. Gilles[2] prepared colloidal ferric oxide by continued boiling of a solution of ferric acetate. The red-brown color which is characteristic of the acetate became brick-red as the boiling continued and the peculiar taste of ferric salts gave place to that of acetic acid. The colloid was distinctly turbid in reflected light, but was perfectly clear in transmitted. Potassium sulphocyanate did not change the color, whereas the solution of the ordinary acetate was appreciably reddened. Potassium ferrocyanide as well as all the other potassium salts, produced a brown ochreous precipitate which assumed a green shade after long standing.

"A trace of sulphuric acid or of an alkaline salt precipitates all the iron in the form of a red-brown deposit that is insoluble in the cold in all acids even the more concentrated. By boiling it is dissolved by hydrochloric acid, but is not attacked by nitric.

"When the liquid is poured into hydrochloric acid there is formed a finely divided, granular, brick-red precipitate which readily settles to the bottom of the vessel. This precipitate, which in appearance in no way resembles the ordinary ferric hydroxide, may be washed without change with the same acid, however concentrated; and even may be treated

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[1] Weiser and Middleton: Jour. Phys. Chem., **24**, 30 (1920).

[2] Comptes rendus, **40**, 568, 1243 (1855).

with water. But if the salt water, together with most of the acid enclosed by the precipitate, is removed by one or two decantations with distilled water, the solid disappears at once with the formation of a brick-red, opalescent liquid, similar in every respect to that originally obtained. An indefinite number of alternate precipitations and dissolutions can be carried out if hydrochloric or nitric acid is employed; but if any other acid is used with the exception of acetic, the precipitate once formed will no longer redissolve in water."

Scheurer-Kestner[1] obtained a similar modification of the hydrous oxide by heating a solution of ferric nitrate for three days at 100°. The addition of a few drops of hydrochloric acid precipitated the oxide, which was dried on a porous plate and later was peptized with water, forming a tasteless brick-red liquid. Krecke[2] prepared it by heating a $^1/_2$ percent solution of ferric chloride for a suitable length of time at 100° to 130°. Giolitti[3] has extended the experiments of Péan de St. Gilles on the colloid prepared by boiling the acetate. He confirmed the interesting observation that the physical character of the precipitated colloid was different with different precipitating agents. He found that the addition of a small quantity of sulphurous, sulphuric, selenious, iodic, periodic, boric or phosphoric acid produced a gelatinous precipitate that was not redissolved by water; while the addition of a small amount of hydrochloric, hydrobromic, hydriodic, nitric, perchloric or perbromic acid caused slight precipitation of a finely divided brick-red powder, which could not be removed by ordinary filtration. The addition of a larger amount of the latter group of acids caused complete precipitation and the powder was readily peptized by water as Péan de St. Gilles observed.[4]

The Graham Colloid.—Graham[5] prepared a colloid that

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[1] Ann. Chim. Phys., (3) **57**, 23 (1850).

[2] Jour. prakt. Chem., (2) **3**, 286 (1871). Cf. Debray: Comptes rendus. **68**, 913 (1869).

[3] Gazz. chim. ital., **35**, II, 181 (1905).

[4] Cf. Weiser and Middleton: Loc. cit.

[5] Jour. Chem. Soc., **15**, 250 (1862).

differs in certain respects from the Péan de St. Gilles colloid by the dialysis of a ferric acetate solution in the cold; or more usually, by peptizing gelatinous ferric oxide in ferric chloride solution and then dialyzing out the excess ferric chloride. This colloid is colored deep reddish brown and is comparatively clear. "The red solution is coagulated in the cold by traces of sulphuric acid, alkalis, alkaline carbonates, sulphates and neutral salts in general; but not by hydrochloric, nitric and acetic acids nor by alcohol or sugar. The coagulum is a deep red-colored jelly resembling the clot of blood, but more transparent." The precipitate can not be peptized by washing by either hot or cold water; but it is readily dissolved in dilute acids. On the other hand, the Péan de St. Gilles precipitate is relatively insoluble in acids and under certain conditions can be peptized by water. Graham considered his colloid to be ordinary hydrated "peroxide" of iron and the Péan de St. Gilles colloid to be "metaperoxide" of iron.

Krecke[1] obtained the Graham hydrous peroxide by hydrolysis of ferric chloride at concentrations ranging from $^1/_{16}$ to 1 percent at temperatures from 20° for the more dilute solutions to 83° for the more concentrated. Solutions of higher concentration up to 32 percent gave the same product at higher temperatures, but ferric chloride was re-formed when the temperature was lowered. Biltz[2] obtained the Graham colloid by dialysis of a dilute solution of ferric nitrate. Grimaux[3] prepared a similar product by pouring an alcoholic solution of ferric ethylate into water. Neidle[4] oxidized ferrous chloride with hydrogen peroxide and dialyzed.

The Composition of Colloidal Ferric Oxide

The Question of Hydrates.—The colloid prepared by boiling the acetate gives much more intense light cones[5] since it is more granular and less hydrous than the Graham colloid.

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[1] Loc. cit.

[2] Ber. deutsch. chem. Ges., **35**, 4431 (1902).

[3] Comptes rendus, **98**, 105, 1434 (1884).

[4] Jour. Am. Chem. Soc., **39**, 2334 (1917).

[5] Zsigmondy-Spear: "Chemistry of Colloids," 163 (1917).

This is due to the dehydration and agglomeration of the particles of the former at the higher temperature. The same thing may be accomplished by long standing of the latter at a lower temperature. Thus Giolitti[1] found that the Péan de St. Gilles colloid was fairly uniform, whereas the Graham colloid changed gradually from the more hydrous to the less hydrous form on standing. Zsigmondy found that certain commercial colloids prepared by the Graham method have properties that lie intermediate between the newly formed Graham colloid and the Péan de St. Gilles colloid. The effect of temperature and time of standing on the degree of hydration of hydrous ferric oxide, both precipitated and colloidal, has been the subject of numerous investigations, chiefly for the purpose of establishing the existence or non-existence of definite hydrates. Thus, Péan de St. Gilles[2] writes: "Having observed the transformation produced by a temperature of 100° on the acetic acid solution of ferric hydrate, I determined what would happen at the same temperature on the same hydrate in the free state.

"I prepared the hydrate by decomposing ferric chloride in the cold with ammonia (brown chocolate hydrate) and also with bicarbonate of soda (yellow ochreous hydrocarbonate). When assured that the precipitate was entirely free from alkali by washing a great number of times with cold water, I suspended it in water and heated it. After boiling some time, manifest action was noted by a change in the color of the precipitate and especially, by the property it had acquired of no longer dissolving completely in concentrated nitric or acetic acid. On continuing to heat the hydrate on the water bath I noted that little by little it took on the brick-red color, characteristic of the modified acetate. In this condition not only acetic but also dilute nitric and hydrochloric acids caused the precipitate to disappear instantly producing a liquid, cloudy by reflected light but clear by transmitted; and colored

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[1] Loc. cit.

[2] Comptes rendus, 40, 1244 (1855).

brick-red. In a word, it was similar in all respects to the substance produced directly from the acetate."

Péan de St. Gilles[1] considers that the brick-red colloid has the composition $Fe_2O_3.H_2O$. Schiff[2] claims to have gotten the same thing by keeping precipitated hydrous ferric oxide for many years at ordinary temperature. Wittstein[3] says that the hydrate $Fe_2O_3.3H_2O$ is obtained by precipitating a ferric salt with ammonia and drying for a short time at 100°. Brescius' experiments[4] indicate that there are no definite hydrates of ferric oxide; but Ramsay[5] believes he prepared the hydrate $Fe_2O_3.H_2O$ by drying the precipitated oxide to constant weight at 100°. Tommasi[6] recognizes two series of oxides, yellow and red, the properties of which depend on the method of preparation. The members of the red series are obtained by precipitating a ferric salt with alkalis. These hydrates dissolve in dilute acids and are dehydrated even by boiling water. The members of the yellow series are obtained by oxidation of ferrous hydrate or carbonate. According to Tommasi the members of the two series are identical in composition, but differ in color and stability. The yellow hydrates are denser; are but sparingly soluble in concentrated acids; and require a higher temperature to dehydrate them. Moreover, they retain a molecule of water even on long boiling with water.[7] Carnelley and Walker[8] conclude from their investigations that no definite stable hydrates are formed, inasmuch as the precipitated hydrous oxide loses water gradually and continuously from 15° to 500° where Fe_2O_3 is formed.

Van Bemmelen[9] has made an extended study of both the yellow and red hydrous oxides under various conditions and

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[1] Ann. Chim. Phys., (3) **46,** 47 (1856).

[2] Chem. Centralblatt, (2) **5,** 1768 (1860).

[3] Ibid., (1) **24,** 367 (1853).

[4] Jour. prakt. Chem., (2) **3,** 272 (1871).

[5] Jour. Chem. Soc., **32,** 395 (1877).

[6] Bull. Soc. chim. Paris, (2) **38,** 152 (1833).

[7] Cf. Muck: Zeit. für Chemie, 41 (1868).

[8] Jour. Chem. Soc., **53,** 89 (1888).

[9] Rec. trav. chim. Pays-Bas., **7,** 106 (1888); Zeit. anorg. Chem., **20,** 185 (1899).

has shown with considerable certainty that there is but one definite crystalline hydrate of ferric oxide and that this can be prepared only under special conditions—the decomposition of sodium ferrite by water at ordinary temperature.[1] In the hydrous oxides as ordinarily prepared, the ratio of oxide to water depends entirely on the method of treatment. Thus a certain reddish brown colloid exposed to air for a year contained 4 to 4.1 moles of water.[2] In dry air this fell to 1.6 moles, in 4 months. By heating to 100° in dry air, the composition fell to 0.96 mole, but the final composition depends on the state of aggregation. A particular sample kept for 6 months contained 1 mole of water at 15°, which went to 0.45 mole in only 5 hours at 100°. Between 100° and 300° the dehydration was slow and regular to about 0.25 mole, but if heated sufficiently long at any intermediate temperature the result was the same. After heating at temperatures between 100° and 300° the oxide regained only a part of its water when placed in an atmosphere saturated with moisture. The yellow colloid showed similar variations. It contained 2.43 moles of water when dry but when kept for a month in a saturated atmosphere it contained 7.4 moles. When heated from 15° to 270° in a stream of dry air, the water fell from 1.7 moles to 0.24 mole. Above 200° the composition was the same as the reddish brown colloid, but between 50° and 300° it retained its water more strongly. From these results, and a large number of others, van Bemmelen concluded that a hydrate with a definite composition was obtained only by chance. "The determinations of the water content of the substances prepared in different ways by different investigators (Davies, Lifort, Péan de St. Gilles, Wittstein, Schaffner, Muck, Tommasi, etc.) are of no value other than representing the transient and accidental state of the colloid."

Mineralogists distinguish at least six hydrates of ferric oxide: Haematite, Fe_2O_3; Turgite, $Fe_2O_3.{}^1/_2H_2O$; Göthite, $Fe_2O_3.H_2O$; Limonite, $Fe_2O_3.{}^2/_3H_2O$; Xanthosiderite, Fe_2O_3.-

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[1] Van Bemmelen and Klobbie: Jour. prakt. Chem., 46, 497 (1892).

[2] Cf. Spring: Rec. trav. chim. Belg., 17, 222 (1898).

$2H_2O$; and Limnite, $Fe_2O_3.H_2O$. Of these, haematite is sometimes found in nature as a well crystallized substance; but of the hydrates, göthite only occurs in a definite crystalline form. Ruff[1] has heated freshly-prepared, red ferric oxide under 5000 atmospheres and claims to have gotten definite hydrates. Between 30° and 42.5° he claims to get limonite; between 42.5° and 62.5° göthite, and above this hydro-haematite. A yellow non-crystalline hydrate, $Fe_2O_3.{}^2/_3H_2O$, prepared by the oxidation of moist hydrous ferrous oxide, was unchanged between 40° and 70° under high pressures. From this he concludes that the yellow hydrate is a compound of constant composition.

In the light of all the investigations it seems probable that not more than one definite crystalline hydrate of ferric oxide exists. The different formulas mean merely that a number of hydrous oxides of variable water content have been analyzed under such conditions that their percentage composition happened to approach that of a definite hydrate. It is very unlikely that any of the colloidal solutions of ferric oxide contain definite hydrates. Bancroft[2] concludes that any number of hydrous ferric oxides can be prepared differing among themselves in the degree of hydration and the size of the particles. This is borne out by Zsigmondy's observation that the small hydrous particles of the Graham colloid go over gradually to the larger, less hydrous particles of the Péan de St. Gilles colloid.

The Question of Basic Salts.—The colloid prepared by Graham's method is comparatively free from electrolytes, but it always contains traces of chlorides that can not be removed completely, however long the dialysis may be continued.[3] On this account a number of investigators consider the various dialyzed colloids as chlorides of condensed ferric hydroxide like, $Fe_2(OH)_6.{}^1/_{150}Fe_2Cl_6$, or as oxychlorides of

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[1] Ber. deutsch. chem. Ges., **34**, 3417 (1901).

[2] Jour. Phys. Chem., **19**, 232 (1915).

[3] Linder and Picton: Jour. Chem. Soc., **87**, 1920 (1905); Ruer: Zeit. anorg. Chem., **43**, 85 (1905); Desch: Liebig's Ann., **323**, 28 (1902).

variable composition. This idea was advanced by Wyrouboff[1] and his pupils and was later taken up by Jordis,[2] Duclaux,[3] Linder and Picton,[4] Nicolardot,[5] Malfitano,[6] Michel,[7] and others.[8] Thus, Nicolardot finds that the colloid in which the ratio of iron to chlorine in equivalents is 6, gives no tests for ferric and chloride ions by adding potassium ferrocyanide or sulphocyanate and silver nitrate, respectively.[9] He concludes that at this point in the dialysis the colloid contains a definite compound, a ferric oxychloride. He states further that after continuing the dialysis for several months, no more hydrochloric acid can be removed; and then the ratio of iron to chlorine in equivalents is 125. He considers this to be another definite compound and believes that all ratios between these two result from mixtures of the two compounds. Neidle[10] points out that Nicolardot's conclusions do not represent the facts and concludes from his own investigations that clear hydrous ferric oxide sols. containing ferric ion may contain a definite oxychloride which is a colloid having the ratio, 21 equivalents of iron to 1 of chlorine. He postulates the existence of other theoretical oxychlorides and attributes the increasing stability of the colloids with increasing hydrochloric acid content, to the reversal of hydrolysis and the formation of stable oxychlorides. On the other hand, Giolitti[11] concludes that there is no evidence for the existence of oxychlorides of definite composition in the colloidal ferric oxides;

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[1] Bull. Soc. chim. Paris, **21**, 137 (1899).

[2] Zeit. anorg. Chem., **35**, 16 (1903); Zeit. Elektrochemie, **10**, 509 (1904).

[3] Comptes rendus, **138**, 144, 809 (1904); **140**, 1468, 1544 (1905); **143**, 296, 344 (1906); Jour. chim. phys., **5**, 29 (1907).

[4] Loc. cit.

[5] Ann. Chim. Phys., (8) **6**, 344 (1905).

[6] Malfitano and Michel: Comptes rendus, **145**, 185, 1275 (1907); Malfitano: Zeit. phys. Chem., **68**, 232 (1909).

[7] Comptes rendus, **147**, 1052, 1288 (1908).

[8] Neidle: Jour. Am. Chem. Soc., **39**, 2334 (1917); Dumanski: Zeit. Kolloidchemie, **8**, 232 (1911).

[9] Cf. Ruer: Loc. cit. and Desch: Ibid.

[10] Loc. cit.

[11] Gazz. chim. ital., **36**, 1157 (1906); cf. Van Bemmelen: Zeit. anorg. Chem., **36**, 380 (1903).

and Fischer[1] points out that if there are any basic ferric chlorides, they can be stable only at low temperatures. From a study of the system: ferric oxide, hydrochloric acid and water, Cameron and Robinson[2] find that no definite basic chlorides are formed at 25°.

It seems to the author that the existence of colloidal oxychlorides of definite composition is doubtful; and moreover, that it is of questionable use to postulate the formation of a series of complex oxychlorides to account for the properties of the different hydrous oxides; particularly, when the independent existence of no single one has been established with any degree of certainty. The properties can be explained from the point of view of specific adsorption. Any number of hydrous ferric oxides are possible, differing among themselves in the degree of hydration and the size of the particles, both of which factors affect the amount of adsorption. The colloid prepared by the Graham method is formed in the presence of ferric chloride, ferric ions and hydrogen ions. Accordingly we might expect the colloid to adsorb some ferric chloride and it will always adsorb ferric, hydrogen, and chloride ions in amounts depending on the nature of the colloid, the specific adsorbability and the concentration. Now it is well known that a substance always shows a strong tendency to adsorb its own ions and hydrogen ion is usually very strongly adsorbed; on the other hand, chloride ion is not strongly adsorbed, as a rule, and this preferential adsorption results in a stable positive colloid. It is likely that most of the chloride ion present in the Graham colloid is not adsorbed by the hydrous oxide but its concentration is a measure of the adsorbed ferric and hydrogen ions which give the colloid its stability. Adsorbed chloride ion will not give a test with silver nitrate. Moreover, Ruer[3] has shown that the presence of small amounts of unadsorbed chloride in the presence of colloidal iron oxide can not be detected by precipitation with silver nitrate, since

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[1] Zeit. anorg. Chem., **66**, 38 (1910).

[2] Jour. Phys. Chem., **11**, 690 (1907).

[3] Zeit. anorg. Chem., **43**, 85 (1905).

the protecting action of the hydrous oxide does not allow the particles of the silver chloride to become large enough to cause turbidity. Since there is an equilibrium between the amount of a substance adsorbed and the amount in solution, prolonged dialysis will result in the loss of part of the adsorbed cations (together with an equivalent amount of anions) and this will decrease the stability of the colloid. It is unnecessary to postulate the existence of oxychlorides of varying composition to account for the observation that only a part of the chlorine present appears to exist as ion.[1]

The Color of Hydrous Ferric Oxide

That hydrous ferric oxide exists in a variety of colors varying from yellow to violet-red is evident from the colors of the minerals. Thus, haematite is black when crystalline and red when powdered; turgite is a deep brown; limonite varies from a light brown to yellow; and limnite is a full yellow.[2] By referring to the formulas usually assigned to these minerals, it might seem that the yellow color is a question of hydration of the oxide. This can not be the case as pointed out by Robinson and McCaughey:[3] "By heating limonite or any hydrate of ferric oxide, it loses water, changes color and becomes in fact red haematite. There is, however, no satisfactory measurement of a temperature of inversion of limonite to haematite, and it is doubtful if such an inversion point exists. At ordinary pressures limonite does not lose water appreciably at any temperatures which may be realized under field conditions."

As has been stated, the preparation of both yellow and red ferric oxides was accomplished a long time ago by Muck, whose work was extended by Tommasi. The latter clearly implied that the color was not a question of degree of hydration, since he assigned the same formula to hydrous oxides of different color. Antony and Giglio[4] and Goodwin,[5] at about

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[1] See Dumanski: Loc. cit.

[2] Dammer's, "Handbuch der anorganische Chemie," **3**, 304 (1893).

[3] Bureau of Soils, Bull. **79**, 18 (1911).

[4] Gazz. chim. ital., **25**, 1 (1895).

[5] Zeit. phys. Chem., **21**, 1 (1896).

the same time and independently, made the interesting observation that the conductivity of a dilute solution of ferric chloride increases on standing and that this is accompanied by color changes. "I observed also that the solution which was as good as colorless at the start became quickly yellow-red and then brown-red." Nicolardot[1] recognized four modifications of hydrous ferric oxide: white, dark brown, yellow and red. He obtained the white hydrous oxide by pouring a concentrated solution of a ferric salt into cold liquid ammonia. He believed that the different colored forms were derived from the colorless oxide by molecular condensation. Moreover, he suggested that the red oxide was an open chain compound while the yellow was of cyclic nature. Malfitano[2] ascribed the different colors of the colloidal oxide to different complex compounds of the general type of the cobalt amines. Although the existence of a series of complex salts of widely varying composition is improbable, the experimental work recorded in Malfitano's paper is of particular importance, since it brings out the relationship between the size of particles and the color of hydrous ferric oxides. Accordingly, I will quote from it in some detail:

"Freshly prepared ferric chloride solutions are clear and run through the collodion membrane completely. After a while, and the quicker the weaker the solution and the higher the temperature, the solution undergoes a marked change. The hydrolysis of the solution produces color changes and the solution appears heterogeneous. Three cases can be distinguished:

"(a) Dilute solutions (*e. g.*, 1 percent) at low temperatures (25° to 50°) and the more concentrated solutions slowly heated to 100° assume an ochre-yellow color, become opalescent and opaque; and if the concentration is sufficiently high, a precipitate forms which settles to the bottom of the clearing solution. In this solution the ultramicroscope reveals particles which appear on an almost entirely dark back-

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[1] Comptes rendus, **140**, 310 (1905).

[2] Zeit. phys. Chem., **68**, 232 (1910).

ground. The ultrafilter retains all the colloid as the filtrate is entirely clear and is not clouded by the addition of potassium chloride and sulphate. If one completes the filtration while exerting a slight pressure on the inside of the filter, the colloid agglomerates on the bottom of the little sack and forms a very thin solid residue.

"(b) Ferric chloride solutions of like concentrations when they are suddenly heated to 100° assume a red-brown color becoming heterogeneous; but less so than in the previous case. However a precipitate never forms. Small particles of very different sizes are seen with the ultramicroscope. In contrast to the former case, the background on which the particles appear is clear, since most of the particles are too small to be observed optically; but they serve to light up the background of the field. By ultrafiltration this solution gives a filtrate, which at the outset is entirely homogeneous, possesses a light yellow color and is not clouded by the addition of electrolytes; soon, however, there passes through the filter a redder solution, which appears homogeneous in the nepheloscope but becomes quite cloudy on the addition of hydrochloric acid, potassium chloride or potassium sulphate. There is, therefore, an extremely finely divided colloid which runs through the membrane. It should be noted that the colloid can exist in complete solution, homogeneous to light.

"If the ochre-yellow liquid in case (a) were filtered through the membrane, the latter is intensely colored after the filtration. It is impregnated with the iron compound and its electrical nature has changed. Before this filtration it became negative during electric osmose; after filtration it became positive. After the membrane was changed in this way, it allowed the red solution through unchanged. The micellae of small dimensions appear to settle firmly in the pores of the membrane or else they fix themselves on these pores only at the outset. After the membrane is impregnated they can run through, but the membrane always retains a part of the colloid as a thick slimy solution or as a doughy precipitate. In order to get a large amount of colloidal material, one must take a slightly permeable collodion membrane.

"(c) If the ferric chloride solution is heated to a high temperature (134°) or is kept for a long time at 100°, the liquid which was red-brown at the outset goes over into a brick-red. The heterogeneity becomes pronounced, and there form differently colored plates and finally even a precipitate. In such a solution one can detect the presence of particles of large dimensions without the ultramicroscope. By ultrafiltration is obtained a red-brown filtrate and within the sack there remains a pulverulent precipitate.

"As we see therefore the colloid is composed of particles of different size, depending on the nature and method of the hydrolysis. * * * * "

"If we dissolve the residue after filtration in pure water we find the dimensions of the micellae easily change.

"(a) The residue of ochre-yellow colloid can be suspended again quite readily and one can repeat this process frequently. It loses in this way a part of its chlorine and at the same time loses the property of dividing itself uniformly in the solution.

"(b) The residue from the filtration of the red-brown colloid which partly runs through the membrane, forms a quite stable colloid with water. If this is filtered again, the iron compound goes through the membrane; and if the solution is put on a new membrane, the latter is not colored at all. Therefore it is proven beyond doubt that impregnation of the membrane is a question of the dimensions of the micellae. By repeated washing, the colloid continues to lose more and more of its chlorine forming cloudy solutions which are stable, nevertheless. The residue, after a long series of filtrations, becomes more doughy and firm. By optical study it appears that the micellae decrease in number and increase in dimensions.

"(c) If the residue, after filtration of the solution which has become brick-red by long heating, is taken up with water, there is obtained a very heterogeneous and unstable solution.

Even after the first washing one can observe particles visible under the microscope and can detect them even with the unaided eye. They remain in solution but a short time and then settle to the bottom with different velocities.

"The dimensions of the particles are different, therefore; but not only this, the dimensions can easily change. In the main, as the colloid loses chlorine, the nuclei appear to group into ever-increasing masses. These masses can either remain in the solution or more or less readily settle out. One can also realize the reverse process:

"(a) If we add a ferric chloride solution to the ochre-yellow colloid which consists of large micellae, it goes into stable solution again. However, this solution is always very cloudy, no matter how much ferric chloride has been added. If this colloid is suspended in hydrochloric acid solution again, it takes up chlorine without appreciably changing its state of division. If a sufficient amount of hydrochloric acid is added, it precipitates the colloid. Afterwards this precipitate is attacked slowly by the acid and dissolves again as ferric chloride. The solutions of all other electrolytes with the exception of hydrobromic and nitric acids are unable to diminish the size of the particles; in general, they cause an increasing of the size and precipitation of the colloid.

"(b) If one adds ferric chloride to the residue after filtration of the red-brown colloid, it undoubtedly forms smaller micellae, for the colloid henceforth appears in the filtrate. If this colloid is now heated with ferric chloride, the color goes over into ochre-yellow and the entire colloid precipitates out. The red colloid can, therefore, be changed into the ochre-yellow colloid which one obtains also by slow heating or by gentle heating for a long time. If there is added to the residue after filtration of the red colloid, a hydrochloric acid solution which is more concentrated than that which has been removed by filtration, it must form small micellae, as the new solution appears a little cloudy and there is less acid in the solution than was added. The colloid adsorbed chlorine and with the same pressure of filtration, the volume of the residue is greater than before the addition of acid. If a larger amount of hydrochloric acid is added, the phenomenon changes. There is found in the filtrate not only the colloid but hydrochloric acid as well; and the residue becomes less voluminous and more doughy. If the amount of acid is further increased, the solution of the colloid is not only cloudy but deposits a sediment. If, soon thereafter, the solution is diluted, the precipitate vanishes and the colloidal solution is relatively stable. However, the precipitate changes slowly in the presence of a large amount of hydrochloric acid; it becomes insoluble and brick-red, exactly like the precipitate which was obtained by continued strong heating of ferric chloride solutions. Finally, the precipitate is attacked by the acid and changed to ferric chloride. The same phenomena can be observed in the presence of nitric acid. The other electrolytes never decrease the dimensions of the micellae; those with univalent anions increase the size of the micellae if they are present in large amount; those with polyvalent anions cause this even in slight concentration, thus precipitating the colloid.

"(*c*) If the brick-red colloid is treated like the two others, the same results obtain; however, the change appears more rapidly than with the ochre-yellow colloid and not stepwise as with the red-brown colloid.

"We see therefore that the size and with this also, the other properties of the colloidal solution alter as a function of the composition of the intermicellar liquid. In a few cases the change in the size is reversible; in a few others it is permanent."

Malfitano's investigations show clearly that a close relation exists between the color and size of the particles of hydrous ferric oxides. As before stated, he considers that the different colored colloids are different compounds of complex nature. This opinion is not shared by Fischer,[1] who believes that the parent substance or "K_0 substance" is a simple well-defined chemical compound: "By a physical-chemical method I have succeeded in showing the probable existence and formulas

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[1] Zeit. anorg. Chem., 66, 37 (1910).

of basic chlorides like $Fe_2Cl_5(OH)$. However, these substances appear to be stable only at low temperatures, say 0°; at 80°, their period of existence is but a few seconds at the most. Then they are decomposed by hydrolysis. For this reason their presence is entirely out of the question among the following mentioned substances prepared by long-continued hydrolysis at high temperatures. Besides, the chlorine content is much too small to suffice for a chemical compound of the normal type. Therefore, the only compounds that can be considered as K_o substances are oxides or hydrated oxides."

Fischer has made some interesting observations on the relationships among the different colored hydrous oxides, natural and artificial: "As van Bemmelen has shown, the gel alters only very slowly at low temperatures, therefore a method must be found for appreciably increasing the ageing process. To do this a method is known which consists of heating in the presence of acids or bases. By this process, the iron hydroxides must dissolve as a compound to a certain, even if small, degree; and must again separate out in a form poorer and poorer in energy and therefore older, in the same way as small crystals grow together into larger ones by prolonged action of the solvent. In this way a form of a definite "age" is obtained, the sooner the greater the solution is hydrolyzed, that is, the diluter and warmer it is.

"The first product of the hydrolysis of a ferric chloride solutions is the red-brown colloid of van Bemmelen. It results whenever one should expect the appearance of $Fe(OH)_3$, that is, by hydrolysis and by the precipitation of iron salts by alkalis. Its composition as a function of the vapor pressure of water is given by van Bemmelen.

"By the action of hydrochloric acid on this there is formed the yellow colloid which, to my knowledge, was first observed by Goodwin. It betrays its presence even in slight amount by a green opalescence; if more is formed the solution becomes very cloudy, opaque and opalescent in reflected light, while it is transparent with a deep red-brown color in transmitted light.

"The time which the yellow colloid needs for its formation can be determined easily by the opalescence; and so one can test the above-mentioned rule that heat and dilution favor the reaction; and it was found to hold true. The vessel must be cleaned by boiling with concentrated hydrochloric acid since an inoculation hastens the clouding. The velocity of the change is influenced also by the amount of hydrochloric acid present. For example, in a solution in which $^1/_5$ of the chlorine is neutralized, no yellow colloid appears in three hours, while the same solution without the addition of a base becomes cloudy in a short time. Likewise the solution in boiling water becomes cloudy in proportion to the amount of base added. If the suspension is carried down with barium sulphate and the partly washed precipitate is analyzed, there will be found a stoichiometrically incomplete amount of chlorine. The yellow colloid differs from the red-brown in its extreme insolubility in acids. Its loss-of-water curve is quite different. It loses more water at the beginning but later less than the brown substance (van Bemmelen). In dry air the water content is 1.7 moles at 15°; 1.68 at 100°; and 1.34 at 150°. The velocity of loss of water is therefore quite small. At 200° there enters in a sudden change: in something like 16 hours it loses its water to 0.38 mole; but then its color goes over to black.

"A final condition is by no means reached with the appearance of this yellow colloid. If the $N/10$ solution is heated a few days at 100° there results a precipitate which shows the red of powdered haematite. To obtain the same substance from a concentrated solution, it must be heated for a few hours at 200° in a bomb tube. The substance that settles on the walls under these conditions appears glistening black like haematite."

Fischer tabulated the results of a number of experiments in which solutions of different concentrations were heated to different temperatures in bomb tubes. His conclusions follow:

"First is shown that the higher the temperature, and the lower the concentration, the greater is the proportion of chlorine in the solution therefore, the further has the hydrolysis proceeded. The oxides obtained fall into two series: (1) into the yellow substances with a water content that amounts to at least 10 percent; however, this rises to as much as 50 percent in the more concentrated solution by the shortest heating (hence the youngest gel); (2) into the red or black substances with a water content under 5 percent. In these, also, the substances have the least water content which are obtained from the most dilute and the longest heated solutions, in spite of the fact that they are much more finely divided. In a particular series the color goes stepwise from red to black with increasing coarseness of grain. The substances obtained from solutions up to approximately tenth normal are black. With increasing dilution there is mixed with them always more and more red until finally at $^1/_{100}$ normal they are a clear, bright red. In the same way, haematite crystals which glisten violet-black give a red streak on a streak plate.

"The regularity is satisfactory throughout, when one thinks how involved is the process taking place by which is formed from red-brown ferric hydroxide, first the yellow colloid and from the latter the black-red colloid; that the velocity of the reaction hinges on so many uncontrollable secondary conditions; and finally that the heating method in the bomb tube is extremely primitive, assuming as it does constant temperature and exact measurement of the time of heating."

From similar observations on the naturally occurring oxides, Fischer concludes that limonite is identical with the yellow colloid and that haematite is identical with the red colloid. A consideration of the loss-of-water curves of the different hydrous oxides under varying conditions, leads Fischer to the conclusion that the parent substance of the brown colloid is $Fe_2O_3.1.5H_2O$; of the yellow colloid, $Fe_2O_3.H_2O$; and of the red colloid, Fe_2O_3.

Neither Fischer nor Malfitano suggested a possible connection between the color of colloidal ferric oxides and the size of the particles, although both showed conclusively that the color of the hydrous oxide went fron brown through yellow to red with increasing coarseness of grain. On the other hand, Wöhler and Condrea[1] conclude, without question, that the different colors of anhydrous ferric oxide are a question of the size of the particles. "These shades are obtained by high heating of ferric oxide with sodium chloride. The color is determined by the temperature, the time of heating and the amount of salt used (2 to 6 percent). According to the directions given in the technical handbooks, 2 percent of salt and 1 hour's heating gives the yellow color; 4 percent of salt and 3 to 4 hours' heating the brown; and 6 percent of salt and 6 to 7 hours' heating the violet. At the same time the rapidity of cooling, and the admission or exclusion of air will have an influence on the color and chemical stability. The statements fail to give the temperature of the reaction and there is nothing conclusive in the directions concerning the cause of the color and the role of the salt in the process. The suggested explanation that a uniform temperature will result from the evaporation of the small amount of salt added, is of course incorrect. Another explanation that the salt serves as a means of removing sulphuric acid thus neutralizing the acid that remains on the caput mortuum, is untenable since by using pure iron oxide the above-mentioned scale of colors is passed through at 800° in the presence of salt, but not without it."

Wöhler and Condrea first showed that the product, after the heating, was pure iron oxide that was almost anhydrous. After discussing the possible causes of the color changes, they conclude that the size of the particles is the all-important thing: "One should expect the following relationships to obtain if the changes in the color are produced by the agglomeration of smaller particles: (a) The mixture must be heated at least to the melting point of the added salt in order to produce the agglomerating effect on the iron oxide powder. (b) The same amounts of different salts at their melting point will act in the same manner on the iron oxide, providing the salt is stable at this temperature and does not react with the

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[1] Zeit. angew. Chem., 11, 481 (1908).

iron oxide. (c) In order to produce a definite color a definite minimum amount of salt and, at the same time, a definite temperature above the melting point, is necessary; within limits a deficiency of salt can be compensated by raising the temperature. Hence the color produced is a function of the amount of salt added and the temperature. (d) By producing a medium of lower viscosity, the water content of the salt and of the oxide will have an influence, even though a lesser one, on the change of the size of the particles and therefore on the color. (e) By the reverse process of fine division, the violet substance may be changed into the reddish yellow color of the original oxide."

By numerous experiments Wöhler and Condrea established each of the above points. Since most of the experiments involved heating to relatively high temperatures, the colors and color changes refer to the anhydrous oxide. However, they consider that certain color changes are influenced by water of composition: "The violet product which results from heating hydrous iron oxide to 250° can be changed back easily into the reddish yellow color by grinding in a mortar. If the powder so obtained is moistened with water and again heated to 250°, it undergoes no further change in color. It follows, therefore, that the original water was a different water chemically combined which escapes at 250° and thereby produces a medium of lesser viscosity and brings about the growth of the particles. Between 250° and 550°, where a further deepening in color takes place, the rest of the water will be freed which is generally evolved from the colloidal hydrous oxides at a surprisingly high temperature.

"A brown coloration of the yellow-red iron oxide can be obtained at ordinary temperatures by rubbing iron oxide with a hydrated salt. For example, if iron oxide is ground with hydrated calcium chloride, the color changes to dark brown. This color is not altered by washing out the calcium chloride. The salt-free product so obtained can readily be changed back into the original yellow-red by rubbing finely in a mortar.

"The cause of the color at ordinary temperatures is the crystal water of the salt just as the color at 250° and 550° is brought about by the water of constitution of the hydrated oxide. In both cases, however, the changing in the size of grain is the reason for the change in color; since the change to the original color is readily obtained by fine grinding."

Inasmuch as the change in color is a question of change in the size of grain, it would seem unnecessary to postulate that water of chemical constitution rather than adsorbed water plays the role to which they ascribe it. Their final experiments are interesting and conclusive: "In a similar manner the violet color obtained by heating to 800° can be changed into a much lighter color, but not into the yellow-red original substance. It was to be expected that the technical product obtained by heating left the edge mill with a color but slightly lighter. However, the lightest color obtained in the agate mortar can be further subdivided by alternate elutriation and grinding. In this way was finally obtained not only the yellow-red color of the original material, but over and beyond this, a color that was more yellow than red and consisted of a still more finely divided reddish yellow iron oxide."

Bancroft[1] has suggested that the yellow color of hydrous limonites may be due to the adsorption of an iron salt. But in a later communication from his laboratory, Keane[2] arrived at the conclusion that the yellow color of the so-called Mars pigments is due to finely divided ferric oxide, which is kept from agglomerating by the presence of hydrous aluminum oxide; and, further, that the yellow color which iron imparts to bricks is due to sufficiently finely divided anhydrous ferric oxide. When the particles are larger, the color is red. This is quite in line with the conclusions reached by Wöhler and Condrea.

EXPERIMENTAL

The experiments to be described in the following pages are concerned with the factors which affect (a) the physical character and (b) the color of hydrous ferric oxide. In so

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[1] Jour. Phys. Chem., 19, 232 (1915).

[2] Ibid., 20, 734 (1916).

far as practicable these will be considered under separate headings.

The Physical Character of Hydrous Ferric Oxide

Attention has been called to the interesting observation that the physical character of precipitated hydrous ferric oxide prepared by the method of Péan de St. Gilles varies with the nature of the precipitating electrolyte: Thus, such acids as hydrochloric and nitric precipitate the colloid as a granular mass; whereas such acids as sulphuric and phosphoric, as well as certain salts, precipitate it in a gelatinous form. In discussing this phenomenon Bancroft[1] says:

"This precipitation of ferric oxide as a sandy mass by hydrochloric acid and as a gelatinous one by sulphuric acid is an important matter about which we appear to know very little theoretically. The formation of the gelatinous precipitates can not be a matter involving the hydrogen ion because we get the effect with sodium sulphate and do not get it with hydrochloric acid. Since it occurs with a number of different acids and salts, the effect can not be due to a specific anion. The one common characteristic is that the anions precipitate in low concentration and are, therefore, adsorbed strongly but this does not enable us to distinguish between the possible hypotheses of the effect being due to the solvent action of the adsorbed salt. It has been shown by von Weimarn that cellulose can be converted into a gelatinous mass by treating with concentrated salt solutions, preferably under pressure. In the particular case of ferric oxide, the salt concentrations are low, which makes it a little more probable that we may be dealing with the effect of the anion rather than of the salt; but, on the other hand, it is open to anybody to postulate a high salt concentration in or at the surface of the ferric oxide."

In order to acquaint ourselves with the exact nature of the differences in the physical character of the precipitates with different electrolytes, a series of precipitations were

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[1] Loc. cit.

carried out on a Péan de St. Gilles colloid. The colloid was prepared as follows: Twenty-five grams of ferric chloride were precipitated with a solution of sodium carbonate and the precipitate thoroughly washed by decantation. This was accomplished by placing the solution and precipitate into two 250 cc. bottles and centrifuging for ten minutes at 1500 r. p. m. The supernatant liquid was poured off and replaced with water, after which the precipitate was stirred up well and the centrifuging repeated. This was done until the removal of the electrolyte was so complete that the oxide started to go into colloidal solution in the wash water. To the precipitate suspended in 200 cc of water were next added 10 cc of glacial acetic acid which is less than the amount necessary to dissolve the oxide completely as ferric acetate. After standing for a few minutes a clear, dark red solution was obtained indicating that the excess oxide had been peptized by the acetate formed. This solution was diluted to 2500 cc and boiled until it became cloudy and of a brick-red color. From 30 to 40 hours were required.

In earlier experiments[1] the solution of the hydrous oxide was accomplished by adding acetic acid in the presence of relatively little water. Under these conditions a considerable amount of oxide remained undissolved unless an excess of acid was employed. There resulted a highly concentrated solution of ferric acetate containing excess acetic acid. The method above given ensures fairly rapid and complete solution with no excess of acetic acid.

Precipitation of the Colloid.—For the sake of uniformity of procedure the precipitations were carried out in the apparatus described in a previous communication.[1] This consists essentially of a glass tube 4 cm in diameter and 20 cm in length, closed with rubber stoppers. Concentric with the larger tube and held in place by the bottom stopper, is a smaller tube 2.5 cm in diameter and 7 cm in length. Twenty cubic centimeters of the colloid were placed in the inner compartment and a definite amount of normal or half-normal

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[1] Weiser and Middleton: Loc. cit.

electrolyte was placed in the outer compartment and diluted to 30 cc. Thus the precipitation took place always in a volume of 50 cc. After precipitation, the liquid was poured into a 50 cc eudiometer tube and at intervals observations were made of the volume and physical character of the precipitates. The volume occupied by the precipitate furnishes a good indication of its character since the most gelatinous precipitates are the most voluminous, and vice versa. Such precipitations were carried out with hydrochloric, nitric, sulphuric and phosphoric acids and with potassium sulphate and potassium chloride. These will be considered in detail.

(a) *Hydrochloric Acid.*—The precipitations with hydrochloric acid were carried out as above described. A portion of the observations are summarized in Table I. Under the heading "Volume of precipitate" is recorded the number of cubic centimeters which the precipitate occupies at the different time intervals. A blank space indicates that no precipitation has taken place. A star (*) after a number indicates that precipitation is incomplete; and the absence of a star shows that all or nearly all is precipitated.

TABLE I
Hydrochloric Acid as Precipitant

N acid cc	Volume of precipitate				Character of precipitate
	1 hr.	2 hr.	3 hr.	5 hr.	
8	—	0.2*	0.3*	0.4*	Granular, orange-red
9	0.6	0.5	0.5	0.5	Granular, orange-red
10	0.6	0.5	0.5	0.5	Granular, orange-red
11	—	—	—	0.3*	Granular, orange-red
12	—	—	—	—	No precipitate for 12 hours
13	—	—	0.3*	0.5*	Granular, orange-red
14	—	0.8*	0.8	0.7	Granular, orange-red
15	1.0	0.9	0.8	0.7	Less granular, brown brick-red

The colloid to which 15 cc of acid were added settled out in 15 minutes, but in all other cases settling was not observed until the solution had stood more than a half hour. The solutions were cloudy from the start, a condition that was less marked with the higher concentrations of acid. Even under the most favorable circumstances the agglomeration was relatively slow and the supernatant liquid continued more or less cloudy for hours. After the addition of acid, the suspensions became orange-red in color and came down as an orange-red powder. After precipitation was complete a portion of the supernatant liquid was tested for iron. A decided test was obtained, showing that the acid had an appreciable solvent action on the hydrous oxide.

From the table it will be noted that almost complete precipitation was obtained with 9 cc of acid in an hour; whereas with 12 cc of acid there was no precipitate in 5 hours. As a matter of fact, precipitation was only partial in this case after standing 24 hours. It is evident that we are dealing here with a so-called "abnormal series" similar to that observed by Freundlich[1] with other colloids. This will be taken up later in the paper.

(b) *Nitric Acid.*—Precipitations were carried out with nitric acid in the same manner as with hydrochloric. The observations are given in Table II.

TABLE II
Nitric Acid as Precipitant

N acid cc	Volume of precipitate				Character of precipitate
	1 hr.	2 hr.	3 hr.	5 hr.	
8	—	—	—	—	Precipitates after long standing, granular, orange-red
9	—	—	0.4*	0.5*	Granular, orange-red
10	1.7	1.5	1.3	0.9	Somewhat gelatinous, brownish brick-red
11	1.8	1.6	1.3	0.9	Somewhat gelatinous, brownish brick-red
12	2.0	1.6	1.3	0.9	Somewhat gelatinous, brownish brick-red
13	2.0	1.6	1.3	0.9	Somewhat gelatinous, brownish brick-red
15	2.1	1.7	1.4	0.9	Somewhat gelatinous, brownish brick-red

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[1] Zeit. phys. Chem., **73**, 385 (1910); Kapillarchemie, 459 (1909); Freundlich and Schucht: Zeit. phys. Chem., **85**, 641 (1913); cf. Bechhold: Ibid., **48**, 385 (1904).

As with hydrochloric acid, immediate precipitation did not take place, but agglomeration was observed much sooner at the higher concentration than with hydrochloric. Precipitation was incomplete after 5 hours with 9 cc of acid; and several days were required with 8 cc. These precipitates came out slowly and were of the same character as the hydrochloric acid precipitate. With higher concentrations agglomeration was more rapid and the precipitate was somewhat gelatinous; much more so than with hydrochloric acid. Moreover, there was no region of non-precipitation above the first precipitation value, such as was observed with the halogen acid.

(c) *Sulphuric Acid.*—With sulphuric acid agglomeration took place at once and in every case the precipitate was distinctly gelatinous and brick-red in color.

TABLE III

Sulphuric Acid as Precipitant

N acid cc	Volume of precipitate				Character of precipitate
	1/2 hr.	1 hr.	2 hr.	3 hr.	
0.5	7.0	4.6	3.2	2.6	Gelatinous, brick-red
5.0	7.0	3.5	2.2	1.6	Gelatinous, brick-red
15.0	7.0	2.0	1.8	1.4	Gelatinous, brick-red

Although the precipitate was gelatinous in every case, it was less voluminous the more concentrated the acid used. After the precipitate settled, a portion of the supernatant liquid was removed and tested for iron with potassium ferrocyanide: The solution containing 0.5 cc of acid gave no test; that containing 5 cc showed a trace; and that containing 15 cc somewhat more.

(d) *Phosphoric Acid.*—The solution used in this experiment was normal $H_2(HPO_4)$.

TABLE IV

Phosphoric Acid as Precipitant

N acid cc	Volume of precipitate				Character of precipitate
	1/2 hr.	1 hr.	2 hr.	3 hr.	
0.5	6.8	5.2	4.4	4.2	Gelatinous, brick-red
5.0	6.0	4.0	3.3	3.1	Gelatinous, brick-red
15.0	5.2	3.3	2.4	2.1	Gelatinous, brick-red

Here, again, it will be noted that the precipitate is quite voluminous; and it is more so the smaller the concentration of acid used. The supernatant liquid gave no test for iron in the solution containing the most dilute acid; but in the most concentrated solution a slight test was obtained.

(e) *Potassium Sulphate.*—A half-normal solution of potassium sulphate was used. The observations are given in Table V.

TABLE V

Potassium Sulphate as Precipitant

N/2 salt cc	Volume of precipitate				Character of precipitate
	1/2 hr.	1 hr.	2 hr.	3 hr.	
0.5	6.5	5.0	4.5	3.5	Gelatinous, brick-red
5.0	6.0	4.2	3.6	3.5	Gelatinous, brick-red
15.0	5.0	4.3	3.7	3.5	Gelatinous, brick-red

The precipitate with potassium sulphate was somewhat more voluminous than with the corresponding acid; and as the electrolyte showed no solvent action, the volume was practically the same in the presence of varying concentrations of electrolyte.

(f) *Potassium Chloride.*—It was found that the stability of the colloid was such that the precipitation value under the conditions chosen was somewhat less than 5 cc of half-normal potassium chloride. Accordingly, 5 cc of salt solution was the smallest amount used. The results are given in Table VI.

TABLE VI

Potassium Chloride as Precipitant

$N/2$ salt cc	Volume of precipitate				Character of precipitate
	1/2 hr.	1 hr.	2 hr.	3 hr.	
5	5.8	4.5	3.9	3.8	Gelatinous, brick-red
10	5.4	4.1	3.8	3.7	Gelatinous, brick-red
15	5.4	4.1	3.8	3.6	Gelatinous, brick-red

From the above table it will be noted that the precipitate was of the same general character and occupied approximately the same volume as that obtained with potassium sulphate; but it is very different from the hydrochloric acid precipitate.

Discussion of Results.—A survey of the results obtained shows the marked difference in the character of the ferric oxide precipitate with different precipitating agents. Under the conditions outlined above, hydrochloric acid gives a distinctly granular precipitate while that obtained with sulphuric acid is gelatinous, as Giolitti observed. It is evident, however, that the formation of a gelatinous precipitate is independent of the valence of the precipitating ion since both potassium chloride and potassium sulphate give the same thing. The outstanding facts disclosed by the experiments are: that the most voluminous precipitate is obtained when there is immediate agglomeration throughout the entire solution; and when the precipitating agent has no solvent action on the particles. As a matter of fact, this is exactly what one might expect:

A gelatinous precipitate consists of a network of particles which has carried down with it a greater or lesser amount of water. It is well known that the slow formation of a precipitate from a supersaturated solution is conducive to the formation of large particles; whereas if the conditions are such that there is a rapid formation of finely divided particles, a gelatinous precipitate may be obtained. This has been observed by von Weimarn[1] in the case of precipitated barium sulphate, which ordinarily comes down in a distinctly granular form but which may, under certain conditions, form a gelatinous precipitate or even a jelly. In a colloidal solution we have very finely divided particles which are essential to the formation of a gelatinous precipitate. Moreover, in the case of the colloidal oxides the particles are hydrated to a greater or lesser extent, depending on the method of preparation. Other things being the same, we should expect to get the most gelatinous precipitate from a colloidal solution containing the most finely divided and the most highly hydrous particles. A low temperature is conducive to the formation of small and highly hydrous colloidal particles, while a high temperature will favor the formation of larger and less hydrous colloidal particles.[2] Therefore, the newly prepared Graham colloid will be more hydrous than that prepared by boiling the acetate. Accordingly, when the latter colloid agglomerates gradually, the particles that are not very highly hydrous, may form into more or less granular masses that will entangle relatively little water. On the other hand, if the colloid agglomerates rapidly throughout the entire solution, the hydrous particles will form a network that will enclose and adsorb a relatively large amount of water and hence will be relatively voluminous. This accounts for the fact that a gelatinous precipitate is always obtained when the precipitating anion is polyvalent. Under such conditions a relatively low concentration causes rapid agglomeration throughout the entire solution with the consequent formation of a gelatinous mass.

Although substances containing anions having a high precipitating power will cause rapid agglomeration and hence gelatinous precipitates, this property is obviously not confined to electrolytes with strongly adsorbed anions. Thus potassium chloride produces a very voluminous precipitate and yet choride ion is not strongly adsorbed as a rule. On the other hand, hydrochloric acid causes the precipitate to come

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[1] "Zur Lehre von den Zuständen der Materie," 10 (1914).

[2] Cf. Bancroft: Loc. cit.

down granular. The difference in the character of the precipitate with these two electrolytes having the same anion results from the difference in the solvent action and the rate of agglomeration. Potassium chloride possesses no solvent action and the stabilizing influence of potassium ion is relatively slight; hence, rapid agglomeration takes place at the precipitation value. With hydrochloric acid conditions are quite different: On account of the stabilizing influence of hydrogen ion, the precipitation value of hydrochloric acid is greater than of its potassium salt. Now it is usually stated that hydrochloric acid has no solvent action on the Péan de St. Gilles colloid since the latter is precipitated even by highly concentrated solutions of the acid. As a matter of fact, however, hydrochloric acid has a marked solvent action on the hydrous oxide, a property which is likewise possessed, but to a lesser degree, by both nitric and sulphuric acids. It is quite obvious that the solvent action will be greater while the oxide is in the colloidal state than after agglomeration into larger particles has taken place. Accordingly, the slower the colloid is agglomerated by a given acid the greater will be the amount dissolved. Although the Péan de St. Gilles colloid is fairly uniform compared to an old Graham colloid, there is unquestionably considerable variation in the size of the individual particles such as Zsigmondy and others have observed with colloids generally.[1] Now it is the smallest particles that are the most readily attacked; hence the solvent action will, to a greater or lesser extent, prevent the formation of a continuous network of particles, thus cutting down the amount of water that can be enclosed and carried down; and so decreasing the volume of the precipitate.

As before stated, hydrogen ion has a marked stabilizing action on the colloidal oxide. The solvent action of the acid replaces hydrogen ions with ferric ions and the latter are slightly more strongly adsorbed than the former. Even above the precipitation value, the combined stabilizing effect of the two cations will cause a gradual rather than an im-

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[1] Cf., however, Tolman: Jour. Am. Chem. Soc., **35**, 307 (1913).

mediate agglomeration and the resulting precipitate will be granular rather than gelatinous in character.

From what has been said, it follows that if a sufficiently high concentration of hydrochloric or nitric acid is added to the colloid to cause quite rapid agglomeration before the solvent action of the acid has had time to manifest itself appreciably, we should get a precipitate that is distinctly more gelatinous than is obtained in the region of the precipitation value. Furthermore, it follows that a less gelatinous precipitate should be obtained with a relatively highly concentrated solution of sulphuric acid than with the quite dilute solutions in the region of the precipitation concentration. As pointed out, this tendency was shown in the precipitation experiments with sulphuric acid, above described. Finally, if the stabilizing influence of the cation tends to cut down the rate of agglomeration, then salts with polyvalent cations and univalent anions will produce a granular precipitate under certain conditions. Fortunately, all of these conclusions are readily verified experimentally.

Effect of the Concentration of Acid.—To determine the effect of the concentration of acid on the physical character of the precipitated oxide, 10 cc of 10-normal acid were diluted to 30 cc and placed in the outer compartment of the mixer; and 20 cc of colloid in the inner compartment. After mixing, the solution was transferred to a 50 cc eudiometer tube and observations made of the volume of the precipitate as previously explained. Precipitations were made with hydrochloric, nitric and sulphuric acids of the above concentration; and for the sake of comparison, a precipitation with 0.5 cc of normal sulphuric. The results are given in Table VII.

The precipitation was immediate in every case and was distinctly gelatinous in character. Indeed the precipitate with nitric acid was quite as gelatinous as with the concentrated sulphuric acid and that with hydrochloric was little less so. Moreover the precipitate with the concentrated sulphuric was not nearly so voluminous as with the dilute. The experi-

TABLE VII

Effect of the Concentration of Acid

Acid	Amount added	Volume of precipitate					Character of precipitate
		1/2 hr.	1 hr.	2 hr.	3 hr.	4 hr.	
Nitric	10 cc of 10 *N*	3.5	2.3	1.6	1.3	1.2	Quite gelatinous
Hydrochloric	10 cc of 10 *N*	3.3	1.6	1.2	0.9	0.9	Gelatinous
Sulphuric	10 cc of 10 *N*	3.6	2.4	1.6	1.3	1.2	Quite gelatinous
Sulphuric	0.5 cc of *N*	6.5	4.5	3.0	2.5	2.4	Very gelatinous

ments show conclusively that if the precipitation is sufficiently rapid, a gelatinous precipitate can be obtained with both nitric and hydrochloric acid; and, furthermore, that the precipitate with very dilute sulphuric acid is much more gelatinous than with the more concentrated acid which has an appreciable solvent action.

The Effect of the Nature of Salts.—Precipitations were carried out with thorium nitrate and with the chlorides of aluminum, iron, chromium, zirconium and potassium. The method was as follows: To 5 cc of colloid in a test-tube was added, drop by drop, a solution of the salt in question until there was noticeable clouding. To a second 5 cc portion was added a relatively large excess of electrolyte. The rate of precipitation and the physical character of the precipitate were noted in each case. The results are given in Table VIII.

TABLE VIII

Effect of the Nature of the Salt

Salt	Physical character of the precipitate on the addition of electrolyte	
	Not in excess	In excess
Potassium chloride	Gelatinous	Gelatinous
Aluminum chloride	Granular	Gelatinous
Chromic chloride	Granular	Granular
Ferric chloride	Granular	Gelatinous
Zirconium chloride	Granular	Granular
Thorium chloride	Granular	Gelatinous

From Table VIII it will be noted that the addition of enough electrolyte to cause clouding produced a granular precipitate with every salt with a polyvalent cation, while potassium chloride gave a gelatinous precipitate under these conditions. As was expected, the granular precipitate came out slowly, owing to the stabilizing influence of the cation and of the hydrous oxide formed by hydrolysis of the electrolytes. The addition of excess electrolyte caused almost immediate formation of a gelatinous precipitate in most cases; but with chromic chloride and zirconium chloride, the precipitate came out gradually and was granular under all circumstances. Again, the results show conclusively that the formation of a gelatinous precipitate of the hydrous oxide is a question of rate of agglomeration; and that it is possible to get either a granular or gelatinous precipitate with certain salts, by suitable variation in the conditions of precipitation.

The Two Precipitation Values with Hydrochloric Acid.—Attention was called in a previous paper[1] to Freundlich's observation that strychnine nitrate has two precipitation values for colloidal arsenious sulphide—one low and another relatively high. He considers that the lower value corresponds to negative arsenious sulphide while the higher value is for a positive colloid formed by the difficultly soluble strychnine base surrounding the particles. Freundlich and Schucht[2] observed a similar thing in determining the precipitation value for mercuric sulphide, of salts of heavy metals, like silver nitrate: "The explanation is the same as was previously recognized. In the lower precipitation zone we have the coagulation of negative mercuric sulphide. In the upper zone of non-precipitation the particles of mercuric sulphide are surrounded by silver oxide or the like, so that we have a positive colloid which is precipitated by nitrate ion in the upper zone of coagulation."

The explanation is a probable one in the cases above cited; but with hydrous ferric oxide, it seemed very unlikely that there

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[1] Weiser and Middleton: Jour. Phys. Chem., **24**, 30 (1920).

[2] Zeit. phys. Chem., **85**, 641 (1913).

could be a change of sign from positive to negative in a strongly acid solution. To make certain of this, however, the direction of migration of the colloid in the second zone of non-precipitation was determined. The colloid was prepared by adding 12 cc of normal hydrochloric acid diluted to 30 cc, to 20 cc of the original colloid. The direction of migration was determined in a modification of the Nernst apparatus recommended by Taylor.[1] It was found that the particles were positively charged.

It will be recalled that the concentration of acid in the immediate region of the first precipitation value caused a marked clouding at once; and that the solution remained distinctly clearer for a long time in the second zone of non-precipitation. A possible explanation seemed to be that the solvent action of the acid of a certain concentration resulted in the introduction of ferric ions which might be more strongly adsorbed and hence exert a greater stabilizing effect than hydrogen ions alone. This hypothesis proved not to be correct since the precipitation value of ferric chloride is not very much higher than that of hydrochloric acid. The following experiment illustrates that the presence of ferric ions has but little more effect than an equivalent amount of hydrogen ions: Thirteen cubic centimeters of normal hydrochloric acid were diluted to 29 cc and 1 cc of normal ferric chloride was added. This solution was mixed with 20 cc of colloid in the usual way and observation made of the time of precipitation. It was found that the agglomeration took place quite as rapidly as with 14 cc of acid instead of more slowly than with 13 cc, which would have been the case if the stabilizing influence of ferric ion was appreciably greater then that of an equivalent amount of hydrogen ion.

A second zone of non-precipitation can be accounted for best from a consideration of possible differences in the adsorption isotherms of hydrogen ion and chloride ion. It is well known that in relatively dilute solutions of hydrochloric acid the adsorption of hydrogen ion by ferric oxide is apprecia-

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[1] "Chemistry of Colloids," 78 (1915).

bly greater than that of chloride ion. Accordingly, the adsorption isotherm of the latter will lie under that of the former until such a concentration is reached that the adsorption of the two is equal; at which concentration, precipitation of the colloid takes place. Now it is quite conceivable that the two isotherms may coincide for a short distance within certain limits of concentration, then separate, and finally come together again at a higher concentration. This may be shown best by a diagram. In Fig. I, *A* and *B* may be considered to represent a portion of the adsorption isotherm of hydrogen and chloride ion, respectively. At a certain concentration they coincide at the point P_1 which corresponds to the lower precipitation value. At a slightly higher concentration of acid, hydrogen ion is again more strongly adsorbed than chloride ion and the colloid is once more stable, although very much less so than the original colloid since the curves are quite close together relatively. At a still higher concentration of acid they come together again at the point P_2 which corresponds to the second precipitation value. At all concentrations above P_2 precipitation takes place. This explanation accounts for the two precipitation values, one above the other; and for the zone of non-precipitation between where the colloid is much less stable than the original colloid. It also accounts for the additional fact that the colloid does not change sign in the upper zone of non-precipitation.

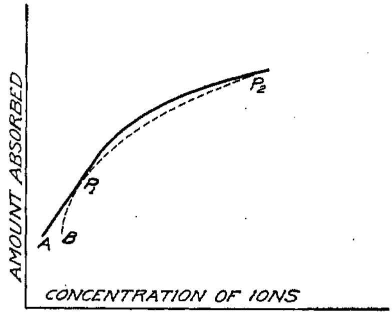

Fig. I

Washing of Precipitated Hydrous Ferric Oxide.—Péan de St. Gilles called attention to the fact that the oxide precipitated with nitric acid or hydrochloric acid was carried back into colloidal solution by washing out the precipitating agent with water. This was not possible when the precipitation was effected with sulphuric acid. Since, in general, the precipitate obtained with hydrochloric acid is granular and with sulphuric acid is gelatinous, Bancroft[1] concludes that the determining factor is not the specific adsorbability of the ions but the physical character of the precipitate: "It seems to me more probable that the insolubility [of the sulphuric acid precipitate] in water is due to the precipitate being gelatinous and therefore coalescing into a continuous mass which is not peptized readily by water." While the physical character of the the deposit unquestionably has an effect, it is not the important factor as Bancroft supposed. Although it is true that the gelatinous precipitate with sulphuric acid is not peptized by washing, the very gelatinous precipitate obtained with potassium chloride is quite as readily peptized as the granular one gotten with hydrochloric acid. The following experiment illustrates this: Two 25 cc portions of colloid were taken and each diluted to 40 cc. To one were added 10 cc of *N*/2 potassium sulphate and to the other 10 cc of *N*/2 potassium chloride. The precipitates were thrown down by centrifuging for ten minutes at 1.500 r. p. m.; after which the supernatant liquid was poured off and the inside of the container carefully rinsed with distilled water so as not to disturb the precipitate. Fifty cubic centimeters of water were added to each and after stirring up thoroughly, the centrifuging was repeated. It was found that practically all of the precipitate obtained with potassium chloride was carried back into a colloidal solution from which the particles were not separated by centrifuging. On the other hand, the precipitate obtained with potassium sulphate was not peptized by eight repetitions of the above process; and no further attempt was made. The experiment is conclusive evidence that the adsorbability

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[1] Loc. cit.

of the ion and not the physical character of the precipitate determines the degree of reversibility of precipitation of hydrous ferric oxide.

The Color of Hydrous Ferric Oxide

From the investigation to which reference has been made in the first part of this paper, it is evident that colloidal ferric oxide exists in three more or less separate and distinct colors: reddish brown, yellow and red. As might be expected, there are numerous intermediate shades. The variation in color of the hydrous oxide from brown, through yellow to red, was shown by Malfitano[1] and by Fischer[1] to be associated with an increase in the size of the particles; but they did not consider the possible connection between the two. Malfitano believes that the different colored substances obtained by hydrolysis of ferric chloride are complex compounds of different composition. Fischer does not share this view, but regards the brown colloid as hydrous $Fe_2O_3.1.5H_2O$; the yellow as hydrous $Fe_2O_3.H_2O$; and the red as hydrous Fe_2O_3. Ruff[1] believes that hydrous $Fe_2O_3.1.5H_2O$ is yellow rather than brown. As stated before, van Bemmelen was unable to prepare any definite hydrates under ordinary conditions, and it is doubtful if any exist. Moreover, Wöhler and Condrea[1] have shown that anhydrous oxides can be prepared that vary in color from yellow to red by simply varying the size of the particles. This has been confirmed by Keane[2] and by Scheetz,[3] who prepared a yellow anhydrous oxide by heating ferrous oxide in the presence of alumina, which prevents agglomeration to the red oxide.

Van Bemmelen[4] has called attention to the fact that the loss of water on heating the yellow hydrous oxide from 15° to 100° was slight; while if it is kept for some time at 200°, there is an appreciable loss of water and the color changes from yellow to red. This behavior led Fischer to the conclu-

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[1] Loc. cit.

[2] Jour. Phys. Chem., **20**, 734 (1916).

[3] Ibid., **21**, 570 (1917).

[4] Zeit. anorg. Chem., **29**, 185 (1899).

sion that the yellow oxide is a hydrous hydrated oxide instead of a hydrous oxide. Wöhler and Condrea have likewise observed a change in color when a certain oxide lost water which they, too, considered was water of constitution rather than adsorbed water. They pointed out, however, that the loss in water favored the growth of particles by decreasing the viscosity of the medium; and that this growth in particles changed the color since the original color of the hydrous oxide was obtained by fine grinding of the dehydrated one. A number of experiments have been carried out which indicate that the different colors of hydrous ferric oxide are due to variation in the size of the particles.

Effect of the Velocity of Hydrolysis of Ferric Chloride.—Malfitano showed that the slow heating to 100° of a ferric chloride solution of suitable concentration resulted in the formation of an ochre-yellow colloid; while sudden heating produced a red-brown colloid that was apparently heterogeneous, but less so than the yellow. Krecke[1] poured a ferric chloride solution into boiling water and obtained a perfectly clear dark red-brown colloid. The difference in appearance of these three colloids is most likely due in part to a difference in the size of particles produced by difference in the rate of hydrolysis. To determine the extent of this influence, a series of experiments was carried out as follows: Fifty cubic centimeters of water were placed in an Erlenmeyer flask and brought to a certain temperature. To the water were then added 10 cc of an approximately 20 percent solution of $FeCl_3.6H_2O$; and the temperature, after mixing, was noted. The flask was then set on an electric hot-plate of constant temperature which brought the solution to the boiling point, where it was kept boiling vigorously for 5 minutes. Since the hydrolysis is most rapid at higher temperatures and is practically complete at 100°, the rate of hydrolysis depends on the temperature of the water to which the ferric chloride is added and the time necessary to bring it to the boiling point. The results of a series of experiments at various temperatures are given

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[1] Loc. cit.

in Table IX. In the first column is given the initial temperature of the solution; in the second and third, the color of the solution after two hours and the stability after standing for a day.

TABLE IX

The Hydrolysis of Ferric Chloride

Temperature (degrees)	Observations	
	Color	Stability (after 24 hrs.)
10	Ochre-yellow	Considerable precipitated
25	Ochre-yellow (brownish)	Considerable precipitated
40	Brownish yellow	Partly precipitated
60	Yellow-brown	Little precipitated
73	Brown	Trace settled out (cloudy)
84	Reddish brown	No precipitate (cloudy by reflected light)
100	Dark red-brown	Clear in both transmitted and reflected light

The above table shows very clearly the effect of the rate of hydrolysis on the size of the particles and hence on the color of the colloid. When the salt solution is added to boiling water the hydrolysis is most rapid and the particles are relatively small and red-brown in color. When added to water at 0° and heated gradually to boiling, the particles form slowly and hence are larger and yellower in color. Between these extremes lie all variations in size of particles and color of the colloid formed.

Effect of Hydrochloric Acid on the Size of Particles Formed during Hydrolysis of Ferric Chloride.—As observed by Goodwin and by Fischer, the brown colloid is apparently transformed into the yellow by the action of hydrochloric acid. This is what one might expect since it is well known that the solvent action of the medium, as well as the rate of formation, determines the size of particles separating from solution. In order to show the extent of this effect, the hydrolysis was carried out by introducing 10 cc of 20 percent ferric chloride solution into water containing a definite small amount of hydrochloric acid at 93°. The resultant solution, the temperature of which was 84°, was placed on the electric hot-plate and heated to boiling, where it was kept for 5 minutes. From the preceding table it will be noted that a stable reddish brown colloid is formed in this way when the salt solution is added to pure water. Under otherwise constant conditions, a difference in the size of the particles, and hence in the color, was noted by adding the salt solution to acid as dilute as $^5/_{100}$ normal. The results with varying concentrations of acid are given in Table X. In the first column is given the amount of normal hydrochloric acid added to 50 cc of water from a 2 cc Mohr's pipette.

TABLE X
Effect of Hydrochloric Acid

N HCl cc	Temperature (degrees)	Observations	
		Color	Stability (after 24 hrs.)
0.0	84	Reddish brown	No precipitate
0.1	84	Light reddish brown	No precipitate
0.3	84	Brown	No precipitate
0.5	84	Brownish yellow	Some precipitate
0.7	84	Ochre-yellow	Most precipitated
0.9	84	Ochre-yellow	Most precipitated

The above results show clearly the influence of the solvent action of hydrochloric acid on the size of the particles and hence on the color. Similar results were obtained with nitric acid. The two factors, rate of hydrolysis and solvent action of the electrolyte, go hand in hand in the formation of hydrous ferric oxide by the hydrolysis of a ferric salt. Which will be the determining factor depends entirely on the conditions under which the hydrolysis is brought about. It is evident that the rapid hydrolysis on slowly pouring a salt solution into water at the boiling point results in the formation of very small particles in spite of the solvent action of the water and of the acid which is a product of the hydrolysis. On the other hand, if the ferric chloride solution is added slowly to water that has been acidified slightly, the solvent action should result in the formation of larger particles, even at the boiling point. This is exactly what happens: To 50 cc of water acidified by the addition of 2 cc. of normal hydrochloric acid, were added slowly 10 cc of 20 percent $FeCl_3.6H_2O$ and the boiling continued for 5 minutes. An ochre-yellow colloid was obtained similar in every way to that prepared by slow heating of the aqueous solution of ferric chloride from room temperature to the boiling point.

The Action of Ferric Chloride.—Malfitano has pointed out that the residue after filtration of the yellow colloid is readily peptized by ferric chloride; but that the solution remains quite cloudy, no matter how much ferric chloride is added. This experiment has been confirmed.

Malfitano observed also that the particles obtained by filtration of the brown colloid are peptized by ferric chloride, forming a clear solution, the particles of which are not removed by the ultrafilter. He states that if this solution is now heated the color goes to ochre-yellow and the colloid precipitates out. From this he concludes that the brown colloid can be changed to the ochre-yellow by the action of ferric chloride. It seems to me that this experiment is open to the objection that heating the ferric chloride solution alone produces an ochre-yellow colloid; so that an ochre-yellow precipitate does not necessarily indicate that the brown colloid has been transformed to yellow by this process. Some experiments have been carried out which indicate that no such transformation takes place:

1. A solution of ferric chloride was precipitated with a slight excess of sodium carbonate and the precipitate thoroughly washed, making use of the centrifuge. The freshly prepared oxide was added to $N/2$ ferric chloride in small amounts at a time until it had taken up all the oxide that it could. In this way a very concentrated brown colloid was obtained. When this solution was heated, no clouding was observed.

2. In the first experiment, the concentration of ferric

chloride was low since most of the ferric ions were adsorbed by the hydrous oxide which was carried into solution thereby. A varying excess of ferric chloride solution was next added to several small portions of the colloid which was then heated. Precipitates were obtained which varied in color from brown to brownish yellow, depending entirely on the excess of ferric chloride and the rate of heating.

The results of the above experiments are quite in line with the observations made by Neidle.[1] The latter found that colloidal ferric oxide, prepared by dissolving the freshly precipitated oxide in excess ferric chloride, could not be dialyzed hot at the start, since the yellow ochreous variety of the oxide was formed. By dialyzing in the cold until the excess of ferric chloride was removed, the colloidal solution could be heated to boiling and the dialysis continued in the hot without the appearance of the yellow colloid.

Attention has been called to Bancroft's hypothesis that the yellow color of certain hydrous oxides may be due to adsorbed ferric salt. If this is the case, one might expect to get a yellow precipitate if the brown or red colloid were thrown down in a highly gelatinous form in the presence of excess ferric salt. In a previous experiment it was shown that the Péan de St. Gilles colloid was precipitated in a gelatinous form by excess ferric chloride. The precipitate so obtained was distinctly red in color even in the presence of a very large excess of electrolyte. Similar results were obtained by precipitating in the presence of excess ferric chloride, the dark red-brown colloid prepared by adding ferric chloride to boiling water. To a 5 cc portion of this colloid was added an excess of ferric chloride and enough potassium sulphate solution to cause agglomeration. A gelatinous red-brown precipitate resulted. Ferric sulphate solution likewise produced a red-brown precipitate. On account of the gelatinous character of the precipitate obtained in each of these experiments, there is certain to be considerable adsorption of ferric salt. The experiments indicate, therefore, that adsorption of ferric

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[1] Jour. Am. Chem. Soc., 39, 71 (1917).

salt by hydrous ferric oxide does not necessarily result in a yellow modification.

The Stepwise Transformation from the Brown to the Red Colloid.—As previously noted, the interesting observation has been made that the first product of the hydrolysis of ferric chloride is the brown colloid which goes over into the larger yellow particles at ordinary temperatures if the solution is sufficiently dilute; and, finally, that the yellow particles are transformed into the still larger brick-red, by continued heating. A number of experiments have been carried out which show the conditions under which this stepwise transformation takes place:

1. A 1 percent solution of ferric chloride was heated slowly; and it was noted that the solution became not only opalescent but that particles sufficiently large to be seen were obtained near the boiling point. On raising the temperature to boiling and then allowing the solution to cool, a yellowish brown colloid was obtained from which no precipitate deposited on standing for several hours. By boiling this solution vigorously for a few days, the oxide went over entirely into the brick-red particles which settled out on standing. From this experiment it is clear that if the conditions are chosen properly, one can bring about the stepwise change from the brown through the yellow to the brick-red.

2. A 4 percent solution of ferric chloride was heated slowly from 25° to 100°; a yellow ochreous colloid was obtained that was heated at 100° for several days with but slight change in color resulting. If this solution were heated to a higher temperature in a bomb tube, a precipitate having the red color of powdered haematite would result (Fischer).

3. 10 cc of a 20 percent solution of $FeCl_3.6H_2O$ were added to 50 cc of boiling water and the solution boiled for several hours. Under these conditions was obtained the brick-red precipitate identical with that resulting from the dilute solution used in Experiment 1.

4. 50 cc of solutions of ferric chloride were prepared of the following concentrations: $N/50$; $N/100$; and $N/500$.

When first prepared the *N*/50 solution was very light and the other two were almost colorless. On standing the *N*/50 solution became orange-yellow in color; the *N*/100 yellow; and the *N*/500 canary-yellow. The solvent action of the water was probably an important factor here, since the concentration of the acid was so low. These solutions were heated to boiling: the *N*/50 became scarlet-red; the *N*/100 orange-red; and the *N*/500 reddish orange. As the boiling was continued the transformation to the brick-red colloid took place gradually. A precipitate settled out of the most concentrated solution after boiling for a day; while the *N*/100 solution required more than twice as long to produce the same result. The *N*/500 acquired a bright red color, but boiling was discontinued before the particles were agglomerated sufficiently large to settle. Here, again, the direct transformation from the yellow to the red colloid was observed.

From the above experiments it is demonstrated that the yellow colloid formed under certain conditions can be transformed into the red colloid by prolonged boiling of the solution; and when formed under other conditions it is not transformed by the boiling process at atmospheric pressure. It will be recalled that Fischer showed that the degree of hydration of the colloids decreases in the order: brown, yellow, red. As previously pointed out, Keane and Scheetz have demonstrated that the yellow color of bricks is due to finely divided anhydrous ferric oxide which is kept from agglomerating by alumina and probably by certain other substances as well. This requires a rather high percentage of alumina. In the so-called Mars pigments which are yellow, the ferric oxide is in the hydrous state; and in this condition it agglomerates less readily to the red oxide and less alumina is required to prevent the transformation. From this it is clear that the failure of the yellow colloid to lose water when formed under certain conditions, accounts for the difficulty with which it is transformed into the red colloid at 100° and the relative ease with which the transformation takes place at higher temperatures.

The Stability of the Yellow Hydrous Oxide.—It has been shown that blue hydrous copper oxide is stabilized to such a degree by the adsorption of certain salts, that a suspension of it may be heated to the boiling point without dehydration taking place.[1] This immediately suggests that the stability of the yellow hydrous ferric oxide may be due to adsorption of some salt. The hypothesis seems all the more probable in view of the fact that the stability of the oxide is much greater under certain conditions of formation than under others, as shown by the results of the experiments in the preceding section. Referring once more to Bancroft's hypothesis, that the yellow color of the hydrous oxide is due to the presence of adsorbed ferric salt, we find that this suggestion was based on Fischer's observation that the brown colloid went over into the red in the presence of hydrochloric acid; on Malfitano's experiment that the brown colloid is transformed into the yellow by boiling with ferric chloride; and on Phillips' method of preparing the yellow oxide by oxidation of ferrous carbonate. The results obtained by Fischer and by Malfitano have been accounted for in another way. Moreover, the hydrous oxide has been precipitated in a gelatinous form in the presence of a large excess of ferric chloride,—a condition that would favor marked adsorption of ferric salt; and yet the oxide was distinctly red. Accordingly, it is probable that the color of the yellow colloid is not due to adsorbed iron salt. Bancroft's hypothesis was the outgrowth of the observation that the yellow colloid was formed under such conditions that the absorption of an iron salt was a possibility. The converse appears not to be the case, namely, that the adsorption of an iron salt always results in the formation of a yellow hydrous oxide. Although the adsorption of an iron salt probably does not impart a yellow color to a hydrous ferric oxide, it is altogether possible that the yellow hydrous oxide which is not converted to the red by heating at 100°, is stabilized by absorbed iron salt. This hypothesis is in line with the results of experiments above described. The

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[1] Blucher and Farnau: Jour. Phys. Chem., 18, 629 (1914).

following may be mentioned: (1) The yellow hydrous oxide resulting from the hydrolysis of a dilute solution of ferric chloride, is formed under conditions that are unfavorable to the adsorption of ferric salt, and this colloid is transformed readily into the red by continued boiling. (2) The yellow hydrous oxide produced by the slow heating of more concentrated solutions of ferric chloride is formed under conditions favorable to the adsorption of ferric salt; and this hydrous oxide is distinctly stable at 100°. (3) The hydrolysis of ferric chloride is very rapid at 100°. Accordingly the hydrous oxide formed by the addition of ferric chloride to boiling water will not be stabilized by adsorption of ferric salt and so will be converted to the brick-red oxide by boiling. (4) Finally, the yellow hydrous oxide formed by hydrolysis of ferric chloride poured into dilute hydrochloric acid solution at elevated temperatures, is stable as we should suppose. These results all support the hypothesis that the yellow hydrous oxide is stabilized by adsorption of ferric salt.

The Color of the Péan de St. Gilles Colloid.—The Péan de St. Gilles oxide is always described as brick-red in color; but early in the investigations on this oxide, I noted that the shade of different preparations varied from a brown-red to a dark brick-red, even though the same general method was employed in the preparation. At first I was inclined to attribute the variation in color to difference in the time of boiling; but some later observations disclosed that this was not the case:

1. A solution of ferric acetate was prepared by adding 10 cc of glacial acetic acid in 200 cc of water to the freshly prepared and thoroughly washed oxide obtained from 25 g. of $FeCl_3.6H_2O$. This solution had stood for three weeks when a portion of it was made up to approximately $N/20$ and boiled for 30 hours. Much to my surprise, the colloid was not even a shade of red, but was distinctly yellow colored and gave a yellow precipitate with salts instead of brick-red. The following experiment was then carried out: From the concentrated acetate solution were prepared 750 cc of an $N/20$

solution which was boiled for 40 hours. Samples of 10 cc each were withdrawn at intervals and the color of the colloid observed. These samples were then diluted to 20 cc; precipitated by the addition of 5 cc of *N*/2 potassium sulphate; and the color of the precipitate noted. The results are given in Table XI.

TABLE XI

Boiling of *N*/20 Ferric Acetate

Time (hours)	Color of colloid	Color of precipitate
0	Light red	Brown
1/6	Light red	Brown
1/2	Orange-red	Light brown
1	Reddish orange	Light brown
3	Light reddish orange	Brownish orange
5	Orange	Reddish orange
10	Orange	Reddish orange
15	Orange	Orange
20	Orange	Orange
30	Orange-yellow	Yellow
40	Orange-yellow	Yellow

From the above experiments it is quite evident that the hydrolysis of the acetate resulted in the formation of the yellow hydrous oxide which was sufficiently stable that it was not converted into the red oxide by boiling.

2. A solution of ferric acetate was prepared by suspending in 150 cc of water, the ferric oxide obtained from 25 grams of $FeCl_3.6H_2O$; adding 10 cc of glacial acetic acid; and diluting to 250 cc. This solution was allowed to stand for 10 days, after which 20 cc were taken and diluted to 100 cc, making a solution which was approximately 2.2 *N*. By diluting the latter, were prepared 50 cc portions of other solutions of various concentrations as given in Table XII. A new solution of ferric acetate was next prepared of the same concentration as the old; and as soon as possible, this new solution was diluted in the same manner as the old. The two series of solutions in 150 cc beakers were placed on an electric hotplate and boiled vigorously for 15 hours, replacing the water

as it evaporated. A difference in the color of the two series of colloids was soon noted, which became quite pronounced as the boiling continued: the colloids from the old ferric acetate were yellow; and from the new were red.

After the boiling, a 2 cc portion of the most concentrated solution of each series was diluted to 45 cc and 5 cc of $N/2$ potassium sulphate added to precipitate the colloid. In the same manner, 4 cc, 8 cc, 16 cc and 32 cc portions of the other solutions of each series were diluted to 45 cc and precipitated. In this way the same amount of precipitate was obtained and the color was observed. The result with the two series are recorded in Table XII and Table XIII.

TABLE XII
Hydrolysis of Old Solution of Ferric Acetate

Solution boiled		Color of colloid	Color of precipitate
Ferric acetate 2.2 N	Water		
50.0	0.0	Reddish orange	Yellow
25.0	25.0	Orange	Yellow
12.5	37.5	Light orange	Yellow
6.25	43.75	Yellow	Yellow
3.13	46.87	Canary	Yellow

TABLE XIII
Hydrolysis of New Solution of Ferric Acetate

Solution boiled		Color of colloid	Color of precipitate
Ferric acetate 2.2 N	Water		
50.0	0.0	Very dark red	Dark brick-red
25.0	25.0	Dark red	Dark brick-red
12.5	37.5	Red	Dark brick-red
6.25	43.75	Light red	Dark brick-red
3.13	46.87	Orange-red	Dark brick-red

It is evident from the above experiments that the formation of the red colloid in one instance and the yellow in another, is not a question of the dilution or the duration of boiling, but of the length of time that the acetate solution is allowed to stand before it is diluted and boiled. This is what one might expect from the previous observations on the stability of yellow hydrous ferric oxide:

Reinitzer[1] showed that a ferric acetate solution can be evaporated to crystallization only in the presence of excess acetic acid. The solution of the normal acetate is fairly stable at low temperatures; but Herz[2] finds that at 44° it decomposes quite rapidly with the precipitation of $Fe(OH)_2C_2H_3O_2$. Rosenheim and Muller[3] prepared a ferric acetate to which they assign the formula $Fe_2(C_2H_3O_2)_5OH$, by the action of glacial acetic acid on ferric oxide. A solution of this salt containing 9.772 grams per liter hydrolyzes completely in 216 hours at 20° with the formation of colloidal hydrous ferric oxide.

The concentrated solutions of ferric acetate prepared by us contained no excess acetic acid and so hydrolysis took place slowly at ordinary temperatures. This was proven by the fact that a few drops of potassium sulphate solution caused no precipitation of the newly formed acetate for almost an hour; whereas a copious precipitate resulted at once in the old. The very slow hydrolysis in the presence of excess ferric salt furnished ideal conditions for the formation of the yellow hydrous particles stabilized by adsorbed ferric salt. Therefore, an old solution of ferric acetate does not go over to the brick-red colloid on boiling. The newly formed solution diluted and heated at once hydrolyzes very rapidly under conditions much less favorable for the formation of the stable yellow colloid and consequently the brick-red colloid is always obtained under such circumstances.

Investigation of the properties of negative hydrous ferric oxide[4] are being made and will be reported on in a subsequent communication.

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[1] Monatshefte f. Chemie, **3**, 256 (1883).

[2] Zeit. anorg. Chem., **20**, 16 (1899).

[3] Rosenheim and Muller: Zeit. anorg. Chem., **39**, 175 (1904).

[4] Fisher: Biochem. Zeit., **27**, 223 (1910); Grimaux: Comptes rendus, **98**, 1485 (1884); Powis: Jour. Chem. Soc., **107**, 818 (1915).

The results of this investigation may be summarized briefly as follows:

1. A survey of the investigations on the composition of colloidal ferric oxide has been made. The existence of no definite basic ferric salt has been established with certainty and but one definite crystalline hydrate has been prepared. The latter is formed only under special conditions: the decomposition of sodium ferrite by water at ordinary temperature. Accordingly it is probable that the different ferric iron colloids are not composed of basic salts of varying composition or of hydrous hydrated oxides; but instead are hydrous ferric oxide.

2. A study has been made of the physical character of colloidal and precipitated hydrous ferric oxide.

3. The difference in properties of colloidal hydrous ferric oxides prepared by different methods and of different ages, is due to a difference in the degree of hydration and in the size of the colloidal particles.

4. It is unnecessary to postulate the existence of basic chlorides or complex salts of varying composition in order to account for the observation that only part of the chlorine present in the dialyzed Graham colloid appears to exist as ion.

5. Certain electrolytes precipitate the Péan de St. Gilles colloid in a gelatinous form while others precipitate it in a granular form. The nature of the precipitate depends on the conditions of precipitation; the same electrolyte may produce either a granular or gelatinous mass under suitable circumstances.

6. The most gelatinous precipitate is obtained when there is very rapid agglomeration of the hydrous particles throughout the entire solution and when the electrolyte possesses no solvent action; the most granular precipitate results when the agglomeration progresses slowly and when the electrolyte possesses a solvent action.

7. Acids and salts with polyvalent anions precipitate the Péan de St. Gilles colloid rapidly in extremely low concentration and so produce a gelatinous precipitate. Similar re-

sults are obtained at somewhat higher concentrations with salts both of whose ions are univalent.

8. Acids with univalent anions and salts with univalent anions and polyvalent cations, precipitate the Péan de St. Gilles colloid only at relatively high concentrations. The stabilizing influence of the cation causes relatively slow agglomeration of a granular mass in the region of the precipitation value. Sufficiently high concentration of such electrolytes may cause rapid agglomeration with the consequent formation of a gelatinous precipitate.

9. The smallest particles in a colloidal solution are most readily attacked by an electrolyte that has an appreciable solvent action. The agglomeration of a colloid by such an electrolyte will tend to make the precipitate more granular by destroying or preventing the formation of the continuous network of particles necessary for producing a gelatinous mass.

10. Hydrochloric acid possesses two precipitating values for the Péan de St. Gilles colloid: one above the other with a zone of non-precipitation between where the colloid is stable but less so than the original colloid. An explanation of this phenomenon has been offered.

11. The degree of reversibility of the precipitation of hydrous ferric oxide is determined for the most part by the specific adsorbability of the precipitating ion, although the physical character of the precipitate doubtless has some effect.

12. An investigation has been made of the factors that affect the color of colloidal ferric oxide. It is not probable that the different colors are due to complex salts or to hydrous hydrated oxides; but to variation in the size of the particles of hydrous ferric oxide.

13. Three different colors of colloidal hydrous ferric oxide are generally recognized: reddish brown, yellow and red. Under suitable conditions, it is possible to make the stepwise transformation from brown through yellow to red by increasing the size of the particles.

14. The rapid hydrolysis of ferric chloride on adding the

salt solution to boiling water, produces very small particles that are reddish brown in color; the slow hydrolysis of a dilute solution at ordinary temperatures or of a more concentrated solution heated slowly to the boiling point, produces larger particles that are yellow. Continued boiling of the brown or the yellow colloid formed under certain conditions causes agglomeration to still larger particles that are red. All variations in shade can be realized from the very small brown to the large dark red particles.

15. The hydrolysis of a ferric chloride solution poured into hot water, produces small brown particles; but if poured into hot, dilute hydrochloric or nitric acid, the solvent action of the acid results in the formation of larger particles that are yellow. All variations in shade from reddish brown to yellow can be realized by suitable variation in acid concentration and hence in the size of the particles.

16. Anhydrous ferric oxide varies in color from yellow to red with increasing coarseness of grain. The yellow anhydrous oxide agglomerates much more readily to the red oxide on heating, than does the yellow hydrous oxide.

17. The yellow colloidal hydrous oxide formed under conditions that favor the adsorption of ferric salt, is not readily dehydrated at 100°, and so does not readily agglomerate to the red oxide until a higher temperature is reached. The stability of this oxide under certain conditions is probably due to adsorbed ferric salt.

18. A yellow colloid has been prepared by the Péan de St. Gilles method by allowing the acetate solution prepared in a given way, to stand for a few days before diluting and boiling. The slow hydrolysis of the acetate favors the formation of yellow hydrous oxide stabilized by adsorbed ferric salt. When such a solution is boiled, a stable yellow colloid is formed instead of the usual brick-red.

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