[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

THE PRECIPITATION, STABILITY AND CONSTITUTION OF HYDROUS FERRIC OXIDE SOLS. I.

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"A critical examination of the results of coagulation experiments will show that comparisons between the work of different persons must not be too rigid because the coagulating power of any given electrolyte varies greatly with the treatment of the sample used. As shown by the work of Spring, Freundlich, Höber and Gordon, Paine, Galecki, and others, the question as to whether a given concentration of an electrolyte will produce coagulation or not depends, within a certain range, on how the electrolyte is added, *e. g.*, slowly, drop by drop, or rapidly, with very gentle stirring or violet stirring, etc., and on how the mixture is treated immediately after the addition, *e. g.*, whether shaken violently, heated and then cooled, heated for some time at the boiling point, etc. Naturally we may suppose that each experimenter carries out all his observations under similar conditions, and consequently that this results may be compared with one another, although the numbers determined by one worker may not agree entirely with those found by another."[1]

The above quotation from Burton fails to recognize two most important factors determining the amount of electrolyte necessary to precipitate a colloid. These are the concentration of the sol with respect to the colloid and its purity. In the present work, of the variations in method of precipitation, only the effect of the rapidity of addition of electrolyte was observed. In a few cases the amount of electrolyte required for the complete precipitation of a hydrous ferric oxide sol was slightly greater when added gradually than when added rapidly. This discrepancy is entirely negligible as compared with the enormous variations to be found in the literature on the precipitation of colloids by electrolytes.

These striking variations can be very largely, if not entirely, attributed to the varying concentrations and purity of the sols of a given colloid employed by different authors. This statement may be made on the basis of the results of this paper, whose object was a systematic study of the precipitation by potassium sulfate solutions of hydrous ferric oxide sols, in which both purity and concentration of colloid were varied.

It is unfortunate that articles on colloids, with few exceptions, do not give the electrolyte content, that is, the purity of the sols used. However, a number of investigators, including the author, have made the general qualitative statement that the stability of a sol decreases with increasing purity and with increasing concentration. In this connection the amount of electrolyte necessary to precipitate a sol, containing a given quantity of colloid, is taken as a measure of its relative stability. An unstable sol is not one in which the colloid settles, but one requiring little salt for precipitation. A sol from which the colloid settles, due to gravity, may be classified as a heterogeneous sol.

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[1] Burton, "Physical Properties of Colloidal Solutions," p. 148 (1916).

It was realized that the above relationship between stability and composition of a sol, if correct and susceptible to accurate measurement, would lead to values for the maximum purity which sols may attain, and might throw some light on their constitution.

To completely specify the problem, it should be added that the sols employed were perfectly clear in both reflected and transmitted light, and that their acid constituent was hydrochloric acid. Hydrous ferric oxide sols which are turbid yield a yellow deposit on standing, and are therefore heterogeneous. This does not happen with the perfectly clear sols, which even in the ultramicroscope are no more heterogeneous than some true solutions.[1]

Preparation of Sols.

A gram equivalent of commercial ferrous chloride was dissolved in 400 cc. of water. The solution, being turbid due to the presence of oxidized insoluble matter, was filtered and diluted to two liters. Three per cent hydrogen peroxide (U. S. P.) was added to the ferrous chloride solution which was stirred mechanically, until no test could be obtained for ferrous iron with potassium ferricyanide. About one liter of hydrogen peroxide was necessary and the completion of the desired reaction was indicated by the appearance of a thick foam. The solution obtained was perfectly clear and brownish red. The reaction between ferrous chloride and hydrogen peroxide has been studied and the results will be published shortly.

For the present research, no better method could be employed for the preparation of the sol since no metal other than iron is introduced and very pure, perfectly clear sols are easily obtained from the ferrous chloride peroxide reaction mixture.

The reaction mixture was diluted to four liters and dialyzed in the cold by the continuous circulation method, until the solution could be heated to 80° without causing the appearance of a turbidity. This required three days, the solution being stirred during the entire time. The resulting solution which will be referred to as solution A, had the following composition: iron, 0.4822 g. equivalents per liter; chlorine, 0.0720 g. equivalents per liter.

Of solution A, 150 cc. were diluted to 900 cc. and dialyzed at 80° for five days in a two-liter beaker, using thirty lb. parchment paper.[2] Towards the end of the dialysis, a brownish yellow foamy scum formed on the surface of the colloidal solution. This was carefully removed by means of a porcelain spatula at the end of the dialysis, and the perfectly clear sol was poured, without filtering, into a Jena bottle.

Some small particles of dried colloid were invariably formed at the

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[1] Spring, *Bull. acad. roy. med. belg.*, [3] 37, 174 (1899); Biltz, *Ber.*, 35, 4431–4438 (1902).

[2] Neidle and Barab, THIS JOURNAL, 39, 71–81 (1917).

surface of the solution. It was desirable to remove them, but every attempt at filtration, however carefully conducted caused the sol to become somewhat turbid. This change of the colloid was avoided by allowing the sol to cool, when the insoluble dried colloid would settle to the bottom, and the solution was then carefully decanted into a three-liter Jena bottle.

The colloidal solution obtained by the above procedure, being very pure, would not keep in the ordinary soda-lime glass bottle. Within a few hours such a bottle would precipitate the colloid at the liquid-glass-air intersection, and after a few days the colloid would be almost completely precipitated. This effect was due to the solution of alkali from the glass. Jena glass vessels proved to be entirely satisfactory containers, and it was also found, later, that Pyrex glass vessels were equally satisfactory.

The above preparation was run in triplicate, and the sols when mixed, had the following composition: iron, 0.0819 g. equivalents per liter; chlorine, 0.00118 g. equivalents per liter; ratio-equiv. Fe: equiv. Cl = 69.4. This sol will be called sol B.

Another very pure sol, of higher iron content, was prepared as follows: A parchment paper (30 lbs.) membrane, made of a 45 cm. disc, was suspended in a three-liter wide mouth, short neck, Pyrex round bottom flask. Of solution A, 750 cc. were diluted to one liter and poured into the membrane. Distilled water circulated through the flask at the rate of about 2 liters per hour, a constant level being maintained by means of suction. The flask was kept at about 80° and the dialysis continued for five days. Each day it was necessary to pour some water into the membrane to prevent concentration of the colloid. The sol thus obtained, which will be called sol C, had the following composition: iron, 0.2156 g. equivalents per liter; chlorine, 0.00342 g. equivalents per liter; ratio-equiv. Fe: equiv. Cl = 63.0.

Analysis of Sols.

The iron was determined gravimetrically after heating with an excess of hydrochloric acid. The chlorine was determined as follows: the sol was treated with concentrated nitric acid and heated until the initial precipitate completely dissolved, and on cooling the solution was colorless. The chlorine was precipitated by adding a known volume of standard silver nitrate solution, weighing the silver chloride in a Gooch crucible, and determining the excess of silver nitrate by titrating with standard potassium thiocyanate, thus obtaining a check on the gravimetric result. The chlorine was also determined nephelometrically; the sol was treated with sufficient nitric acid to give a colorless solution, silver nitrate was added, and then comparisons made with standards by aid of the Kober nephelometer. It had been first ascertained that the presence of considerable ferric nitrate had no appreciable influence on the tubidity produced by the silver chloride precipitate. The great importance of the correct determination of the chloride will be seen later.

Preparation of Sols Used in Precipitation Experiments.

A series (Series I) of sols having the same iron content but varying hydrochloric acid content, were prepared as follows: 25 cc. portions of sol B were transferred into a number of 100 cc. Jena or Pyrex erlenmeyers, and all were diluted to the same volume with varying amounts of water and standard dilute hydrochloric acid solutions. Four such series of sols were prepared with the following relative iron concentration: 1, 2, 4 and 6. The details of the preparation of the four series of sols are given in Tables I to IV.

The sols thus prepared came to equilibrium in a very short time, with the exception of the last members of Series I and II, to which such large amounts of hydrochloric acid were added that they ultimately became mixtures of ferric chloride and hydrochloric acid. The constancy of the precipitation value was taken as an indication of equilibrium. It was assumed that the mixture of sol, water and standard dilute hydrochloric acid, at equilibrium, was identical in constitution with a sol of the same composition obtained directly by dialysis. The consistency of the results was considered sufficient support for this assumption.

Thus it is claimed that the nature of the deep brownish red colloidal hydrous ferric oxide is entirely determined by the content of iron and hydrochloric acid and not by the method of preparation. It is also assumed that the changes which take place during dialysis are reversible. Usually dialysis is regarded as an irreversible process, because the addition of concentrated hydrochloric acid causes the precipitation of the colloid.

The essential nature of dialysis involves the fundamental principle of reversibility—that is, the gradual displacement of equilibrium by the gradual removal of electrolyte. Naturally, to reverse the process, the electrolyte must be returned gradually, in small quantities, and preferably in dilute solution. In this way practically all the sol may be converted by the addition of dilute hydrochloric acid into ferric chloride, and without the preliminary formation of a precipitate.

Precipitation Experiments.

The nature of colloid precipitation is not clearly understood, nor is there general agreement as to when a colloid is completely precipitated by the electrolyte. The method here adopted is entirely arbitrary and adapted to the needs of the problem at hand.

Ten cc. of each sol were transferred to a 50 cc. centrifuge tube and standard potassium sulfate solution was added until a precipitate was formed. In general, the first portions of potassium sulfate solution only caused a turbidity which increased with further additions of salt, until a flocculent precipitate was formed. The mixture was centrifuged to determine whether precipitation was complete, this being indicated by a colorless supernatant liquid. If the latter was not colorless, the centrifuge tube was shaken so as to bring the sediment into suspension and more salt was added until centrifuging indicated complete precipitation. In a duplicate experiment the potassium sulfate was added rapidly to within

TABLE I.—SERIES I.

Precipitation by K_2SO_4 of a series of hydrous ferric oxide sols all 0.03107 *N* with respect to ferric iron and with varying HCl content, prepared by diluting 25 cc. sol B with H_2O and standard HCl to 65.9 cc.

	HCl added.		*M*/1600 K_2SO_4 to precipitate 10 cc. solution.			
Solution.	Conc.	Cc.	I. Cc.	II. Cc.	Average. Cc.	Test for Fe^{+++} in supernatant liquid from precipitation.
a........	0.01 *N*	0	0.90	0.92	0.91	No test
b........	0.01 *N*	1.5	2.45	2.45	2.45	No test
c........	0.01 *N*	3.0	3.74	3.72	3.73	No test
d........	0.01 *N*	5.0	4.88	4.90	4.89	No test
e........	0.01 *N*	6.61	5.11	5.13	5.12	No test
f........	0.1 *N*	0.85	5.30	5.28	5.29	No test
g........	0.1 *N*	1.25	5.44	5.47	5.46	No test
h........	0.1 *N*	2.50	5.80	5.77	5.79	No test
i........	0.1 *N*	5.00	5.91	5.90	5.91	Good test
j........	0.1 *N*	7.50	5.95	5.94	5.95	Good test
k........	0.5 *N*	2.00	5.91	5.89	5.90	Good test
l........	0.5 *N*	2.50	5.90	5.88	5.89	Good test
m.......	0.5 *N*	7.95	3.78	3.82	3.80	Good test

TABLE II.—SERIES II.

Precipitation by K_2SO_4 of a series of hydrous ferric oxide sols all 0.06214 *N* with respect to ferric iron and with varying HCl content, prepared by diluting 25 cc. sol B with H_2O and standard HCl to 32.95 cc.

	HCl added.		*M*/800 K_2SO_4 to precipitate 10 cc. solution.			
Solution.	Conc.	Cc.	I. Cc.	II. Cc.	Average. Cc.	Test for Fe^{+++} in supernatant liquid from precipitation.
a'.......	0.01 *N*	0.00	1.00*	1.02*	1.01*	No test
b'.......	0.01 *N*	1.50	2.06	2.08	2.07	No test
c'.......	0.01 *N*	3.00	3.52	3.53	3.53	No test
d'.......	0.01 *N*	5.00	4.68	4.67	4.68	No test
e'.......	0.01 *N*	6.61	5.04	5.00	5.02	No test
f'........	0.1 *N*	0.85	5.17	5.21	5.19	No test
g'.......	0.1 *N*	1.25	5.44	5.44	5.44	No test
h'.......	0.1 *N*	2.50	5.74	5.74	5.74	Good test
i'........	0.1 *N*	5.00	5.79	5.76	5.78	Good test
j'........	0.1 *N*	7.50	5.64	5.68	5.66	Good test
k'.......	0.5 *N*	2.00	5.44	5.46	5.45	Good test
l'........	0.5 *N*	2.50	5.27	5.25	5.26	Good test
m'.......	0.5 *N*	7.95	3.07	3.05	3.06	Good test

* *M*/1600 K_2SO_4 used.

TABLE III.—SERIES III.

Precipitation by K_2SO_4 of a series of hydrous ferric oxide sols all 0.1242 *N* with respect to ferric iron and with varying HCl content, prepared by diluting 25 cc. sol C with H_2O and standard HCl to 43.36 cc.

Solution.	HCl added.		$M/800$ K_2SO_4 to precipitate 5 cc. solution.			Test for Fe^{+++} in supernatant liquid from precipitation.
	Conc.	Cc.	I. Cc.	II. Cc.	Average. Cc.	
1	0.05 *N*	0	0.75*	0.77*	0.76*	No test
2	0.05 *N*	0.8	2.22	2.22	2.22	No test
3	0.05 *N*	1.6	3.56	3.56	3.56	No test
4	0.05 *N*	2.2	4.36	4.34	4.35	No test
5	0.1 *N*	1.5	5.00	4.98	4.99	No test
6	0.1 *N*	1.71	5.26	5.22	5.24	No test
7	0.1 *N*	2.80	5.78	5.75	5.77	Good test
8	0.5 *N*	0.80	5.94	5.98	5.96	Good test
9	0.5 *N*	1.10	5.96	....	5.96	Good test
10	0.5 *N*	1.30	5.99	6.04	6.02	Good test

TABLE IV.—SERIES IV.

Precipitation by K_2SO_4 of a series of hydrous ferric oxide sols all 0.1863 *N* with respect to ferric iron and with varying HCl content, prepared by diluting 25 cc. sol C with H_2O and standard HCl to 28.92 cc.

Solution.	HCl added.		$M/800$ K_2SO_4 to precipitate 5 cc. solution.			Test for Fe^{+++} in supernatant liquid from precipitation.
	Conc.	Cc.	I. Cc.	II. Cc.	Average. Cc.	
1′	0.05 *N*	0	0.84*	0.87*	0.86*	No test
2′	0.05 *N*	0.8	2.94	2.92	2.93	No test
3′	0.05 *N*	1.6	5.16	5.16	5.16	No test
4′	0.05 *N*	2.2	6.52	6.50	6.51	No test
5′	0.1 *N*	1.5	7.60	7.56	7.58	No test
6′	0.1 *N*	1.71	7.97	7.95	7.96	No test
7′	0.1 *N*	2.80	8.75	8.78	8.77	Good test
8′	0.5 *N*	0.80	9.53	9.50	9.52	Good test
9′	0.5 *N*	1.10	9.28	9.22	9.25	Good test
10′	0.5 *N*	1.30	9.23	9.22	9.23	Good test

a few drops of the first volume required, and then the precipitation was brought to completion. Usually a third titration was run, which lead to checks agreeing, as a rule, within a few hundredths of a cc.

In some of the more concentrated sols, the solution would gel as a whole at a certain stage in the addition of potassium sulfate. After breaking up the gel by shaking, the precipitation was continued as above.

Results.

The observations are given in Tables I–IV, and from these the values in Tables V–VIII were calculated, giving the equivalents of potassium sulfate necessary to completely precipitate sols containing 1 g. equiv. of ferric iron. In Figs. 1 and 2 the equivs. of potassium sulfate required to precipitate one equivalent of iron are plotted against the hydrochloric acid

* 10 cc. sol used.

Table V.

Total Cl content of colloid and K_2SO_4 required for precipitation.
Series I: Conc. Fe = 0.03107 g. equiv. per liter.

Solution.	Cl per g. equiv. Fe milli-equiv.	$\frac{\text{Equiv. Fe}}{\text{Equiv. Cl}}$ ratio.	K_2SO_4 to precipitate 1 g. equiv. Fe milli-equiv.
a	14.41	69.4	3.665
b	21.73	46.0	9.841
c	29.06	34.4	15.02
d	38.83	25.8	19.68
e	46.69	21.4	20.60
f	55.92	17.9	21.28
g	75.46	13.3	21.99
h	136.5	7.32	23.31
i	258.6	3.86	23.79
j	380.7	2.63	23.94
k	503.1	1.99	23.75
l	625.2	1.60	23.71
m	1956.0	0.511	15.30

Table VI.

Total Cl content of colloid and K_2SO_4 required for precipitation.
Series II: Conc. Fe = 0.06214 g. equiv. per liter.

Solution.	Cl per g. equiv. Fe milli-equiv.	$\frac{\text{Equiv. Fe}}{\text{Equiv. Cl}}$ ratio.	K_2SO_4 to precipitate 1 g. equiv. Fe milli-equiv.
a'	14.41	69.4	2.032
b'	21.73	46.0	8.327
c'	29.06	34.4	14.22
d'	38.83	25.8	18.84
e'	46.69	21.4	20.20
f'	55.92	17.9	20.88
g'	75.46	13.3	21.87
h'	136.5	7.32	23.11
i'	258.6	3.86	23.27
j'	380.7	2.63	22.79
k'	503.1	1.99	21.95
l'	625.2	1.60	21.16
m'	1956.0	0.511	12.31

Table VII.

Total Cl content of colloid and K_2SO_4 required for precipitation.
Series III: Conc. Fe = 0.1242 g. equiv. per liter.

Solution.	Cl per g. equiv. Fe milli-equiv.	$\frac{\text{Equiv. Fe}}{\text{Equiv. Cl}}$ ratio.	K_2SO_4 to precipitate 1 g. equiv. Fe milli-equiv.
1	15.86	63.1	1.530
2	23.28	43.0	8.938
3	30.70	32.6	14.33
4	36.27	27.6	17.51
5	43.69	22.9	20.10
6	47.58	21.0	21.10
7	67.80	14.7	23.23
8	90.06	11.1	24.00
9	99.34	10.1	24.00
10	136.4	7.33	24.24

Table VIII.

Total Cl content of colloid and K_2SO_4 required for precipitation.

Series IV: Conc. Fe = 0.1863 g. equiv. pr liter.

Solution.	Cl per g. equiv. Fe milli-equiv.	Equiv. Fe / Equiv. Cl ratio.	K_2SO_4 to precipitate 1 g. equiv. Fe milli-equiv.
1'..............	15.86	63.1	1.154
2'..............	23.28	43.0	7.87
3'..............	30.70	32.6	13.86
4'..............	36.27	27.6	17.46
5'..............	43.69	22.9	20.36
6'..............	47.58	21.0	21.38
7'..............	67.80	14.7	23.56
8'..............	90.06	11.1	25.58
9'..............	99.34	10.1	24.84
10'..............	136.4	7.33	24.80

content per equivalent of iron. Examining the graph in Fig. 1, representing the results for Series I, we see that the precipitation value first increases more rapidly than the hydrochloric acid content, then, after a fairly sharp bend, increases only slightly, and finally decreases. The curves for the other series are of the same type.

It is remarkable how little potassium sulfate is necessary for the precipitation of the first member of each series. A mere glance at the graph shows that there is no simple stoichiometric relation between the hydrochloric acid content of the colloid and the potassium sulfate necessary for precipitation.

The curves showing the relationship between the precipitation value and the hydrochloric acid content are established experimentally for sols up to a purity represented by the first member of each series. Continuing along any curve to the left, towards the hydrochloric acid axis, we obtain the precipitation values for sols of greater and greater purity. Graphical extrapolation is a dangerous procedure, but in this research could not be avoided since the dotted part of the curves represent sols which are entirely too sensitive to work with, being precipitated by mere traces of electrolyte. No small amount of difficulty was experienced in working with the purest sols used, and it is here that the greatest experimental errors were incurred.

If we continue along any of the curves (Fig. 2) from the continuous to the dotted part, we obtain the relationship between precipitation value and hydrochloric acid content for sols with less and less hydrochloric acid per gram equivalent of iron. The intersection of the dotted curve with the hydrochloric acid axis indicates the hydrochloric acid content at which zero potassium sulfate is required for precipitation. This gives the purity of the sol of minimum stability for the particular iron concentration.

Continuation of the dotted curve beyond the hydrochloric acid axis

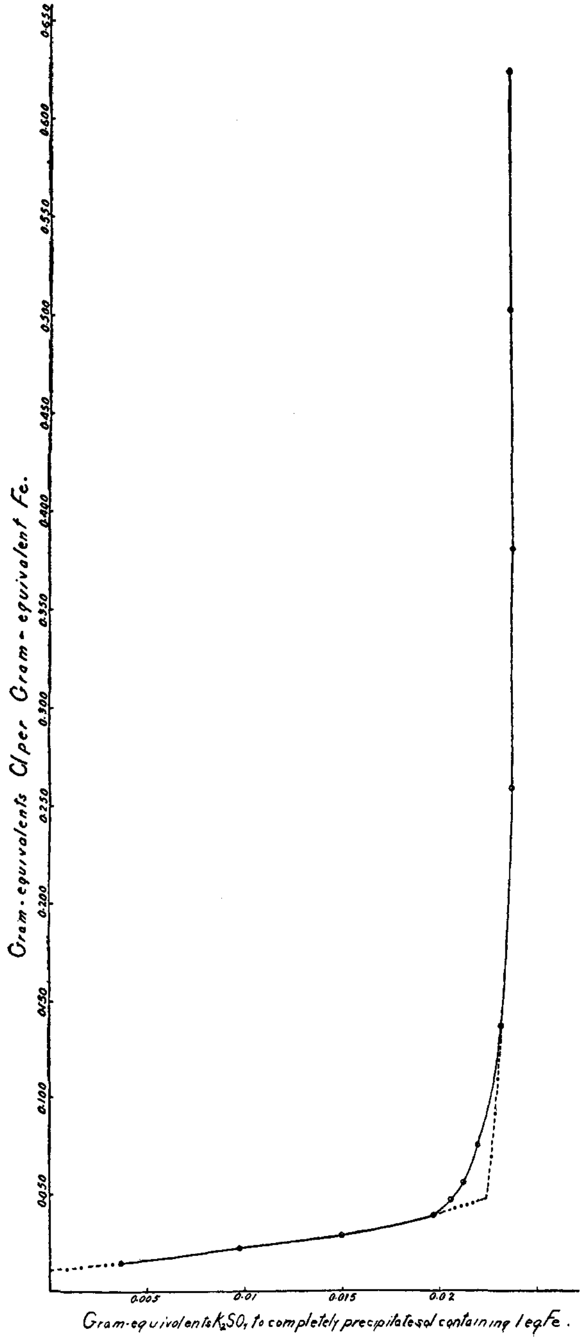

Fig. 1.

represents sols which require a negative amount of potassium sulfate for precipitation, that is, have negative stability. Such sols are purely hypothetical. We will now postulate that only sols having a positive stability can be prepared. Furthermore, all such sols will keep indefinitely if contained in vessels, the substance of which will not react with the sols.

Theoretically, the purest sol obtainable is that which has zero stability; but, experimentally, the maximum purity attainable is limited by the solubility of the container in the sol. The purity of hydrous ferric oxide sols will be represented by the ratio of iron to chlorine in equivalents, which is the reciprocal of the equivalents of hydrochloric acid per equivalent of iron.

It is thus seen that extrapolation of any precipitation curve to intersection with the hydrochloric acid axis yields the maximum purity for any particular iron concentration. For example, Curve 1 shows that the sol has zero or minimum stability when the hydrochloric acid content is 0.0107 equivalent per equivalent of iron, the concentration of the latter being 0.03107 equivalent per liter. Hence, in a sol of this iron concentration the purity cannot exceed 93 at room temperature. Similarly, the maximum purity for sols of iron concentrations represented in Series II, III and IV were obtained, the results being given in Table IX. Fig. 2 also shows that above the ratio of about 30 the stability of sols of a given purity decreases with increasing concentration, this being most conspicuous for the very pure sols.

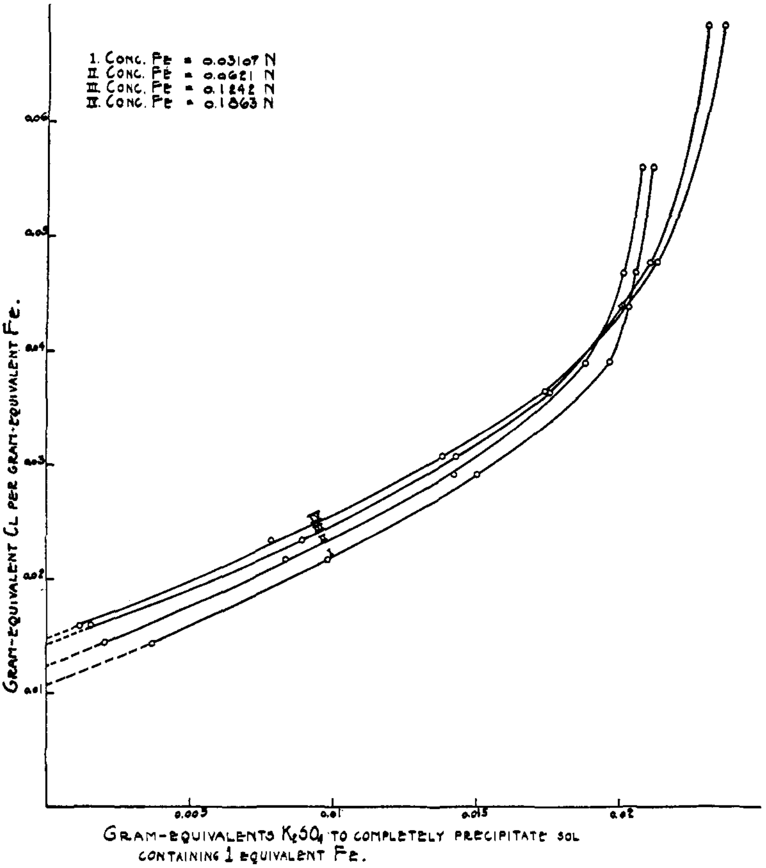

Fig. 2.

The relationship between the maximum purity and iron concentration is shown in Fig. 3, which demonstrates clearly that the lower the iron concentration of the sol the greater the purity obtainable. The values of the maximum ratios are probably all low, but within 5% of the correct ones. Fig. 3 also enables one to predict how far a sol may be concentrated before gel will begin to separate out. It is seen that the purer the sol the lower the iron concentration at which gel will appear upon evaporation.

TABLE IX.

The Iron content of hydrous ferric oxide sols and the maximum purity.

Conc. equiv. Fe.	Max. purity Equiv. Fe / Equiv. Cl'
0.03107	93
0.06214	81
0.1242	70
0.1862	67

TABLE X.

Ratio limits between which hydrous ferric oxide sols cease to give the test for Fe^{+++} with potassium sulfocyanate.

Fe content g. equiv. per l.	Limits of Equiv. Fe / Equiv. Cl'
0.03107	3.86– 7.32
0.06214	7.32–13.3
0.1242	14.7 –21.0
0.1862	14.7 –21.0

The question now arises: What will take place if a sol is dialyzed beyond the maximum purity? The answer has been given by Linder and Picton[1] and by Jordis:[2] gel containing a smaller proportion of electrolyte than the sol separates out, leaving a sol with a correspondingly slightly lower purity and slightly lower colloid concentration. The sol remaining, if in equilibrium with the separated gel, should be a sol of maximum purity, which plotted against the iron concentration, should fall on the curve in Fig. 3. This suggested a method of verifying the validity of the graphical extrapolation used above. The method of cold dialysis would mean an experiment of over six months' duration and then would require extreme precautions.

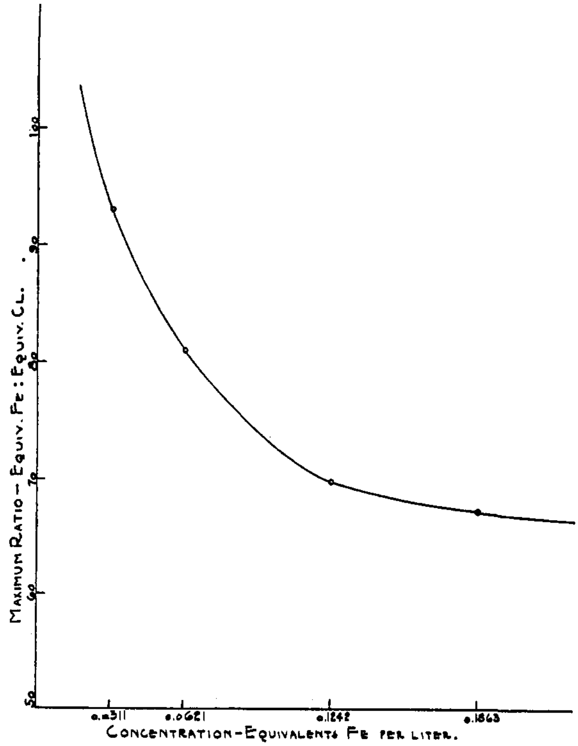

Fig. 3.

The method of hot dialysis, however, furnished the desired result in nine days, as follows: 150 cc. of solution A

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[1] *Trans. Chem. Soc.*, **87**, 1909 (1905).

[2] *Kolloid Z.*, **3**, 161 (1908).

were diluted to 900 cc. and dialyzed at 80° for nine days. At the end of this period gel had already been formed, and therefore the sol was at its maximum purity, although not corresponding to room temperature. However, after allowing to cool, the latter was probably approximated. The sol had the following composition: Fe = 0.0463 N : Cl = 0.000552 N : ratio equiv. Fe equiv. Cl = 84. Thus the maximum purity at room temperature for a sol which is 0.0463 N with respect to iron should be a little above 84, since the Pyrex glass vessel used in the experiment must slightly reduce the maximum purity attainable. The curve in Fig. 3 indicates 86, which is very satisfactory agreement and justifies the graphical extrapolation resorted to.

The Constitution of Hydrous Ferric Oxide Sols.

In 1905 Nicolardot[1] advanced the following theory of the constitution of hydrous ferric oxide sols, based on the views of Béchamp and his own extensive experimental work. The clear brownish red sols contain two ferric oxychlorides in varying proportions, one having a ratio of 6, and the other the ratio of 125. Nicolardot found that a sol in which the ratio of iron to chlorine in equivalents was 6 no longer gave tests for ferric and chloride ions, and concluded that the sol contained a definite colloidal compound—a ferric oxychloride. He states that after dialyzing a sol for many months the ratio became 125, and no more hydrochloric acid passed through the membrane, thus fixing the ratio for the second oxychloride. He also claimed that the sol with the ratio 125 is the purest possible.

Clearly, Nicolardot overlooked the importance of concentration. Had he worked with sols of varying concentrations with respect to iron, he would have found limiting ratios other than 6 and 125. Furthermore, even if the existence of two definite compounds did correspond to the limiting ratios, no evidence is advanced to support the contention that sols in which the ratio is between 6 and 125 contain only mixtures of these two compounds.

Nicolardot examined sols for ferric and chloride ions by adding potassium ferrocyanide or sulfocyanate and silver nitrate, respectively. The failure of these tests for ferric and chloride ions in the presence of colloidal particles is only conclusive if the latter do not interfere. The color intensity of the colloid and its reactions with electrolytes may explain the negative tests for chloride ion which is *always* present, and for ferric ion which is present in some instances.

To the author it seemed more logical to test for the ferric ion after the colloid had been precipitated by potassium sulfate, and separated by the aid of a centrifuge. The supernatent liquid will contain some of the ferric iron of the original sol and is suitable for testing with potassium

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[1] *Ann. chim. phys.,* [8] 6, 334–393 (1905).

sulfocyanate. Adopting this procedure, the results shown in the last columns of Tables I–IV were obtained, and these determined the ratio limits (Table X), between which a sol of given iron concentration ceases to give the analytical test for ferric ion. It is thus seen that the maximum ratio at which a sol still gives a test for ferric ion increases with rising concentration, and for our highest concentration the value obtained is more than twice that given by Nicolardot.

If we slowly concentrate a sol containing 0.03107 equivalent of ferric iron per liter and with a ratio of 3.86, so as to insure equilibrium at every stage, the amount of ferric ion will steadily increase, while the proportion of free hydrochloric acid will decrease. This is simply a case of hydrolytic dissociation, hydrochloric acid and colloid reacting as the sol is concentrated, to form ferric chloride and water, or conversely for dilution. A fundamental question is—"Does the colloid in this equilibrium represent a distinct molecular species and, if so, what is its composition?" The data already presented permit a tentative reply to this question, while research which promises to yield conclusive evidence is at present in progress.

The precipitation curves going from left to right all consist of an almost straight line, a fairly sharp bend, a part which is almost perpendicular, and a line approaching the HCl axis. Going along any of the curves from left to right represents the addition of hydrochloric acid at "constant volume." In all cases ferric ion begins to appear somewhere on the bend. If the first part of the curve is continued to intersection with a continuation of the almost perpendicular part, a point is obtained for which the ratio is practically 21 for all four curves. The intersection for Series I is shown in Fig. 1.

The author believes that clear hydrous ferric oxide sols containing ferric ion contain a definite oxychloride whose ratio is 21 (Fe/3) : 1 (Cl). This definite oxychloride is a colloid and enters in the following hydrolysis equilibrium:

$$\text{Ferric chloride} + \text{water} \rightleftharpoons \text{Colloid No. 1} + \text{hydrochloric acid} \quad (1)$$

The equation is written out in words because the molecular formula of the colloid, indicated as Colloid No. 1, is not known. As the concentration of ferric ion decreases, Colloid No. 1 begins to hydrolyze, giving rise to hydrochloric acid and a second oxychloride, Colloid No. 2, with a ratio higher than 21. The progress of the latter hydrolysis which is superposed on the first may be responsible for the bends in the curve. The data do not indicate the ratio of Colloid No. 2, nor do they preclude the hydrolysis of this oxychloride. Thus when a sol no longer contains ferric ion, the progressive removal of hydrochloric acid causes a series of successive hydrolyses which overlap to some extent, and oxychlorides of increasing molecular weight were formed. These successive overlapping hydrolyses do not cause any discontinuity in the precipitation curves as shown by the almost horizontal lines beginning from the sharp bends.

The equations for the hydrolysis of the various oxychlorides may be written as follows:

$$\text{Colloid No. 1} + \text{water} \rightleftarrows \text{Colloid No. 2} + \text{hydrochloric acid} \quad (2)$$

$$\text{Colloid No. 2} + \text{water} \rightleftarrows \text{Colloid No. 3} + \text{hydrochloric acid}, \quad (3)$$

etc.

Further evidence in support of the theory that the first colloidal oxychloride has a ratio of 21 is found in the behavior of ferrous sulfate solutions when oxidized by the air. A precipitate is formed in which the ratio of iron to sulfate radical is 16.89, but in the presence of platinum the oxidation is accelerated, and the precipitate contains 20 equivalents of iron to one equivalent of sulfate radical.[1]

The hydrolysis equilibria of the oxychlorides are established rapidly, as shown by the very short time within which constant precipitation values were obtained with most of the synthesized sols. But the behavior of the sols in which ferric chloride was formed, particularly *m* and *m'*, proved that the first hydrolytic equilibrium, Equation 1, requires considerable time.

Below the ratio 21, the proportion of free hydrochloric acid increases rapidly and ferric chloride begins to appear. It is interesting to note that dilute ferric chloride solutions will give a precipitate with potassium sulfate, and centrifuging yields a clear colorless liquid. This indicates that the color of dilute ferric chloride solutions is due to the presence of the oxychloride, Colloid No. 1.

Dissociation of the Oxychlorides.—Duclaux,[2] in a much quoted article, published data on the precipitation of brownish red hydrous ferric oxide sols of the clear variety, showing that the potassium sulfate required for precipitation was equivalent to the chlorine present in the sol taken. He therefore concluded that all of the chlorine in the colloid was ionizable, the precipitation by potassium sulfate being similar to the precipitation of a chloride, like barium chloride by potassium sulfate. The formula $n\text{Fe}_2(\text{OH})_6.\text{Fe}_2\text{Cl}_6$ was ascribed to the colloid. Duclaux employed sols of purities varying within a wide range, and found slight deviations from the above rule only for the purer sols. For these the equivalents of potassium sulfate were slightly less than the equivalents of chlorine, but no particular importance was attached to this fact. Duclaux also clearly implied that the potassium sulfate necessary for precipitation will be zero only when the chlorine content is zero.

Examination of the results in Tables V–VIII, Cols. 2 and 4, shows that the number of equivalents of potassium sulfate required for the pre-

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[1] Jordis, *Z. Elektrochem.*, 10, 679–682 (1904).

[2] *J. chim. phys.*, 5, 29–56 (1907).

cipitation of a sol may be a very small fraction of the hydrochloric acid content of the sol, expressed in equivalents; and, so far as the experimental data indicate, the fraction is always less than one-half. The smallest fraction was obtained for sol 1′, for which the potassium sulfate was equivalent to about one-fourteenth part of its hydrochloric acid content.

Evidently Duclaux's and the author's results are completely at variance. Since a fundamental question in colloid chemistry is at issue, it is important to establish the reason. The following three causes suggest themselves: (1) Different methods employed for the precipitation of sols; (2) the aging phenomenon in hydrous ferric oxide sols; (3) incorrect analysis of sols.

Duclaux's method of precipitation consisted in adding varying volumes of potassium sulfate solution to a number of samples of the same sol, and observing the smallest quantity of electrolyte which caused complete precipitation upon standing. This method of precipitation in several test experiments gave results identical with those obtained by the author's method. Thus, the method of precipitation is not responsible for the contradictory results.

It is claimed that perfectly clear hydrous ferric oxide sols age.[1] The author's ability to reproduce certain sols by mixing other sols with dilute hydrochloric acid, and the consistent results obtained throughout, justify the statement already made—that the nature of a clear hydrous ferric oxide sol is determined by its composition and temperature—not by its history. The aging of clear hydrous ferric oxide sols, in the absence of more conclusive evidence, might be attributed to the action of the alkali of the glass container.

There remains the third possible explanation of the disagreement between the results of Duclaux and the author. Picter and Lindon,[2] Duclaux,[3] and several others, have demonstrated beyond question that in a colloid precipitation similar to that of this research, the amount of electrolyte displaced from the colloid is equivalent to the electrolyte necessary for precipitation. In the present case, the liquid in which the precipitated colloid is suspended, will contain potassium chloride equivalent to the potassium sulfate required for precipitation. It accordingly follows that if the potassium sulfate is equivalent to chlorine content of the sol, it should be possible to determine this chlorine content by precipitating with potassium sulfate, filtering, and analyzing for chlorine in the filtrate.[4] The author's experience indicates that the method always

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[1] Zsigmondy, "Kolloid chem.," p. 185.

[2] *Trans. Chem. Soc.*, **87**, 1909 (1905).

[3] *J. chim. phys.*, **5**, 29–56 (1907).

[4] This method of analysis is no doubt responsible for the high ratios reported by some investigators. Duclaux does not give his method for determining the chlorine in his sols.

yields very low results. Hence Duclaux's relationship appears to be incorrect. If Duclaux determined the chlorine content of his sols by precipitating with potassium sulfate and estimating the chlorine in the filtrate, his relationship is immediately explained.

Interpretation of the Relationship between Chlorine Content of Colloid and the Potassium Sulfate Required for Precipitation.—Taking the first theoretical oxychloride at the intersection of the dotted line in Fig. 1, we find that 0.0224 equivalent of potassium sulfate completely precipitate colloid containing 0.047 equivalent of hydrochloric acid. Only a small fraction of the chlorine of the sol is in the form of free hydrochloric acid. Hence, a plausible explanation is that about one-half of the chlorine of the first oxychloride, Colloid No. 1, is ionizable, the other half being masked or non-ionic. According to this theory only the ionic chlorine of the oxychloride is replaceable by sulfate radical.

Above the ratio 21, as evidenced by the increasing difficulty of dialysis, the chlorine as hydrochloric acid becomes an increasingly smaller fraction of the total chlorine of the sol, and consequently may be disregarded in considering the higher oxychlorides. Now, purification of Colloid No. 1 leads to the appearance of new oxychlorides of higher order, *i. e.*, with higher ratios. At the same time, the number of equivalents of potassium sulfate required for precipitation becomes an increasingly smaller fraction of the chlorine content of the sols, which is practically equal to that of the oxychlorides. Therefore, the proportion of ionic chlorine decreases as the order of the oxychlorides increases, or as the purity of the sol increases.

The increasing stability of a sol as the hydrochloric acid content increases may now be explained by the reversal of hydrolysis and the formation of more stable oxychlorides. This explanation seems more satisfactory than that which says that the hydrochloric acid or hydrogen ion protects the colloid.

Experiment shows that the stability of a sol, with a ratio above 30, decreases as the concentration increases. But, according to the equation, Colloid No. x + Water $\rightleftarrows$ Colloid No. $(x + 1)$ + Hydrochloric acid, concentration of a sol will result in a reversal of hydrolysis, and the formation of more stable oxychlorides. Hence, the theory that the ionic chlorine of the oxychlorides determines the precipitation value is not complete, *i. e.*, colloid precipitation cannot be regarded simply as a metathesis reaction. However, the decrease of stability with increase in concentration, is considerable only for very pure sols as may be seen from Fig. 2. Probably the formation of more stable oxychlorides upon concentrating a sol is more than compensated by the greater tendency of the colloidal molecules to gel or flocculate in concentrated solutions.

The study of colloidal precipitation is being continued in this laboratory, and the physical properties, including viscosity and conductivity, of sols of the type of hydrous ferric oxide are also being investigated.

Summary.

The lack of agreement between the colloid precipitation data of different investigators is shown to be attributable very largely to the varying purities and concentrations of the sols employed.

A number of series of perfectly clear hydrous oxide sols were carefully prepared. In each series the iron concentration was constant while the chlorine content varied. The sols were precipitated by potassium sulfate solution, and the amount of salt required for the complete precipitation of the sol was taken as a measure of its relative stability.

The data show that for a given iron concentration the stability increases with the chlorine content, while for sols of a given purity, *i. e.*, ratio equivalents Fe : equivalents Cl, the stability decreases as the concentration increases, this being most pronounced for very pure sols.

It is shown how the maximum purity of a sol may be found by graphical extrapolation. The maximum purities corresponding to four iron concentrations are obtained. The maximum purity obtainable decreases as the iron concentration increases.

The results of Nicolardot and Duclaux are discussed.

A chemical theory of the constitution of hydrous ferric oxide sols is advanced to explain the relation between stability and composition.

PITTSBURGH, PENNA.

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE UNIVERSITY OF ILLINOIS, NO. 28.]

AN IMPROVED VICTOR MEYER VAPOR-DENSITY APPARATUS.

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The Victor Meyer vapor-density apparatus has remained in nearly its original form since its introduction, in spite of the fact that many thousand molecular-weight determinations are made with it every year in research and instructional laboratories. The few modifications that have been called to the attention of the authors are concerned with the introduction of the substance to be vaporized. Weiser[1] has, however, described a compact form of the apparatus, which has a number of advantages.

The substance whose molecular weight is desired is usually introduced by removing the stopper at the top, and dropping into the apparatus a diminutive glass-stoppered bottle or a bulb with a capillary outlet. Another method consists in breaking the sealed capillary of a bulb hung near the top of the vaporization tube. Either of these methods involves

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[1] *J. Phys. Chem.*, 20, 532 (1916).