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

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

## Summary

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

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY, NO. 421]

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

BY ARTHUR W. THOMAS AND LUCILLE JOHNSON

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

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

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

other, but the recent discovery by Freundlich and Nathansohn[3] showing that arsenious sulfide hydrosol and sulfur (Odén) hydrosol precipitate each other, although both are "negatively charged," is not amenable to explanation by this hypothesis. A satisfactory chemical explanation is available, however.

A short paper by Lottermoser[4] in 1910 suggested a chemical mechanism for mutual precipitation of colloids which was based upon a few experiments with silver iodide hydrosol peptized by silver nitrate (or by silver ion) and silver iodide sol peptized by potassium iodide (or the iodide ion). He found sharpest and most complete mutual precipitation in those mixtures where the amounts of peptizing silver nitrate and potassium iodide were in, or very near, chemical equivalence.

In the belief that mutual precipitations of colloids are chemical phenomena this investigation was undertaken. A series of "positively charged" ferric oxide hydrosols was treated with a number of "negatively charged" silicic oxide hydrosols and the precipitation quantitatively studied from the contents of peptizing electrolyte. The reaction between ferric oxide sols and arsenious sulfide sols was followed qualitatively.

## Preparation and Analysis of Ferric Oxide Sols

**Preparation.**—Ferric oxide sols were prepared by adding 2 *M* ammonium hydroxide very slowly, by dropping from a buret, to 2 *M* ferric chloride solution which was vigorously stirred until the precipitated ferric hydroxide ceased to peptize or "dissolve" easily. The sols, which were very dark in color, were dialyzed in collodion bags against distilled water until the desired degree of "purity" was reached.

**Analysis.**—IRON. Three cc. of concd. sulfuric acid was added to 25 cc. of sol and the solution evaporated to dryness on a hot-plate. This was to insure removal of chlorine. The dried residue was dissolved in 150 cc. of water, 10 cc. of 18 *M* sulfuric acid added, the solution passed through a Jones reductor and titrated with standard potassium permanganate. Correction was made for the reducing of a blank of sulfuric acid.

CHLORINE BY VOLHARD'S METHOD.—Ten cc. of nitric acid prepared by diluting concd. acid (d., 1.42), from which all oxides had been removed, with an equal volume of water, was added to 50 cc. of the sol and the mixture allowed to stand in a dark, cool place until the solution was clear. An excess of standard 0.1 *M* silver nitrate solution was added, the silver chloride filtered off and the excess titrated with 0.1 *M* potassium thiocyanate solution using the iron as indicator.

TABLE I

COMPOSITION OF FERRIC OXIDE SOLS

| No. | Moles $FeCl_3$ | Moles $Fe_2O_3$ | $Fe_2O_3/FeCl_3$ | No. | Moles $FeCl_3$ | Moles $Fe_2O_3$ | $Fe_2O_3/FeCl_3$ |
|---|---|---|---|---|---|---|---|
| 1 | 0.00895 | 0.0482 | 5.35/1 | 15 | 0.00518 | 0.0507 | 9.8/1 |
| 2 | .01075 | .0509 | 4.8/1 | 17 | .00267 | .0346 | 13./1 |
| 3 | .00889 | .0483 | 5.37/1 | 20 | .00145 | .0267 | 18.5/1 |
| 4 | .00338 | .0294 | 8.65/1 | 21 | .00230 | .0367 | 15.9/1 |
| 6 | .00178 | .0191 | 10.6/1 | 23 | .00238 | .0339 | 14.3/1 |

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[3] Freundlich and Nathansohn, *Kolloid Z.*, **28**, 258 (1921); **29**, 16 (1921).

[4] Lottermoser, *Kolloid Z.*, **6**, 78 (1910).

The amount of iron as iron chloride was calculated from the chlorine and this subtracted from the total iron gave the iron from which ferric oxide was calculated.

## Silicic Acid Sols

**Preparation.**—Silicic acid sols were prepared by dissolving water glass (d., 1.4) in 10 times its weight of water and partially neutralizing to various degrees with hydrochloric acid. The sodium chloride formed was not removed because (1) the freshly prepared sols diffused quite readily through unglazed porcelain dialyzers and through ordinary collodion sacks; these sols after standing showed aggregation of particles (became opalescent) and then would not diffuse through the septa mentioned; but removal of sodium chloride by dialysis would also remove sodium hydroxide formed by hydrolysis of sodium silicate, which was not desired; (2) the presence of the sodium chloride did not complicate the results, as shown later.

**Analysis.**—SILICIC ACID. To a portion of the sol was added several cubic centimeters of 12 *M* hydrochloric acid and the mixture was evaporated to dryness. The residue was twice wet with hydrochloric acid and evaporated to dryness, after which it was washed free from chlorides and weighed as silicon dioxide.

SODIUM SILICATE.—A portion of the sol was diluted with four or five times its volume of water, making a total volume of 100 or 200 cc., depending on the concentration of the sol. Ten cc. of a concd. solution of sodium chloride was added to replace sodium hydroxide which might be held in the dispersed phase, and the solution titrated with 0.1 *M* hydrochloric acid, using phenolphthalein as indicator. After neutrality was apparently reached the solution became pink upon standing, and a few drops of acid were necessary to discharge the color. To avoid errors due to this, a check was run by adding an excess of acid and titrating with sodium hydroxide; the results checked within 2%, which is well within the error of the subsequent determinations of precipitation ratios.

SODIUM CHLORIDE.—The sodium chloride was calculated from the amount of hydrochloric acid added to the water glass to form the silicic acid sol.

As no definite formula can be given for the sodium silicate, the concentrations are expressed in terms of silicon dioxide for silicic acid and sodium hydroxide for the stabilizing sodium silicate.

TABLE II

COMPOSITION OF SILICIC ACID SOLS

In moles per liter

| No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $SiO_2$ | 0.221 | 0.208 | 0.305 | 0.437 | 0.186 |
| NaOH | 0.0327 | 0.0356 | 0.0294 | 0.135 | 0.0115 |
| $SiO_2$ : NaOH | 6.7/1 | 5.8/1 | 10.4/1 | 3.5/1 | 1.6/1 |
| NaCl | 0.091 | 0.081 | 0.142 | 0.111 | 0.093 |

## Procedure

Various amounts of one sol were run from a buret into hard glass, bacteriological tubes of uniform diameter and clearness and about 20 cc. in volume. Equal volumes of the other sol were run from a pipet or buret into the tube as quickly and as quietly as possible to avoid mixing. The tubes were inverted two or three times with as little agitation as possible, to insure complete mixing of the sols. This was sufficient if the tubes were not more than $^3/_4$ full and were revolved as they were inverted. The point of maximum precipitation could be clearly seen by successive stages; first, the greatest cloudiness in the series, followed by the first separation of particles, and usually the first sediment. The last was frequently over a wider range than the first two stages as the precipitating zone widened rapidly. All observations were made immediately after mixing by holding the series of tubes against a clean or open window. Artificial light was found to be quite unsatisfactory, as was the light late in the afternoon or on a dark day.

Some series precipitated more easily than others, probably because of greater agitation. Vigorous shaking usually precipitated the whole series immediately. A tube of greater diameter than the others or of cloudy or marked glass appeared more cloudy and consequently was misleading. A few series were centrifuged, but the time required in placing them in the centrifuge and the force to throw out the fine particles resulted in complete precipitation over a wide range.

To avoid errors due to an unclean tube or some other factor, three or four determinations were made in each instance.

The effect of dilution of the sols is given in Table III.

TABLE III

EFFECT OF DILUTION UPON MUTUAL PRECIPITATION

| Cc. $Fe_2O_3$ sol No. 6 | Cc. $SiO_2$ No. 1 | | Precipitation results | Millimoles | |
|---|---|---|---|---|---|
| | | | | HCl | NaOH |
| 1. (Dilution 1:0 | 1:10) | | | | |
| 5.3 | 1 to 10 | | All coagulated to solid | | |
| 2. (Dilution 1:10 | 1:50) | | | | |
| 5.3 | 3.0 | | Partial | 0.00284 | 0.00268 |
| 5.3 | 3.5 | | Almost complete | | |
| 5.3 | 4.1 | | Complete | | |
| 5.3 | 4.5 | | Almost complete | | |
| 3. (Dilution 1:50 | 1:250) | | | | |
| 5.3 | 4.5 | | Partial | 0.00057 | 0.00064 |
| 5.3 | 4.8 | 4.9 | Complete | | |
| 5.3 | 5.1 | | Complete | | |
| 5.3 | 5.4 | | Partial | | |
| 4. (Dilution 1:100 | 1:250) | | | | |
| 10 | 4.7 | | Much slower | 0.00065 | 0.00053 |
| 10 | 5.0 | | First to ppt. | | |
| 10 | 5.3 | | Much slower | | |
| 10 | 5.6 | | Much slower | | |

This table shows that the dilution of mutually precipitating sols narrows and sharpens the zone of maximum precipitation, and that the variation in ratio between the sols varies no more than in successive experiments with the same dilution. If carried beyond certain dilutions coagulation is almost imperceptible or is so slow that it is very difficult to determine. The dilutions used for the work were the greatest giving sharp precipitations. Very unstable sols show considerably different ratios with dilution. This will be discussed later.

To avoid possible differences due to order of mixing, the order was always reversed at least once.

Table IV gives the data found in determining the points of maximum precipitation in cases typical of 37 experiments made, and Table V shows results obtained with one silica sol and several ferric oxide sols, which are typical of two other similar series.

TABLE IVA

MUTUAL PRECIPITATION OF SILICIC ACID HYDROSOL NO. 1 WITH FERRIC OXIDE HYDROSOL NO. 20

Dilutions: $Fe_2O_3$ sol = 1:25 $SiO_2$ sol = 1:200

5.3 cc. of ferric oxide sol added to silicic acid sol

| First test | | Second test | |
|---|---|---|---|
| Cc. $SiO_2$ sol | Results | Cc. $SiO_2$ sol | Results |
| 4.0 | Partial precipitation | 4.5 | Partial later precipitation |
| 5.0 | First and heaviest precipitate | 5.0 | First to precipitate |
| 6.0 | Partial precipitation | 5.5 | |
| 7.0 | Only slightly cloudy | 6.0 | Partial later precipitation |

It was evident that 5.2 cc. of silicic acid sol with 5.3 cc. of ferric oxide sol gives the maximum precipitation.

TABLE IVB

Silicic acid sol added to 5.3 cc. of ferric oxide

| Cc. $SiO_2$ sol | Results | Cc. $SiO_2$ sol | Results |
|---|---|---|---|
| 4.8 | Fourth to precipitate | 5.4 | Second to precipitate |
| 5.0 | Second to precipitate | 5.6 | Third to precipitate |
| 5.2 | First to precipitate | | |

Maximum precipitation is obtained with 5.2 cc. of silicic acid sol and 5.3 cc. of ferric oxide sol.

TABLE V

THE RATIO AT MAXIMUM PRECIPITATION OF SILICIC ACID SOL NO. 1 TO DIFFERENT FERRIC OXIDE SOLS

| | $Fe_2O_3$ sol | | Milli equivalents | | $SiO_2$ sol | |
|---|---|---|---|---|---|---|
| No. | Dilution | Cc. | Chloride | Sodium | Cc. | Dilution |
| 1 | 1:100 | 10.0 | 0.00199 | 0.00151 | 4.6 | 1:100 |
| 2 | 1:100 | 5.3 | .00171 | .00124 | 3.8 | 1:100 |
| 3 | 1:100 | 10.0 | .00267 | .00180 | 5.5 | 1:100 |
| 4 | 1:100 | 10.0 | .00102 | .00112 | 3.5 | 1:100 |
| 6 | 1:100 | 10.0 | .00054 | .00065 | 5.0 | 1:250 |
| 15 | 1:50 | 5.3 | .00165 | .00155 | 9.5 | 1:200 |
| 17 | 1:50 | 5.3 | .00085 | .00085 | 5.2 | 1:200 |
| 20 | 1:25 | 5.3 | .00085 | .00085 | 5.2 | 1:200 |
| 21 | 1:25 | 5.3 | .00147 | .00164 | 10.0 | 1:200 |
| 23 | 1:25 | 5.3 | .00151 | .00155 | 9.5 | 1:200 |

Silicic acid sol No. 4 was precipitated at different dilutions against ferric oxide sols Nos. 4, 6 and 20. No clear zones could be determined, but in every case the milli-equivalents of sodium exceeded the milli-equivalents of chloride.

The precipitating volumes checked within 10% in all cases except that of the very impure silicic acid sol No. 4.

To test the effect of the sodium chloride present upon the point of maximum precipitation 0.03 g. of sodium chloride (an amount equal to 60% of the amount of sodium chloride already present in the sol), was added to silicic acid sol No. 2 (diluted 1: 200), and the sol precipitated with several ferric oxide sols.

The results showed that the sodium chloride is without influence on the mutual precipitation of silicic acid sols and ferric oxide sols, and consequently no error was introduced by its presence in the silicic acid sols used.

TABLE VI

THE RATIO OF FERRIC CHLORIDE EXPRESSED IN EQUIVALENTS OF HYDROCHLORIC ACID TO SODIUM SILICATE

Expressed in equivalents of sodium hydroxide in the thirty-seven precipitations of ferric oxide sol and silicic acid cited in the foregoing tables. The values are milli-equivalents of sodium hydroxide per 0.001 milli-equivalents of hydrochloric acid.

The sols are arranged in the order of their purity, the ratio of sodium silicate in terms of sodium hydroxide to silicon dioxide decreasing from left to right, and the ratio of ferric chloride to ferric oxide decreasing from top to bottom

| | | Silicic Acid Sols | | | | |
|---|---|---|---|---|---|---|
| Number | | 4 | 2 | 1 | 3 | 5 |
| Moles $NaOH/SiO_2$ | | 1/3.5 | 1/5.8 | 1/6.7 | 1/10.4 | 1/16.1 |
| Ferric oxide sols No. | Ferric oxide sols Moles $FeCl_3/Fe_2O_3$ | | | | | |
| 2 | 1/ 4.8 | | 0.00061 | 0.00073 | 0.00080 | .... |
| 1 | 1/ 5.35 | | .00080 | .00055 | .00077 | .... |
| 3 | 1/ 5.37 | | .00073 | .00069 | .00077 | .... |
| 4 | 1/ 8.65 | >100% | .00096 | .00091 | .00090 | .... |
| 15 | 1/ 9.8 | | .00090 | .00100 | .00080 | 0.00029 |
| 6 | 1/10.6 | >100% | .00106 | .00094 | .00082 | .... |
| 17 | 1/13 | | .00101 | .00090 | .00080 | .00043 |
| 23 | 1/14.3 | | .00101 | .00091 | .00090 | .00048 |
| 21 | 1/15.9 | >100% | .00098 | .00110 | .00080 | .00044 |
| 20 | 1/18.5 | | .00093 | .00100 | .00080 | .... |
| Av. (Excl. of 2, 1, 3) | | >100% | .00098 | .00095 | .00083 | .00041 |

Table VI shows that over a wide range of ratios between peptizing agent and dispersed phases of sols, there is a constant ratio between the peptizing agents of mutually precipitating sols and a greatly varying ratio between the dispersed phases. This leads to the conclusion that the precipitation is due to removal of the peptizing agents by a chemical action between them. As no definite formula can be given for the silicates it is impossible to express the reaction between sodium silicate and ferric chloride in an equation. However, the peptizing ferric chloride and sodium silicate can be given in terms of their hydrolysis products which are in equilibrium with the dispersed phase complexes, and consequently in the mutual precipitation of ferric oxide and silicic acid sols the reaction may be expressed as $HCl + NaOH \longrightarrow NaCl + H_2O$.

Another indication of such a reaction is given by the difference of hydrogen-ion concentration in the supernatant liquid of precipitation of varying degrees. Various amounts of silicic acid sol No. 3 (diluted 1:25) were added to 25 cc. of ferric oxide sol No. 4 (diluted 1:10), the precipitates allowed to settle and the hydrogen-ion concentrations of the supernatant liquids determined with the results given in Table VII. The ferric oxide sol showed a Sörensen value (*P*H) of 5 while the silicic oxide sol was slightly alkaline to phenolphthalein.

TABLE VII

CHANGE IN HYDROGEN-ION CONCENTRATION WITH VARYING PRECIPITATION OF FERRIC OXIDE AND SILICIC ACID SOLS

| Silicic acid sol Cc. | Remarks | Negative log hydrogen-ion concentration |
|---|---|---|
| 10 | Very slight pptn.<br>Excess of $Fe_2O_3$ sol | 5.6 |
| 16 | Maximum pptn. | 6.8 |
| 18 | 2nd of series to ppt. | 7.8 |
| 20 | Slow pptn. Excess of $SiO_2$ sol | >8.3 (Alkaline to phenolphthalein) |

Thus it is evident that maximum precipitation occurs at neutrality as the chemical equivalence of peptizing electrolyte demands and that the acidity increases with excess ferric oxide sol, and the alkalinity increases with an excess of silicic acid sol.

The ferric oxide sols, excluding Nos. 1, 2 and 3 (which contain the greatest amount of the peptizing agent in proportion to the dispersed phase), give a 1:1 ratio with silicic acid sols Nos. 1 and 2. With silicic acid sol No. 3, the same ferric oxide sols give a constant ratio with the ferric chloride of the same ferric oxide sols. As the sol becomes purer in respect to peptizing agent, it becomes more unstable and the precipitating ratios become more inconstant. This agrees with the general experience with "pure" ferric oxide sols. It is known that when a certain degree of "purity" is passed in a sol, the sol precipitates. The sol containing only a little more than the necessary minimum of peptizing agent is in a metastable condition, and the least disturbance will precipitate it. This may easily account for the ready precipitation of the pure ferric oxide sols.

The effect of diluting unstable sols in mutual precipitation is shown in Table VIII.

TABLE VIII

PRECIPITATION OF FERRIC OXIDE SOL NO. 17 WITH SILICIC ACID SOL NO. 5 OF VARIOUS DILUTIONS

| $Fe_2O_3$ sol, 1:50 | Milli-equivalents of HCl, 0.00160 | | |
|---|---|---|---|
| $SiO_2$ sol | 1:50 | 1:100 | 1:200 |
| NaOH, milli-eq. | 0.00057 | 0.00069 | 0.00080 |
| NaOH eq. of HCl eq. % | 35 | 43 | 50 |

Thus it is seen that the reaction between very "pure" sols tends to approach chemical equivalence upon dilution, which is to be expected since the individual particles becoming widely separated upon dilution have less chance of aggregating and thus settling out. In the mean time there is more chance for a complete reaction between the peptizing agents.

Both ferric oxide and silicic acid sols show erratic results in precipitation, if they contain large amounts of peptizing agent. This is undoubtedly due to the fact that some of the unaffected peptizing agent is adsorbed in the coagulum and carried down with it.

## Investigation of the Mutual Precipitation of Ferric Oxide and Arsenic Trisulfide Sols

The ferric oxide sols used in this work were the same as those used with silicic acid sols and the method of procedure was the same.

### Arsenic Trisulfide Sols

**Preparation.**—Hydrogen sulfide was passed into a warm solution of arsenic trioxide prepared by dissolving from 5 to 10 g. of finely powdered resublimed arsenic trioxide in a liter of boiling water that had been boiled first to remove dissolved oxygen.

Analysis.—Attempts were made to drive over the excess hydrogen sulfide and thus determine it directly, but in every instance there was decomposition of the arsenic trisulfide. For example, 100 cc. of sol containing only 1 cc. of phosphoric acid (d., 1.7) was completely dissolved by 15 minutes' boiling. This was surprising in view of the generally accepted ideas of the stability of arsenic trisulfide, and may be due to its fine subdivision in the sol. At no time was there precipitation during the heating, unless electrolytes had been added to the point of precipitation.

Ward[5] states that at temperatures below 35°, the adsorbed hydrogen sulfide can be evolved from arsenic sulfide without decomposition of the latter, but several attempts to remove only the hydrogen sulfide by passing carbon dioxide gas through the pure sol, or through the sol previously precipitated by neutral salts, resulted in appreciable decomposition and this technique was thereby proved valueless.

Freshly prepared sols were analyzed for total arsenic and sulfur. From the arsenic percentage, the amount of trisulfide present was calculated and the sulfur found in excess of that to give this amount was calculated as hydrogen sulfide of peptization. But the amount was so small that a very small error in the determination of either the arsenic or sulfur renders the results useless; thus, in one case an error of 0.1% in analysis made an error of 100% in the calculation of hydrogen sulfide of peptization.

Since a quantitative study of this mutual reaction is precluded, at least a qualitative test is justifiable. If in the mutual precipitation of ferric oxide sol and arsenious sulfide sol a chemical reaction takes place between the ferric chloride and hydrogen sulfide of peptization, one of the following reactions may take place: (1) $H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + S + 2HCl$; (2) $3H_2S + 2FeCl_3 \longrightarrow 2FeS + S + 4HCl$.

In most precipitations there is no evidence of the latter reaction, as the precipitate is yellow. When, however, the sol contains a great amount of hydrogen sulfide, a blackening develops which can be explained by the formation of ferrous sulfide.

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[5] Ward, *Am. Chemist.* **4**, 10 (1873).

To test the supposition that the mutual precipitation between ferric oxide sol and arsenious sulfide is due to the oxidation of the sulfide ion of the peptizing hydrogen sulfide by the ferric ion of the peptizing ferric chloride, the following experiment was performed.

Five hundred cc. of an arsenic trisulfide sol was precipitated with ferric oxide sol No. 4, the precipitate dried and extracted with carbon disulfide. *Sulfur was recovered.* Since arsenious sulfide sols are most likely to contain sulfur after exposure to air, a "blank" was run wherein an equal quantity of sol was precipitated by aluminum sulfate, the precipitate dried, extracted, and the sulfur found subtracted from that obtained in the main experiment.

It has been generally considered that hydrogen sulfide is always the stabilizing agent of arsenic trisulfide sols. In this investigation it was found that sols that contained an excess of arsenious acid, either through decomposing the arsenic trisulfide and driving out some hydrogen sulfide, or by failure to add an equivalent or slight excess of the hydrogen sulfide for the arsenious acid in solution when preparing the sols, were very stable. They gave a sharp range of precipitation with the ferric oxide sols, if sufficiently dilute, and acted in every way as did the arsenic trisulfide sols peptized by hydrogen sulfide. They have the advantage of having a nonvolatile peptizing agent, and one that does not oxidize as readily as does hydrogen sulfide, thus being more dependable for quantitative work. The arsenic trisulfide sols peptized by arsenious acid will probably be found more satisfactory for further quantitative work on the mutual precipitation of ferric oxide and arsenic trisulfide sols than those peptized by hydrogen sulfide have been.

## Summary

1. The precipitating ratios of certain mutually precipitating hydrosols depend upon the peptizing agent.
2. There is chemical equivalence between the peptizing agents of ferric oxide hydrosol peptized by ferric chloride, and silicic acid sols peptized by sodium silicate, provided the ratio of peptizing agent to the dispersed phase falls within a certain range. Outside of this range the precipitation is erratic.
3. Ferric-oxide—silicic-acid sol precipitations showing chemical equivalence between the peptizing agents at maximum precipitation exhibit little variance in precipitation ratios with dilution, while those showing a divergence from chemical equivalence approach chemical equivalence with dilution.
4. Mutual precipitation of ferric oxide and silicic acid sols is due to the removal of peptizing agents by chemical reactions between them.
5. Qualitative experiment shows that the mutual precipitation of arsenious sulfide hydrosol and ferric oxide hydrosol may be due to the

chemical reaction $S^{--} + 2Fe^{+++} \longrightarrow S^{\circ} + 2Fe^{++}$. It was impossible to verify this quantitatively because of restrictions in the analytical procedures.

New York, N. Y.

[Contribution from the Department of Chemistry of Cornell University]

# AZIDO-CARBONDISULFIDE. I. FORMATION, PREPARATION AND GENERAL PROPERTIES[1]

By A. W. Browne, A. B. Hoel, G. B. L. Smith and F. H. Swezey
With Microscopical Studies by C. W. Mason

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It was found by F. Sommer,[2] during an investigation of the properties of sodium azido-dithiocarbonate, that treatment of aqueous solutions of this salt with such oxidizing agents as ferric chloride, iodine in potassium iodide, and potassium permanganate, potassium dichromate, or ceric salts in sulfuric acid solution, results in the precipitation of an unstable white solid, surmised by him, from the method of its formation, to possess the formula $N_2—N—CS—S—S—CS—N—N_2$. No analysis was made of this compound, or study of its properties, aside from the observation that a sample of the insoluble needles, when heated under water, exploded violently at a temperature below 100°.

The formation of this substance, to which the name azido-carbondisulfide is provisionally assigned, has been repeatedly observed in this Laboratory[3] to take place when aqueous solutions of potassium trinitride and iodine are brought together under certain conditions in the presence of carbon disulfide. Azido-carbondisulfide has been shown to have an important catalytic effect upon the reaction between potassium trinitride and iodine, as does the related compound, potassium azido-dithiocarbonate. In fact, these two substances, the relationship between which is very similar to that between iodine and potassium iodide, behave in this reaction in the manner characteristic of what might be termed a *reciprocal catalytic pair.*[4]

**Formation and Preparation.**—The action of various oxidizing agents

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[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 4 under Heckscher Grant No. 4. For Articles 1, 2, and 3 see This Journal, **44,** 2106, 2116, 2315 (1922). This paper was presented at the New Haven meeting of the American Chemical Society in April, 1923.

[2] Sommer, *Ber.*, **48,** 1833 (1915).

[3] Browne and Hoel, This Journal, **44,** 2106 (1922).

[4] This term is intended to apply to any pair of chemical compounds that undergo repeated mutual conversion into each other while having their catalytic effect upon a given chemical reaction.