

225. *Some Observations on Colloidal Solutions of Silver and Copper.*

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(1) NEEDING silver sols of various particle sizes, free from organic substances, we did not use dextrin for reduction (Wiegel, *Kolloid-Z.*, 1929, **47**, 323; 1930, **51**, 112; **53**, 96; *Z. physikal. Chem.*, 1929, *A*, **143**, 81), but obtained a very clear, yellow nuclear sol by reduction of silver oxide in ammoniacal solution with hydrazine hydrate. A stock silver solution was prepared by dissolving the freshly precipitated oxide in aqueous ammonia ($\text{Ag} : \text{NH}_3 = \text{ca. } 1 : 4$), and diluting this to 0.01M with regard to silver. For preparation of the sol, 10 c.c. of this solution were diluted to 100 c.c. and reduced by addition of 100 c.c. of water containing 2 c.c. of a stock 0.1% hydrazine hydrate solution (B.D.H.).

From this nuclear sol, coarser, but fairly homodisperse sols were prepared by treating suitable amounts of the sol with hydrogen peroxide, as in Wiegel's method. Some of the silver particles are dissolved in the peroxide, and this silver is deposited upon the remaining nuclei. The colour changes with increasing particle size in the following series: yellow, orange, red, violet, deep blue, pale blue. If the number of nuclei is very small, they grow so much at the expense of the dissolved silver that visible flakes are formed, mostly floating on the liquid. The colour series mentioned is similar to that observed when using a nuclear sol prepared with dextrin or with a solution of phosphorus in ether. There are, however, a few minor differences which are not readily explained owing to insufficient knowledge of the rate of crystallisation of silver in solutions of this kind and of the decomposition of hydrogen peroxide in presence of ammonia.

The foregoing results were obtained when using ordinary distilled water, but if the stock solutions were diluted with conductivity water, good nuclear sols were not obtained. They were decidedly coarser, markedly opaque, especially in reflected light, and less homodisperse: if used as a nuclear sol, the sols containing larger particles did not show the clear, strong colour distinctive of homodisperse sols. Now it was known that the distilled water contained copper to the extent of 0.3—0.4 mg. per litre (as determined colorimetrically with potassium ferrocyanide), so a nuclear sol was prepared by using a solution of conductivity water containing 0.002 millimol. of copper sulphate (somewhat less than the amount in distilled water); a clear, homodisperse sol was formed, exactly like one prepared with distilled water. Hence the presence of copper is obviously the factor favouring the formation of a transparent, homodisperse sol, when using distilled water.

There is an optimum in the concentration of copper sulphate between 0.003 and 0.007

millimol. per litre. This amount of copper is not the most suitable for all silver concentrations : for much smaller concentrations, the amount of copper present in the distilled water may be large enough to cause coagulation. At higher copper sulphate concentrations, markedly above 0.015 millimol./litre, flocculation becomes evident, the colour of the sol being very dark in reflected, and brown in transmitted, light.

The presence of small amounts of copper is essential to the formation of good silver mirrors on glass; *e.g.*, by reducing alkaline silver solution with glucose. According to Kohlschütter and Fischmann (*Annalen*, 1912, **387**, 86), the formation of such mirrors depends on a number of factors; among others, the silver must be precipitated in a homodisperse, colloidal state, such a precipitation being favoured by small amounts of copper. Our results confirm this statement. Those authors found that small, but somewhat larger amounts of lead and zinc act in the same way as copper in improving the deposition of mirrors. Correspondingly, we found that the preparation of a nuclear silver sol with conductivity water is improved by addition of small amounts of lead nitrate or zinc sulphate. Mirror and sol formation are also similar in that in both cases the favourable influence of foreign metals is confined to a narrow range of concentrations : slightly larger amounts cause coagulation of the silver particles; black silver is formed instead of a mirror, and the sol changes its colour owing to coagulation.

The mechanism of the action of these metals is not known with certainty. Perhaps highly disperse particles of the metal oxides (or hydroxides) are present and are able to act as nuclei or are instrumental in distributing the primary silver nuclei in a similar dispersion ("orientating action" of Kohlschütter).

Zsigmondy and his collaborators (*e.g.*, Zsigmondy and Thiessen, "Das kolloide Gold," Leipzig, 1925; Hiege, *Z. anorg. Chem.*, 1915, **91**, 145; Reitstötter, *Kolloidchem. Beih.*, 1917, **9**, 222) investigated the influence of foreign substances upon the formation of gold sols. To a certain extent they were able to distinguish between substances which change the rate of formation of nuclei (a) and others which change the rate of crystallisation (b); *e.g.*, ammonia, hydrazine sulphate, ferro- and ferri-cyanide ions strongly reduce (a) without influencing (b); when present, they therefore only allow the preparation of more or less coarse sols. These substances have a similar effect on the preparation of silver sols as described above. Addition of small amounts of potassium ferro-, ferri-, or nickelo-cyanide or of an excess of ammonia to conductivity water prevents the formation of yellow, highly disperse sols. At higher concentrations (*e.g.*, 0.15 millimol./litre of the nickelocyanide) the formation of silver particles is delayed for many hours or entirely inhibited. Obviously also, hydrazine, as with gold sols, is not a reducing agent which naturally would favour the formation of highly disperse silver sols; it needs the presence of substances like copper, etc., to give satisfactory results.

Potassium cyanide acts like the complex cyanides. The ferrocyanide is able to dissolve colloidal silver, as reported by Beutel and Kutzligng (*Monatsh.*, 1929, **51**, 369) and confirmed by us. This might suggest that the cyanide ion acts directly by rapidly and preferentially dissolving the very small silver nuclei, the larger ones surviving and growing at the expense of the dissolved silver. It might be objected that complex ions such as ferrocyanide are very stable : no ferrous ion can be detected in ferrocyanide solutions by the polarographic method (Sanigar, *Rec. trav. chim.*, 1925, **44**, 549; Emelianova, *ibid.*, p. 528). This result does not rule out the possibility that cyanide ion may be split off, leaving some other complex ion, and hitherto no extensive investigation on the concentration of cyanide ion in solutions of complex cyanides appears to have been carried out.

An excess of ammonia might act like cyanides, dissolving the small nuclei preferentially.

Phosphorus in ether is a reducing agent not only for gold but also for silver, causing a very rapid formation of metal nuclei and hence of most highly disperse sols. Those of silver are obtained also when conductivity water is used, *i.e.*, in absence of copper, or with an excess of ammonia. Sols prepared by passing phosphine through an ammoniacal solution of silver oxide (*M*/1000 with regard to Ag) are highly disperse, like those made with phosphorus. They may be used as nuclear sols in presence of an excess of ammonia, etc.

These experiments were confirmed by observations with the cardioid-ultramicroscope, as is shown by the following summary.

Silver sol prepared with :	Observation.
Phosphorus in ether	No particles visible
N ₂ H ₄ , H ₂ O in distilled water (Cu present)	Very small particles; a few larger ones
„ in conductivity water (Cu absent)	Many larger particles, also some smaller ones
„ and excess of NH ₃	Mainly large particles
„ and a small amount of K ₄ Fe(CN) ₆	Mainly large particles

(2) Red, fairly stable, aqueous sols of copper, not containing large amounts of a protective substance, have only occasionally been described (Gutbier, *Z. anorg. Chem.*, 1902, **32**, 355; Meyer, *ibid.*, 1903, **34**, 60; cf. Sauer and Steiner, *Kolloid-Z.*, 1935, **72**, 35). When an ammoniacal solution of copper oxide was reduced with hydrazine hydrate, red copper sols were sometimes obtained, but it was not possible to find conditions regularly yielding this result. The sols generally obtained were rather coarse, bluish-green in transmitted and copper-red in reflected light, and distinctly opaque. Since phosphorus in ether produces highly disperse gold and silver sols, we hoped it would be equally effective for preparing highly disperse copper sols, but mere addition of phosphorus in ether to an ammoniacal copper solution did not give satisfactory results. At room temperature, the liquid became dark only when the phosphorus concentration was large; on heating, a brownish-black colloidal solution was formed over a wide range of concentrations. This appears to be a copper phosphide sol: its formation is favoured by an excess of phosphorus and it is easily oxidised by air. The tendency of copper to form phosphides is known to be greater than that of gold and silver (cf. Gmelin-Friedheim, 1909, Vol. 5, I, 958), and the rate of this reaction seems to surpass all others. The successive action of hydrazine hydrate and phosphorus, however, produces highly disperse, transparent, beautifully red copper sols, looking like copper ruby glass, the results being reproducible. 3 C.c. of a solution of copper oxide in aqueous ammonia ($\text{Cu} = M/100$; $\text{NH}_3 = 1.0M$) are diluted with 10 c.c. of water and heated to boiling; 3 c.c. of hydrazine hydrate (0.5%) are added, and immediately afterwards 1.5 c.c. of a solution of phosphorus in ether (the saturated solution diluted to 10 times its volume). On addition of the hydrazine hydrate the bluish liquid turns colourless (reduction to univalent copper), and on addition of the phosphorus it becomes first yellow and then red.

This sol is amicroscopic, no particles being seen under the cardioid-ultramicroscope, and they mainly consist of metallic copper. This was proved by an X-ray analysis, for which we are very indebted to Mr. H. Terrey. The sol, containing 2.5 millimols. (*i.e.*, 0.16 g. Cu/l.), was just coagulated with lithium nitrate, centrifuged for a short time, the excess of water poured off, and the sediment, in presence of some water, sealed into a glass capillary. The Debye-Scherrer diagram was that of metallic copper. The particles of this sol are negatively charged, as shown by electrophoresis.

The mechanism of the formation of this sol is complicated. First, a highly disperse sol of some other substance is formed whose particles appear to act as nuclei for the copper sol: the liquid turns yellow, at room temperature, if the ammoniacal solution of bivalent (or also of univalent) copper is mixed with hydrazine hydrate and phosphorus solution; on heating it becomes darker. The dark brown solution, appearing on heating with an excess of phosphorus, turns yellow on shaking or in course of time. The same yellow colloidal solution is produced, if phosphine is passed through an ammoniacal copper solution to which some hydrazine hydrate has been added, or if the latter substance is poured on the ammoniacal solution after it has been treated for a very short time with phosphine. If the treatment with phosphine is too prolonged, a black sol is formed, which turns yellow again when oxidised by being shaken with air and then mixed with hydrazine hydrate. The formation of this yellow sol also always precedes that of a red copper sol on heating according to the standard method described above.

This primary substance might be a very highly disperse copper phosphide. This assumption, however, is not free from objection: it would mean that the copper has to be deposited on the nuclei of the phosphide, because the latter is not readily reduced by hydrazine hydrate; if a brownish-black sol of the phosphide is produced by adding an excess of phosphorus in ether, it cannot be reduced to a red sol, even with an excess of hydrazine hydrate. Moreover, if phosphine acts upon an ammoniacal copper solution, heated to boiling and containing hydrazine hydrate, only a transitory formation of a red sol is observed, the liquid finally becoming black (copper phosphide). Also it is not clear why the formation of the primary, yellowish sol appears to proceed particularly easily with phosphine. The possibility that the primary nuclei consist of some other copper compound cannot yet be excluded.

These experiments agree with v. Weimarn's conception (*Kolloid-Z.*, 1929, **47**, 231) that the preparation of highly disperse metal sols need not depend mainly on the rate of formation of metal nuclei from dissolved substances; nuclei of an intermediate, insoluble compound may be produced which are particularly liable to form highly disperse sols. The nuclei of this intermediate substance may be reduced to the metal or be coated with it.

When hydrazine hydrate acts upon an ammoniacal copper solution in absence of phosphorus, an excess of ammonia is inimical to the production of highly disperse copper sols. As with silver, the ammonia may dissolve the very small metal nuclei formed. Perhaps pre-formed nuclei are again essential; particles of copper oxide (or hydroxide), present from the start,

may act in this way, either as such or after having been reduced to copper. They, too, would only be in the solution when the excess of ammonia is small, *i.e.*, when the copper-ammonia complex is dissociated to a sufficiently high degree. This colloidal oxide is most probably positively charged, whereas the copper particles are negative; hence there is always the danger that the oxide will coagulate the freshly formed copper sol, thus preventing or impeding the production of a highly disperse sol. There is probably a narrow range in the concentration of the copper-ammonia complex favourable for producing the sol. The amount and dispersion of the copper oxide are not alone responsible; other factors influencing the rate of reduction and coagulation must also be taken into account and are not easily kept constant. In agreement with this conception, the transitory formation of a red, clear sol is frequently observed; the final sols are, however, generally coarser, being copper-red in reflected and bluish-green in transmitted light. Their particles also consist of metallic copper, as proved by *X*-ray analysis.

Amicronic red sols are probably produced so much more easily in presence of phosphorus because the primary nuclei formed there, *i.e.*, the particles of the yellow sol, are negatively charged (as shown by an electrophoretic experiment) like the copper particles, thus rendering coagulation unlikely.

These experiments led to many observations on the formation of copper mirrors on the walls of the glass vessels, the reduction of an ammoniacal copper solution by hydrazine hydrate being a particularly suitable method of preparing them. As Kohlschütter and Fischmann (*loc. cit.*) observed with silver mirrors, the substance which is specially important is the metal oxide: this must be present in sufficiently large amount; hence only a small excess of ammonia is favourable, the degree of dissociation of the copper-ammonia complex then being high. The copper oxide is markedly adsorbed on the glass, the two substances having opposite charges, and it must be reduced there more rapidly than in the liquid. Since a rapid reduction is also favoured by a higher temperature, the glass wall of the vessel must be sufficiently hot. If a test-tube filled with cold water is dipped into the solution in which the copper compound is being reduced, no mirror is formed on its wall. With the same total amount of ammonia, the copper-ammonia complex may be considered to be more dissociated than the silver complex (Gaus, *Z. anorg. Chem.*, 1900, **25**, 236; Dawson and McCrae, *ibid.*, 1901, **26**, 94); hence a large excess of ammonia, causing a decrease in the amount of colloidal metal oxide, need not be avoided so carefully with copper as with silver.

Under the conditions favouring the production of good copper mirrors, copper sols are formed in the liquid which appear to be coagulated by copper oxide (or hydroxide). They are dark brown in reflected and greyish-green in transmitted light; if the reduction is allowed to continue, the colour changes to copper-red in reflected and bluish-green in transmitted light, *i.e.*, the adsorbed oxide is reduced, a coarse copper sol being formed. The amount of oxide advantageous for the mirror is obviously too large for the sol, for it may cause coagulation. For preparing more highly dispersed sols, a larger but not too high concentration of ammonia is favourable.

(3) Mercury sols of diverse particle size and colour could also be prepared by mixing various amounts of hydrogen peroxide solution with a nuclear mercury sol made by reducing mercuric chloride with hydrazine hydrate in an aqueous solution containing sodium hydroxide and sodium protalbinat.

SUMMARY.

1. Highly disperse silver sols, free from organic substances and suitable as nuclear sols, may be prepared by reducing an ammoniacal silver oxide solution with hydrazine hydrate, provided that small amounts of copper be present. The favourable influence of traces of copper for making silver mirrors is well known. Other metals, such as lead and zinc, similarly facilitate the formation of both sols and mirrors.

2. Substances, such as complex cyanides or excess of ammonia, known to have an unfavourable influence on the production of highly disperse gold sols, are equally disadvantageous with silver sols.

3. As with gold sols, phosphorus (in ether) favours the formation of a highly disperse silver sol so strongly that it is not necessary either to add an advantageous substance such as copper or to avoid impeding reagents such as excess of ammonia. Hydrogen phosphide acts like a solution of phosphorus.

4. Clear, amicronic, red sols of metallic copper, free from protecting colloids, are reproducibly prepared by reducing an ammoniacal solution of copper oxide with hydrazine hydrate and adding phosphorus (in ether), at higher temperatures. Phosphorus without

hydrazine hydrate does not produce such a sol, but instead, provided that the amount of phosphorus be sufficiently large, a brownish-black sol, probably containing copper phosphide particles. The production of the red copper sol is connected with the primary formation of a yellow sol whose particles, consisting presumably of copper phosphide, act as nuclei.

5. With ammoniacal copper oxide solution and hydrazine hydrate in absence of phosphorus, much coarser copper sols are produced. In these solutions copper mirrors are also readily formed. Mirrors are favoured by a smaller excess of ammonia than is advantageous for the formation of fairly disperse copper sols.

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