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LXI. Allotropic silver.—Part III. Blue silcer, soluble and insoluble forms

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LXI. *Allotropic Silver.*—Part III. *Blue Silver, soluble and insoluble forms.* *By* M. Carey Lea*.

WHEN my first paper on the subject of allotropic silver was published about two years ago, that product seemed to be the result of a very limited number of reactions closely allied to one another. Further study has shown that it is a much more common product than at first appeared to be the case. Wherever in the reduction of silver a reddish colour shows itself, that may be taken as a probable indication that allotropic silver has been formed, even although it may be destroyed before it can be isolated.

What is rather remarkable, is that allotropic silver is produced abundantly in certain very familiar reactions in which its presence has never been suspected: so abundantly, in fact, that some of these reactions constitute the best methods of obtaining silver in the soluble form. In photographic operations silver has often been reduced by tannin in the presence of alkalies. It has not been imagined that by slightly varying the conditions, the whole of the silver may be made to pass into solution as a soluble metal with its characteristic intense blood-red colour.

Some of these new reactions will be here described in detail.

Allotropic Silver formed by Dextrine and Alkaline Hydroxide.

When dextrine is dissolved in a solution of potassium or sodium hydroxide, and silver nitrate is added, keeping the hydroxide in moderate excess, the silver is at first thrown down in the form of the well-known brown oxide. This brown colour presently changes to a reddish-chocolate shade, and at the same time the silver begins to dissolve. In a few minutes the whole has dissolved to a deep-red colour, so intense as to be almost black. A few drops poured into water give it a splendid red colour of perfect transparency. Examination with the spectroscope leaves no doubt that we have to do with a true solution.

It is interesting to observe that silver can be held in solution in neutral, acid, and alkaline liquids. In the first process which I published, in which silver citrate is reduced by a mixture of sodic citrate and ferrous sulphate, the latter may be used either in acid solution, or it may be first neutralized with alkaline hydroxide, so that that form of silver is held in solution in either a neutral or an acid liquid. The form that

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* Communicated by the Author.

is obtained with the aid of dextrine dissolves most freely in the strongly alkaline liquid in which it is produced, and when dilute nitric or sulphuric acid is added, the silver is precipitated. But with acetic acid the precipitation is very incomplete: the solution retains a brown colour, and contains silver. Even the addition of a large excess of strong acetic acid fails to throw down any more silver. It follows, therefore, that whilst this form of silver is most freely soluble in a strongly alkaline liquid it is also soluble, to some extent, in one that is either neutral or acid.

The precipitate, when once formed, appears to be almost insoluble. A small portion of it stirred up with distilled water gives no indication of solution. But if a quantity is thrown on a filter and washed, as soon as the mother-water is washed out, the liquid runs through of a muddy red; and if this filtrate be allowed to stand, it deposits an insoluble portion, and then has a fine rose-red colour and perfect transparency. Notwithstanding the beautiful colour, it contains a trace of silver only, so great is the colouring-power of the metal. Sometimes, if the alkaline solution stands for a month or two, the silver becomes spontaneously insoluble; most of it falls to the bottom as a deep-red substance, but part remains in suspension, with a bright brick-red colour. The difference between this and the true solution as originally formed is extremely well marked.

Dextrine is a very variable substance, and different specimens act very differently. Common brown dextrine seems to do better than the purified forms.

Convenient proportions are as follows:—In 2 litres of water 40 grammes of sodium hydroxide may be dissolved and an equal quantity of dextrine, filtering if necessary. 28 grammes of silver nitrate are to be dissolved in a small quantity of water, and added by degrees at intervals. Complete solution readily takes place. Although the liquid contains less than 1 per cent. of metallic silver, it appears absolutely black, when diluted red, by great dilution yellowish. With some specimens of dextrine the solution remains clear; with others it soon becomes a little turbid.

Perhaps the most interesting reaction which this solution shows is that with disodic phosphate. A little phosphate is sufficient to throw down the whole of the silver, although both solutions are alkaline. When a gramme of phosphate in solution is added to 100 cub. centim. of silver solution, the colour becomes bright red, sometimes scarlet, and the whole of the silver is presently precipitated. This precipitate on the filter has a colour like that of ruby copper, which colour it retains during the first washing; but after a few hours' washing with distilled water, the colour changes to a deep Nile-green, and at the same time it becomes slightly soluble, giving a port-wine coloured solution. With more washing, this solubility may disappear.

It is a general fact that all these forms of silver, however various their colour, have both a body- and a surface-colour; and these two colours tend always to be complementary. The body-colour is that shown by the precipitate while still moist; it is also visible when a thin coat is brushed over paper, a coat so thin that light passes through it, is reflected by the paper, and returned again through the film. But when a thick and opaque film is applied, the body-colour disappears, and only the complementary surface-colour is visible.

So in the case of the precipitate by phosphate, when the substance resembling ruby copper is spread thickly on paper, it dries with a bright-green metallic surface-colour. But when the substance itself becomes green by continued washing, it assumes, on drying, a dark gold or copper colour, the surface-colour changing with the body-colour and maintaining its complementary relation. In observing these effects one is constantly reminded of certain coal-tar colours, both by the great intensity of coloration and by the metallic surface-colour. I am not aware that any other inorganic substance shows this resemblance to a similar extent.

These forms of allotropic silver have a great tendency to attach to themselves foreign matters. Although the dry substance has all the appearance of a pure metal, it may contain as much as 8 or 10 per cent. of organic matter, which it is utterly impossible to detach. I have taken much trouble to eliminate this substance. In one attempt hot distilled water was forced through with the aid of a filter-pump for over one hundred hours, without effect. The presence of this organic substance becomes evident when the metal is heated in a tube. A vapour arises which condenses into small brownish drops having an empyreumatic odour. The residue of bright white metallic silver, when dissolved in nitric acid, leaves behind black flakes of carbon. When the allotropic silver is dissolved in dilute nitric acid and the silver precipitated by hydrochloric acid, on evaporation a small residue of a yellowish gummy substance is obtained.

Analyses.—Four silver determinations were made of material rendered as pure as it was found possible to obtain it. Results:—

No. 1	93·77	per cent.	Ag.
„ 2	94·27	„	„
„ 3	92·86	„	„
„ 4	96·64	„	„

Allotropic Silver obtained with Tannin and Alkaline Carbonates.

Tannin (gallotannic acid) in alkaline solution reduces silver nitrate to metallic silver in the allotropic form. Tannin acts more strongly than dextrine, and therefore does best with carbonated alkali, dextrine best with alkaline hydroxide, although either substance will produce the reaction with either form of alkali and, though less advantageously, with ammonia. Tannin with sodium carbonate gives a very perfect solution of silver, quite free from the turbidity that is apt to characterize the dextrine solution. The colour of this solution is likewise very intense: one containing 1 per cent. of silver is quite black, on dilution deep yellowish red. It has very much the same characters as the preceding, but is rather more stable. To obtain it, 24 grammes of dry sodium carbonate may be dissolved in 1200 cub. centim. of water. A 4-per-cent. solution of tannin is to be made and filtered; of this, 72 cub. centim. are to be added to the solution just named: of silver nitrate, 24 grammes dissolved in a little water are to be added by degrees. Solution takes place almost instantly as each successive portion is added. The solution, after standing a day or two, may be decanted or filtered from a small quantity of black precipitate.

When the solution is treated with a very dilute acid, as, for example, nitric acid diluted with twenty times its bulk of water, allotropic silver is precipitated in the solid form. It dries with a brilliant metallic surface-colour of a shade different from the foregoing, and somewhat difficult to exactly characterize, a sort of bluish steel-grey.

I do not find that the blue allotropic silver (in which is included the green and steel-grey varieties) can be reduced to any one definite type. On the contrary, its variations are endless. Slight differences in the conditions under which the solutions are formed, or in the mode of precipitation, give quite different products. For example: of ten products obtained with tannin and sodium carbonate in different proportions, several were easily and completely soluble in ammonia, some were slightly soluble, and some not at all. Some specimens not at all soluble in water became so by moistening with dilute phosphoric acid: they did not dissolve in the acid, but when it was removed they had become soluble in water. On other specimens phosphoric acid had no such effect. Some solutions are scarcely affected by acetic acid, others are partly precipitated, others almost, but not quite, wholly. The films spread on paper vary very much in their relations to light; some are readily converted into the yellow intermediate form, whilst others are very insensitive. The least sensitive specimens seemed to be those for which dilute nitric acid had been used as a precipitant: they had a steel-grey colour. Precipitation by acetic acid seems to tend to a greenish metallic surface, colour, and greater sensitiveness. Different specimens also vary very much as to permanency; this character is also affected by the amount of washing received: thorough washing tends to permanency.

In some way the blue, grey, and green forms seem more closely related to the black or dark grey forms of normal silver, for they tend, in time, to pass into them; whilst, on the contrary, gold-coloured silver, if pure, tends, with time, to change to bright white normal silver on the surface with dark, or even black, silver underneath.

Action of other Carbonates.

Tannin is capable of producing allotropic silver, not only in the presence of the carbonates of potassium and sodium, but also with those of lithium and ammonium, and also with the carbonates of calcium, magnesium, barium, and strontium. The action of the last-named carbonate has been more particularly examined. It yields allotropic silver of a dark-red colour whilst moist, drying with a rich bluish-green metallic surface-colour in thick films, in very thin films transparent red. It is probable that the substances with which tannin produces these reactions would be further increased by investigation.

I have found some additional modes of production of these forms of silver, modes which are very curious and interesting. They are now being studied, and will be reported on hereafter.

Nature of the "Intermediate Substance."

It has been mentioned in previous papers that when allotropic silver is converted into normal silver by the action of heat, it passes through a perfectly well-marked intermediate state. In this state it retains the gold-yellow colour and high lustre, but none of the other properties of the original form. Oxidizing and chlorizing agents show nearly the same indifference as with ordinary silver. Whilst allotropic silver is soft and easily reduced to powder, the intermediate substance is hard and tough. When a glass rod is drawn over a film of allotropic silver, it leaves behind it a white trace of ordinary silver. The intermediate substance shows no such reaction: the trace of a glass rod does not differ from the rest of the film; and even hard burnishing produces no change in the colour. Continued exposure to sunlight brings about the same alteration to the intermediate form, and it takes place spontaneously with time.

At that time no explanation could be found as to the nature of the change. It proves, however, to be a passage into a crystalline form. Some films spread on paper were exposed to the action of very dilute solution of ferric chloride. It chanced that one of these films had undergone a partial change into the intermediate form; the unchanged portion was darkened by the ferric solution, whilst the portion that had passed into the intermediate form retained its bright gold-yellow colour and lustre, rendering it thus distinguishable. The figures which it exhibited were strikingly crystalline. One portion showed a foliated structure, such as is formed by interpenetrating crystals; other parts showed ramifications with something of a plant-like form. Another part exhibited a sheaf of acicular crystals nearly parallel in direction half an inch to an inch long, and as fine as hairs. These appearances indicated with certainty crystalline structure. Other specimens have been obtained, though none so well defined as that just mentioned, which happened to be taken at exactly the right stage of spontaneous alteration to make the structure manifest. The alteration is not apparent to the eye, as the colour does not change.

This change to the crystalline condition does not seem to be peculiar to gold-coloured silver. The blue form, when gently heated in a tube, becomes yellow. By continued heat it changes to white normal silver. A film on glass began to change from blue to yellow at about 180° C. Light also produces this change on blue silver. The specimens obtained by different processes act very differently; some change with a few hours of strong sunlight, others require many days.

From what has been written in this and preceding papers, it appears that allotropic and even soluble silver may be formed in a great variety of reactions. The reducing agent may be either a ferrous or a stannous salt, or any one of a variety of organic substances of very different constitutions. From the solubility and activity of this substance and the parallelism which many of its reactions show to those of silver in combination, I have been disposed to think that silver in solution might, like silver in combination, exist in the atomic form. It is certain that, up to the present time, we have no positive knowledge of the existence of any element in the atomic form as a solid. We know that four or five metals are atomic in their vapours, and that in iodine vapour at a certain temperature the molecules separate into atoms.

But it may be questioned whether we have not seen solid elements in the atomic form without recognizing them as such. There are forms of iron, nickel, cobalt, and lead which exhibit very remarkable properties, properties that have been hitherto very unsatisfactorily explained. Lead tartrate reduced by gentle ignition in a nearly closed tube, and allowed to cool and then shaken out into the air, forms a stream of fire. The oxides of iron, nickel, and cobalt reduced in closed tubes by hydrogen show similar properties. It is customary to explain this action by affirming that the metals are left in an extremely fine state of division. This explanation is not satisfactory. Sulphur, for example, is far more inflammable than any of the metals just mentioned, and may be obtained in a state of exceedingly fine division, either by sublimation or by precipitation; but does not, in consequence, show any greater tendency to spontaneous inflammation. It seems more natural to suppose that these metals are reduced in the atomic form; and this view of the matter seems to be much strengthened by the following considerations.

The experiments of Ramsey and of Heycock and Neville, cited in a previous paper, lead to the conclusion that in the case of a dilute solution of one metal in another the dissolved metal exists in the atomic form. But still more, the experiments of Tammann on amalgams indicate that in these alloys the dissolved metal is atomic; and it is stated that Joule, by distilling off the mercury from an iron amalgam, found that the iron was left in a pyrophoric condition. The amalgam of manganese, carefully distilled, gives a pyrophoric powder. Chromium amalgam, distilled in a current of hydrogen, gives a similar result if the temperature is not raised too high. The enormous affinity which these forms of metals exhibit for oxygen renders their study very difficult. It has not been before suggested that their activity is due to their being atomic; but this would seem to be a much more rational explanation than that of extreme division*. A broad distinction must of course be drawn between chemical and mechanical division: a substance may be atomic and yet appear in masses; may be in the finest mechanical division and yet be molecular

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* M. G. Rousseau, in the new *Encyclopédie Chimique*, seems to entirely abandon the old view of extreme division, and considers these forms to be allotropic, and comparable with the allotropic forms of phosphorus, &c., Vol. iii. p. 56.

or polymerized. Silver being a metal with a very low affinity for oxygen, could not be expected to show in the atomic state the same inflammability as more oxidable metals.

In conclusion, it may be said that there is much reason to suppose that elements may exist in the atomic form, and that allotropic silver may present such a case. This is, of course, far from being proved, and is offered only as a "working hypothesis." As such, it may afford a useful aid in further investigations.

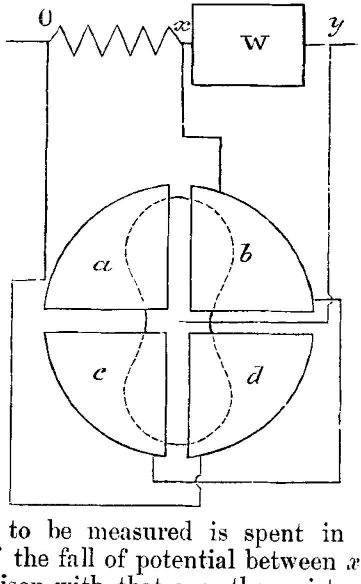
Philadelphia, April, 1891.

LXII. *The Electrometer as a Wattmeter.* *By* J. Swinburne [*].

IN 1881, when M. Joubert published his experiments on a Siemens machine, in the course of which he had used a Thomson or Mascart electrometer as a voltmeter, Professors Ayrton and Fitzgerald simultaneously proposed to use the quadrant electrometer as a wattmeter.

The ordinary method of arranging the instrument is shown in fig. 1. The resistance is wound so as to be non-inductive; and the power to be measured is spent in the apparatus marked W. If the fall of potential between x and y is very great in comparison with that over the resistance, the instrument reads like a charged electrometer, and it may be taken to read in watts. In practice such conditions do not occur;

Fig. 1.



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[*] Communicated by the Physical Society: read March 6, 1891.