

ART. L.—*On Allotropic Forms of Silver*; by M. CAREY  
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SILVER is capable of existing in allotropic forms possessing qualities differing greatly from those of normal silver. There are three such forms, or rather three modifications of one form, differing from each other in many respects, but all more nearly related to each other than any one of them to normal silver. One of these forms is soluble in water, passing readily to an insoluble form, and this last may, by the the simple presence of a neutral substance exercising no chemical action upon it, recover its solubility. Another form closely resembles gold in color and lustre.

Whether metallic silver shall be reduced from its compounds in its normal or in an allotropic form, depends upon the reducing agent applied, so that it cannot be said with any certainty whether it exists in its compounds in its ordinary normal form, or in an allotropic condition: the latter alternative seems at least equally probable.

These allotropic forms of silver are broadly distinguished from normal silver by color, by properties, and by chemical reactions. They not improbably represent a more active condition of silver, of which common or normal silver may be a polymerized form. Something analogous has already been observed with other metals, lead and copper.

Much having been written, especially within the last few years, on the products of the reduction of silver compounds, a brief summary of what has appeared may be desirable before proceeding further. The study of this subject has led to remarkable divergencies of opinion on the part of the

\* Young's General Astronomy.

chemists engaged in it. Almost all the views advanced have been successively disproved by each subsequent publication. It follows that what has obtained a place in the text books is almost wholly incorrect.

The earliest experimental work was Faraday's, but his product has been proved to be a mixture.\* The next was the well known paper of Wöhler published in 1839. It is not my purpose here to enter upon a criticism of this memoir. If this illustrious chemist succeeded in obtaining by the means employed a true citrate of silver hemioxide,—as would appear from his analyses—no chemist since his time seems to have done so. The next publication to Wöhler's was that of Von Bibra, who used Wöhler's method and, whilst affirming that he obtained a similar citrate, found an entirely different constitution for the corresponding chloride. For instead of obtaining a hemichloride  $\text{Ag}_2\text{Cl}$ , he gives, as the result of 15 concordant analyses, the constitution of his product as  $\text{Ag}_3\text{Cl}$ .† A citrate, to yield such a chloride, (if such a chloride exists,) by the simple action of hydrochloric acid, could scarcely have the constitution assigned to it by both Wöhler and V. Bibra.

In 1882, Pillitz published two papers.‡ He commences by disputing the probability of the existence of  $\text{Ag}_4\text{O}$  on grounds of valency; namely as implying that oxygen may be quadrivalent. Although it is very doubtful that any one has up to the present time obtained  $\text{Ag}_4\text{O}$ , the argument seems futile as are many arguments deduced from supposed laws of valency. Similar reasoning would make  $\text{Ag}_2\text{Cl}$  impossible, which substance undoubtedly exists, and it would also deny the existence of  $\text{K}_2\text{Cl}$  which stands upon such authority as that of Rose, Kirchhoff, and Bunsen.§ Pillitz carefully examined the so-called hemioxide precipitated by alkaline solutions of antimony and tin and could find no trace of  $\text{Ag}_4\text{O}$  in any of them. He did not examine Wöhler's products.

The first person to deny categorically the existence of Wöhler's series of hemi-compounds of silver appears to have been Dr. Spencer Newbury. In two interesting papers,|| he describes a repetition of Wöhler's methods and declares it to be impossible to obtain products of constant composition. The red solution taken by Wöhler to be argentous citrate, Dr.

\* G. H. Bailey and G. J. Foster, Chem. Soc. 1887, 416. Bericht D. Ch. G., xx, Ref. 360.

† Erdmann, J. prakt. Chim. 1875. 120, 39. Von Bibra precedes his paper with a brief summary of the conclusions reached by previous chemists on the subject of the action of light and chemical reducing agents on silver compounds. The collection is interesting as showing to what inconsistent and even contrary opinions careful observers have come on these reactions.

‡ Zeitschrift für Ann. Chemie, xxi, p. 27, p. 496.

§ Gmelin Kraut, ii, 1, 72.

|| Am. Chem. Jour. vi. 407; viii, 196.

Newbury concludes to be a suspension of finely divided silver. Muthmann\* after a careful examination of Rautenberg's products concludes that that chemist was wholly in error in asserting the formation of compounds of chromic, molybdic and tungstic acids with silver hemioxide. He next studies the red liquid obtained by Wöhler's process and comes to the same conclusion as Newbury, that it consists of finely divided silver suspended in water.

I shall not dispute the correctness of this opinion in the case of the liquid examined by these two chemists. At the same time I cannot accept the tests of solution employed by Muthmann. That a substance will not pass through a dialyser shows that it is colloidal and is no proof whatever that it is not in solution. Animal charcoal takes up many substances from true solutions. Decolorization by animal charcoal is no proof whatever that the color removed was not in true solution. By freezing, the molecular condition of a substance may be changed. Muthmann found that when the red liquid was mixed with gum water and precipitated by alcohol, the precipitated gum carried down with it the red substance, thence deducing that it was only in suspension. This conclusion is scarcely justified. A solution of litmus was mixed with gum water and precipitated with alcohol: the mass of the litmus went down with the gum, a trace only appeared in the filtrate. With Hoffmann's violet, the same result. Yet no one, I think, will assert that these two substances do not make true solutions in water. Even however, if these arguments could be admitted they would not apply to the solutions presently to be described, which can be proved by optical means to be true solutions. I propose presently to show that silver may exist in a perfectly soluble form, dissolving easily and abundantly in water. Starting from this, it may show all degrees of solubility down to absolute insolubility, still however, existing in an allotropic form and quite distinct from normal or ordinary silver. The solutions formed are as perfect as those of any other soluble substance.

Wöhler's process was next repeated by G. H. Bailey and G. J. Foster, who came to the conclusion that no citrate of hemioxide was formed, and that Wöhler's results must be rejected.

Von der Pfordten† endeavored to obtain hemi-compounds of silver by acting on the nitrate with an alkaline solution of sodium tartrate, and also with phosphorous acid. His determinations were made volumetrically, based on an opinion that a permanganate solution acidified with sulphuric acid would dissolve silver hemioxide, but not metallic silver. Previously to receiving his paper I had found that sulphuric acid, even

\* Bericht der D. Ch. Ges., xx, 983.

† Ibid., xx, 1458.

diluted with ten times its bulk of water, was capable of acting on finely divided normal silver and of dissolving an easily recognized quantity. V. d. Pfordten's conclusions were thus vitiated entirely. It should however be remarked that the difficulties of the subject are extremely great. In his last paper\* this chemist abandons his views as to the existence of silver hemi-oxide; so that at the present time the formation of  $\text{Ag}_4\text{O}$  by Wöhler's method, or by any other known method, is admitted by no one. That such an oxide may exist appears by no means improbable. The existence of  $\text{Ag}_2\text{Cl}$  and  $\text{K}_2\text{Cl}$  seems almost to involve that of  $\text{Ag}_4\text{O}$  and  $\text{K}_4\text{O}$ . This latter product Davy believed that he had obtained. The black substance which V. d. Pfordten formerly regarded as  $\text{Ag}_4\text{O}$  he now takes to be silver hydrate  $\text{Ag}_4\text{H}_2\text{O}$ .

The reduction products described by V. d. Pfordten are strongly distinguished from those which I shall presently describe by two decisive reactions:—

1. None of his products could be amalgamated with mercury (l. c., 2296). All of mine readily amalgamate.
2. None of my products give off the slightest trace of gas when treated with dilute sulphuric acid. All of his do so. (l. c., 2291.)

Moreover, the difference of appearance is extremely great.

Early in the year 1886, I took up the study of the reduction products of silver in connection with that of the photosalts. I commenced with Wöhler's process, giving it up after a few trials as affording no satisfactory results, and sought for a more reliable means. This I found, in March 1886, in a reaction which I still use; namely the reduction of silver citrate by ferrous citrate. At first, however, the results obtained were most enigmatical, the products very unstable, and impossible to purify. Much time was lost and the matter was given up more than once as impracticable. Eventually, by great modifications in the proportions, stable products, and capable of a fair amount of purification were got. Even the earlier and less pure forms were exceedingly beautiful; the purer are hardly surpassed by any known chemical products.

The forms of allotropic silver which I have obtained may be classified as follows:—

*A.* Soluble, deep red in solution, mat lilac, blue, or green whilst moist, brilliant bluish green metallic when dry.

*B.* Insoluble, derived from *A*, dark reddish brown while moist, when dry somewhat resembling *A*.

*C.* Gold silver, dark bronze whilst wet, when dry exactly resembling metallic gold in burnished lumps. Of this form there

\* Ber. D. Ch. Ges., xx, 2288.

is a variety which is copper-colored. Insoluble in water, appears to have no corresponding soluble form.

*Properties possessed by all the varieties in common and distinguishing them all from normal silver.*

All these forms have several remarkable properties in common.

1. *That of drying with their particles in optical contact, and consequently, forming a continuous film.*—If either is taken in a pasty condition and is spread evenly over paper with a fine brush, it takes on spontaneously in drying a luster as high as that of metallic leaf. C when so treated would be taken for gold leaf. But this property is much better seen by brushing the pasty substance over glass. When dry, an absolutely perfect mirror is obtained. The particles next the glass, seen through the glass, are as perfectly continuous as those of a mercurial amalgam, and the mirror is as good. A and B form bluish-green mirrors, C, gold or copper-colored mirrors.

2. *The halogen reaction.*—When any of these allotropic forms of silver are brushed over paper and the resulting metallic films are exposed to the action of any haloid in solution, very beautiful colorations are obtained. The experiment succeeds best with substances that easily give up the halogen, such as sodium hypochlorite, ferric chloride, iodine dissolved in potassium iodide, etc. But indications are also obtained with alkaline salts such as ammonium chloride etc., though more slowly and less brilliantly. With sodium hypochlorite the colors are often magnificent, intense shades with metallic reflections, reminding one of the colors of a peacock's tail. Blue is the predominating tint. These are interference colors, caused by thin films, but whether of a normal silver haloid or a hemisalt, cannot be said. When silver leaf (normal silver) is fastened to paper and a comparative trial is made, the contrast is very striking.—This matter will be more particularly examined in the 2d part of this paper, and is mentioned here as one of the reactions distinguishing allotropic from ordinary silver.

3. *The action of acids.*—The stronger acids, even when much diluted, instantly convert the allotropic forms of silver into normal gray silver; even acetic acid, not too much diluted, does this. It is important to remark that this change takes place absolutely without the separation of gas. I have more than once watched the whole operation with a lens and have never seen the minutest bubble escape.

4. *Physical condition.*—All these allotropic forms of silver are easily reduced to an impalpable powder. One is surprised to see what is apparently solid burnished metal break easily to pieces and by moderate trituration yield a fine powder.

*A. Soluble Allotropic Silver.*

A solution of ferrous citrate added to one of a silver salt produces instantly a deep red liquid. (Ferrous tartrate gives the same reaction but is less advantageous.) These red solutions may either exhibit tolerable permanency or may decolorize, letting fall a black precipitate. It is not necessary to prepare the ferrous salt in an isolated form, a mixture of ferrous sulphate and sodic citrate answers perfectly.

When, however, concentrated solutions are used with a large excess of ferrous sulphate and a still larger one of alkaline citrate, the liquid turns almost completely black. It should be stirred very thoroughly for several minutes, to make sure that the whole of the precipitated silver citrate is acted upon by the iron. After standing for ten or fifteen minutes, the liquid may be decanted and will leave a large quantity of a heavy precipitate of a fine lilac-blue color. It is best to adhere closely to certain proportions. Of a ten per cent solution of silver nitrate, 200 c. c. may be placed in a precipitating jar. In another vessel are mixed 200 c. c. of a thirty per cent solution of pure ferrous sulphate and 280 c. c. of a forty per cent solution of sodic citrate. (The same quantity of ferrous sulphate or of sodic citrate in a larger quantity of water will occasion much loss of the silver product.) I think some advantage is gained by neutralizing the ferrous solution, which has a strong acid reaction, with solution of sodium hydroxide: as much may be added as will not cause a permanent precipitate. To the quantities already given, about 50 c. c. of 10 per cent soda solution. The reaction takes place equally well without the soda, but I think the product is a little more stable with it.—The mixed solution is to be added at once to the silver solution.

The beautiful lilac shade of the precipitate is rather ephemeral. It remains for some time if the precipitate is left under the mother water, but when thrown upon a filter, it is scarcely uncovered before the lilac shade disappears and the precipitate takes a deep blue color, without losing its solubility. It may be washed either on a filter or by decantation, with any saline solution in which it is insoluble and which does not affect it too much. On the whole, ammoniac nitrate does best, but sodic nitrate, citrate, or sulphate may be used, or the corresponding ammonia salts. Although in pure water the precipitate instantly dissolves with an intense blood red color, the presence of five or ten per cent of any of these salts renders it perfectly insoluble. I have usually proceeded by adding to the precipitate (after decanting the mother water as completely as may be and removing as much more as possible with a pipette), a moderate amount of water; for the above quantities about 150 c. c. Much less would dissolve the precipitate but for the

salts present: this much will dissolve the greater part but not the whole, which is not necessary. A little of a saturated solution of ammoniac nitrate is to be added, just enough to effect complete precipitation.

As the material appears continually to change, the amount of washing needed must depend upon the object in view. If wanted for analysis, the washing must be repeated many times until ferric salt ceases to come away, but no amount of washing will entirely eliminate it. After seven or eight solutions in pure water and as many precipitations, the material is to be thrown on a filter, the liquid forced out as completely as possible with a pump and then the ammoniac nitrate washed out with 95 per cent alcohol until the filtrate leaves nothing on evaporation. The substance at this point is still soluble in water, though much less so than at first. During the washing the solubility slowly but steadily diminishes, a fact rendered noticeable by less and less ammoniac nitrate being needed to precipitate it from its solution.

*Analysis.*—The product after thorough washing as above described with alcohol, was dried at ordinary temperatures or a little above, and was then reduced to very fine powder and washed again with water as long as anything dissolved. It was then dried at 100° C. in water bath. Three silver determinations were made.

A1.....	97.31	per cent	silver.
A2.....	97.18	“	“
B.....	97.21	“	“

A1 and A2 were made with different portions of the same material, B with different material prepared in exactly the same way.

The substance therefore contained on an average 97.27 per cent of silver. The nature of the residue would decide whether the material was silver with a certain amount of impurity firmly attached to it, or whether we had to do with silver in chemical combination with other elements.

The filtrate from the silver chloride in analysis A2 was evaporated to dryness and was found to contain chiefly iron and citric acid. The iron was thrown down as sulphide, redissolved in nitric acid, precipitated hot, washed with boiling water and gave 0.8947. The residue therefore consisted of ferric oxide and citric acid, probably in the form of ferric citrate and attached so strongly that even the very careful and prolonged washing given failed to remove them. Stronger means would be required than could be used without altering the condition of the substance. The conclusion therefore seemed to be justified that the material consisted of uncombined silver simply mixed with impurity.

To verify this conclusion by additional evidence, the substance was examined as to its behavior when heated. For if any other element were chemically combined with the silver it would only be (in view of the high percentage of silver) hydrogen or oxygen. We might have to do with a hydride, analogous to Wurtz's hydride of copper, or possibly an oxide, but not probably as  $\text{Ag}_2\text{O}$  would contain only 96.43 per cent of silver.

The presence of either hydrogen or oxygen in combination with silver seems to be pretty certainly negated by the action of dilute sulphuric acid on this (and the two other substances, B and C, to be described farther on). They are all converted into gray metallic silver without the slightest escape of gas. This seems tolerably conclusive in itself; and the result of exposing a great number of specimens of all the forms A, B and C to the action of heat was equally so. As the object was to expose the fresh and moist material to a gradually increasing heat from that of boiling water to a low red heat without interrupting the process, the following arrangement was found convenient.

A piece of Bohemian glass tube about six inches long was sealed in the lamp at one end, the other closed with a rubber cork, through which passed a small gas delivery tube and another tube passing into a small test tube partly filled with water and having another tube through the cork passing under the surface of the water, thus preventing regurgitation. The material was thus first exposed for some hours to a heat of about  $150^\circ \text{C}$ . in a chloride of calcium bath; this was next removed and the heat continued to low redness. Only traces of gas were evolved and this was found to be in all of the many trials made, carbonic acid, derived from the citric acid adhering. This treatment was repeated many times with all the different varieties of the substance and with the same result. The temperature was always raised sufficiently high to ensure the complete conversion of the material into normal gray silver, but in no case was oxygen or hydrogen set free.

It could not be overlooked that in all these trials the material had passed into an insoluble form before the silver determination was made. There remained therefore this possibility: that the silver, so long as soluble, might be in combination with citric acid and that its change to the insoluble condition was caused by its separating from the citric acid. It seemed desirable that this view should be tested. As the object was to determine the condition of the silver in the substance as originally formed, avoiding as far as possible to change that form by attempts at purification, the only course available was



to determine the ratio between the silver on the one hand and the citric acid on the other, either excluding from the determination, or else removing, that portion of the citric acid which was combined with sodium (sodic citrate being used in excess) or with iron. The first attempt was to exclude without removing it, by using Wolcott Gibbs's ingenious method of precipitating the base by hydrogen sulphide, and determining the acid thus set free in a solution originally neutral. It was ascertained by careful experiment on weighed quantities of pure anhydrous citric acid, that exact titration could be made with the aid of phenolphthalein. The silver was next redissolved and estimated as chloride. A large number of determinations were made, but the method proved unsatisfactory. It was found that portions of the same material operated upon separately gave different (even widely different) results. In fact, this very discordance was in itself a proof that no stoichiometrical combination existed between the silver and the citric acid.

The importance of the matter led me to take it up again with different means, estimating the citric acid by Creuse's method. In this method the solution, after being reduced to a small bulk, is exactly neutralized (with ammonia or acetic acid), is treated with a slight excess of barium acetate and then mixed with twice its bulk of 95 per cent alcohol, let stand a day and filtered and washed with 65 per cent alcohol. In igniting, a few drops of sulphuric acid convert the barium salt into sulphate in which form the estimation is made. A preliminary trial with a weighed quantity of citric acid showed that this method gave fairly good results. I was obliged to vary the method somewhat: the precipitate of barium citrate carried down with it enough iron to render it ochrey in appearance. It was, therefore, after thorough washing with 65 per cent alcohol till every trace of barium acetate was removed, dissolved on the filter with dilute hydrochloric acid (acid 1, water 10) in which barium citrate is extremely soluble and washed through. This was followed by still weaker acid and finally with water. From the filtrate, sulphuric acid precipitated snow-white barium sulphate.

But this method requires that both the sulphates and the excess of sodic and ferric citrate shall first have been perfectly removed. The blue precipitate was therefore washed with dilute solution of ammonic nitrate until this was effected. The necessity for this purification was regrettable as introducing a possibility of a change during the treatment. It was, however, indispensable that the ferrous, ferric and sodic citrates present should be got rid of. The material after this treatment was still freely soluble in water, to a dark-red solution. An ex-

amination of its absorption spectrum showed it to be still a true solution. From this solution the silver was first removed by  $H_2S$  and then the citric acid was determined in the above described way. (If the silver were thrown down by hydrochloric acid, the reliability of the citric determination would be impaired.) Next, the silver sulphide was converted into chloride and weighed. The result gave the ratio

1 gram silver to .03195 gram citric acid.

In this case washing out the sulphates, etc., was an affair of several days. The work was repeated, reducing the time as much as possible. The material was precipitated, decanted as soon as settled, thrown upon a filter pump and the funnel kept constantly full of ammoniac nitrate in dilute solution by a wash bottle. By using very thick paper and a powerful pressure the entire washing was rapidly finished so that in about six hours from first precipitation the material was thoroughly washed, redissolved and again filtered and placed under the action of  $H_2S$ . The result was

1 gram silver to .0130 citric acid.

When these relations are reduced from weights to equivalents, they become:

No. 1, 1 equiv. citric acid to 55.63 equivs. silver.  
No. 2, 1 " " 193.7 "

indicating both that the proportion of citric acid present is variable and that it is certainly not in stoichiometrical combination with the silver in the substance examined.

It has been already said that these solutions before being acted upon by  $H_2S$  were examined optically and found to be true solutions. The inference therefore seems to be very strong that there exists an allotropic form of silver freely soluble in water. This is a property so exceptional in a metal that I have admitted it with much hesitation. The principal arguments are as follows:

The content of silver in the various products was very carefully, and I believe I may say quite accurately, determined: it was extremely high, always above 97 per cent. As already remarked, this virtually excludes the presence of all elements except hydrogen and possibly oxygen. These elements were carefully searched for, but their presence could not be detected. To suppose that we had to do with a mixture in which some compound of silver was mixed with metallic silver was not possible, for as the whole was soluble we should still have to admit the solubility of silver.

We have consequently to deal with a substance containing over 97 per cent of silver, and neither hydrogen nor oxygen in

combination with it, the remaining 2 or 3 per cent fully accounted for by ferric oxide and citric acid determined as present as accidental impurity; the substance itself readily amalgamating with mercury by simple friction, nevertheless abundantly soluble in water. If I had been able to find any other explanation for these facts without admitting the solubility of silver, I should have adopted it. But none presented itself.

Whether in solution it exists as a hydrate, that is, in more intimate combination with one or more equivalents of water, cannot be said with entire certainty; but the easy amalgamation with mercury seems hardly to favor that view. No means could be found for settling the question absolutely. Certainly at 100° C. all water is expelled, but this is of course not an argument. All the water is not expelled by indefinite exposure to a vacuum over sulphuric acid. But the proportion left is very small.

The material examined was in all cases as nearly as possible the same as that originally precipitated, but absolute identity could not be obtained. The purification absolutely necessary effects some change. This is shown by the color. The freshly precipitated material dissolves to a blood red liquid, by great dilution yellowish red. The purified substance gives a darker red solution, which with dilution remains still red. Of the nature of the substances in the condition in which they were analyzed, I can speak with some positiveness, and these include a substance soluble in water and nevertheless appearing to be nearly pure silver.

The constitution of the lilac blue substance at the moment of formation and whilst still under its mother water is a matter of more difficulty; it could not be said with certainty that it was not in some way altered in the purification. Much time and labor were spent in endeavoring to settle this point, without entirely satisfactory results, and I am at present engaged in the search for a better method.

When this blue soluble substance, purified either by washing very moderately by ammonium nitrate, or by washing with pure water, using those portions which remain undissolved after most has been carried through the filter, is brushed over paper and dries rapidly, it exhibits a very beautiful succession of colors. At the moment of applying it appears blood red; when half dry it has a splendid blue color with a lustrous metallic reflection; when quite dry this metallic effect disappears and the color is mat blue. Examined with a polarizer it shows the same characters as to two reflected beams of light polarized in planes perpendicular to each other that are described further on under B.

When the blue substance prepared in either way dries more slowly in lumps the result is very variable; sometimes it is bright bluish metallic; sometimes dull lead color, with a metallic reflection only where it has dried against a smooth surface.

### *B. Insoluble Form of the foregoing.*

The solution of the blue product just described is influenced in a remarkable way by the addition of almost any neutral substance. So far I have not found any that does not precipitate it. Not only saline solutions do this, but even a solution of gum arabic.

Neutral salts may precipitate the silver in either a soluble or an insoluble form. Alkaline sulphates, nitrates and citrates throw down the soluble form, magnesium sulphate, cupric sulphate, ferrous sulphate, nickel sulphate, potassium bichromate and ferro cyanide, barium nitrate, even silver nitrate and other salts throw down a perfectly insoluble form. The soluble form constitutes a blue or bluish black precipitate; the insoluble, a purple brown, which by repeated washing, by decantation or otherwise, continually darkens.

What is very curious is that the insoluble form may be made to return to the soluble condition. Many substances are capable of effecting this change. Sodium borate does so, producing a brown solution, potassium and sodium sulphate produce a yellowish red solution and ammonium sulphate a red one. None of these solutions has the same blood-red color as the original solution; the form of silver seems to change with the slightest change of condition.

The solutions used must be extremely dilute, otherwise the silver, though rendered soluble in pure water by them, will not dissolve in the solution itself, a singular complication of effects. So that if a moderately strong solution of one of the above substances is poured over the insoluble silver substance it does not dissolve, but by pouring off the saline solution and replacing it with pure water, the substance now dissolves readily. The insoluble substance is also readily soluble in ammonia. The solution has a fine red color, and not the yellowish red of the sodium sulphate solution.

Most neutral salts act in one or other of the ways just described, precipitating the solution of the blue substance A in either the soluble or the insoluble form, the latter soluble in ammonia, but sodium nitrite is an exception; its solution effects an entire change and renders the substance wholly insoluble, probably reconverting it to normal silver.

Sometimes the substance will spontaneously pass into a soluble form. A specimen, rendered insoluble by precipitation with ferrous sulphate, after much washing began to run through, not only as a suspension, which often happens, but as a solution, clearing itself, after a day or two, of insoluble portions and furnishing a rose-red solution. I have kept this solution in a corked vial for eight months, during which time it has remained unchanged.

The general properties of this substance can be much better observed in the thin films obtained by brushing the moist substance over paper than in the lumps. The films thus obtained are bright greenish metallic, and this green evidently results from a mixture of blue and yellow, as in some lights the blue, in others the yellow, is most evident. When these films are examined by light reflected from them at a large incidence with the normal and a Nicol's prism or an achromatized prism of calc-spar is interposed between the film and the eye, it becomes at once apparent that the blue and yellow light are oppositely polarized. The yellow light is polarized in the plane of incidence, the blue light perpendicularly to that plane. All specimens show the yellow light, but the quantity of blue light is very variable and is directly connected with the amount of washing applied to the precipitate. The more it is washed the more the yellow predominates. To see the blue form in its full beauty, a little of the red solution may be precipitated with a very little magnesium or aluminium sulphate and be thrown on a filter. As soon as the liquid has drained off and without any washing, the deep bronze-colored substance is to be brushed over paper. On drying it has all the appearance of a bright blue metal with a remarkable luster. The mirrors obtained by brushing the substance over glass are so beautiful and so perfect that it seems as if this property might have useful applications, especially for silvering irregular surfaces. Much care, however, would be necessary in the preparation to obtain a permanent product.

*Crystallization.*—On one occasion this substance was obtained in a crystalline form. Some crude red solution had been set aside in a corked vial. Some weeks after, it was noticed that the solution had become decolorized, with a crystalline deposit at bottom. The bottle was carefully broken; the deposit, examined by a lens, consisted of short black needles and thin prisms. Evidently the saline matters present had balanced the silver in solution so nearly as not to cause an immediate precipitation, but a very gradual one only. The mother water was drained off and a few drops of pure water were added. No solution took place, the crystals were therefore of the material B, the insoluble form. The contact of pure water instantly

destroyed the crystallization and the substance dried with a bright green metallic luster. Contact with pure water evidently tends always to bring this form of silver into the colloidal state, sometimes soluble and sometimes not; whilst the contact with certain neutral salts renders it crystalline.

The extraordinary sensitiveness which allotropic silver shows to external influences contrasts strongly with the inertness of normal (probably polymeric) metallic silver. When we place this fact alongside of the well known sensitiveness of many silver compounds to light, heat and (as I have elsewhere shown) to mechanical force,\* we are led to ask whether silver may not exist in this form in these very sensitive compounds.

To obtain the substance in a pure condition suitable for analysis, it is necessary to choose a precipitant not giving an insoluble product with either citric or sulphuric acid. Magnesium sulphate or nickel sulphate answers well; I have generally used the first named. A very dilute solution is made of it and the red solution of A is to be filtered into it. The precipitate soon subsides. A large quantity of water is to be poured on, and then washing by decantation can be continued to three decantations, after which the substance remains suspended. It can be made to subside by adding a very small quantity of magnesium sulphate; one four-thousandth part (0.25 gram to one liter) is sufficient. The substance may then be thrown on a filter and washed with pure water.

*Analysis.*—A specimen dried in vacuo over sulphuric acid gave

No. 1	.....	97.17	per cent silver.
No. 2	.....	97.10	“ “

A specimen dried first in vacuo and then at 100° C., lost in the second drying .88 per cent water.

So that the substance dried at 100° contained 97.96 per cent. of silver. The remaining 2.04 per cent consisted of ferric oxide and citric acid.

### *C. Gold-Yellow and Copper-colored Silver.*

It has been long known that golden-yellow specks would occasionally show themselves in silver solutions, but could not be obtained at will and the quantity thus appearing was infinitesimal. Probably this phenomenon has often led to a supposition that silver might be transmuted into gold.† This yel-

\* Production of an image on silver iodide capable of development by simple pressure.

† I have a little volume published in Paris in 1857 by a chemist named Tiffereau who was firmly convinced that in many reactions, minute portions of silver are converted into gold, especially with the aid of powerful sunlight. In Mexico, he affirmed, he had artificially produced several grams of gold, a portion of

low product, however, is only an allotropic form of silver, but it has all the color and brilliancy of gold, a fact which was apparent even in the minute specks hitherto obtained.

By the means presently to be described, silver can be converted wholly into this form. It is a little curious that its permanency seems to depend entirely on details in the mode of formation. I found many ways of obtaining it, but in a few months the specimens preserved changed spontaneously to normal silver. This happened even in well closed tubes. The normal silver produced in this way is exquisitely beautiful. It has a pure and perfect white color like the finest frosted jewelers' silver, almost in fact exceeding the jeweler's best products. I found, however, one process by which a quite permanent result could be obtained. Specimens made by it in November of 1886 are now, at the end of thirty months, unchanged.

In forming the blue product which I have called A, very concentrated solutions were necessary. C on the contrary is best obtained from very dilute ones. The following proportions give good results.

Two mixtures are to be prepared: No. 1, containing 200 c. c. of a ten per cent solution of silver nitrate, 200 c. c. of twenty per cent solution of Rochelle salt and 800 c. c. of distilled water. No. 2, containing 107 c. c. of a thirty per cent solution of ferrous sulphate, 200 of a twenty per cent solution of Rochelle salt and 800 of distilled water. The second solution (which must be mixed immediately before using only) is poured into the first with constant stirring. A powder, at first glittering red, then changing to black, falls, which on the filter has a beautiful bronze appearance. After washing it should be removed whilst in a pasty condition and spread over watch glasses or flat basins and allowed to dry spontaneously. It will be seen that this is a reduction of silver tartrate by ferrous tartrate. The metallic silver formed by reduction with ferrous citrate and ferrous tartrate is in an allotropic condition; with ferrous oxalate this result does not seem to be produced.

Although the gold-colored silver (into which the nitrate used is wholly converted) is very permanent when dry, it is less so when wet. In washing, the filter must be kept always full of water: this is essential. It dries into lumps exactly resembling highly polished gold, especially the surfaces that have dried in contact with glass or porcelain. For this substance has in a

which he presented to the French Academy with one of his papers. To his great disappointment he did not succeed in repeating these experiments in Paris, with more than an infinitesimal result. All gold in his opinion had been originally silver, and this belief, he affirms, is universal amongst Mexican miners. The book has for title "*Les Métaux sont des Corps composés.*"

high degree the property already described in forms A and B—that of drying with the particles in optical contact. When the thick pasty substance is extended over glazed paper, it dries with the splendid luster of gold leaf, with this essential difference, that these allotropic forms of silver B and C assume spontaneously in drying the high degree of brilliancy which other metallic surfaces acquire by elaborate polishing and burnishing. By brushing a thick paste of this substance evenly over clean glass, beautiful gold-colored mirrors are obtained; the film seems to be entirely continuous and the mirror is very perfect.

By continued washing the precipitate changes somewhat, so that in drying it takes on a coppery rather than a golden color, and is rather less lustrous, though still bright and permanent.

Two silver determinations by conversion into chloride made in Nov., 1886, gave :

No. 1 .....	97·81 per cent silver.
No. 2 .....	97·86 “ “

Recently these experiments have been repeated and the washing was more successful. Ferric tartrate adheres very obstinately and after a time washing with water ceases to remove it. Stronger means cannot be employed without affecting the substance itself. These last determinations gave :

No. 1 .....	98·750 per cent of silver.
No. 2 .....	98·749 “ “

The residue of No. 2 was examined and consisted almost wholly of ferric citrate.

Chestnut Hill, Phila., April, 1889.

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NOTE.—The editors have received, from the author of the above paper, samples of the three allotropic forms of silver which he describes, and also strips of glass and paper coated with them. Mr. Lea is to be congratulated on his very important results. The coated strips, including the gold-colored mirror made with the “gold-silver,” answer fully to his description. The mirror is remarkable for its perfection and brilliancy.