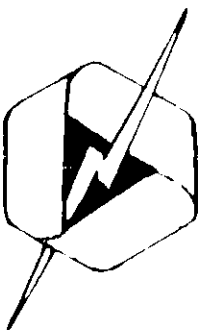


INFO



REX RESEARCH
P O BOX 19250
JEAN
NV 89019
USA

MR. L.S. LEA

TITLE:

LEA, Carey

ALLOTROPIC SILVER



Results of comparison with Solar Spectrum.—It will be seen by inspection of the tabulated results that nine out of the eleven lines of copper are reversed in the sun, and four of the five of zinc. The conclusion reached in each of these cases was after repeated examination when the conditions were such as to show a clear space between the components of the E line. The latest available authority* gives copper among the doubtful elements in a list of those found in the sun, and on the same list zinc does not appear at all. The present investigation makes it quite probable that zinc, and almost completely demonstrates that copper exists in the solar atmosphere.

Bowdoin College, March 14, 1889.

ART. L.—*On Allotropic Forms of Silver*; by M. CAREY LEA, Philadelphia.

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 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.

Ame



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 hemi-chloride Ag_2Cl , he gives, as the result of 15 concordant analyses, the constitution of his product as Ag_2Cl_3 †. 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 1852, Pillitz published two papers.‡ He commences by disputing the probability of the existence of Ag_2O on grounds of valency; namely as implying that oxygen may be quadri-valent. Although it is very doubtful that any one has up to the present time obtained Ag_2O , the argument seems futile as are many arguments deduced from supposed laws of valency. Similar reasoning would make Ag_2Cl impossible, which substance undoubtedly exists, and it would also deny the existence of K_2Cl 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 Ag_2O 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 argenteous citrate, Dr.

* G. H. Badley 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.

‡ Zeit-schrift für Ann. Chemie, **xxi**, p. 27, p. 496.

§ Gmelin Kraut, ii, 1, 72.

¶ Am. Chem. Jour. vi, 407; viii, 196.

Amer. J. Sci. [3] 37(222) 476-491 (June 1882)

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 Pfordter† 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, 1158.

dilat
fincl
nize
entir
of t
chem
oxid
Wöh
by n
imp
to n
belic
d. F
silv
T
stro
deso
1.
(l. c
2
tre
M
I
pro
cou
tria
reli
wh
ro
em
pu
tha
in
of
we
an
cla
me
wh
re

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 hemioxide; so that at the present time the formation of Ag_2O 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 Ag_2Cl and K_2Cl seems almost to involve that of Ag_2O and K_2O . This latter product Davy believed that he had obtained. The black substance which V. d. Pfordten formerly regarded as Ag_2O he now takes to be silver hydrate $\text{Ag}_2\text{H}_2\text{O}$.

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., ix, 2283.

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 so
produ
the sam
tions n
ize, let
prepar
rous su

Wh
excess
citrate,
stirred
the wh
the iron
may be
cipitate
to cert
nitrate
another
of pur
tion of
or of
much
gained
acid r
may be
the qu
solutio
soda, b
The n

The
erul.
the me
uncove
tate fa
may be
saline
it too
sodic r
ing au
instan
of five
insolu
tate (a
and r
moder
c. c.

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 ammonic 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 ammonic 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 ammonic 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 Ag_2O would contain only 96.13 per cent of silver.

The presence of either hydrogen or oxygen in combination with silver seems to be pretty certainly negatived 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°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 Wolecott 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
true solution
by H₂S and
described
chloric acid
be impaired
chloride and

In this case
several days
much as per
soon as set
constantly
bottle. But
the entire
hours from
washed, re
action of

When t
lents, they

No
No

indicating
variable a
nation wit

It has
acted upon
true solution
strong than
soluble in
that I have
arguments.

The con
fully, and
was extreme
remarked,
except by
carefully s
To support
compound
possible, f
admit the

We have
over 97 pe

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 slowly i
bright
metallic
surface.

The s
in a re
substance
tate it.
of gum

Neutr
or an in
throw d
phate, f
and ferr
salts thr
constitu
purple
otherwis

What
to return
ble of ef
a brown
yellowis
None of
original
slightest

The s
silver, t
not dissc
effects.

above su
it does n
replacing
readily.

ammonia
lowish re

Most
described
in either
ammonia

effects a

insoluble

AM. JOU

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.

column 4 of the table. Eifel, described by Hussak, is given for the purposes of comparison, it corresponding more closely in chemical composition to the Ishawood rock than any other published analysis. It is, however, like most leucite rocks, richer in alkalis with potash in excess of the soda.

ART. V.—*On Allotropic Forms of Silver*; by M. CAREY LEA.

[Continued from page 491, vol. xxxvii.]

In the first part of this paper were described certain forms of silver; among them a lilac-blue substance, very soluble in water with a deep red color. After undergoing purification it was shown to be nearly pure silver. During the purification by washing it seemed to change somewhat, and consequently some uncertainty existed as to whether or not the purified substance was essentially the same as the first product: it seemed possible that the extreme solubility of the product in its first condition might be due to a combination in some way with citric acid, the acid separating during the washing. Many attempts were made to get a decisive indication and two series of analyses, one a long one, to determine the ratio between the silver and the citric acid present, without obtaining a wholly satisfactory result, inasmuch as even these determinations of mere ratio involved a certain degree of previous purification which might have caused a separation.

This question has since been settled in an extremely simple way, and the fact established that the soluble blue substance contains not a trace of combined citric acid.

The precipitated lilac-blue substance (obtained by reducing silver citrate by ferrous citrate) was thrown on a filter and cleared of mother water as far as possible with a filter pump.

AMER. J. SCIENCE 138 (#223) p 47
(1889)

solutions, under the influence of which the substance itself slowly but continually changes. Next, the saline solution used for washing must be removed by alcohol. During this treatment, the substance, at first very soluble, gradually loses its solubility and when ready for analysis, has become wholly insoluble. It is impossible at present to say whether it may not have undergone other change: this is a matter as to which I hope to speak more positively later. It is to be remarked, however, that these allotropic forms of silver acquire and lose solubility from very slight causes, as an instance of which may be mentioned, the ease with which the insoluble form B recovers its solubility under the influence of sodium sulphate and borate and other salts as described in the previous part of this paper.

The two insoluble forms of allotropic silver which I have described as B and C; B, bluish green, C rich golden color, show the following curious reaction. A film of B, spread on glass and heated in a water stove to 100° C. for a few minutes becomes superficially bright yellow. A similar film of the gold-colored substance C treated in the same way, acquires a blue bloom. In both cases it is the surface only that changes.

Sensitiveness to Light.—All these forms of silver are acted upon by light. A and B acquire a brownish tinge by some hours' exposure to sunlight. With C the case is quite different, the color changes from that of red gold to that of pure yellow gold. The experiment is an interesting one, the exposed portion retains its full metallic brilliancy, giving an additional proof that the color depends upon molecular arrangement, and this with the allotropic forms of silver is subject to change from almost any influence.

Stability.—These substances vary greatly in stability under influences difficult to appreciate. I have two specimens of the gold yellow substance C, both made in Dec. 1886, with the same proportions, under the same conditions. One has passed to dazzling white, normal silver, without falling to powder, or undergoing disaggregation of any sort; the fragments have retained their shape, simply changing to a pure frosted white, remaining apparently as solid as before, the other is unchanged and still shows its deep yellow color, and golden luster. Another specimen made within a few months and supposed to be permanent has changed to brown. Complete exclusion of air and light is certainly favorable to permanence.

Physical condition.—The brittleness of the substances B and C, the facility with which they can be reduced to the finest powder, makes a striking point of difference between allotropic

and normal silver. It is probable that normal silver, precipitated in fine powder and set aside moist to dry gradually, may cohere into brittle lumps, but these would be mere aggregations of discontinuous material. With allotropic silver the case is very different, the particles dry in optical contact with each other, the surfaces are brilliant and the material evidently continuous. That this should be brittle indicates a totally different state of molecular constitution from that of normal silver.

Specific Gravities.—The allotropic forms of silver show a lower specific gravity than that of normal silver.

In determining the specific gravities it was found essential to keep the sp. gr. bottle after placing the material in it for some hours under the bell of an air pump. Films of air attach themselves obstinately to the surfaces and escape but slowly even in vacuo.

Taken with this precaution, the blue substance B gave specific gravity 9.58 and the yellow substance C, sp. gr. 8.51. The specific gravity of normal silver, after melting was found by G. Rose to be 10.5. That of finely divided silver obtained by precipitation is stated to be 10.62.*

I believe these determinations to be exact for the specimens employed. But the condition of aggregation may not improbably vary somewhat in different specimens. It seems however clear that these forms of silver have a lower specific gravity than the normal, and this is what would be expected.

Chestnut Hill, Philadelphia, May, 1889.

ART. IV.—*The Peridotite of Pike County, Arkansas*, by JOHN C. BRANNER, State Geologist of Arkansas, and RICHARD N. BRACKETT, Chemist of the Geological Survey of Arkansas. With Plate I.

PART I, by John C. Branner.

Two and a half miles southeast of Murfreesboro in Pike county, Arkansas, is a small exposure of peridotite whose position and topographic features are shown in detail upon the accompanying map (Plate I.) The entire exposure is about 2400 feet long by 1600 feet wide, and lies upon the middle of the line between sections 21 and 28 of township 8 south, range 25 west.

From a geological standpoint this exposure is an important one, for, small as it is, it offers a suggestion regarding the time and character of the disturbing influences, which, about the

* Watts' Dict., orig. ed., v, 277.

the acid present is nearly neutralized with sodium hydroxide, the neutralization being completed by hydrogen sodium carbonate added in excess to an amount corresponding to 10 cm.³ of the saturated solution for every 0.1 gram. of antimonious oxide present. Titration with decinormal iodine standardized against tartar emetic gives the antimony quickly and with a fair degree of accuracy. The whole process requires about an hour and a half for completion.

ART. XXX.—Notes on Allotropic Silver; by M. CAREY LEA.

Relations of the Yellow to the Blue Forms.—The gold and copper-colored forms on the one hand, and the blue, bluish-green and steel-gray on the other hand stand in close relations to each other. In previous papers there has been described a crystalline state intermediate between these active forms and ordinary silver, which intermediate condition, while retaining the bright yellow color of the active form is nearly as indifferent to reagents as ordinary silver. Into this intermediate state both the yellow and blue forms are capable of passing, and apparently the intermediate states of both kinds of allotropic silver are identical: *the intermediate form of blue silver is yellow.* Thus when lumps of blue silver are heated in a test tube to about 180° C. they assume a gold color and luster. The same change takes place at the same temperature when films of blue silver are placed in a hot air bath.

But relations much closer than these exist. Blue silver can be converted into yellow at ordinary temperatures and consequently with retention of its active properties. This is accomplished through the agency of sulphuric acid. When a solution of silver is obtained by the action of sodium hydroxide and dextrine on silver nitrate* it appears to contain the blue variety, for if allowed to precipitate spontaneously by long standing, or if precipitated by acetic acid, dilute nitric acid, or by many neutral substances, it gives a form of silver which is dark red while moist and dries with a blue surface

* Forty grams each of sodium hydroxide and of yellow or brown dextrine (not white) are dissolved in two litres of water and 28 grams of silver nitrate in solution are added in small quantities at a time, with frequent stirring, so that several hours shall elapse before the last portion is added. The solution is always slightly turbid when viewed by reflected light, by which it shows a beautiful deep green color. By transmitted light it is deep red, and when diluted, absolutely transparent. By diminishing the proportion of silver nitrate to one-half, a solution nearly or quite clear by reflected as well as by transmitted light is obtained.

Amer J Sci 42 (250) Oct, 1891

when dry—characteristic to their color with more characteristic by that.)

The behavior of dextrine with dilute. When 100 water to which 3 added, a dark red in films, is blue. tate is formed is 5 and 6 c.c. sucrose surface color becomes the acid is increased no longer dries and acid produce substance

It will be seen substance only as of different forms proportions of the

That these forms sulphuric acid in presence of this ordinary silver. obtained with few water containing or three hours the silver.

It is observable least acid, have diminishes steadily to 6 c.c. to 100 comes more marked

But we can also as the solution very can be made to strong acid, so the substance, may silver by adding ferrous sulphate of silver nitrate of gold-colored ide, either to the get a bluish green belongs to the

color. (It is always a little difficult to characterize these substances by their colors since the surface color which they show when dry—either in mass or in films—is mostly complementary to their color when wet. As the surface color is much the more characteristic, I have adopted the course of naming them by that.)

The behavior of the red solution obtained by soda and dextrine with dilute sulphuric is very interesting and instructive. When 100 c.c. of solution are poured into 100 c.c. of water to which 3 c.c. of sulphuric acid have been previously added, a dark red precipitate falls, which, when dry, especially in films, is blue. The mixed liquid from which the precipitate is formed is acid. Increasing the proportion of acid to 4, 5 and 6 c.c. successively, the substance obtained has a green surface color becoming more yellowish green in proportion as the acid is increased in quantity. With $7\frac{1}{2}$ c.c. the substance no longer dries green but yellow. Increased proportions of acid produce substances drying with a coppery shade.

It will be seen that from a single solution, and using one substance only as a precipitant, we can obtain the whole range of different forms of allotropic silver, by simply varying the proportions of the precipitant.

That these forms of silver should subsist in the presence of sulphuric acid in excess is remarkable. For the most part the presence of this acid tends to quickly convert allotropic to ordinary silver. For example, bright yellow allotropic silver obtained with ferrous tartrate was washed on a filter with water containing $\frac{1}{500}$ its volume of sulphuric acid: in two or three hours the entire mass was converted into gray ordinary silver.

It is observable that the substances precipitated with the least acid, have a very splendid luster, and that this luster diminishes steadily as the proportion of acid is increased. Up to 6 c.c. to 100 the effect is hardly noticeable, after that it becomes more marked.

But we can also obtain the converse of this reaction. Just as the solution which naturally would yield the blue product, can be made to yield the yellow by the presence of excess of strong acid, so the solution which normally yields the yellow substance, may be made to produce blue (or rather green) silver by adding alkali. Thus a mixture of dilute solutions of ferrous sulphate and of Rochelle salt added to mixed solutions of silver nitrate and of Rochelle salt, results in the formation of gold-colored silver. But if we add a little sodium hydroxide, either to the iron solution or the silver mixture, we shall get a bluish green product, whose properties show that it belongs to the blue class and not to the yellow. Even if a

solution of the hydroxide is added immediately after the iron solution has been poured into the silver, the result is the same.

There is therefore a well marked tendency of acids to give rise to the formation of the yellow product and of alkalies to the blue. But this is a tendency only. Both substances can be produced from neutral solutions, and slight changes are sufficient to alter the product formed. Thus, ferrous tartrate, in dilute solution acting on silver tartrate gives rise to the formation of the gold-colored substance, but when citrates are substituted, the blue substance is obtained.

Production of Allotropic Silver by Inorganic Substances.—

For reasons which will be mentioned presently, the reduction of silver must take place gradually to produce the allotropic form, and for a time it seemed an invariable condition that an organic substance of some sort should be present. This, however, proves not to be essential. In a paper presented to the American Academy and kindly read for me by Professor Remsen at the meeting in April last, I alluded briefly to having found a reaction depending upon inorganic agents only. It is as follows: Sodium hypophosphite added to silver nitrate does not effect reduction, but when hypophosphorous acid is set free, by the addition of phosphoric acid, a red coloration appears, indicating the presence of allotropic silver. The coloration is transitory, no doubt because of the strong tendency of free mineral acids to convert allotropic to normal silver, but red and blue stains form on the sides of the vessel.

Phosphorous acid gives similar results, though perhaps less well marked.

Action of Light on Blue Silver.—This action differs with different varieties: it was more especially examined with the form that is obtained from the soda dextrine silver solution already described by pouring the solution into an equal bulk of water to which sulphuric acid had been added in the proportion of 4 c.c. to each 100 c.c. of water. This form was selected because it is easy to obtain with great constancy of result, and because it is one of the forms of blue silver most sensitive to light.

Exposed to light, this substance first becomes more distinctly blue, losing a slight greenish shade. With continued exposure it passes to a yellow-brown shade, and finally to a perfectly pure golden-yellow of great brilliancy and luster. The last is the intermediate or crystalline form.

The action of light on this form of silver is remarkable in this respect, that its first effect is to *increase* the sensitiveness to reagents.

This result was so unexpected and *a priori* so improbable, that it was subjected to the most careful verification before

being accepted. The film of the substance with an opaque screen exposure to strong sunlight into a one per cent solution. The part exposed colorless, that which was covered by placing the film in a fringed absolutely opaque by translucent paper (the brown paper) and leaving five hours action of sunlight treated with weak ferrous having passed into the blue exposure has been the part covered by the transparently wholly protected is moderately acted on by sensitiveness thereby. It follows that upon exposure, first exalting its color.

It is impossible to observe this action of light, bromide.

The latter substance, light, is subject to the sensitiveness to reduction, becoming less sensitive, commonly known as solarization.

Causes determining the Allotropic or the Normal.—I have examined the phenomenon of silver under a great variety of conditions, but part do not deserve particular generalization: the indirect, direct when normal salt or oxide change is first to suboxide, far as my observation shows the reduced silver always when the reduction is of its allotropic states.

The following reactions are: (1) reduction of silver are: (1) reduction of nitrate or tartrate; (2)

being accepted. The action is very easily shown by exposing a film of the substance to light, covering part of the surface with an opaque screen. After twenty or thirty minutes of exposure to strong summer sunshine, the film may be plunged into a one per cent solution of potassium ferridecyanide, when the part exposed colors much sooner and more strongly than that which was covered. The effect is shown still better by placing the film in a frame, covering part with paper rendered absolutely opaque by coating it with thick tin foil, part with translucent paper (thick white writing paper or very thin brown paper) and leaving part wholly exposed. After four or five hours action of strong summer sunshine, the film is to be treated with weak ferridecyanide. The part wholly exposed having passed into the gold-colored crystalline condition (if the exposure has been sufficient) is wholly unacted upon, the part covered by the translucent paper is rapidly attacked, that wholly protected is attacked slowly. So that the portion moderately acted on by light has very markedly increased in sensitiveness thereby.

It follows that upon this form of silver *light has a reversing action*, first exalting its sensitiveness, then completely destroying it.

It is impossible to overlook the analogy which exists between this action of light, and that which light exerts on silver bromide.

The latter substance though incomparably more sensitive to light, is subject to the same reversing action, first gaining in sensitiveness to reducing agents and then, by continued exposure, becoming less sensitive than originally, a change commonly known as solarization.

Causes determining whether in the reduction of Silver, the Allotropic or the Normal form shall be produced.—I have examined the phenomena connected with the reduction of silver under a great variety of conditions. These for the most part do not deserve particular mention but seem to lead up to this generalization: that the reduction of silver may be direct or indirect, direct when it passes from the condition of the normal salt or oxide to that of the metal, indirect when the change is first to sub-oxide or to a corresponding sub-salt. So far as my observation has gone when the reduction is *direct* the reduced silver always appears in its ordinary form. But when the reduction is *indirect* the silver presents itself in one of its allotropic states.

The following reactions support this view.

Three of the principal modes of formation of allotropic silver are: (1) reduction of silver citrate or tartrate by ferrous citrate or tartrate; (2) acting on silver nitrate or oxide by

dextrine and fixed alkaline hydroxide; (3) acting on silver nitrate or carbonate by tannin and fixed alkaline carbonate. Now, if in either of these three cases we interrupt the action before it is complete by adding an excess of dilute hydrochloric acid we shall obtain a dark chestnut-brown or sometimes purple-brown substance which on examination proves to be a mixture of silver subchloride and photochloride. When, after complete removal of the excess of hydrochloric acid by thorough washing or better by boiling with distilled water, the substance is treated with cold dilute nitric acid that portion of the sub-chloride which is not combined with the normal chloride is broken up and there remains photochloride of a very rich and intense rose-color.*

The production of silver sub-chloride in all these cases would seem to indicate that the reduction when the acid was added was incomplete, and that in case (1) a sub-salt, and in cases (2) and (3) a sub-oxide was first formed as an intermediate step before complete reduction. Either of these substances would of course give rise to the formation of subchloride when treated with hydrochloric acid. It is important to observe that this result is to be obtained only by interrupting the reaction before it is complete. When, for example, allotropic silver in solution is produced by the action of sodic hydroxide and dextrine and after complete reduction, hydrochloric acid is added, the liquid becomes filled with gray normal silver, which presently collects to a cake. When this cake is well washed and boiled with water, and then treated with dilute nitric acid, solution takes place: a trace of photochloride is left behind. It has been mentioned elsewhere that hydrochloric acid, though without action on ordinary silver, is capable of forming a variable quantity of protochloride when placed in contact with allotropic silver.

I have not met with any exception to this general principle that when a reaction leading to the formation of allotropic silver is interrupted by the addition of hydrochloric acid, subchloride is abundantly formed as one of the products.

In all such cases the reduction is evidently indirect. The silver does not lose at once the whole of its oxygen, but apparently passes through an intermediate form, probably Ag_2O , the reduction of which tends to the formation of allotropic silver.

These facts lead directly up to the question: does silver exist in its subsalts in the allotropic form? There are some

* This is a very beautiful reaction and deserves more particular mention than can be given here. It is perhaps the best means for obtaining silver photochloride, for which purpose I have often employed it, both on account of its facility and certainty, and the very beautiful color of the product.

facts that would varied coloration infinite variety of silver when On the other hand its less specific molecular consti

ART. XXXI.—
tario; by

STEEP ROCK
Canada, northwest
adian Pacific Ra
the center of the
Pacific Railway
the northwest, th
and the shore of
Arthur, on the so
inc. (scale 1 inch
Département, Ton
extreme southern
waters of the At
52' N. and long.
halfway upon the
Lake.

Steep Rock La
nected by lodger
Some from Atlan
Atleokan River
the map, an irreg
the western or lat
and the eastern d
peculiar form is
structure of the r
what follows. Th
hundred feet acro
some three hund
at a point about a
the eastern arm.
end of the western

AM. Jour. Sci.—Th
22

facts that would support this view, especially the very rich and varied coloration of the subsalts corresponding to the almost infinite variety of color of allotropic silver, while normal salts of silver when formed with colorless acids are mostly colorless. On the other hand, the greater activity of allotropic silver and its less specific gravity would seem to indicate a simpler molecular constitution than that of normal silver.

ART. XXXI.—*Structural Geology of Steep Rock Lake, Ontario*; by HENRY LLOYD SMYTH. With Plate XI.

GEOGRAPHY.

STEEP ROCK LAKE is situated in the Province of Ontario, Canada, northwest of Lake Superior and south of the Canadian Pacific Railway. It lies about twenty-five miles east of the center of the rough quadrilateral formed by the Canadian Pacific Railway on the northeast, the Lake of the Woods on the northwest, the United States boundary on the southwest, and the shore of Lake Superior from Pigeon River to Port Arthur, on the southeast. As given on the map of the Province, scale 1 inch = 30 miles, published by the Crown Lands Department, Toronto, 1884, the geographical position of the extreme southern point of the lake, where it receives the waters of the Atlicokan River from the east, is about lat. $48^{\circ} 52' N.$ and long. $91^{\circ} 30' W.$ from Greenwich; or, it is about halfway upon the map between Lac des Milles Lacs and Rainy Lake.

TOPOGRAPHY.

Steep Rock Lake is one of the many that, collectively, connected by longer or shorter links of river, make up the River Seine from Island Falls as far as, and doubtless below, the Atlicokan River. In shape the lake resembles, as shown on the map, an irregular and slightly distorted letter M, of which the western or left arm, (looking north) runs north and south, and the eastern or right arm, northwest and southeast. This peculiar form is closely related to the character and to the structure of the rocks in which the lake lies as will be seen in what follows. The Seine River, after a beautiful fall, two hundred feet across, and forty to fifty feet high, over granite, some three hundred yards northeast of the lake, flows into it at a point about a mile southeast of the northwest extremity of the eastern arm. It leaves the lake at the extreme southern end of the western arm. Between the points of entrance and

taking this with the above number for the B. A. unit, we have
as the length of the mercury column corresponding to the ohm,

106.84 CMS.

COLOR

ART. XXXIV.—*The Properties of Allotropic Silver*; by
M. CAREY LEA.

THE three forms of allotropic silver which were described in the June number of this Journal—the blue soluble and the blue and the yellow insoluble—are not to be understood as the only forms which exist, but as the best marked only. The substance is protean, and exhibits other modifications not yet studied. No other metal than silver appears to be capable of assuming such a remarkable variety of appearances. Every color is represented. I have obtained metallic silver blue, green (many shades of both), red, yellow and purple. In enumerating these colors I do not refer to interference colors produced superficially by reagents, also wonderfully brilliant, but to body colors. As a single instance of coloration the following may be mentioned. I recently obtained a solution of allotropic silver of an intense yellow brown. A little solution of disodic phosphate changed this to bright scarlet (like Biberich scarlet) presently decolorizing with formation of a purple precipitate. Washed on a filter this changed to bluish green. The colors I have met with in this investigation can only be compared with the coal-tar products, of which one is constantly reminded by their vividness and intense colorific power.

Two of the insoluble forms of allotropic silver, the gold-colored and the blue, show in many respects a close relationship and almost identical reactions. There are other respects in which they differ strikingly and amongst these, in stability. Blue allotropic silver (dark red whilst moist, becoming blue in drying) is very stable. It may be exposed for weeks in a

AMER. J. SCI.

(JULY, 1889)

moist state on a filter, or be placed in a pasty condition in a corked vial and so kept moist for months, without alteration.

The gold-colored form on the contrary, tends constantly to revert to ordinary silver. This is especially the case whilst it is moist, so that from the time of its formation, it must be separated from its mother water and washed as rapidly as possible, otherwise it loses its brilliancy and purity of color and changes to a dark dull gray form of normal silver. On the filter, its proper color is pure black with a sort of yellow shimmer (the gold color appearing as it dries) often, especially if allowed to become uncovered by the water during washing, it will change superficially to gray.* But if the washing is done rapidly with the aid of a filter pump and a pressure of four or five inches of mercury, the allotropic silver obtained, when allowed to dry in lumps, or brushed over paper or glass, is at least equal to pure gold in color and in brilliancy. With the blue product such precautions are wholly superfluous.

Of the facility with which the gold colored form is converted into normal silver, I have recently had a somewhat singular proof. I brought with me to my summer home a number of specimens in tubes, some recently prepared, some dating back as far as two and a half years, together with other tubes containing specimens of white silver spontaneously formed from the gold colored. On opening the box no tubes of gold colored silver were to be found, all had changed to white. But the same box contained pieces of paper and of glass on which the same material had been extended; these were wholly unchanged and had preserved the gold color perfectly. Apparently the explanation was this, the mere vibration caused by the jarring of a journey of 600 miles by rail and steamboat had had no effect in changing the molecular form, but the material contained in the partly filled tubes had been also subjected to *friction* of pieces moved over each other, and this had caused the change. To verify this explanation I prepared fresh material, filled three similar tubes each one quarter full, but in one forced in cotton wool very tightly to prevent frictional motion. These tubes were packed in a small box and sent over 2400 miles of railway. The tubes with loose material came back much altered, one was nearly white, and as the change has been set up will probably in a few days be entirely so,† another with loose material was also changed but not as much as the first mentioned. The tube filled up with cotton came back unaltered. So that continued friction of pieces sliding over each other will cause a change to take place in a few days which otherwise might have

* When well washed, this form can also be preserved for a time in the moist condition in a corked vial, as I have lately found.

† It has since become so.

required
permanence
so that wh
permanent
placed in
unaffected
lowed to n

When g
test tube
fore heati
After heat
be pulveriz

Both the
silver in di

These t
stability an
of formati
ly ordinary
They show
also sensiti
mirrors by
glass was m

Many su
nary silver,
silver with
formation o
reflected ra
gen reactio
stances whic
found that n
effects. Th

Sulphides
copper colo
vapor of an
of it, assum
obtained in

Potassium
red and gre

Potassium
gradually att
blue, purple

Phosphor

ation.
The color
readily part
sodium hyp
bichromate

required years or might not have occurred at all. The permanency of this substance is greatly influenced by moisture, so that when simply air-dried before placing in tubes it is less permanent than when dried at 70° or 80° C. in a stove. Tubes placed in the same box containing the blue form remained unaffected by the motion, though only partly filled and allowed to move freely.

When gold-colored allotropic silver is gently heated in a test tube it undergoes a remarkable change in cohesion. Before heating, it is brittle and easily reduced to fine powder. After heating it has greatly increased in toughness and cannot be pulverized at all.

Both the gold-yellow and the blue forms resemble normal silver in disengaging oxygen from hydrogen peroxide.

These two forms though differing so much in color and stability and differing also in specific gravity and in their mode of formation, have many properties in common, not possessed of ordinary silver, and differentiating them strongly from it. They show a vastly greater sensitiveness to reagents, and are also sensitive to light. The ability to form perfect metallic mirrors by being simply brushed in the pasty condition over glass was mentioned in a previous paper.

Many substances which react little if at all with ordinary silver, attack the gold-colored and the blue allotropic silver with production of very beautiful colors due to the formation of thin films and resulting interference of two reflected rays. In my previous papers I called this the "halogen reaction" because first obtained by the action of substances which easily parted with a halogen. But I have since found that many other reagents will produce the same or similar effects. These are

Sulphides. Paper brushed over with either the gold, the copper colored, or the bluish green substance exposed to the vapor of ammonium sulphide, or immersed in a dilute solution of it, assume beautiful hues, though less brilliant than those obtained in some other ways.

Potassium permanganate in dilute solution produces blue, red and green colors.

Potassium ferricyanide in moderately strong solution gradually attacks allotropic silver with production of splendid blue, purple and green coloration.

Phosphorous acid produces gradually a rather dull coloration.

The color reaction is produced finely by substances which readily part with a halogen such as ferric and cupric chlorides, sodium hypochlorite, hydrochloric acid to which potassium bichromate has been added, and by corresponding, bromine

and iodine compounds. In some earlier experiments I obtained effects of the same sort, but in much weaker degree with alkaline haloids. But with purer products, the results have been different. There is at first some darkening, but no true color reaction and the allotropic silver appears to be gradually converted into normal, so that it is no longer capable of giving the brilliant color reaction with potassium ferridcyanide, but, like normal silver, takes a pale and faint coloration only.

The perchlorides of platinum, gold and tin do not give the color reaction, though by analogy one would expect that they should, since they can lose chlorine with formation of a lower chloride.

Action of Light.—In a previous paper was mentioned the remarkable fact that the gold- and copper-colored forms of allotropic silver can be converted first into yellow and finally into white normal silver by the continued action of light. The earlier specimens of the blue form became brown by exposure, but purer ones since obtained are likewise converted into yellow by exposure, becoming continually lighter as the action is continued. The conversion from the darker shades to a bright yellow with full metallic luster is very easy, but when the previous paper was written I had been only able to obtain the white by keeping the paper, on which the silver was coated, moist by a wet pad and by exposing for five or six days. Since then I have obtained the gold-colored silver in a more sensitive form, giving a perfectly white product by exposure dry for half that time.

The white silver thus obtained has all the character of ordinary silver and does not show the color reaction with ferric and cupric chloride, potassium ferridcyanide, etc. Just in proportion to the exposure to light, the ability to give this color reaction diminishes, so that after a day's exposure, when the exposed part has become bright yellow, the color reagents scarcely affect this yellow, whilst the protected part becomes intense blue, purple, or green. In this way it is easy to observe the gradual effect of light as it changes the allotropic silver, finally converting it into what resembles in every way, and is undoubtedly, ordinary silver.

July, 1889.

ART. XX
product

ALLOTTIC
brushed o
iant coatin
of iodine
of colored
beaker sha
by irregul
produced
results. I

window, t
affects the
principally
shaped cur
the air cur
place a be
to set it w
a fire, or e

That ic
(Nobili's ri
Robert H
normal silv
gummed p
gently rub
and faded-
lustrous an
striking.†
tion could
by photogr

As to th
with posit
for several
silver B, an
colored is th

July, 1889.

* Described i
† I was desir
printing for th
found that he c
parent, and ye
imitate in print

ART. XXXV.—*On Ring Systems and other Curve Systems produced on Allotropic Silver by Iodine*; by M. CAREY LEA.

ALLOTROPIC silver, in its moist and plastic state, may be brushed over paper and gives on drying a continuous and brilliant coating resembling metallic leaf.* When a small crystal of iodine is placed on paper that has been thus coated, a system of colored rings of remarkable beauty is obtained. A funnel or beaker should be inverted over the paper to prevent distortion by irregular currents of air. One form of distortion, however, produced by a slight current in one direction, gives interesting results. If the paper with the crystal on it is set near a closed window, the slight current which makes its way through, affects the air under the glass enough to carry the iodine vapor principally in one direction and there result oval or pear-shaped curves of great elegance and much variety according as the air currents are stronger or weaker. Another method is to place a bell glass, not fitting too closely, over the paper and to set it where it will be influenced by the draught created by a fire, or even by a gaslight.

That iodine is capable of producing interference rings (Nobili's rings) on metallic surfaces has long been known, and Robert Hunt has described their formation on surfaces of normal silver. I have made these for comparison, pressing gummed paper on silver leaf, bringing to a smooth surface by gently rubbing after drying. The contrast between the pale and faded-looking effects produced on normal silver, and the lustrous and glowing hues given by the allotropic, is very striking.† One cannot help wishing that this splendid coloration could be made to do service for obtaining natural colors by photographic processes.

As to the durability of these products, I cannot yet speak with positiveness. Protected from light and air they endure for several months at least. Both the bluish green insoluble silver B, and the gold-colored C produce these effects; the gold-colored is the better suited of the two.

July, 1889.

* Described in this Journal, June, 1889.

† I was desirous of having some of these curve systems reproduced in color printing for this Journal, but on conferring with an experienced color printer, found that he could give no assurance of a successful result. The colors are transparent, and yet have a metallic brilliancy, a combination almost impossible to imitate in printing.



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
bright gr
dently ter
loidal sta
contact w

The ex
to extern
normal (
this fact
silver co
shown) t
may not

To ob
analysis,
insoluble
sium sul
used the
the red s
soon sub
and then
decentati
can be r
magnesi
one liter
a filter a

Analysis
gave

A spe
the second
So the
of silver
oxide an

It has
occasion
be obtai
nitesima
position

* Produ
pressure.

† I have
reau who
are conver
he affir

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
—that of d
the thick pa
with the spl
ence, that t
spontaneous
other metall
nishing. B
over clean g
the film seen
perfect.

By contin
that in dryin
and is rather

Two silver
in Nov., 188

Recently
washing was
obstinately a
remove it.
affecting the

The residu
wholly of fer
Chestnut Hill,

NOTE.—The
paper, samples
describes, and
Mr. Lea is to
The coated str
the "gold-silve
remarkable for

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.

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.

ART. LVI.—Notes on Silver; by M. CAREY LEA.

Action of Ammonia.—Aqueous ammonia is supposed to be without action on normal silver but this is not so: under favorable conditions, silver is gradually taken up by this solvent.

The first experiments were made with silver reduced from the nitrate by the action of sodium hydroxide and milk sugar. The silver was very carefully purified from any possible trace of oxide. Placed in contact with ammonia for a few hours, silver was taken up. Its presence could be recognized either by ammonium sulphide or by adding a drop or two of hydrochloric acid and then supersaturating with dilute sulphuric acid; a dense cloud of silver chloride forms and this result can be obtained any number of times in succession by acting with ammonia on the same portion of silver.

A similar reaction was obtained with silver reduced from chloride by cadmium and hydrochloric acid removing afterwards all traces of cadmium. Silver reduced in this way is liable to contain traces of chloride. These were removed by covering the silver with strong ammonia, letting it stand over night and thoroughly washing out. This was repeated five times. From this silver, ammonia by twenty-four hours contact always took up enough to give a dense white cloud when treated as above.

Portions of solutions obtained in the last mentioned manner were evaporated to dryness over the water bath and left brownish black films. These were non-explosive and therefore did not consist of silveramine; they yielded a large proportion of silver to acetic acid, leaving behind a little metallic silver. The ammonia therefore, does not dissolve the silver as metal but as oxide. The presence of a little metallic silver in the residue left by evaporation was probably due to slight traces of oxidable organic matter contained in the ammonia. This opinion was confirmed by the fact that the solution when heated acquired a transparent red color.

It appears therefore that in the presence of ammonia, silver has a tendency to oxidize, for when the silver was placed in a vial with an air-tight fitting stopper, filling it about half full, and was then completely filled with liquid ammonia and tightly closed, it was found that in twenty-four hours a mere trace of silver was taken up. On the other hand when the silver was placed in a flat basin and merely moistened with ammonia more silver was taken up in five minutes than in the preceding case in twenty four hours.

This action of ammonia in promoting oxidation recalls its behavior with cobaltous salts and with copper. It is probably

(Nov 1892.)

[the only case in which silver is oxidized (at ordinary temperatures) by atmospheric oxygen.]

Action of Dilute Sulphuric Acid.—It is generally held that silver is insoluble in cold dilute sulphuric acid. Almost any form of silver, providing it is finely divided, is slightly soluble in sulphuric acid diluted with four or five times its bulk of water. With more dilute acid different varieties of silver act very differently. The most easily attacked is that which is obtained by reducing the oxide with alkaline hydroxide and milk sugar; from this a distinct trace is dissolved by sulphuric acid diluted with 100 times its bulk of water. From silver reduced from the chloride by cadmium this very dilute acid takes up nothing.

Nitric acid, sp. gr. 1.40, diluted to ten volumes and allowed to stand for an hour with finely divided silver, took up an extremely faint trace.

Hydrochloric acid, sp. gr. 1.20, was totally without action. The silver after being well boiled with water to remove every trace of acid, dissolves completely in nitric acid.

Acetic acid has no action upon metallic silver.

Various Reactions of Normal Silver.

Normal metallic silver even in a state of very fine division does not abstract the slightest trace of nitric acid from perfectly neutral cupric nitrate obtained by acting on pure cupric sulphate with barium nitrate. After fifteen hours of contact not a trace of silver had been dissolved.

But silver easily reduces cupric chloride with formation of purple photochloride. If the copper salt is present in slight excess the silver is so thoroughly acted upon that nitric acid does not extract a trace of it from the purple photochloride.

Metallic mercury instantly reduces silver nitrate but metallic silver takes chlorine from corrosive sublimate. The precipitate contains calomel and blackens with ammonia.

Silver in fine division slowly reduces a neutral solution of potassium permanganate.

Silver nitrate, as is well known, is reduced by ferrous sulphate, or ammonia ferrous sulphate, the iron at the same time becoming peroxidized and the silver assuming the gray metallic form. On the other hand silver powder rapidly reduces a neutral solution of ferric sulphate. A solution of iron alum readily dissolves metallic silver without the aid of heat;* in a few seconds the solution strikes a blue color with potassium

* The statement in the new *Encyclopédie Chimique* that heat is required and that the metal separates again on cooling (Tome iii, earlier 15, p. 248) appears to be incorrect.

ferrieyanide and if the iron alum is in excess the whole of the silver is dissolved. It has been before noticed that the reactions between silver salts on the one hand and iron salts on the other are to some extent reversible, the observations just described place the matter in a somewhat clearer light. With a view of ascertaining whether ferrous sulphate could be completely oxidized by argentic oxide a portion of the ferrous solution was treated with successive portions of the oxide until the latter was no longer affected by it. But when this stage was reached the solution no longer contained a trace of iron, the whole of it had entered into combination with the silver. This combination is perfectly black and may probably have consisted of the compound described by H. Rose, as $Ag_2O, 2FeO, Fe_2O_3$, and obtained in the same way.

When ammonia iron alum is placed in contact with finely divided silver in considerable excess in a tightly closed vial the solution after a few days standing with frequent shaking acquires a deep red color. This may last for a week or more. The solution then decolorizes and becomes greenish but still contains abundance of ferric salt. Thus it appears that although silver has a powerful reducing action on ferric salts the action is self-limited and ceases long before complete reduction is effected for after many weeks contact in a closed vial there are abundant indications of the presence of ferric salt, although silver has been present in large excess.

ART. LVII.—Notes on Silver Chlorides; by M. CAREY LEA.

EXPERIMENTS made by J. J. Aeworth* at the suggestion of E. Wiedeman showed that by heating silver chloride to a temperature of 220° C. it passes into a modification that was insensitive to light.

I think this change may be due to the complete driving off of moisture. Abney showed by a well-known experiment that silver chloride when exposed perfectly dry in vacuo in a glass tube was totally unaffected by light, but I have shown that fused silver chloride poured into petroleum and placed in the sun-light without removing it from the liquid, was instantly darkened.

These three experiments taken together lead to the following conclusions:

1. Silver chloride dry and perfectly isolated is insensitive to light. (Abney's experiment.)

* Wied. Referate, 1890, p. 518.

2 T
sensitiv
drated
3. T
the dar
not ess
capable
ment a
Ther
of wate
silver e
by fusio
which
thence
the wat
ver chl
experim
So lon
easily b
applicat
moisture
been lat
upon col
energetic

ART. LV
Wington
Rena
IN the
Hally, in
occure
assigned
Pike cou
at the bas
along to
terizing
Burling
This
one
consider

* Published
Survey of Mi
† Geol. Sur
AM. Journ.

2. The presence of atmospheric air does not restore the sensitiveness, if the silver chloride has been absolutely dehydrated at 220° C. (Aeworth's experiment)

3. The presence of oxygen is not necessary or important for the darkening of silver chloride. The presence of moisture is not essential; its place may be taken by another substance capable of taking up chlorine. This follows from my experiment above mentioned.

There is no doubt that silver chloride retains the last portion of water with great obstinacy. I have frequently tried to dry silver chloride in hot air so that it should lose nothing further by fusion, but never quite succeeded. There is always a loss which may be roughly taken at a half a milligram and from thence upwards to nearly one milligram, in a gram. When the water is thoroughly driven off it is probable that the silver chloride is left in an insensitive condition. Aeworth's experiments seem to show this.

So long as moisture is present the molecule of silver chloride easily breaks up, not merely by the action of light but by the application of any form of energy. The part played by moisture in chlorine reactions is somewhat remarkable. It has been lately stated that absolutely dry chlorine has no action upon copper foil. As soon as a trace of moisture is introduced, energetic action sets in.

ART. LVIII. — A remarkable Fauna at the Base of the Burlington Limestone in Northeastern Missouri. BY CHARLES RUTLIS KINGS

In the description of a certain gasteropod (*Purcellia nebulosa* Hall), in the third volume of the Illinois Geological Survey occur the following paragraph, in connection with the assigned horizon and locality: "Lower Carboniferous; Barry, Pike county, Illinois; from a peculiar cherty calcareous band at the base of the Burlington limestone, formerly supposed to belong to that rock, but now known to contain fossils characterizing the dolitic upper bed of the Kimmswick group, at Burlington, Iowa."

This allusion though merely incidental is the only direct one ever known to be made to the particular beds now under consideration.

* Published by permission of Mr. Arthur S. Lawson, Director of the Geological Survey of Missouri, from work prosecuted during the years 1891-92. † Geol. Surv. Illinois, vol. iii, p. 459. (1868).

ART. XL.—On Silver Hemisulphate; by M. CAREY LEA.

THE existence of those substances which I described some years ago under the name of photosalts of silver* necessarily implied the existence of the hemihaloids of silver also, as these latter entered into the composition of the photosalts. Similar inferences, though less definite, had long been drawn from the action of light on silver haloids. Two of these, the chloride and bromide, lost by the action of light their complete solubility in ammonia without becoming completely soluble in nitric acid. Evidently there was indicated an intermediate compound between the normal haloid and metallic silver. During the last ten or twelve years I have devoted much time to the attempt to isolate these lower compounds of silver and to gain some certain knowledge as to the hemioxide, whose existence seemed almost a necessary inference from that of the hemihaloids. Some eight years ago, I obtained a substance having all the properties which one would be disposed to ascribe to Ag_2Cl and a large number of analyses made seemed to confirm the view. I hesitated, however, to publish a description of it, not feeling entire certainty that it might not be a mixture, as to which a concordance of the proportions found of Ag and Cl with theory gives no sufficient information. Since then M. Guntz has described a subchloride obtained by acting on silver hemifluoride with phosphorus pentachloride and a hemioxide derived from it. Up to the present time no combination of silver hemioxide with an oxyacid has been known.

Such a combination I have been able to obtain as a double salt of hemisulphate and normal sulphate containing one molecule of each. The new salt has a light bright brown color, and exhibits a stability which in view of its composition, is something remarkable. It has no tendency either to oxidation or to reduction. Nitric acid, unless very strong, has but little action upon it. Acid of 1.42 poured over it in large excess and let stand for several days gradually dissolves it completely, but the same acid diluted with with two or three times its volume of water has so little action that it forms a convenient means of purification. On the other hand, ferrous sulphate which instantly reduces argentic sulphate has no action whatever on the new substance even with several days' contact. Hot strong sulphuric acid has no action. It might almost be expected that under its influence, the argentous salt would gradually take up oxygen and be converted into argentic sul-

* This Journal, xxxiii, May and June, 1857.

phate. I
of undilu
ing water
strong pr
The ap
cession of
the moist
lilac, at 1
temperatu
acquires a
almost to
color is li
as the su
vapors are

It was
nitrate is
phorous a
transient c
presence o
was publi
study. It
with a sol
phuric aci
that whic
It became
free the h
with form
A reman
between th
silver. TH
but acquir
the same v
capable of
union with
analogy lie
occurs in c
case with t

The new
sulphuric a
phosphoron
already pre
is formed in
Several s
employed t
perhaps the
rapid, and v

(Oct 1892)

phate. But a specimen which was covered with a large excess of undiluted sulphuric acid in a flask and was kept under boiling water for ten hours was not altered thereby. Another strong proof of its stability is found in its resistance to heat.

The application of heat produces a somewhat curious succession of colors. The terra cotta or warm brown shade of the moist substance changes by drying above 100° to pale lilac, at 165° – 170° it becomes grayish, at a somewhat higher temperature, yellowish green. Considerably below red heat it acquires a fine ruby red color. In cooling, this red darkens almost to black, then becomes lighter again and when cold the color is light olive-green. The changes are repeated as often as the substance is heated and cooled. No sulphuric acid vapors are disengaged even at a low red heat.

It was mentioned in a previous paper that when silver nitrate is reduced by solutions of phosphorous or hypophosphorous acid or by acidified solutions of their alkaline salts, transient colorations were produced that seemed to suggest the presence of some form of allotropic silver. Since that paper was published this reaction has been taken up for further study. It soon appeared that when the silver salt was treated with a solution of alkaline hypophosphite, acidified with sulphuric acid, the result obtained was entirely different from that which presented itself under any other circumstances. It became clear that sulphuric acid did not act solely by setting free the hypophosphorous acid, but also acted on the silver with formation of a double sulphate.

A remarkable though limited analogy here presents itself between the substance just described and the photosalts of silver. The silver hemihaloids are very unstable substances, but acquire stability by uniting with the normal haloids. In the same way the hemisulphate, which is not known to be capable of separate existence, becomes perfectly stable by union with the normal sulphate. The limitation to this analogy lies in the fact that the last mentioned combination occurs in definite proportions, which does not seem to be the case with the halogen compounds.

The new substance then is formed by the joint action of sulphuric and hypophosphorous acid on a silver salt. Hypophosphorous acid has but little action on silver sulphate already precipitated, but it is different when the silver sulphate is formed in presence of hypophosphorous acid.

Several silver salts may be used. I have at different times employed the nitrate, phosphate and carbonate. The latter is perhaps the best, because the action with the nitrate is too rapid, and with the phosphate, too slow, and for other reasons.

A weighed quantity of silver nitrate is precipitated with an excess of alkaline carbonate and washed. The carbonate, as well as all the other reagents employed must be absolutely free from chlorides, otherwise the product becomes contaminated with silver chloride which cannot be removed. The silver carbonate is then treated with a solution of alkaline hypophosphite acidified with sulphuric acid. All the alkaline hypophosphite of commerce contains much more than a trace of chloride: this is best got rid of by adding to its solution a little solution of silver nitrate, stirring well at intervals, letting stand for twenty-four hours and filtering. This filtrate with addition of sulphuric acid is to be poured over the moist silver carbonate and constantly stirred. The reaction is complete in twenty or twenty-five minutes, when a bluish-black film of reduced silver begins to form on the surface. Further action is then cut short by neutralizing the liquid with alkaline carbonate. The precipitate is next to be washed several times by decantation. Very pure distilled water is, of course, needed throughout.

Convenient proportions are: 40 grams silver nitrate precipitated with excess of alkaline carbonate. Of sodium hypophosphite, 100 grams, dissolved in 650 c. c. of water are treated with a little silver nitrate, and after standing and filtering, 4 c. c. of sulphuric acid are to be added and the liquid poured over the silver carbonate. After a few minutes, 6 c. c. more of sulphuric acid, diluted with a little water, are added by degrees. With this second quantity of sulphuric acid the characteristic reddish-brown color of the substance first appears.

This process may be varied by precipitating with disodium phosphate (which must be perfectly free from chloride) instead of alkaline carbonate. The action is much slower, about 24 hours being needed. Silver nitrate itself may be used, but the action is too rapid and the product is less in quantity.

The crude product obtained in either way is to be purified with nitric acid. Acid of 1.42 is diluted with three times its volume of water, and of this dilute acid a quantity is taken about double in volume to that of the precipitate and of the water left after decanting closely. After a time some effervescence takes place, but the mixture does not become warm. After standing for three or four hours over the precipitate, it is to be poured off and the precipitate washed. This treatment with acid is applied three times: the first removes a good deal of silver, the second a little, the third a trace. Each time the acid is left three or four hours in contact. The product is then washed by pouring on it a large quantity of boiling water. This is repeated four or five times, each time (except

the first) placed several hours.

The product is dried at 100° C. It fuses in air, changing color. It has the peculiar appearance of a sharp hissing substance as well as with the formation of the product.

The substance is weighed of the product.

These properties I have found. It is formed under conditions suitable to bring a hypophosphite acidified with sulphuric acid less of it. Its reduced silver.

It might be supposed to leave, when treated with the double sulphuric acid with the photometric mass, containing chlorides will be into bright purple.

All the species of phosphoric acid, phosphoric anhydride, Three determinations 2-19.

It is apparent that it is united so firmly that it is detached. If it were the nitric acid would be converted and dissolved.

Another attempt at heating the substance for several hours, followed by water to wash off the product formed at the expense of silver. I believe that a simple quantitative determination of phosphoric anhydride.

Other modes of experiment are free from phosphorus.

the first) placing the vessel in a water bath kept at 100° C. for several hours.

The product is either dried in the air or (for analysis) at 100° C. It forms a bright brown substance, permanent in the air, changing to violet when kept for some time at 160° C. It has the peculiarity that when water is poured on it, it makes a sharp hissing noise. This takes place with the air-dried substance as well as that dried at higher temperatures and as much with the former as with the latter.

The substance after purification has about one-half the weight of the silver nitrate taken.

These proportions and this mode of operating are those that I have found to give the best result. But the substance is formed under a great variety of conditions. It seems impossible to bring a silver salt into contact with alkaline hypophosphite acidified with sulphuric acid without producing more or less of it. Its presence is often completely obscured by reduced silver. But a mass which looks perfectly black and might be supposed to contain nothing but metallic silver will leave, when treated with nitric acid, a bright brown residue of the double sulphate. We have here, as before, an analogy with the photosalts. For it will often happen that a blackish mass, containing metallic silver and mixed or combined silver chlorides will, when treated with nitric acid, resolve itself into bright purple or rose colored photochloride.

All the specimens of this new substance contain a little phosphoric acid which cannot be removed. Reckoned as phosphoric anhydride it amounts to a little over two per cent. Three determinations gave respectively, 2.30; 2.09; 2.18, mean 2.19.

It is apparently united with silver and this silver phosphate is united so firmly with the double sulphate that it cannot be detached. If it were not so united it would be dissolved in the nitric acid with which the substance is three times treated if it were normal phosphate, and if it were hemiphosphate it would be converted (if in a free state) to normal phosphate and dissolved.

Another attempt to remove this phosphate was made by heating the substance with sulphuric acid to 100° C. for ten hours, followed by copious treatment with boiling distilled water to wash out the sulphate which it was hoped would be formed at the expense of the phosphate. It seems difficult to believe that a silver phosphate could resist this treatment, but a quantitative determination showed that the proportion of phosphoric anhydride is not even diminished by it.

Other modes of formation than those described here were experimented on with the view of obtaining the substance free from phosphate, but without good result.

THE
AMERICAN JOURNAL OF SCIENCE

[THIRD SERIES.]

[3] 41 (243)
(March, 1891)

ART. XX.—*On Gold-colored Allotropic Silver*; by M.
CAREY LEA. (Part I, with 3 Plates.)*

THE object of the present paper (which may be considered as a continuation of that published in this Journal for June, 1889) will be:

1st. To describe the reactions of gold-colored allotropic silver.

2d. To show that there exists a well characterized form of silver intermediate between the allotropic silver previously described and ordinary silver, differing in a marked way from both.

3d. To prove that all the forms of energy act upon allotropic silver, converting it either into ordinary silver or into the intermediate form. Mechanical force (shearing stress) and high tension electricity convert it directly into ordinary silver. Heat and chemical action convert it first into the intermediate form, then into ordinary silver. The action of light is to produce the intermediate form only, and even the most prolonged action at ordinary temperatures does not carry it beyond this.

4th. To show that there exists a remarkable parallelism between the action of these forms of force on allotropic silver and their action on the silver haloids, indicating that it is not improbable that in these haloids silver may exist in the allotropic condition.

REACTIONS.

The most characteristic reactions of gold-colored allotropic silver are those with the strong acids. When normal silver

* Numbered I, II, III, being Plates XI, XII, XIII of the volume.

reduced with milk sugar and alkaline hydroxide is left in contact with strong hydrochloric acid even for several hours there is no action, and the silver after thorough washing dissolves in warm dilute nitric acid without residue. With allotropic silver similarly treated chloride is always formed. But strong hydrochloric acid instantly converts allotropic to ordinary silver and consequently only a trace of chloride is produced. By largely diluting the acid the conversion is retarded and the proportion of chloride is greatly increased. Thus for example when ordinary hydrochloric acid is diluted with fifty times its volume of water and is made to act on allotropic silver, about one-third of the latter is converted to chloride. Probably the whole would be but for the simultaneous conversion to normal silver. This double action is very curious and strongly differentiates allotropic from ordinary silver. Even with the same acid diluted with a hundred times its volume of water, there is a gradual but complete conversion to white silver accompanied by the production of a not inconsiderable quantity of silver chloride.

Neutral chlorides also act strongly upon allotropic silver even when much diluted. So sensitive is this form of silver to the action of chlorides that if in washing it on the filter, river water containing a mere trace of chlorides is by an oversight used instead of distilled water, a thin gray film of normal silver will form on the surface.

The reactions above described were obtained with the moist precipitate freshly prepared. By standing for some time even if kept moist it appears to undergo a change. When freshly prepared it is slightly soluble in acetic acid but after standing for a week or two ceases to be so.

Sulphuric acid diluted with fifty times its volume of water has no action upon normal silver. When made to act upon allotropic silver, it quickly converts it to normal but at the same time dissolves a little of it.

It is rather curious that the dry film of gold-colored allotropic silver seems to be more easily acted upon by some reagents than the moist precipitate. I have noticed for example that oxalic, citric and tartaric acids do not convert the moist precipitate to normal silver, but films on pure paper are gradually whitened by these acids. It is not a question of strength of solution, for the moist precipitate remained unchanged for twenty-four hours under the same solution which whitened the same material as a dry film.

Ammonia seems to be without converting action but dissolves a trace. It will be shown in a future paper that there exists a form of allotropic silver abundantly soluble in ammonia.

In those r
a reducing a
and perman
differs from
activity. Th
The formati
scribed at th

Allotropic
of forms ar
bluish green
these varietie
of which one

If we coat
colored allotr
hour or two
the plate can
sufficient heat
golden yellow
than the por
heat. This r
mediate form

Its proper
paper, one en
perature just
is sudden and
a flash. Exa

1st. That i
gold color.

2d. When
or change col

3d. It is n
ing it.

4th. It no
ferricyanide a
deepening of

Of these c
remarkable.

changes with
touch, any fr

which a film

gray. Exposu

change, and it

tected from lig

some remarka

the anomaly l

In those reactions in which allotropic silver acts the part of a reducing agent, as for example with potassium ferricyanide and permanganate and with ferric chloride, etc., its behavior differs from that of ordinary silver chiefly in showing greater activity. The difference is rather of degree than of kind. The formation by these reagents of colored films will be described at the end of this paper.

INTERMEDIATE FORM.

Allotropic silver presents itself in an almost endless variety of forms and colors, gold-colored, copper-colored, blue and bluish green (these last in thin films red or purple). Most of these varieties seem to be capable of existing in two conditions, of which one is more active than the other.

If we coat a chemically clean glass plate with a film of gold-colored allotropic silver, let it dry, first in the air, then for an hour or two in a stove at 100°C ., and then heat the middle of the plate carefully over a spirit lamp, we shall obtain with sufficient heat a circle of whitish gray with a bright, lustrous, golden yellow ring round it, somewhat lighter and brighter than the portion of the plate that has not been changed by heat. This ring consists of what I propose to call the "intermediate form."

Its properties are better seen by using a film formed on pure paper, one end of which is heated over a spirit lamp to a temperature just below that at which paper scorches. The change is sudden and passes over the heated portion of the surface like a flash. Examining the changed part, we find:

1st. That it has changed from a deep gold to a bright yellow gold color.

2d. When subjected to a shearing stress it *does not whiten or change color in the slightest degree.*

3d. It is much harder, as is readily perceived in burnishing it.

4th. It no longer shows the color reaction with potassium ferricyanide and ferric chloride, changing only by a slight deepening of color.

Of these characteristic changes the second is the most remarkable. The gold-colored silver in its original condition changes with singular facility to white silver: almost any touch, any friction, effects the conversion. If the paper on which a film is spread, is creased, the crease is found to be gray. Exposure to heat or to light destroys this capacity for change, and it is often lost by mere standing (even though protected from light) for a few weeks. This evidently indicates some remarkable molecular change. It will be noticed that the anomaly lies in this, that pressure instantly effects the

complete change from the original form to normal silver, heat effects the same change but with an intermediate stage at which stage *pressure no longer produces any action.*

The intermediate form is distinguished from normal silver almost solely by its bright yellow color and its higher luster. This last difference is very striking when a film on glass is heated in the manner above described. The central parts in changing to white silver become wholly lusterless, while the circle of "intermediate" retains all its original luster. Its continuity is still complete, so that if viewed through the glass, it still acts as a mirror.

This change may be either molecular or depend on dehydration.

The latter seems doubtful for the change can not be brought about by desiccation. Films on paper, on glass and also solid material were kept over sulphuric acid in vacuo for twelve days* without bringing about this modification (they were of course thoroughly protected from light).

Light is also capable of effecting to some extent this change, as will be described farther on:

COPPER-COLORED ALLOTROPIC SILVER.

The color of allotropic silver depends to a remarkable extent on the amount of washing, which the freshly prepared material receives. With a short washing the material dries to a bright yellow gold color; with more washing to a reddish color; with still more, the color is a deep rich copper shade. The washing, when conducted in the ordinary manner, is exceedingly troublesome, the material soon begins to run through the filter and blocks it up. This trouble may be completely avoided by washing with a two per cent solution of Rochelle salt instead of pure water, until towards the end of the operation.†

* A longer time was inadmissible on account of the tendency to spontaneous alteration.

† The mode of preparing the gold and copper colored forms is as follows, the difference is in the length of washing only.

In a precipitating jar are placed,	800 ^{cc}
Water.....	200
20% sol. Rochelle salt.....	50
40% sol. silver nitrate.....	
In another vessel are placed,	800 ^{cc}
Water.....	200
20% sol. Rochelle salt.....	107
30% sol. ferrous sulphate (crystallized).....	

(The substances must be added in the order above given and be mixed immediately before using. It is scarcely necessary to say that distilled water must be used exclusively.) As soon as the mixtures are made the iron solution is to be poured into the silver and vigorously stirred for some time. The white silver tartrate becomes almost immediately bright red, then deepens in color and finally becomes black.

Substance described acting on s more trouble product is in this way probably depending to sis gave 10 first case th 84.12 per formula. the iron p not carried

ACTION OF

High t ver to the gold-color Holtz ma A powerf small ma off. The several sli between the latera silver. purplish

When ductors to the other; by silver

That th mal silver solution o electricit; film show Plate I which el similar s ricyanide has becom

Substances of a character nearly related to those that I have described in this and the previous paper, are obtained by acting on silver tartrate with stannous nitrate. The method is more troublesome and gives inferior results, the gold-colored product is less pure: A beautiful steel-blue substance obtained in this way was found to contain a considerable quantity of tin, probably present as stannic oxide, 10.87 per cent of tin corresponding to 13.80 SnO₂, was found by analysis. Another analysis gave 10.66 per cent corresponding to 13.61 SnO₂. In the first case the quantity of silver found was 83.61, in the second 84.12 per cent. These results do not lead to any satisfactory formula. The tin is no doubt present as an impurity and as the iron process gave far better results, the examination was not carried farther. Silver citrate gives similar results.

ACTION OF DIFFERENT FORMS OF ENERGY ON ALLOTROPIC SILVER.

1. *Action of Electricity.*

High tension electricity instantly converts gold-colored silver to the ordinary form. When paper covered with a film of gold-colored silver is held between the conductors of a Töpler-Holtz machine, each spark forms a gray dot of ordinary silver. A powerful discharge is not necessary; an inch spark from a small machine is effectual, even when the condensers are cut off. There is also a lateral action which is best seen when several slips of such paper are held loosely together and placed between the conductors. When the slips are opened a little the lateral branches are beautifully seen, playing through the silver. Their fine emerald-green color contrasts with the purplish shade of the spark.

When several pieces are in this way held between the conductors together, there is a transfer of silver from one piece to the other, so that the back of each piece of paper is blackened by silver carried over from the one behind it.

That the branching gray spots in this way formed, are normal silver, is easily proved by immersing the piece in a dilute solution of potassium ferricyanide. The part acted upon by electricity is not affected by the reagent, while the rest of the film shows the coloration characteristic of allotropic silver. In Plate I the upper figure shows a slip of paper, at one end of which electricity has been transmitted, and the figure below, a similar slip that has been subjected to the action of the ferricyanide, showing that where electricity has passed the silver has become normal and is not affected by the reagent.

2. Action of heat.

Allotropic silver is converted by heat to normal silver in either the wet or dry state.

Dry heat.—When films of allotropic silver on glass are placed in a water desiccator and are kept at 100 C. for eight or nine hours the central portions are converted into the intermediate form, while at the edges there is a border of grayish white ordinary silver. In fact the change to white silver at the edge commences before the central part is fully converted to the intermediate form.

At higher temperatures the change is much more rapid and better marked. At 180° C. the first effect is to darken a little: (this is usually the first effect of heat) this continues about five minutes. Continuing the heat for ten minutes more the slight darkening disappears and the film has a bright pure gold color sometimes with a slight salmon tinge. The change to the intermediate form is now complete, the film burnishes yellow and does not react with potassium ferrieyanide. It is of interest to remark that the color reaction persists as long as there is a trace of unconverted material, *so that a film may burnish yellow and yet show a well-marked color reaction.* This is because most, but not all of the material has undergone conversion.

At 200° C. the film begins in about ten minutes to show a white border and in half an hour or thereabouts it whitens completely. In these experiments the best support for the film is chemically clean glass. Except that for testing the burnishing a film on paper is needed. The paper should be very pure.

Allotropic silver in the solid form heated to 180° or 190° for about fifteen minutes undergoes a similar change: whereas before it was easily pulverized, it is now almost impossible to reduce it to powder and the powder is yellow instead of being grayish black.

Moist Heat.—A film spread on pure paper and placed in distilled water maintained at 99° or 100° without actually boiling, at the end of half an hour is converted almost wholly to the intermediate form. It burnishes pure yellow but still shows traces of the color reaction.

A better plan of operating is to immerse a film spread on glass in distilled water and to place it in a desiccator with a water jacket. After keeping for twenty-four hours close to 100° C. the film has become pure white. It is not disintegrated by the change but may be detached from the glass in films exactly resembling ordinary silver leaf.

The effects of heat are shown in Plate I, lower pair of figures.

3. Ac

The slight gold-colored with a rounded on paper, heat to cause this were it not there is the and as brilliant of pure white potassium f color, whilst through a represented freshly-made should have used within easy partial ate state, in as to partial

When the the effect is of the pure, trace of color

In an early that, having containing the journey ing undergo shape of the frosted white to the friction by the motion by finding t part of the ment, the su without alter

It was also that when a alteration w at rest, until mens of all bright white thoroughly p

Out of o packed in a

3. Action of Mechanical Force. (Shearing Stress.)

The slightest application of force suffices to instantly convert gold-colored allotropic silver to normal silver. A glass rod with a rounded end drawn lightly over the surface of a film on paper, leaves a white trace behind it. The force sufficient to cause this change is so slight that one might doubt its reality were it not for the decisive proof immediately at hand. First, there is the characteristic change of color: the film is as yellow and as brilliant as gold-leaf; the line drawn by the glass rod is of pure white silver. Immersing the film in a solution of potassium ferricyanide the white lines simply change to gold color, whilst the film surface on which they are drawn passes through a brilliant succession of colors. (These effects are represented in Plate II, the uppermost figures.) For this use, freshly-made material should be employed, and the film itself should have been freshly spread on pure paper or card and used within a few hours after drying. This because of its easy partial passage, especially in thin films, to the intermediate state, in which it gives a yellow streak. (See also remarks as to partial conversion *ante*.)

When the experiment is performed under proper conditions the effect is very striking by reason of the instant conversion of the pure, deep yellow metal to perfect whiteness without a trace of color.

In an earlier communication to this Journal it was mentioned that, having taken with me on a journey several small vials containing gold-colored silver, they were found at the end of the journey to be all converted into white silver without having undergone any disaggregation, and retaining the original shape of the fragments. The white silver formed had the fine frosted white color of pure silver. This change was attributed to the friction of the fragments against each other, occasioned by the motion of the journey; a conclusion that was confirmed by finding that when cotton wool was forced into the empty part of the vial in such a way as to prevent all internal movement, the substance could be sent over a four-fold distance without alteration.

It was also observed (and this is a matter of special interest) that when a partial change had been effected by friction, this alteration went on, although the substance was left perfectly at rest, until it became complete. With time, all solid specimens of allotropic silver undergo this spontaneous change to bright white silver, apparently normal silver, even when thoroughly protected from light.

Out of over twenty specimens in tightly corked tubes, packed in a box and left in a dark closet for a year, not one

* Emmens began here, & cold (-20°C.)

escaped conversion. Spread on paper or on glass and duly protected, the change is slower.

4. Action of Strong Acids.

The action of acids upon allotropic silver has been already described; it remains only to add here that the conversion to normal silver is entirely unaccompanied by the escape of gaseous matter; not a bubble can be detected by the closest observation.

By acting on dry films with dilute sulphuric acid it is easy to make the conversion gradual and so to trace its passage through the intermediate form.

With sulphuric acid diluted with four times its bulk of water and allowed to cool, an immersion of one or two seconds converts a film on glass or on pure paper wholly to the intermediate form. It is then bright gold-yellow but shows no color with the ferricyanide reagent. With sulphuric acid diluted with twice its bulk of water and used while still hot, the action is instantaneous and the allotropic silver is converted into light gray normal silver. The silver obtained in this way is very indifferent and gives no reaction with potassium ferricyanide, whereas even ordinary silver leaf gives a pale-colored reaction. (See Plate II, lower pair of figures.) The same acid after cooling acts more slowly; the product is more yellowish, owing to the presence of a certain quantity of the intermediate form.

5. Action of Light.

When allotropic silver is spread as a thin film on glass or on pure paper it may be preserved for a length of time apparently unchanged. This appearance is deceptive. From the moment that the film is formed a slow but steady change commences which can be best explained by supposing that a gradual polymerization takes place. Even after eight or ten hours' exposure to ordinary diffuse light a distinct loss of activity can be detected by careful testing with potassium ferricyanide. The change which occurs is in the nature of a tendency to a very gradual passage into what I have called the intermediate form in which the gold-yellow color remains unchanged while the chemical activity is lost or much diminished. Although a commencement of this change can be detected in a few hours, it goes on very slowly. By exposure to one or two days of summer sunshine (a much longer time is required in winter), the change is nearly complete. The exposed portions are lighter and brighter, and in solution of ferricyanide they color very slowly.

The question long continued to answer the following

At a window constructed light paper. Some an opaque design but uncovered from the end of this time bright yellow. portions had retained their that the uncovered in the frame. that if two film ing frame under the last mentioned of this silver is always light. The glass becomes hot to a temperature that is freely of the effect of the

It appears, similar to that slower. Experience it is the more

With light, very satisfactory change to the white much better result

When a film or two days of exposed portions their chemical bath of potassium figure of Plate of an immense

* Since this was a known fact in the case more rapidly producing the cause, with chloride darkens to the same light

The question naturally arose whether light by a sufficiently long continued exposure could complete the change and convert allotropic to ordinary white silver. To obtain a decisive answer the following experiment was made:

At a window having a southeastern exposure and unobstructed light there were placed films on glass and on pure paper. Some of these were placed in a printing frame under an opaque design. The others stood side by side with the first but uncovered. The exposure was continued for four months from the end of January to the end of May. At the expiration of this time the uncovered paper and glass films were still bright yellow. But of those in the printing frame the exposed portions had become nearly white, while the protected parts retained their full deep gold color. It may at first seem strange that the uncovered pieces were less affected than those exposed in the frame. But this difference was always observed, namely, that if two films were exposed side by side, the one in a printing frame under glass, the other simply fastened to a board, the last mentioned was always the less affected. The explanation of this seeming anomaly lies in the fact that allotropic silver is always much more easily affected by heat than by light. The glass in the printing frame by exposure to sunlight becomes hot to the touch, and thus the film under it is kept at a temperature many degrees higher than that of the other film that is freely exposed to the air: the higher temperature aids the effect of the light.*

It appears, therefore, that the agency of light is somewhat similar to that of the other forms of energy but very much slower. Experiments made for the purpose demonstrated that it is the more refrangible rays that effect the change.

With light, the production of the intermediate form is never very satisfactory. Long exposures are needed, and before the change to the intermediate form is complete, the further alteration to white seems to commence. With heat the changes are much better marked.

When a film on pure paper has received an exposure of one or two days of summer sunshine under an opaque design, the exposed portions are sufficiently changed to have lost much of their chemical activity, so that when the film is plunged into a bath of potassium ferricyanide, the effect given in the lower figure of Plate III is obtained. The color represented is one of an immense variety of tints produced by this reagent on the

* Since this was written I find that both Herschel and Hunt noticed an analogous fact in the case of silver chloride, viz: that paper prepared with it darkens more rapidly under glass than when freely exposed; without, however, suggesting the cause, which is the same in both cases. I have observed that silver chloride darkens more rapidly when exposed under warm water than under cold to the same light in vessels side by side.

unaltered or active form. The upper figure of the same plate gives the effect of a very protracted exposure (as above described) on pure paper (or glass) under glass. With some kinds of sized paper, this effect is produced by a much shorter exposure; apparently owing to the presence of traces of a hyposulphite,* which appears to aid the action of light.

These seem to be not merely new facts but to belong to a new class of facts. No instance has been hitherto known of an element existing in so great a variety of forms and passing so readily under the influence of any form of energy from one to another of them.

It is evident that a connection must almost certainly exist between these varied transformations and the changes which many silver salts undergo through the action of light and other forces. This connection will form the subject of the second part of this paper. The present part will be concluded by a somewhat fuller description of the color reaction which is especially characteristic of allotropic silver.

THE COLOR REACTION.

When allotropic silver is immersed in a solution of a substance readily parting with oxygen or sulphur or with a halogen, a film is formed which exhibits the colors of thin plates. Such phenomena are familiar and are seen in the blueing or yellowing of steel in tempering and the coloring of other metals when covered with films of oxide or sulphide. With allotropic silver the colors are very brilliant, probably because silver is the best of all reflectors for rays having a nearly perpendicular incidence, sending back about 90 per cent of such. Light gold colored silver gives the most-brilliant effects.

The substances which produce these reactions are potassium ferricyanide and permanganate, ferric and mercuric chlorides, alkaline hypochlorites and sulphides, mixtures of potassium bichromate with hydrochloric or hydrobromic acid, solution of iodine, etc.

Potassium ferricyanide in a five or ten per cent solution is the best of these reagents because its action is more distinctive.

* The behavior of these varieties of paper led me to make inquiries of an intelligent paper manufacturer from whom I learned that every sort of paper pulp is now treated with chlorine. As any portion of the bleaching material left in the paper would eventually destroy its strength, it becomes necessary to add hyposulphite in excess to remove it. Accordingly every specimen of sized paper that I have examined contained hyposulphite, even the purest photographic papers were not free from it, though containing greatly less than most others. Apparently, the only difference is that with photographic paper more care is taken to avoid any considerable excess of hyposulphite.

In particular the purples & especially a peculiarly diluted, until straw shade. does not appear shade only, though has been dipped in manganate allotropic

A ferricyanide substance comes to say whether potassium ferricyanide silver suspended carried to its yellowish white ferrocyanide

Of the many allotropic silver in spark, heat, and variety potassium be seen by an pressure each this form potassium silver color to has nothing to produced in the f

When potassium silver, its first brown, passing bright white & this gold stage thickness of f

The success potassium ferr

In particular the blues which it gives are of great purity and the purples very rich. Ferric chloride gives beautiful tints, especially a peculiar glittering rose color. It must be very much diluted, until the solution loses its yellow color and takes a straw shade. It often happens that the characteristic color does not appear whilst the film is in the solution but a bronze shade only, the permanent color appearing only after the film has been dipped into water and blotted off. Potassium permanganate also gives rise to a beautiful succession of colors on allotropic silver but is somewhat uncertain in its action.

A ferricyanide is therefore the best reagent. As to the substance constituting the film which is formed, it is difficult to say whether it is silver suboxide or ferrocyanide. When potassium ferricyanide is allowed to act on moist allotropic silver suspended in it, and the action of the ferricyanide is carried to its limit, the silver is entirely converted into a yellowish white powder, consisting almost wholly of silver ferrocyanide mixed with a little silver ferricyanide.

Of the many varieties of ordinary silver which exist allotropic silver is convertible into two only. The high tension spark, heat, and acids convert it to dull gray silver: on this variety potassium ferricyanide has no action whatever, as will be seen by an inspection of the plates. Light under glass and pressure each convert allotropic to bright white silver, and in this form potassium ferricyanide acts slightly, converting the silver color to gold. It is needless to say that this gold color has nothing to do with allotropic silver: it seems to be produced in the following way.

When potassium ferricyanide acts on films of allotropic silver, its first effect is to deepen the gold color to a gold brown, passing rapidly on to other shades. The action on the bright white silver is very slight and apparently just reaches this gold stage, which corresponds to an air film having a thickness of from 0.000150^{mm} to 0.000160^{mm} .

The succession of colors obtained on allotropic silver with potassium ferricyanide is as follows:

First Order.

Russet brown.
Brown red.

Second Order.

Rich and deep purple.
Dark blue.
Bright blue.
Pale blue.
Green russet.
Red.

Third Order.

Reddish purple.
Bluish purple.
Rich green.

The fourth order is not reached, for after this the colors become much mixed, probably the action is no longer sufficiently uniform. The other differences, beside the absence of the fourth order, as will have been observed, are that in place of the yellow of the second order corresponding to a thickness of air of 0.000432^{mm}, there is a green, though of a more russet shade than that of the third order.

In the third order there is at no time a pure blue corresponding to 0.000602, but only a succession of beautiful red and blue purples, gradually passing into green.

There are few more beautiful experiments than to watch these changes. Purity of color, however, depends much on the purity of the paper employed. Want of this purity will often cut short the changes at the pale blue of the second order.

I have endeavored to give some idea of these colors in the Plates which accompany this paper, but it has proved to be a most difficult task. The colors represented are,

Plate I, purple and blue of the 2d order.

Plate II, purple of the 2d order and green of the 3d order.

Plate III, brown red of the 1st order.

It has not, however, been found possible to correctly reproduce the brilliancy and depth of color of the originals.

Philadelphia, Jan. 24, 1891.

(To be continued.)

EXPLANATION OF THE PLATES.

In each pair of figures the upper one represents the effect of exposing allotropic silver to some form of energy. The changes are in all cases similar in character.

In the lower of each pair of figures the effect is represented which would be produced by immersing the upper one in a solution of potassium ferricyanide. This affords proof of the completeness of the change by showing that gold-colored silver in passing into the ordinary form has lost its power of reacting with a ferricyanide. In these lower figures an attempt has been made to show some of the colors produced in this way. But they fall far short of the originals in brilliancy and intensity. These last are so remarkable that the lithographer who executed the work remarked that even an artist with a brush and palette of colors could not imitate them, and that therefore it was hopeless to expect to reproduce them by lithography—in other respects the Plates represent fairly well the changes that take place.

IN the School
brief description
about the Great
now able to add
terest to those b

The Great Fa
Belt and Highw
the north Th
Rocky Mountai
Archaean nucle
Cambrian rocks
This formation
underlies the su
phur Springs to
losures of the
on the road fro
numerous altern
and argillaceous
and slate. Near
converted into
this group is gra
fossils were fou
matter abound
ently overlies al
Primordial trilob

On the summit
the Archaean gra
full of *Scolithus*
merous large dyl
stone.

Succeeding the
zoic limestone, s
which has been
most picturesque
with buttes imita
ing to form scen
gist. In the lim
erous fossils. N
unconformably o
fresh water lime
smaller seams of
soon covered wit

THE
AMERICAN JOURNAL OF SCIENCE

[THIRD SERIES.]

[3] 51 (244)

p 259-267

(April 1891)

ART. XXVIII.—*On Allotropic Silver*; by M. CAREY LEA.

Part II.—*Relations of Allotropic Silver with Silver as it exists in Silver Compounds.*

THE first part of this paper* was devoted to the examination of one of the well marked forms of allotropic silver,—the gold-colored. The blue form in its soluble and insoluble varieties will be more particularly described in a future paper. The subject at present to be considered is the relation existing between the allotropic forms of silver taken generally and silver as it exists in its compounds and more especially in the silver haloids.

It is a well established law that when a substance is capable of existing in two forms, of which one is a polymer of the other, the polymeric form possesses greater density and less chemical activity. Combination is usually accompanied with loss of activity, and the polymerization of a body consists in its combination with itself. When a substance is capable of existing in two allotropic forms and of being converted from the one to the other by pressure, the body resulting from pressure is always the more dense of the two and is a polymer of the first.† In the case of allotropic silver these laws appear to be verified. I have shown elsewhere that gold-colored silver has a specific gravity of 8.5, while that of normal silver is 10.5 to 10.6. The greater chemical activity of the gold-colored form is demonstrated by its greater affinity for oxygen, sulphur and

* In the March number, pp. 179-190.

† See examination by Spring of the effect of pressure, Ber. D. Ch. Ges., xvi, p. 1002, 1003.

the halogens. Also it is conspicuous by the remarkable facility with which it passes from the one state to the other. Spring, in the examinations above referred to, used pressures of many thousands of atmospheres. Allotropic silver is changed readily to normal by the mere pressure of the finger or by a temperature of 100° C.

One form of allotropic silver has the property of solubility in water. The solution of a solid in a liquid is often accompanied by change to a more simple molecular structure. Hitherto the only solvent known for a metal has been another metal, and the behavior of metals when so dissolved has been the subject of late years of very interesting examinations by several chemists. Ramsay* examined the lowering of the vapor pressure of mercury by other metals dissolved in it. Heycock and Neville examined the fall in the freezing point of metals, more especially of tin, caused by the solution in it of other metals.† Both of these investigations led directly to the conclusion that in the case of a dilute solution of one metal in another, the dissolved metal existed in the atomic form. (In each case a few metals gave exceptional results, but silver was not among these.) Tammann's investigations on the alloys of mercury led to precisely similar general deductions. Great weight attaches to conclusions supported in these several ways.

The fact that a metal in dissolving in another metal appears to assume the atomic form affords no positive proof that it does the same in dissolving in water. In fact the solution of a metal in water is something so new that we have little ground for argument by comparison. So far, however, as the above mentioned analogy may be considered to go, it rather tends to the view that the solubility of silver may be due to its having assumed a very simple and perhaps an atomic form. It may be said therefore that all considerations tend to show that the allotropic forms of silver taken as a whole have a more simple molecular nature than what I have described as the intermediate form, and that this again is more simply constituted than ordinary silver.

In the present case we have to consider three distinct forms, (1) allotropic, (2) intermediate, (3) ordinary silver. We notice that (1) can with the utmost facility and in several ways be converted into (2) and (3), and that (2) can always be converted into (3), but that *these transformations can by no possibility be reversed*. To convert ordinary silver into allotropic we must as a first step dissolve it in an acid: that is, *convert it from a polymerized to an atomic form*, and only from this atomic form can allotropic silver be obtained.

* R. Trans., 1889, p. 521, also Wiedemann, *Referate* 1889, p. 993.

† Jour. Chem. Soc., 1890, p. 376.—Nature, Jan. 1891, p. 262.

Bearing
five proper
be allowab
they may r
viz: *atomic*

As silver
in the atom
rates from
not unite to
but the phe
does not t
least concei
may be pre
At least fo
state. Wh
not know, l
the case. S
form: if th
for oxygen
it should r
properties a

There is
edge is so
stitution of
can be said
constitution
many atoms
fering from
either adopt
must suppo
merized. T
views it is be
between the
known to ex
For this ex
chloride) wi

Action of Fl

It is a fa
especially, a
already said
silver, it see
their action
far a paralle

Bearing this capital fact in mind and considering the respective properties exhibited by the three forms of silver, it may be allowable to adopt as a working hypothesis the view that they may represent the three possible molecular forms of silver, viz: *atomic, molecular and polymerized*.

As silver in its compounds and in its saline solutions exists in the atomic form, it is easily conceivable that when it separates from such solutions by reduction, the atoms may or may not unite to molecules. Usually elementary atoms do so unite, but the phenomena of nascent action indicate that this union does not take place at the instant of separation, and it is at least conceivable that under particular circumstances this union may be prevented. In some cases no such union takes place. At least four metals exist in the form of vapor in the atomic state. Whether this state continues after condensation we do not know, but there is no impossibility but what such may be the case. Similarly allotropic silver may represent an atomic form: if this were so it should exhibit more active affinities for oxygen and the halogens than the ordinary form; also it should readily pass into the ordinary form. And these properties are undoubtedly exhibited by allotropic silver.

There is no branch of chemical statics in which our knowledge is so defective as it is in relation to the molecular constitution of solids and more especially of the metals. All that can be said is that in metals, as we ordinarily know them, this constitution is probably very complex, the molecules containing many atoms. When substances assume a variety of forms differing from each so much as do the forms of silver, we must either adopt a theory of the character now suggested or else we must suppose that the different forms are differently polymerized. To decide which is the most probable of these two views it is best to examine as to whether an analogy can be traced between these allotropic forms of silver and silver where it is known to exist in an atomic form, namely, in its compounds. For this comparison the silver haloids (and chiefly silver chloride) will be taken.

Action of Forms of Energy on Silver Haloids. Parallelism with Allotropic Silver.

It is a familiar fact that certain forms of energy, light especially, affect the silver haloids. In view of what has been already said as to the action of all forms of energy on allotropic silver, it seemed desirable to make a general examination as to their action on the silver haloids and thus to determine how far a parallelism could be traced.

It is to be observed that the action of different forms of energy on the silver haloids is apt to be partial: the influence seems to be antagonized by opposing and almost equally matched forces. Thus in the case of light, its tendency to condense the atoms of silver to molecules is largely counteracted by the strong affinity of chlorine for *atomic* silver. The action of high tension electricity, as will presently be seen is similar to that of light in that it produces a visible effect. In the case of heat and of contact action on these silver haloids, it will be shown that there is at first a mere indication of effect, invisible to the eye, but readily brought out by the action of a reducing agent, as described below. The action of each form of energy seems to be almost counteracted by opposing affinities. But in every case action does take place and *always in a direction corresponding to the action of that form of energy upon allotropic silver.*

High tension electricity it is well known impresses sensitive films of silver haloids, which on development exhibit remarkable ramifications. When electric sparks are passed through paper on which a coating of silver chloride has been made, the point of passage of each spark is marked by a minute circle of violet color indicating a visible change, probably to a subchloride.

Mechanical force.—More than twenty years ago I noticed that by a slight pressure, an invisible effect, capable of development, could be impressed on silver iodide. Lines drawn with a glass rod or any other hard, neutral substance were reproduced. An embossed card pressed gently on the film, gave an image of all its details on development. These experiments were extensively repeated by others with concordant results.

I have recently repeated them with silver bromide with similar effect.

Heat.—To determine the effect of heat on silver bromide, pieces of bromide paper were placed in a desiccator (of course using inactive light) and heated to the extent indicated. For each piece so heated, a corresponding piece cut from beside it in the same sheet was preserved, and these two pieces, that heated (after complete cooling) and that not heated, were placed side by side in an oxalate developer. Comparison between these developments indicated the effect of the heat. The following results were obtained.

A piece kept for 3 minutes at 145° C. was strongly affected and blackened quickly in the developer, the companion piece remaining white.

A piece kept for 15 minutes at a temperature commencing at 131° C. and ending at 136° was still more thoroughly affected than the foregoing, the longer exposure more than making up for the lower temperature. Companion piece remained white.

A piece was distributed before.

A piece was also brought its composition.

It was as these, in the development by which if the process on the surface by the effect of light.

The result of the effect up to 100° 126° a slight temperature well marked.

It may be said should be able to bear a heavy load lies in the bromide of moisture. A silver 130° and weight. have been

It remains to a moderate position in

For the process of by a glass tube half a meter all these of light. If added to the almost complete as far as possible was used calcium bromide operation.

The silver was forced

A piece kept for 8 minutes at a temperature 107° to 108° was distinctly but not strongly affected. Companion piece as before.

A piece kept for 17 minutes at a temperature of 100° to 102° was almost unaffected. A long and careful development brought out a faint difference between the piece so heated and its companion piece.

It was found that to obtain accuracy in determinations such as these, the paper must rest on a glass, and not a metal, shelf in the desiccator, as the metal shelf is always hotter than the air by which the thermometer is affected. In using a metal shelf, if the paper curled by reason of the heat, the part that rested on the shelf developed darker than that which was simply acted on by the air. By substituting a glass shelf this difference of effect disappeared.

The result of the foregoing and other experiments was that the effect of heat on AgBr commences at about 100° C., that up to 108° it is still slight and acts slowly, but that at 120° to 126° a strong action commences, which further increases as the temperature is raised. The analogy with allotropic silver is well marked.

It may at first seem strange that a temperature of 100° C. should produce a permanent change in a substance which will bear a high heat without decomposition, but the explanation lies in the presence of water in the former case. When silver bromide is formed in paper and dried in the air it still retains moisture. Even at 100° C. this moisture is not driven off. A silver haloid requires to be heated to a temperature between 130° and 140° for several hours before it ceases to lose weight. Therefore in all the foregoing cases moisture must have been present.

It remains to be shown that by a sufficiently long exposure to a moderate heat in the presence of moisture a visible decomposition results.

For this purpose silver chloride was precipitated with an excess of hydrochloric acid, after thorough washing was placed in a glass tube of about a centimeter in internal diameter and one-half a meter long, and was sealed up with a blast lamp. During all these operations the chloride was thoroughly protected from light. Five or six cubic centimeters of pure water were first added to the chloride. It was intended to exclude completely or almost completely the effect of pressure and to act on the chloride as far as possible by heat only, and for this reason a longer tube was used and one end only was immersed in the chloride of calcium bath, the other end remained cold throughout the operation.

The silver chloride formed itself into a compact plug and was forced by the steam which generated below it up to the

middle of the tube. This effect, though not intended, answered very well as the chloride was kept constantly under the influence of steam at about 100° . It soon began to darken and at the end of three or four hours all the lower part was violet brown, the upper part gray, the change taking place entirely through the mass. Some thin smears of silver chloride on the lower inside part of the tube were completely blackened.

On opening the tube next day there was no escape of gas. The water sealed up with the silver chloride had acquired a faint but distinct alkaline reaction showing that enough alkali had been dissolved from the glass to overcome any acidity arising from decomposition of the chloride. The water contained traces of alkaline chloride.

A similar examination was made with silver bromide precipitated with excess of hydrobromic acid and thoroughly washed with distilled water. The action of diffuse light on silver bromide is very different from that on silver chloride. A portion of that prepared as above mentioned changed in diffuse light very quickly from yellow to greenish yellow, but after that first change the alteration was extremely slow and in an hour had only reached to a dirty greenish gray. The action of direct sunlight was quite different; fifteen minutes' exposure changed the greenish gray to dark chocolate brown.

In the tube the silver bromide did not form a plug like the chloride but separated into balls which remained in the bottom of the tube. By keeping the chloride of calcium bath considerably above 100° C. the water in the tube was kept actively boiling; it condensed in the upper part of the tube and returned. Six hours of this treatment only brought the bromide to the same greenish color which it would have acquired by a few minutes' exposure to diffuse light.

The conclusion to be drawn as respects both the silver haloids is that they undergo actual decomposition by the action of moist heat, but that this effect is much more marked in the case of chloride than that of bromide.*

Chemical action.—Dilute sulphuric acid quickly changes allotropic silver to normal, and therefore if the parallelism which I have indicated really exists, marks made on bromide paper with dilute sulphuric acid should be capable of development.

The experiment was made by drawing characters on silver bromide with a glass rod dipped into sulphuric acid diluted with twice its bulk of water. After allowing the acid to

* Light and heat act differently on silver chloride. Heat can not decompose it in the absence of moisture but light can. This was proved by an investigation made by the writer in 1839, in which it was shown that fused silver chloride poured into petroleum and exposed after cooling to the sun's rays was instantly blackened.

remain
immerse
two

On ap
ing conti
repeated
On one s
but reve
darkened
gave a c
strongly
develop
time aft
water to
ten or fi
washed o
was app
came out

Cold s
no action
strong a
leave no
effect inv
give way
the acid
and heat
ble until
the agent
continued
a visible c

Light.
show an
When fo
of hydroc
contains a
trace of s
compositi
ever this
essential p

This ha
binations
capable of
that it can
is rapidly

* In some
I found that
water, with
silver to stro

remain in contact for two or three minutes, the paper was immersed in running water and was washed for an hour or two.

On applying the oxalate developer nothing appeared. Feeling confident that effect must be produced, the experiment was repeated several times and the results were closely examined. On one specimen it was found that the characters had appeared, but reversed, that is, lighter than the ground which had darkened by the development being pushed. This at once gave a clue; it showed that traces of the acid adhered too strongly to be removed by washing and by locally checking the development, interfered with the reaction. Accordingly, next time after a very short washing, the paper was immersed in water to which a trace of ammonia had been added, and after ten or fifteen minutes' action the ammonia was thoroughly washed out. The result was striking: as soon as the developer was applied the characters which had been traced with acid came out strongly as brown marks on a white surface.

Cold sulphuric acid even undiluted is generally held to have no action on silver haloids, but it is well known that the hot strong acid decomposes them. The foregoing experiments leave no doubt that the cold dilute acid produces an initial effect invisible to the eye but revealed by greater tendency to give way under the action of a reducing agent. This action of the acid comes therefore exactly into line with that of light and heat. In all three cases an effect is produced inappreciable until a reducing agent is applied. But in all three cases the agent which produced this invisible effect is capable by continued action under favorable conditions of bringing about a visible change without the aid of a reducing agent.

Light.—The silver haloids in their sensitiveness to light, show an important relationship to that of allotropic silver. When for example silver chloride precipitated with an excess of hydrochloric acid is exposed to light, the darkened product contains apparently no metallic silver* (it is probable that the trace of silver given up to nitric acid may arise from the decomposition of a very small quantity of subchloride). However this may be the subchloride and not metallic silver is the essential product.

This has always seemed a very enigmatical result. Two combinations of silver and chlorine exist; the one very stable, capable of fusion without decomposition, the other so unstable that it can hardly exist isolated, and yet the stable compound is rapidly broken up by light, even by a weak diffuse light,

* In some (unpublished) experiments made some years ago to test this point, I found that silver chloride exposed for several days to strong sunlight under water, with frequent stirring up, and subsequent washing yielded only a trace of silver to strong cold nitric acid after a contact of an hour.

while the unstable compound resists many days' exposure to the strongest sunlight.

In examining the action of light upon allotropic silver (see Part I) an equally remarkable effect was described. Although all the other forms of energy applied readily and quickly convert allotropic to ordinary silver, light (at ordinary temperatures), fails to effect this change even by exposures lasting for several months. If we conceive that the atomic form of silver which exists in AgCl corresponds to the allotropic form, and that the more condensed form of subchloride corresponds to the "intermediate form," we shall obtain a reasonable explanation of the action of light.

The inability of light to carry the change which it produces in allotropic silver beyond the "intermediate form" exactly corresponds to its inability to carry the decomposition of silver chloride further than to subchloride or rather to photochloride. (It is understood that the silver chloride here spoken of is that which is formed by precipitation with excess of hydrochloric acid). This explanation appears to remove a real difficulty, and at the same time establishes a perfect parallelism between that action and the action of light on allotropic silver.

Although the foregoing study of the silver haloids was made for the purpose of fixing the relations which exist between them and allotropic silver, the results nevertheless have much interest in relation to the haloids themselves and place their nature in a somewhat new light. For it is shown that these haloids, though substances in some respects of very great stability have their equilibrium so balanced as to respond to the slightest influence, not merely of light, but of any form of energy, not receiving a momentary but a permanent impression which, though so slight as to be invisible, still greatly increases the tendency of the molecule to fall to pieces under the action of a reducing agent. Further, four of these forms of energy, light, heat, electricity and chemical action, when more strongly applied totally disrupt the molecule. One form of energy, mechanical force, though capable of producing the invisible effect makes an apparent exception in respect of this ability to disrupt. This matter is now under examination and it will probably be shown hereafter that the analogies are complete and without exception.

The same completeness holds with regard to the analogies which form a principal subject of this paper, namely, those existing between allotropic silver and the metal as it exists in the salts of silver. No other salts but those of silver show this wonderfully balanced equilibrium, sensitive to all forms of

energy. I
similar cap
manifestat

The info
as follows.
tropic silve
insoluble in
have almos
exhibits pl
smooth sur
brilliant m
intermediate
metallic lus
chemically
that allotro
intermediat
intermediat
but that th
from ordina
atomic by
metallic for
ing. That
and that thi
condensation
the same ag
able between
that in the
restrained b
atomic silver
pose that in
form.

Philadelphia,

ART. XXIX

[Published t

IN the gra
the rock spl
is by taking
regular bloc
An expert qu
pected of the
factor is the
places there

energy. But allotropic silver also shows an almost exactly similar capacity to respond to the influence of energy in all its manifestations by undergoing changes of a like character.

The inferences to be drawn from the foregoing seem to be as follows. That silver may exist in three forms: 1st. Allotropic silver which is protean in its nature; may be soluble or insoluble in water, may be yellow, red, blue or green, or may have almost any color, but in all its insoluble varieties always exhibits plasticity, that is, if brushed in a pasty state upon a smooth surface its particles dry in optical contact and with brilliant metallic luster. It is chemically active. 2d. The intermediate form, which may be yellow or green, always shows metallic luster, but is never plastic and is almost as indifferent chemically as white silver. 3d. Ordinary silver. . . . Further, that allotropic silver can always be converted, either into the intermediate form, or directly into ordinary silver; that the intermediate form can always be converted into ordinary silver, but that these processes can never be reversed, so that to pass from ordinary silver to allotropic it must first be rendered atomic by combination, and then be brought back to the metallic form under conditions which check the atoms in uniting. That allotropic silver is affected by all forms of energy, and that this effect is always in one direction, namely, towards condensation. That the silver haloids are similarly affected by the same agencies. That a remarkable parallelism is noticeable between the two actions, especially if we take into account that in the haloids the influence of energy is to some extent restrained by the strong affinity which the halogens show for atomic silver. There is therefore reasonable ground to suppose that in the silver haloids silver may exist in the allotropic form.

Philadelphia, March, 1891.

ART. XXIX.—*The Phenomenon of Rifting in Granite;* by
RALPH S. TARR.

[Published by permission of the Director of the U. S. Geological Survey.]

In the granite at Cape Ann and elsewhere it is noticed that the rock splits most easily in certain fixed directions; and it is by taking advantage of these lines of weakness, that large regular blocks are easily split from their bed in the quarry. An expert quarryman knows full well just what may be expected of the granite and in making his calculation, the prime factor is the direction and strength of the "rift." In many places there are other lines of weakness along which the

By carefully regulating the pressure, we may give to the jet a velocity which shall equal the speed of combustion for the mixture of gas and air. The flame will now hang balanced in the air, as shown in fig. 8, the tendency of the fire to spread downward being exactly neutralized by the upward motion of the column. On examining this flame the cause of the bright blue and faint green lines in the mirror is discerned. Around the base of the flame the mixture burns with an intense blue light (fig. 8 A); surmounting this is a cone of greenish fire B, while above this the flame has a light purple tinge.

ART. LVIII.—*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 substance seemed to be the result of a very limited number of reactions closely allied to each other. 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 color 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

a splendid reaction with the specter of a true solution.

It is interesting in neutral, acid, I published, in sodic citrate and in acid solution hydroxide, so either a neutral with the aid of alkaline liquid or sulphuric or acetic acid then retains a brown of a large excess more silver. silver is most also soluble to

The precipitate insoluble. A water gives thrown on a washed out the filtrate be allowed then has a fine withstanding only, so great if the alkaline becomes spongy tom a de

of alkalis. 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 color.

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

Allotropic Silver obtained with 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 color 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 color, so intense as to be almost black. A few drops poured into water give it a splendid red color 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 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 color 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 while 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 color and perfect transparency. Notwithstanding the beautiful color it contains a trace of silver only, so great is the coloring 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 color. 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 two liters of water forty grams of sodium hydroxide may be dissolved and an equal quantity of dextrine, filtering if necessary. Twenty-eight grams 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 one 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 gram of phosphate in solution is added to 100 c.c. of silver solution the color becomes bright red, sometimes scarlet, and the whole of the silver is presently precipitated. This precipitate on the filter has a color like that of ruby copper, which color it retains during the first washing, but after a few hours' washing with distilled water the color changes to a deep Nile green and at the same time it becomes slightly soluble, giving a port wine colored solution. With more washing this solubility may disappear.

It is a general fact that all these forms of silver, however various their color, have both a body and a surface color and these two colors tend always to be complementary. The body color 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 color disappears and only the complementary surface color 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 color. But when the substance itself becomes green by continued washing it assumes on drying a dark gold or copper color, the surface color changing with the body color and maintaining its complementary relation. In observing these effects one is constantly reminded of certain coal tar colors, both by the great intensity of coloration and by the metallic surface color. I am

not aware that
blance to a sim

These forms
attach to them
stance has all t
much as 8 or 1
impossible to c
this substance.
through with t
out effect. T
evident when
which condense
rennatic odor
when dissolve
carbon. Whe
acid and the si
ration a small
tained.

Analyses.—
rial rendered
Results—

N
N
N
N

Allotropic Silver

Tannin (gall
nitrate to met
more strongly
bonated alkali,
either substanc
of alkali and,
Tannin with so
silver, quite fr
the dextrine so
very intense: c
black, by dilut
same character
To obtain it,
solved in 1200
is to be made a
solution just na
little water are
almost instantly
tion after stand
from a small qu

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 100 hours without effect. The presence of this organic substance becomes evident when the metal is heated in a tube. A vapor arises which condenses into small brownish drops having an empyreumatic odor. 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	p. c.	Ag.
No. 2	94.27	"	"
No. 3	92.86	"	"
No. 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 color of this solution is likewise very intense: one containing one per cent of silver is quite black, by dilution deep yellowish red. It has very much the same characters as the preceding, but is rather more stable. To obtain it, 24 grams of dry sodium carbonate may be dissolved in 1200 cc. of water. A 4 per cent solution of tannin is to be made and filtered, of this 72 cc. are to be added to the solution just named: of silver nitrate, 24 grams 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 color of a shade different from the foregoing and somewhat difficult to exactly characterize, a sort of bluish steel-gray.

I do not find that blue allotropic silver (in which is included the green and steel-gray 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-gray color. Precipitation by acetic acid seems to tend to a greenish metallic surface color 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, gray and green forms seem more closely related to the black or dark gray forms of normal silver, for they tend in time to pass into them, while on the contrary, gold-colored 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 color while moist, drying with a rich bluish green metallic surface color in thick films, in very thin films transparent red. It is probable

that the subst
would be fur

I have fou
forms of silv
They are nov

N
It has be
tropic silve
heat it pass
state. In th
luster but r
Oxidizing a
ference as w
and easily r
hard and to
allotropic si
silver. The
the trace of
film and eve
Continued
tion to the i
with time.

At that t
of the chan
talline form
action of v
that one of
the interm
by the ferr
the interpo
luster, rend
exhibited v
foliated str
tals, other
plant-like
crystals ne
long and a
certainty
obtained t
which hap
taneous alt
tion is not

This cha
peculiar to
heated in
changes to

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 color and high luster but none of the other properties of the original form. Oxidizing and chlorizing agents show nearly the same indifference as with ordinary silver. While 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 color. 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, while the portion that had passed into the intermediate form retained its bright gold-yellow color and luster, 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 color does not change.

This change to the crystalline condition does not seem to be peculiar to gold-colored 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 agents 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 vapors and that in iodine vapor at a certain temperature the molecules separate to 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. Chro-

mium amalgam
similar result
enormous aff
oxygen rende
before sugges
but this wou
than that of c
course be dra
substance ma
the finest me
merized. Si
oxygen could
same inflamm

In conclus
suppose that
allotropic sil
far from be
hypothesis."
investigations

Philadelphia, A

ART. LIX:
*River and
Middle
With Plat*

THE Ame
article by th
the Appre
given of a re
Hook and an
of this depre
of the adja
Professor
of this depre
map and ref
1863, takes
Journal, tr
vations on th

* M. G. Rous
don the old vie
and comparable
† Vol xxix, p
and Geodetic St
‡ Vol. xl, pp.

mium 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 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.

ART. LIX:—*Notes on the sub-marine channel of the Hudson River and other evidences of Post-glacial Subsidence of the Middle Atlantic Coast Region*, by A. LINDENKOHLE. With Plate XVIII.

THE American Journal of Science of 1885† contained an article by the writer entitled "Geology of the Sea Bottom in the Approaches to New York Bay," in which a description was given of a remarkable depression in the sea bottom off Sandy Hook and an attempt was also made to account for the origin of this depression and to trace its connection with the geology of the adjacent coast region.

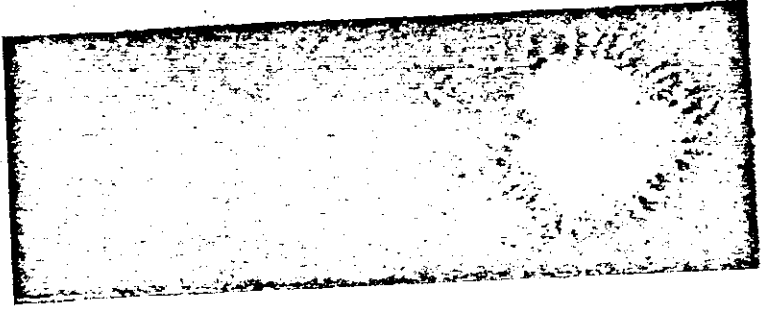
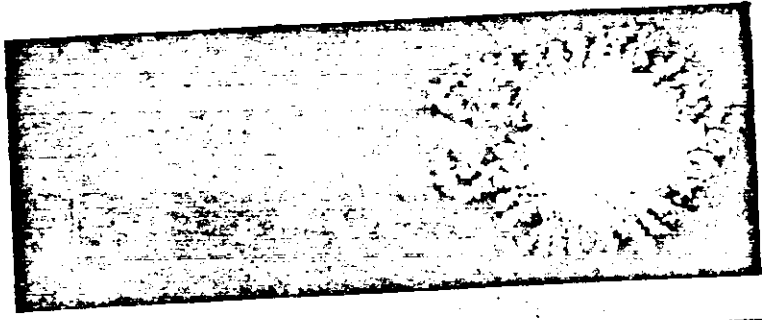
Professor Dana, who was the first to recognize the true shape of this depression and to direct attention to its existence by a map and reference in his "Manual of Geology," published in 1863, takes up the subject again in a recent number of this Journal,†† treating of Long Island in the Quaternary with observations on the sub-marine Hudson River channel, and carefully

* 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, etc. Vol. iii, page 56.

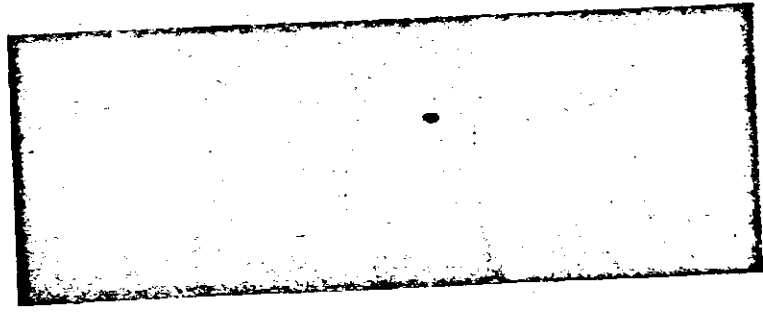
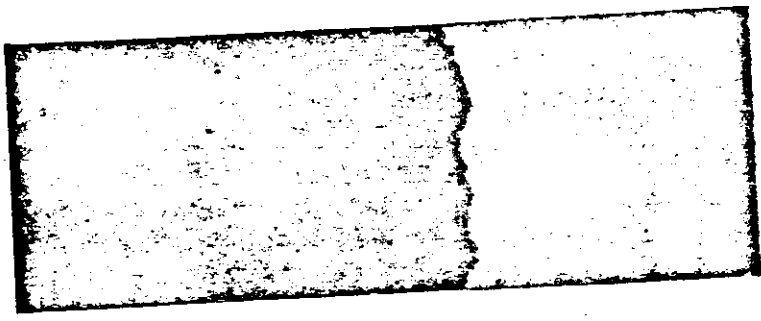
† Vol. xxix, pp. 475 et seq., also republished as Appendix No. 13, U. S. Coast and Geodetic Survey, Report of 1884.

‡ Vol. xl, pp. 425-437.

Effect of Electricity.

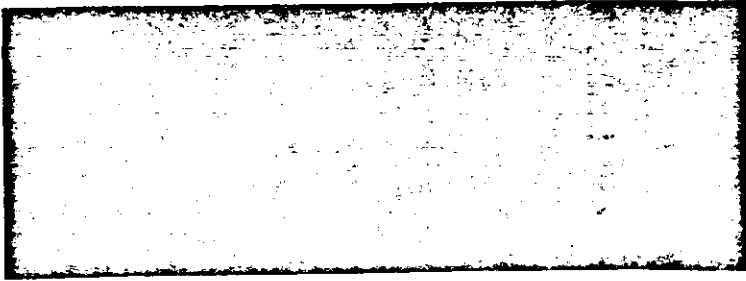


Effect of Heat.



ALLOTROPIC SILVER.

Effect of Mechanical Force.

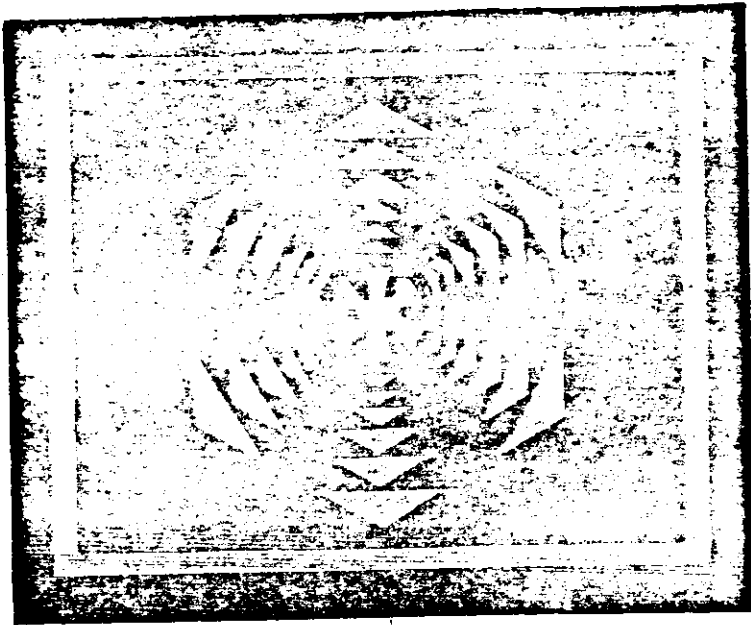
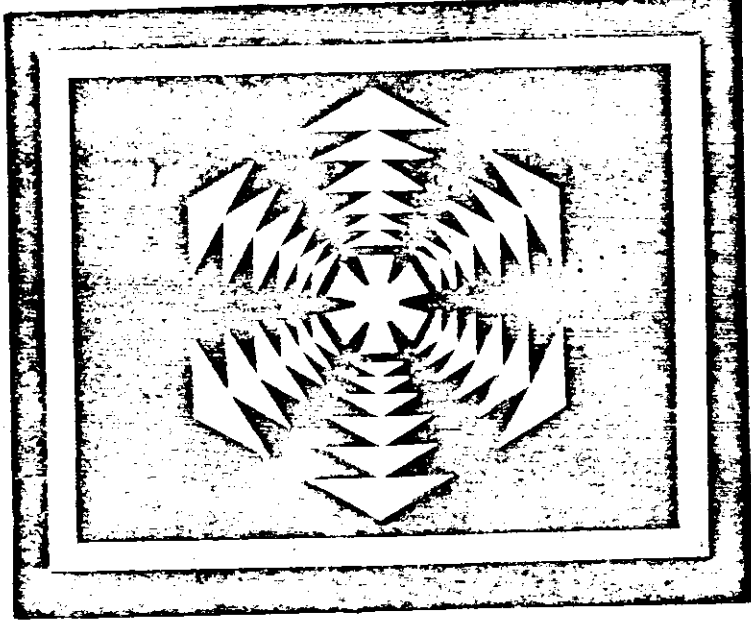


Effect of Chemical Action.



ALLOTROPIC SILVER

Effect of Light



ALLOTROPIC SILVER.

Über Lösungen von metallischem Silber.

Von

M. CAREY LEA.

Alle Lösungen von metallischem Silber, welche ich früher beschrieben habe, sind kolloidal, und seit Veröffentlichung jener Beobachtungen habe ich alle die bezüglichen verschiedenen Präparate weiterhin untersucht und gefunden, daß keines derselben durch Membranen diffundiert. Eine Silberlösung, welche durch Einwirkung von Ferrocitrat erhalten wird, ist auch von Herrn PRANGE, sowie von Herrn Dr. BARUS untersucht worden und zwar mit dem gleichen Erfolge.

Die Silberlösungen sind kolloidal; ob sich jedoch das Silber in denselben im Zustande der Polymerisation befindet, ist durchaus nicht sicher. Polymere Körper sind im allgemeinen indifferentere als die entsprechenden Körper mit einfachem Molekül. Nun werden aber alle Formen des allotropen Silbers, einschließlic der löslichen Form, leichter oxydiert und chloriert, als das Silber in gewöhnlichem Zustande, so daß dieses Verhalten durchaus nicht auf Polymerisation hinweist.

Es sind diese kolloidalen Lösungen von Silber zum mindesten so vollkommene Lösungen wie diejenigen irgend welcher anderer, vollkommen löslicher kolloidaler Körper. Eine gute Methode, um die vollkommene Löslichkeit festzustellen, besteht darin, die Flüssigkeit im Licht von oben derart zu betrachten, daß man das auffallende Licht rechtwinklig zur Gesichtslinie die Flüssigkeit durchstrahlen läßt. Viele Substanzen, deren Lösungen im einfachen, durchfallenden Lichte nicht nur durchsichtig, sondern glänzend klar erscheinen, zeigen bei Untersuchung in der soeben beschriebenen Weise nicht mißzuverkennde Trübung.

Die Lösungen des Silbers halten diese Probe jedoch vollkommen aus, und es scheint dieser Versuch gegen die Ansichten von BARUS und von SCHNEIDER zu sprechen, daß diese Modifikation des Silbers keine allotrope ist, sondern gewöhnliches Silber in feinverteiltem Zustande darstellt.¹ Nach sorgfältiger Bereitung sind diese Silberlösungen sehr beständig; so besitze ich eine Lösung, die durch Ein-

¹ Zeitschr. phys. Chem. 8, 298.

wirkung von Alkalihydroxyd und Dextrin bereitet wurde und welche trotz dreijähriger Aufbewahrung noch stark gefärbt ist. Ein beträchtlicher Teil des Silbers hat sich aus derselben allerdings ausgeschieden; da jedoch die Abscheidung in Form von glänzendweißem, metallischem Silber stattfand, gerade da, wo das Licht am stärksten auffiel,¹ so scheint diese Veränderung prinzipiell, ja vielleicht lediglich durch die Einwirkung des Lichtes bedingt gewesen zu sein.

Gerade diese überstehende Lösung, welche sich so lange gehalten hatte, schien nun eine besonders günstige Gelegenheit zum strengen Nachweis ihrer kolloidalen Natur zu bieten. Sie wurde in einen Dialysator gebracht, und es zeigte sich nach zwei Wochen, daß keine Spur diffundiert war.

Diese Ergebnisse müssen uns also wohl zu der Anschauung führen, daß die Silberlösungen kolloidal sind. Die Löslichkeit ist aber eine vollkommene, so daß diese Lösungen dieselben Proben auf Durchsichtigkeit wie die Lösungen von Krystalloiden aushielten.

¹ Die Flasche stand auf dem Tische in einem hellerleuchteten Zimmer.

Bei der Redaktion eingegangen am 16. September 1894.

Über Triam

Wenn man
gewöhnlichen
phosphats, so
von Magnesium
Ähnlichkeit m
daher leicht In
wenn man den
zugesezt hatt
des Magnesium

Jener Ni
welches ich i
keine Analys
gehalt liegen
nach durch V
in einer Amm
die andere in
enthalte nac
wie nachsteh
stalle erhalten
3H₂O besitzt

Hierzu
lösungen ver
mit 3 Vol. S
erwärmten
spez. Gewic
dünn hatte
langsamen
nur 180 cm
lange derbe
Die gut an

¹ Jahre

² 4. Au

Stabilitätsverhältnisse der Fraktionen.

Ohne Zusatz von Koagulatoren sind die Fraktionen sehr gut haltbar und scheinen ihren Dispersitätsgrad nicht merkbar zu verändern.

Aus den Beobachtungen obiger Tabelle geht die verminderte Teilchengröße der Fraktionen bei den grösseren Schwellenwerten deutlich hervor. Es wurden auch einige Versuche ausgeführt, um die Einwirkung verschiedener Koagulatoren auf die Fraktionen direkt zu untersuchen.

Als Ausgangsmaterial dienten die gereinigten Fraktionen, welche in der Konzentration von 1 g Schwefel 0.085 g NaCl per 100 ccm Sol verwendet wurden. Die freie Salzkonzentration beträgt bei $Fr(-0.25)$

ca. 0.015 g und somit nur ca. 0.0025-norm. bei den grobdispersen 100 ccm Sol

ein wenig mehr. Zu 5 ccm dieser Sole wurden nun im Probiergläschen 4 ccm Wasser gesetzt, und unter Umschütteln Kristalloiddösungen bekannter Konzentration bis zur beginnenden Ausflockung hineingetropt. Die Konzentration der Kristalloiddlösung wurde so gewählt, dass die hierzu erforderliche Menge zwischen 1 und 2 ccm betrug. Aus der zugesetzten Kristalloidmenge und dem totalen Volumen der Flüssigkeit konnte somit die Schwellenkonzentration bestimmt werden. Derartige Bestimmungen sind ja nur annähernd, denn die beginnende Ausflockung lässt sich nicht scharf bestimmen. Die in folgender Tabelle angeführten Zahlen besitzen jedoch relative Bedeutung.

Tabelle 2.

Einwirkung der Koagulatoren auf Schwefelhydrosole verschiedenen Dispersitätsgrads.

Fraktion	(-0.25)	(0.25 - 0.20)	(0.20 - 0.16)	(0.16 - 0.13)	(0.13 - 0.10)	(0.10 - 0.07)	(0.07 -)
Teilchendiameter in μ	—	—	—	(ca. 25)	ca. 90	ca. 140	ca. 210
Schwellenwert für HCl	4.80	3.75	3.40	1.85	1.00	0.65	0.50
" " NH_4NO_3	1.02	0.75	0.67	0.46	0.32	0.25	—
" " NaCl	0.30	0.24	0.20	0.15	0.11	0.09	0.07
" " KCl	0.034	0.029	0.026	0.025	(0.020)	(0.020)	—
" " $\text{Ba}(\text{NO}_3)_2$	0.0017	0.0014	0.0012	0.0012	(0.0010)	(0.0010)	—

Bemerkungen zur Tabelle.

Die Schwellenwerte sind in Molen per Liter angegeben. Die Schwefelkonzentration beträgt bei Ausflockung ca. $\frac{1}{2}\%$. Die in Klammern gesetzten Werte sind der Schwierigkeit wegen, die Koagulation zu beobachten, sehr unsicher.

¹⁾ HCl wirkt in kleinen Konzentrationen zuerst stabilisierend, um bei grösseren Koagulation hervorzurufen.

Aus
gulierfähig
Fraktionen
nicht nur
Lösung von
gulatoren
reversiblen
plizierter g
dem Rahm

F

Das a
der von C
nitrat durc
Es ist mi
fraktioniert
deren Farb
und Lila r

Die S
gegenüber
halten eine
persitätsver
langsam. D
persitätsgra
dern nach
nach Grün.

In die
H. W. Wou
gegen Koag
hervor, dass
Koagulation
Methoden
wurden jed

Die Sil

¹⁾ Zeits
²⁾ Amer
gesammelt in
Dresden 1908

³⁾ Disse

Aus diesen Untersuchungen geht hervor, dass bei grösserer Koagulierungsfähigkeit des Koagulators die verschiedene Empfindlichkeit der Fraktionen weniger scharf hervortritt. Freundlich¹⁾ hat gefunden, dass nicht nur die Endkonzentration, sondern auch die Stärke der zugesetzten Lösung von Bedeutung ist. Dies wurde auch bei den intensiveren Koagulatoren HCl , $BaCl_2$ beobachtet. Es treten hier jedoch irreversible nebst reversiblen Zustandsänderungen auf, welche die Ergebnisse viel komplizierter gestalten. Die nähere Untersuchungen hierüber liegen ausser dem Rahmen dieser Mitteilung.

Fraktionierte Koagulation von Silberhydrosolen.

Koagulator: $(NH_4)NO_3$.

Das als Ausgangsmaterial verwendete Silberhydrosol wurde nach der von Carey Lea²⁾ entdeckten Methode durch Reduktion von Silbernitrat durch Ferrosulfat bei Gegenwart von Natriumcitrat dargestellt. Es ist mir gelungen, das so erhaltene kaffeebraune Hydrosol durch fraktionierte Koagulation in eine Reihe von Fraktionen zu zerlegen, deren Farbe sich mit abnehmendem Dispersitätsgrad von Gelb über Rot und Lila nach Graugrün erstreckt.

Die Silberhydrosole bieten in mancher Hinsicht Verschiedenheiten gegenüber den Schwefelhydrosolen dar. Die Teilchen der letzteren behalten eine längere Zeit ihre Grösse, und von selbst eintretende Dispersitätsverminderungen finden nicht statt, oder auch sie verlaufen sehr langsam. Die Hydrosole des Silbers dagegen vermindern stets ihren Dispersitätsgrad schnell, so dass die erhaltenen Fraktionen nicht stabil, sondern nach einigen Tagen verändert sind; die Farben verschieben sich nach Grün, mikroskopische Sole lassen Submikronen erscheinen usw.

In diesem Zusammenhang mag darauf hingewiesen werden, dass H. W. Woudstra³⁾ gefunden hatte, dass Silberhydrosole mit der Zeit gegen Koagulatoren mehr und mehr empfindlich werden. Er hebt auch hervor, dass die Ursache hierzu in der Annäherung an den freiwilligen Koagulationspunkt zu suchen ist. Ultramikroskopische oder auf andere Methoden gegründete Feststellungen der Dispersitätsverminderungen wurden jedoch nicht ausgeführt.

Die Silberhydrosole lassen sich nur mit grösster Vorsicht reversibel

¹⁾ Zeitschr. f. physik. Chemie 44, 129 (1903).

²⁾ Amer. Journ. of Science [3] 37, 476—491 (1889) und folgende Abhandlungen, gesammelt in Carey Lea-Lüppo-Cramer: Kolloides Silber und die Photohaloide. Dresden 1908.

³⁾ Dissertation Leiden 1906; Zeitschr. f. physik. Chemie 61, 607—632 (1905).

A

koagulieren. Am besten hierfür geeignete Salze scheinen Ammoniumnitrat und -citrat zu sein. Das erstere wurde stets verwendet. Man muss sich bei totalen Koagulationen immer hüten, grössere Überschüsse an Koagulator zu verwenden, da die Koagulation dann irreversibel verläuft. In dieser Hinsicht scheinen eigentümlicherweise die grössten graugrünen Fraktionen weniger empfindlich zu sein als die höchst dispersen gelben. Die erstern scheinen den allmählich eintretenden Dispersitätsvermindernngen auch weniger zu unterliegen.

Die Silberhydrosole sind auch, besonders wenn sie gereinigt sind, gegen Einflüsse verschiedener Art sehr empfindlich. So erleiden sie durch Stehenlassen in gewöhnlichen Glasgefässen irreversible Veränderungen und werden undurchsichtig, schmutziggrau. Man muss daher stets gereinigte Jenaer Glasgefässe verwenden. Gegen Spuren von Cl^- -Ionen sind die Sole besonders empfindlich; wenn die Glasgefässe in gewöhnlichem, schwach chlorhaltigem Wasserleitungswasser ausgespült waren, und die nachherige Reinigung mit destilliertem Wasser vernachlässigt wurde, wurden die Sole zerstört¹⁾.

Gegen Temperaturschwankungen sind die Schwellenkonzentrationen dagegen weniger empfindlich; die Temperatur betrug $17.5^{\circ} \pm 0.5$.

Trotz Vorsichtsmassregeln geschah es oft, besonders bei totalen Koagulationen, dass durch irreversible Veränderungen die Sole verdorben wurden, und es erwies sich als schwierig, die bei Schwefel durchgeführten Reinigungen in bezug auf die Gleichkörnigkeit durchzuführen.

Nach den Vorschriften Pranges²⁾ wurden folgende drei Lösungen bereitet:

- 12.5 g $AgNO_3$ in 125 cem Wasser gelöst;
- 37.5 g $FeSO_4$ in 125 cem Wasser gelöst;
- 70 g Natriumcitrat in 175 cem Wasser gelöst.

Die Natriumcitratlösung wurde der Ferrosulfatlösung zugesetzt und dann dieses Gemisch unter Rühren schnell in die Silbernitratlösung gegossen.

Der sich ausscheidende schwarzbraune Niederschlag von kolloidem Silber wurde durch Zentrifugieren schnell von der Lösung getrennt. Die überstehende, grüngelbe Flüssigkeit scheint von frühern Forschern nicht näher untersucht worden zu sein. Ausser den Eisensalzen und

¹⁾ Dies wurde schon von Carey Lea beobachtet [Amer. Journ. of Science [3] 37, 476—491 (1889). Vgl. Carey Lea-Lüppo-Cramer, loc. cit. S. 81.

²⁾ Recueil de Trav. chim. Bay.-Pas. 9, 125 (1890).

Natriumcitrat
wärmen mit
eine starke C
Gegenwart v
nicht durch
konzentrierte
lieren. $Zn($
jedoch fast
braungrüner

Bei der
Farbenüberg
dagegen dire
 $AlNO_3$ -Lösun
hineindiffund
purpurne Trü
in Grün, wel
grasgrünen F

Dass da
befindet, geh
Flüssigkeit z
Koagulatoren
Zusatz zahlre

Ich geh

Wie fr
mit reinem V
in verdünnter

Diese F

NH_4NO_3 unt

Fr (— 0.25).

Hier wurde
gearbeitet.

Die Bez
und die Arb
wähten Sch
rungen mach
jedem Schwe

³⁾ Vgl. O.
9, 88 (1911).

Natriumcitrat enthält sie beträchtliche Mengen Silber, welches bei Erwärmen mit konzentrierter HNO_3 und Zusatz von Chloriden sich als eine starke Chlorsilberfällung kundgibt. Wahrscheinlich verursacht die Gegenwart von Citrationen, dass die hochdispersen Silbertheilchen sich nicht durch die Kationen koagulieren lassen¹⁾. Auch durch Zusatz von konzentriertem Ammoniumsulfat gelingt es nicht, dieselben zu koagulieren. $Zn(NO_3)_2$, $Al(NO_3)_3$ lassen ein Koagulum ausfallen, welches jedoch fast irreversibel ist, denn es löst sich nur schwer und mit braungrüner Farbe auf.

Bei der Koagulation mit Zn^{++} -Ionen bemerkt man einen deutlichen Farbenübergang ins Orange → Rot → Braun → Olivgrün, mit Al^{+++} -Ionen dagegen direkt eine olivgrüne Farbe. Schichtet man jedoch über eine $AlNO_3$ -Lösung eine verdünnte Lösung des Sols und lässt die Al^{+++} -Ionen hineindiffundieren, so bemerkt man in der Grenzschicht anfänglich eine purpurne Trübung. Die Cl^- -Ionen verursachen keinen Farbenumschlag in Grün, welcher, wenn Sol und Koagulator verdünnt sind, einen hellen grasgrünen Farbenton besitzt.

Dass das Silber sich in sehr disperser Form in der Flüssigkeit befindet, geht aus der ultramikroskopischen Beobachtung hervor. Die Flüssigkeit zeigt nur sehr schwachen Lichtkegel, durch Zusatz von Koagulatoren wird dieser Lichtkegel heller, bläulich, um bei starkem Zusatz zahlreiche Submikronen erscheinen zu lassen.

Ich gehe jetzt zu den Untersuchungen über das Koagulum über.

Wie frühere Autoren gefunden haben, entsteht beim Behandeln mit reinem Wasser eine dunkle, wie Brom aussehende Flüssigkeit, die in verdünntem Zustand kaffeebraun ist.

Diese Flüssigkeit wurde nun der fraktionierten Koagulation mit NH_4NO_3 unterworfen, und in folgende fünf Fraktionen zerlegt:

Fr (— 0.25), Fr (0.25 — 0.15), Fr (0.15 — 0.11), Fr (0.11 — 0.08),
Fr (0.08 —).

Hier wurde im allgemeinen mit einer Silberkonzentration von 5—8% gearbeitet.

Die Bezeichnungen sind denen bei den Schwefelhydrosolen analog und die Arbeitsmethode ist im Prinzip dieselbe. Sowohl die oben erwähnten Schwierigkeiten als auch die ständigen Dispersitätsvermindierungen machten es jedoch notwendig, die wiederholte Koagulation bei jedem Schwellenwert zu inhibieren.

¹⁾ Vgl. O. Gengou, Arch. intern. de physiologie 1908; ref. in Koll. Zeitschr. 9, 88 (1911).

Über das Bindungsvermögen des Koagulums durch den Koagulator wurden keine Versuche angestellt, und die Schwellenzahlen in obigen Bezeichnungen beziehen sich auf:

$$\frac{\text{zugesezte Menge Koagulator im Mol.}}{\text{Volumen des Sols im Liter}}$$

Die Sole enthalten geringe Mengen Eisen und Natriumcitrat. Spezielle Reinigungen wurden im allgemeinen nicht vorgenommen. Es wurde jedoch eine orangegelbe Fraktion durch wiederholtes Fraktionieren so weit von Eisen befreit, dass sie beim Überführen in Eisenrhodanid nur eine schwache Rosafärbung ergab, und an dem so gereinigten Sol festgestellt, dass die Farbe nicht vom Eisengehalt herrührte. Inwieweit die Citrationen für die Reversibilität des Koagulationsvorgangs notwendig sind, wurde nicht näher untersucht¹⁾.

Die Eigenschaften der Fraktionen.

Nach Beendigung der Koagulation wurden 0.1 %ige Lösungen dargestellt und einer näheren Untersuchung unterworfen.

Wie erwähnt, vermindert sich stets die mittlere Teilchengröße, indem einzelne grössere Teilchen nach einiger Zeit erscheinen. Man kann sich von diesen Teilchen befreien, wenn man vorsichtig den ihnen entsprechenden Schwellenwert entstehen lässt und das meistens sehr kleine Koagulum absondert.

Ultramikroskopische Untersuchungen der Silberhydrosole liegen von R. Zsigmondy²⁾, J. Reissig³⁾ und H. Siedentopf⁴⁾ vor. Die genannten Autoren haben immer Submikronen beobachtet, welche oft bunt (rot, grün, blau, violett) gefärbt waren. Nur aus Amikronen bestehende Lösungen scheinen bis jetzt nicht beschrieben worden zu sein.

In folgender Tabelle sind die bei den fünf Fraktionen gemachten Beobachtungen zusammengestellt.

Die Farbenvariationen stimmen mit den von Wo. Ostwald in seiner Monographie: „Über Farbe und Dispersitätsgrad kolloider Lösungen“⁵⁾ zusammengestellten Beobachtungen verschiedener Forscher überein und verschieben sich mit abnehmender Dispersität von Gelb nach Grüngrau, eine nach Wo. Ostwald allgemeine Eigenschaft disperser Systeme.

¹⁾ Vgl. O. Gengou, loc. cit.

²⁾ Zur Erkenntnis der Kolloide, 147, 148 (Jena 1905).

³⁾ Dissertation Erlangen 1908. Ann. d. Phys. [4] 27, 186—212 (1908).

⁴⁾ Verh. d. d. physik. Ges. 12, 43 ff. (1910).

⁵⁾ Koll. Beihefte 2, 409—486 (1911).

Herr B
meiner Frak
Silbernitrat
Keimmenge
Es ergab si
der von Lü
Hydrosole
Cramer he
bilden müss
nicht ausge

Die Ei
Bezeichnung
der Fraktion

I
Fr(—0.25)

II
Fr(0.25—0.15)

III
Fr(0.15—0.11)

IV
Fr(0.11—0.08)

V
Fr(0.08—)

¹⁾ Koll. Z
1910, S. 143—1

²⁾ Vgl. TI

Herr Pr.-Doz. Dr. The Svedberg liess mich freundlichst die Farben meiner Fraktionen mit den von Lüpko-Cramer¹⁾ durch Reduktion von Silbernitrat in Gelatine durch Hydrochinon bei Gegenwart variierender Keimmengen dargestellten Serie von kolloiden Silberpräparaten vergleichen. Es ergab sich eine gute Übereinstimmung zwischen meiner Serie und der von Lüpko-Cramer; nur ist es mir nicht gelungen, die blauen Hydrosole Lüpko-Cramers zu erhalten. Mit Recht hebt Lüpko-Cramer hervor, dass bei grössern Keimmengen sich grössere Teilchen bilden müssen²⁾. Eine ultramikroskopische Feststellung wurde von ihm nicht ausgeführt.

Tabelle 3.

Die Eigenschaften von Silberhydrosolen verschiedener Teilchengrösse.

Bezeichnung der Fraktion	Das allgemeine Aussehen in 1 cm dicker Schicht	Ultramikroskopische Charakteristik
I Fr(-0.25)	0.2 %ige Lösungen tief braun-gelb. Völlig klar in der Durchsicht. In der Aufsicht schwarz. Bei 0.01 % hellgelb und in Durch- und Aufsicht völlig klar.	0.1 %ige Lösungen mit sehr schwachem Lichtkegel von bläulicher Farbe. Koagulatoren machen die Lichtkegel stärker und lassen dann Submikronen von bläulicher Farbe erscheinen.
II Fr(0.25 - 0.15)	0.05 %ige Lösungen dunkelrot 0.01 " " scharlach bis orange. Konzentrierte Lösungen in der Aufsicht schwarz. Verdünnte keine Trübung.	0.1 %ige Lösungen mit starkem Lichtkegel, welcher infolge Absorption rötlich erscheint. Beim Verdünnen wird der Lichtkegel gelblich. Koagulatoren wirken wie bei Fr(-0.25).
III Fr(0.15 - 0.11)	0.05 %ige Lösungen tief purpur 0.01 " " starke Purpurfarbe 0.002 " " blassrosa. Konzentrierte Lösungen in der Aufsicht schwarz. Verdünnte etwas trüb.	0.02 %, deutlicher und starker Lichtkegel, dessen einzelne Teilchen an der Grenze ultramikroskopischer Sichtbarkeit liegen. Die Teilchen von gelber Farbe.
IV Fr(0.11 - 0.08)	0.01 %ige Lösungen undurchsichtig 0.002 " " rot bis braunlila. Lösungen in der Durchsicht klar, in der Aufsicht trüb.	Sichtbare gelbweisse Teilchen von lebhafter Bewegung. Teilchendurchmesser ca. 40 μ .
V Fr(0.08 -)	0.002 %ige Lösungen graugrün, beim Verdünnen mehr blaulila. Konzentrierte Lösungen schwarz, verdünnte sowohl in Durchsicht als in der Aufsicht trüb.	Die Teilchen erscheinen grösser als bei Fr IV, schwach rötlich. Teilchendurchmesser ca. 75 μ .

¹⁾ Koll. Zeitschr. 7, 99-103 (1910); Gedenkboek van Bemmelen (Helder 1910), S. 143-146.

²⁾ Vgl. The Svedberg, Koll. Zeitschr. 6, 238-240 (1910).

Anmerkungen zur Tabelle.

Die Farben wurden im direkten Tageslicht beobachtet. Die ultramikroskopische Untersuchung wurde im Spaltultramikroskop ausgeführt unter Verhältnissen, die unter Tabelle 1 näher mitgeteilt sind. Das spezifische Gewicht des Silbers wurde gleich 10.47 gesetzt und die Teilchen auch hier als Sphären betrachtet. Zu bemerken ist, dass man die Sole nicht längere Zeit als zur Observation nötig ist in der Kuvette stehen lässt, da durch das gewöhnliche Glas (Kittung usw.) leicht Dispersitätsveränderungen eintreten.

Durch Zusammenschlagen der Fraktionen entsteht eine Flüssigkeit, welche beim Verdünnen die kaffeebraune Farbe des Ausgangsmaterials zeigt.

Die verschiedenen Lichtabsorptionskurven der Fraktionen wurde auch (von Herrn Magister phil. N. Pihlblad¹⁾ gemessen, worüber er bereits berichtet hat. Die von Svedberg²⁾ für viele kolloide Lösungen gefundene Verschiebung des Absorptionsmaximums mit steigender Teilchengrösse nach den grössern Wellenlängen hat sich auch hier bewährt.

Einige Bemerkungen zur Polychromie der Silbersole.

Wie erwähnt, haben frühere Autoren, R. Zsigmondy, H. Siedentopf, J. Reissig³⁾, im Ultramikroskop stark gefärbte Teilchen beobachtet. Einige von mir gemachte Beobachtungen über die Polychromie mögen hier erwähnt werden. Bei frisch dargestellten und gereinigten Solen habe ich keine gefärbten Teilchen sehen können. Zwar ist das von den kleinsten Teilchen ausgesandte Licht bläulich, um bei grössern Teilchen eine mehr gelbe oder rötlichgelbe Nuance anzunehmen; ausgeprägte Farben treten jedoch nicht auf. Lässt man aber diese in der Aufsicht fast schwarzen Sole in Bechern aus schlechtem Glas stehen, oder werden sie mit kleinen Mengen chlorhaltigen Wasserleitungswassers versetzt, so verändern sie sich und werden in der Aufsicht grau, während die Farbe in der Durchsicht ein wenig mehr schmutzig aussieht. Betrachtet man diese Sole im Ultramikroskop, so kommt das von Zsigmondy⁴⁾ beschriebene farbenprächtige Bild mit blauen, roten und grünen Teilchen zum Vorschein. Man kann diese polychromen, grauen Hydrosole auch dadurch bekommen, dass man sie mit kleinen Mengen verdünnten Bromwassers versetzt; grössere Mengen führen die Sole in die sogenannten Photohaloide über.

Die Versuche, diese Sole reversibel zu koagulieren, um die verschiedenfarbigen Teilchen in Fraktionen von nur einer Farbe zu isolieren, sind

¹⁾ Koll. Zeitschr. 9, 156—158 (1911), daselbst wurde auch ein Auszug obiger Tabelle publiziert.
²⁾ Zeitschr. f. physik. Chemie 61, 513—536 (1910).
³⁾ Vgl. S. 698, Anm. 2, 3, 4.
⁴⁾ Zur Erkenntnis der Kolloide (Jena 1905), S. 147, 148.

en, sind
irreversibel ve

Bedenkt
Lichtreduktion
Reissig ihre
lich längere Z
wahrscheinlich
veränderungen
Beobachtung S
mikroskop vor
chromen Teilc
chromie versch
licher, dass b
fortschreitet, u
durch Oxydati
lichkeit des Si
folge deren ei
sich im Dispe
In welche
chen zur Poly

An diesen
Farben beim
Von F. K
dass gelatineh
nehmen. Dass
Solen wahrger
Lässt ma
platten sich a
bilden sich Si
von schwach

¹⁾ Es ist
von Silberhydro
Verfasser.)
²⁾ Noyes
³⁾ Vgl. Th
jedoch, dass man
schen den polyc
verschieden gros
⁴⁾ Ann. d.

en, sind ohne Erfolg geblieben, da die Koagulation grösstenteils irreversibel verläuft.

Bedenkt man, dass das von Siedentopf beobachtete Sol durch Lichtreduktion von $AgBr$ entstanden war, und dass Zsigmondy und Reissig ihre Sole nicht selbst dargestellt hatten, diese also wahrscheinlich längere Zeit aufbewahrt gewesen waren, so erscheint es nicht unwahrscheinlich, dass die Polychromie durch chemische Oberflächenveränderungen an den Teilchen hervorgebracht ist. Besonders die Beobachtung Siedentopfs, nach der, wenn man die im Kardiodultramikroskop vorgenommene Bestrahlung nach Ausscheidung der polychromen Teilchen weiter fortsetzt, Ausbleichung eintritt, und die Polychromie verschwindet, verdient Beachtung. Es scheint mir wahrscheinlicher, dass bei fortgesetzter Belichtung die Reduktion bis zum Silber fortschreitet, und nicht, wie Siedentopf annimmt, die gelben Teilchen durch Oxydation entstanden sind¹⁾, speziell wenn man die grosse Löslichkeit des Silberoxyds [bis $2.16 \cdot 10^{-4}$ normal bei 25°]²⁾ bedenkt, infolge deren ein Oxydteilchen nur vorübergehende Existenz besitzt und sich im Dispersionsmittel auflöst.

In welchem Grade die kristallinische oder andere Gestalt der Teilchen zur Polychromie beitragen können, lässt sich zurzeit nicht sagen³⁾.

Die Trockenfarben der Fraktionen.

An diesen Betrachtungen mögen sich einige Ergebnisse über die Farben beim Eintrocknen der Sole anschliessen.

Von F. Kirchner und R. Zsigmondy⁴⁾ ist beobachtet worden, dass gelatinehaltige rote Silbersole beim Eintrocknen blaue Farbe annehmen. Dasselbe wurde auch an den hier dargestellten gelatinefreien Solen wahrgenommen.

Lässt man einige Tropfen der Fraktionen auf gereinigten Glasplatten sich ausbreiten, so verdunstet das Wasser allmählich, und es bilden sich Silber Spiegel, bei den grössten Fraktionen in der Aufsicht von schwach gelber Nuance.

¹⁾ Es ist Herrn cand. phil. H. Nordensson gelungen, durch Bestrahlung von Silberhydroxydlösungen Silbersole darzustellen. (Privatmitteilung an den Verfasser.)

²⁾ Noyes und Kohr, Zeitschr. f. physik. Chemie 42, 336 (1903).

³⁾ Vgl. The Svedberg, Koll. Zeitschr. 9, 49—53 (1911); zu beachten verdient jedoch, dass man alle möglichen Farbenübergänge (vgl. Zsigmondy, loc. cit.) zwischen den polychromen Teilchen beobachten kann, was sich möglicherweise durch verschieden grosse Haloidschicht (falls Bronzusatz) erklären lässt.

⁴⁾ Ann. d. Phys. [4] 15, 573 (1904).

Betrachtet man diese Platten in der Durchsicht, so treten Farben hervor, die mit denen der wässerigen Sole nicht übereinstimmen, bzw. sich nicht aus dem kaffeebraunen Ausgangssol herstellen lassen.

So erscheint:

- die Fraktion (— 0.25) rosenrot,
 " " (0.25 — 0.15) himmelblau,
 " " (0.15 — 0.11) tief dunkelblau,
 " " (0.11 — 0.08) unbestimmte schwarze Farbe.

Die Farbe der Fraktion (0.25 — 0.15) stimmt mit der blauen Gelatineprobe in Lüppo-Cramers oben erwähnter Serie überein. Trotz zahlreicher Versuche ist es mir nicht gelungen, in Lösung Fraktionen zu isolieren, welche mit den in Trockenpräparaten auftretenden Farben übereinstimmen. Die Farben der Sole und die der Trockenpräparate stellen zwei Farbenserien dar, welche in keinem Falle übereinstimmen. Feuchtet man sofort nach dem Eintrocknen die Platten mit Wasser an, so treten die Farben der Sole wieder auf. Nach längerem Stehen zeigen sich die Durchsichtsfarben der trocknen Platten mehr und mehr schmutzig und gehen schliesslich in unbestimmtes Grau über. Durch Anfeuchten lassen sich aus diesen alten Platten die Sole nicht wieder herstellen, die Zustandsänderungen sind irreversibel geworden.

Mit den Fraktionen ausgeführte Koagulationsversuche.

Die Fraktionen wurden nun mit möglichst geringer Ammoniumnitratmenge koaguliert, das Koagulum durch langwieriges Zentrifugieren von der Flüssigkeit getrennt und in Wasser gelöst. Es wurden dann Lösungen bereitet, die auf das Liter 0.1 g Ag enthielten. Mit diesen Solen wurden dann Koagulationsversuche ausgeführt. Es erwies sich hierbei schwer, für die Fraktionen vergleichbare Werte der Schwellenkonzentrationen zu bekommen. Am deutlichsten tritt die verschiedene Stabilität hervor, wenn man den Fraktionen die gleiche Kristalloidmenge beigebracht hat und den zeitlichen Verlauf der Koagulation beobachtet.

Eine solche Versuchsreihe ist in Tabelle 4 wiedergegeben, wobei die $Al(NO_3)_3$ -Konzentration 0.000025-norm. betrug.

Wenn man den Koagulator schnell bis zur Ausflockung zutröpfelt, so entsteht eine Schwierigkeit dadurch, dass schon vor der Ausflockung Veränderungen in der Farbe eintreten, die für verschiedene Fraktionen nicht völlig gleich verlaufen. Meistens verschiebt sich die Farbe bis zu schmutzig Graugrün. Diese graugrüne Farbe ist jedoch für die verschiedenen Fraktionen von verschiedener Nuance, und es ist schwer, einen gemeinsamen Endzustand festzustellen. Bei den in folgender Tabelle

Zeitlich

Der Dispersionshalt per Liter

Fraktion

I

II

III

V

mitgeteilte
terium der
abgesehen
als die vor
Änderung

Koagulations

Der Dispersionshalt
(von 0.1 g Ag)
zutröpfelt.
nötig

Fraktion

Schwellenkonzentration

"

"

"

Wie bei
heit in der
starken Koagulation

Besondere
einige Versuche

Die NaCl-Konzentration
die Farbe ohne
ist für Sole

dispersen ist
sten schmutzig

NaCl-Konzentration
und E. v. Me

*) Zeitschrift
*) Journ.

Tabelle 4.

Zeitliche Beobachtungen über die Koagulation von *Ag*-Hydrosolen verschiedener Teilchengrösse.

Der Dispersitätsgrad nimmt von I—V ab. Es wurde 2 ccm *Ag*-Sol von 0.1 g Gehalt per Liter mit 7 ccm H_2O versetzt und dann vom Koagulator $Al(NO_3)_3$ 0.6 ccm einer 0.0004-norm. Lösung zugegeben.

Fraktion	Sofort beobachtet	Nach 10 Minuten	Nach 1 Stunde
I	keine Veränderung	keine Veränderung	keine Veränderung
II	keine Veränderung	dunklere Farbe	zarte Trübung
III	keine Veränderung	deutliche Trübung	deutliche Ausflockung
V	schwache Trübung	starke Trübung	deutliches Koagulum

mitgeteilten Versuchen ist das Auftreten von Koagulationsflocken als Kriterium der Koagulation benutzt und von den Farbenänderungen ganz abgesehen worden. Die erhaltenen Zahlen sind daher beträchtlich höher als die von Woudstra¹⁾ gefundenen, wo als Koagulationskriterium die Änderung der Farbe benutzt wurde.

Tabelle 5.

Koagulationskonzentrationen einiger Salze bei *Ag*-Hydrosolen verschiedener Teilchengrösse.

Der Dispersitätsgrad nimmt von Fraktion I—V ab. Es wurde zu 10 ccm *Ag*-Hydrosol (von 0.1 g Gehalt per Liter) unter Schütteln von der Salzlösung zur Ausflockung zugetropft. Die Konzentration der Salzlösung war so gewählt, dass hierzu 1—2 ccm nötig waren. Die Schwellenwerte sind in Mol per Liter angegeben.

Fraktion	I	II	III	IV	V
Schwellenwert für NH_4NO_3	0.30	0.20	0.14	0.10	0.06
" " $Ba(NO_3)_2$	0.0020	0.0013	0.0010	0.009	0.008
" " $Al(NO_3)_3$	0.00006	0.00004	0.00004	0.00003	0.00003
" " $NaCl$		0.0005 bis 0.0003			

Wie beim Schwefel gefunden wurde, zeigt sich die Verschiedenheit in der Stabilität weniger ausgesprochen bei der Anwendung von starken Koagulatoren als bei der von schwachen.

Besonders für $NaCl$, welches irreversibel koaguliert, ist es schwierig, einige Verschiedenheiten festzustellen.

Die $NaCl$ -Koagulation weist auch die Eigentümlichkeit auf, dass die Farbe ohne Zwischenfarben in Grün umschlägt. Diese grüne Farbe ist für Sole verschiedener Dispersität eine verschiedene; bei den höchsten dispersen ist sie meist lebhaft klargrün (grasgrün), um bei den größten schmutzig olivgrün zu werden. Nur bei weiterer Steigerung der $NaCl$ -Konzentration flocken die Sole, wie schon von A. Lottermoser und E. v. Meyer²⁾ beobachtet worden ist, heraus.

¹⁾ Zeitschr. f. physik. Chemie 61, 619 (1908).

²⁾ Journ. f. prakt. Chemie [2] 56, 241—247 (1897); [2] 57, 540—543 (1898).

Irreversible Koagulationsversuche mit Solen verschiedener Teilchengrösse.

Im vorstehenden wurden einige neue Verwendungen der fraktionierten Koagulation auf reversible disperse Systeme besprochen. An den dadurch dargestellten Fraktionen, von denen jede einem gewissen Dispersitätsgrad entspricht, wurden Koagulationsversuche ausgeführt. Es zeigte sich, dass, wenn man die Konzentration der dispersen Phase in

$\frac{\text{Masse}}{\text{Volumen}}$ rechnet und die Sole von gleicher Konzentration vergleicht,

die höchst dispersen grössere Schwellenkonzentration brauchen als die weniger dispersen. Will man Sole von gleicher Teilchenzahl pro Volumen vergleichen, so ist für die erstern die höchste, für die letztern die geringste, bzw. gar keine Verdünnung erforderlich. Da ganz allgemein mit steigender Verdünnung der dispersen Phase die Schwellenkonzentrationen wachsen, so sieht man, dass, wenn die Konzentration der

dispersen Phase in $\frac{\text{Zahl der Teilchen}}{\text{Volumen}}$ berechnet wird, man noch grössere

Verschiedenheiten bei den Schwellenwerten bei verschiedenen dispersen Solen bekommt.

Gleichzeitig wurde auch gefunden, dass, wenn die Intensität des Koagulators gross ist und wir irreversible Zustandsänderungen vermuten oder konstatieren können, die ausgesprochenen Verschiedenheiten der Schwellenwerte weniger scharf hervortreten.

Es scheint daher von grossem Interesse, die Stabilitätsverhältnisse einiger typisch irreversiblen Sole in dieser Hinsicht näher zu untersuchen.

Wie vermutet, treten die verschiedenen Schwellenkonzentrationen bei den verschiedenen Teilchengrössen weniger scharf hervor und lassen sich schwer zahlenmässig bestimmen. Es scheint mir daher überflüssig, die ausführlichere Beschreibung der Einzelheiten in den Darstellungsmethoden und Versuchsergebnissen der Sole wiederzugeben. Es wurden stets Methoden zur Erzielung der verschiedenen Dispersitätsgrade verwendet, die als Schlussresultate Sole mit gleichen Mengen von Fremdstoffen ergaben.

Goldhydrosol. Ein Reaktionsgemisch aus $HAuCl_4 + K_2CO_3$ wurde in fünf Portionen geteilt, diese mit verschiedenen Mengen eines nach Zsigmondys Phosphormethode dargestellten Keimhydrosols versetzt und unmittelbar mit einigen Tropfen H_2O_2 reduziert¹⁾. Nach vollendeter Reduktion wurden solche Mengen der Keimlösung zugesetzt, dass der totale Zusatz der Keimlösung in allen fünf Lösungen derselbe war.

¹⁾ Vgl. The Svedberg und K. Inouye, Zeitschr. f. physik. Chemie 77, 150 ff. (1911).

Das erste
Amikrone
grosse Su

Bei
vorher be
als Kriteri
meinsamer
den höchst
verminderu

So vie
0.020-norr
noch nach

Die z
bei 0.020-
weisen lies

Bei di
der dispers
deutliche, a
besitzen als

Einige
koagulation
sind, schein

Die vo
aldehydmeth
auch Amikr
2.48 + 0.16
zugesetzt, b
gesunken un
Koagulation
sich fortwäh
sich die Teil
waren versch
Teilchenzahl,
Teilchen zur
aber mit an
ebenfalls zu
der Teilchen
einander näh

¹⁾ Koll. Z

²⁾ Zeitsch

Zeitschrift f. p

Das erste mit grösster Keimmenge dargestellte Hydrosol enthielt nur Amikronen, das fünfte ohne Keime dargestellte war blau und enthielt grosse Submikronen.

Bei den mit KCl ausgeführten Koagulationsversuchen tritt die vorher bei den Silbersolen erwähnte Schwierigkeit zutage, dass man als Kriterium für die Koagulation der verschiedenen Sole keinen gemeinsamen Endzustand bestimmen kann. Kleine Salzmengen rufen bei den höchst dispersen Veränderungen hervor, die sich als Dispersitätsverminderungen kennzeichnen, ohne dass Koagulation eintritt.

So viel lässt sich jedoch deutlich sagen, dass eine Salzkonzentration, 0.020-norm. KCl , welche Sol V nach 10 Minuten völlig ausgeflockt, noch nach mehreren Tagen Sol I (Amikronen) kaum beeinflusst hatte.

Die zwischen diesen Dispersitätswerten liegenden Sole koagulierten bei 0.020—0.025-norm. KCl , ohne dass sich Verschiedenheiten nachweisen liessen. Für Sol I liegt der Schwellenwert zwischen 0.024—0.028.

Bei diesen Solen zeigt es sich somit, dass auch bei gleicher Menge der dispersen Phase pro Volumeinheit die höchst dispersen Sole eine deutliche, aber verhältnismässig weniger ausgesprochen grössere Stabilität besitzen als die weniger dispersen.

Einige ultramikroskopische Untersuchungen von Goldhydrosolkoagulationen durch Elektrolyte, die von G. Wiegner¹⁾ ausgeführt sind, scheinen dies auch zu bestätigen.

Die von ihm untersuchten Sole waren nach Zsigmondys Formaldehydmethode²⁾ dargestellt und enthielten sowohl Submikronen als auch Amikronen. Ohne Elektrolytzusatz enthielt das Sol pro 10^{-10} ccm 2.48 ± 0.16 Teilchen. Dann wurde in wachsender Menge Schwefelsäure zugesetzt, bei 0.001-norm. H_2SO_4 war die Teilchenzahl auf 2.24 ± 0.11 gesunken und bei 0.0022-norm. auf 2.01 ± 0.14 . Dies scheint mir die Koagulation der grössern Teilchen zu bedeuten. Es zeigte sich, dass sich fortwährend Amikronen im Sehfeld befanden. Bei 0.005-norm. hatte sich die Teilchenzahl auf 2.64 ± 0.07 vermehrt, und die Amikronen waren verschwunden, bei weiterm Zusatz vermindert sich stets die Teilchenzahl, was man auf die jetzt eintretende Koagulation der kleinern Teilchen zurückführen kann. In einer zweiten gleichfalls mit H_2SO_4 , aber mit anderm Ausgangsmaterial ausgeführten Versuchsserie tritt ebenfalls zuerst eine Verminderung und sodann eine Vermehrung der Teilchenzahl auf, die entsprechenden Konzentrationen liegen hier einander näher.

¹⁾ Koll. Zeitschr. 8, 231 (1911).

²⁾ Zeitschr. f. Elektrochem. 4, 546 (1898); Lieb. Ann. 301, 29—54 (1898).
Zeitschrift f. physik. Chem. LXXVIII.

Interessant ist es auch, dass beim Verwenden des viel intensiver wirkenden Koagulators $BaCl_2$ das erste Minimum nicht beobachtet worden zu sein scheint, es tritt sofort Vermehrung der Teilchenzahl ein und sodann stetige Verminderung. Dies steht gut im Einklang mit meinen oben erwähnten Beobachtungen, dass sich die verschiedene Empfindlichkeit der kleinen und grossen Teilchen bei starken Koagulatoren weniger bemerkbar macht.

Sb_2S_3 -Hydrosole. Es wurden nach der von W. Biltz¹⁾ gefundenen Methode Sb_2S_3 -Hydrosole von verschiedener Teilchengrösse dargestellt. Eine als Ausgangsmaterial dienende Kaliumantimonyltartratlösung vom Gehalt 25 g pro Liter wurde in fünf gleiche Portionen geteilt; V wurde unverdünnt mit H_2S bis zur Sättigung behandelt, I wurde zuerst auf das 20fache verdünnt, II—IV auf zwischenliegende Konzentrationen.

Nach beendigter Einleitung von H_2S wurde zwecks Entfernung des Schwefelwasserstoffs Luft durch die Lösungen gesaugt und durch Wasserzusatz die fünf Sole auf gleiches Volumen gebracht. Die ultramikroskopische Untersuchung der Sole bestätigte die von Biltz gefundenen Tatsachen²⁾: Sol I zeigte nur Amikronen, Sol V nur Submikronen.

Gegenüber den Koagulatoren konnte hier bei gleicher Mengenkonzentration der dispersen Phase keine Verschiedenheit im Schwellenwert bei den fünf Solen konstatiert werden. Nimmt man an, dass die Teilchen von Sol V mindestens doppelt so gross sind (was natürlich nur eine Minimalgrösse ist) als bei Sol I, und verdünnt man dieses zur Hälfte, um gleiche Teilchenzahl pro Volumeinheit zu bekommen, so liegt jetzt die Schwellenkonzentration für Sol I höher als für Sol V.

Man könnte vermuten, dass aus einer Mischung der Sole I und V durch vorsichtigen Zusatz von Koagulatoren die grössten Teilchen zum Koagulieren zu bringen seien, und dass sich dann ein nur aus Amikronen bestehendes Sol gewinnen liesse. Versuche in dieser Richtung sind ohne Erfolg geblieben. Zwar kann man durch vorsichtigen Zusatz von Koagulator (NH_4NO_3) eine partielle Koagulation zustande bringen; die Restflüssigkeit enthielt jedoch immer Submikronen, die wahrscheinlich durch Polymerisation der Amikronen entstanden sind. Die fraktionierte Koagulation bleibt daher bei irreversibler Koagulation wahrscheinlich ohne Bedeutung.

¹⁾ Nachr. d. Kgl. Akademie d. Wissensch. Göttingen, math.-phys. Klasse 1906, 141—156.

²⁾ Loc. cit. S. 150.

Mast.

Teilchengr
nachgewie

Die

Es gelingt
konzentration

feinerung

gulationen

wurde, be

1. Es
niger und

letztern zu

2. Die

Verwendu

3. E

Koagulation

persistenzgr

einer Tab

4. Die

hydrosolen

5. Die

mikroskop

in den pu

schaften d

6. Es

Silbersole

7. Die

hydrosolen

gleichen V

trolytkonze

Sol ist. E

weniger de

8. Ver

auf irrever

sicheren R

Upsal

Mastixsuspensionen. Auch für Mastixsuspensionen verschiedener Teilchengrösse konnten keine Verschiedenheiten im Schwellenwerte nachgewiesen werden.

Die Resultate sind somit für irreversible Koagulation zweifelhaft. Es gelingt nicht, durch die gewöhnlichen Methoden die Schwellenkonzentration mit einiger Genauigkeit zu bestimmen. Ob sich bei Verfeinerung unserer Methoden in dieser Hinsicht der für reversible Koagulationen gefundenen Gesetzmässigkeit, wie sie hier für Gold gefunden wurde, bestätigen wird, lässt sich zurzeit nicht sagen.

Zusammenfassung.

1. Es wurde die Bedeutung der Auseinanderhaltung ungleichkörniger und gleichkörniger disperser Systeme, sowie die Methoden, die letztern zu bekommen, besprochen.

2. Die Resultate der fraktionierten Koagulationsmethode und ihre Verwendung in der organischen Chemie wurden kurz erwähnt.

3. Es wurde die Verwendung der Methode der fraktionierten Koagulation zur Darstellung von Schwefelhydrosolen verschiedenen Dispersitätsgrads beschrieben und die Eigenschaften der Fraktionen in einer Tabelle zusammengestellt.

4. Dieselbe Methode liess sich auch zur Zerlegung von Silberhydrosolen in Fraktionen verschiedener Dispersität verwenden.

5. Die gelben und roten Silberhydrosole erwiesen sich bei ultramikroskopischer Untersuchung als nur aus Amikronen bestehend, erst in den purpurn bis lila gefärbten treten Submikronen auf. Die Eigenschaften der Sole wurden in einer Tabelle zusammengestellt.

6. Es wurden einige Beobachtungen über die Polychromie der Silbersole sowie über die Trockenfarben der Fraktionen mitgeteilt.

7. Die Koagulationsversuche mit sowohl Schwefel- als auch Silberhydrosolen verschiedenen Dispersitätsgrads ergaben, dass unter sonst gleichen Verhältnissen bei reversibler Koagulation grössere Elektrolytkonzentrationen zur Ausflockung nötig sind, je höher dispers das Sol ist. Bei intensiv wirkenden Koagulatoren tritt dies Verhältnis weniger deutlich hervor als bei schwach wirkenden.

8. Versuche, die angestellt waren, um die Gültigkeit dieser Regel auf irreversible Koagulationen zu prüfen, ergaben keine unzweideutig sicheren Resultate.

Upsala, Chemisches Universitätslaboratorium.

November 1911.

MATTHEW CAREY LEA died at his residence on Sunset Avenue, Chestnut Hill, Philadelphia, on the 15th of March, 1897. He was born in 1823, and was the eldest son of Isaac Lea, the publisher, well known as a geologist and mineralogist, but especially as a conchologist, in connection with his investigations on the genus *Unio*. Mr. Lea was a member of one of the old Quaker families of Philadelphia, his ancestor John Lea who was an active member of the Society of Friends having come to this country with William Penn in 1700. Carey Lea was educated at home by private tutors and studied law in the office of the late Wm. M. Meredith, being subsequently admitted to the bar. On account of chronic ill health, however, he never practised his profession. His early associations giving him a special interest in scientific matters, he entered the laboratory of Professor James C. Booth and there acquired great proficiency in chemistry. To this science he devoted his life, his chemical researches being numerous and important, by far the greater number having been published in the pages of this Journal. He was elected to membership in the National Academy of Sciences in 1892 and the list of his more important papers then published contained fifty four titles. These investigations for the most part related to the chemistry of photography, and especially to the action of light and other forms of energy upon silver salts. He described photo-bromide and photo-iodide of silver and in 1887 published a paper on the "Identity of the photo-salts of silver with the material of the latent Photographic Image." His most remarkable discovery however, made in 1889, was that silver is capable of existing in three allotropic states. The first is allotropic silver proper, "which is protean in its nature, may be soluble or insoluble in water, may be yellow, red, blue or green or may have almost any color but in all its insoluble varieties always exhibits plasticity: that is if brushed in a pasty state upon a smooth surface its particles dry in optical contact and with brilliant metallic luster. It is chemically active." The second is intermediate in character, may be yellow or green, always shows metallic luster, is never plastic, and is chemically indifferent. The third is ordinary silver. In 1868 Carey Lea published a "Manual of Photography" which reached a second edition in 1871.

Henry Charles Lea the eminent historical writer, was a brother of Carey Lea. His first wife was a Miss Bakewell of Cincinnati who died in 1881 leaving a son, George H. Lea, who still survives. His second wife was Eva Lovering, a daughter of the late Professor Lovering of Harvard.

G. F. D.

JOSEPH F. JAMES died on the 29th day of March at Hingham, Mass. Dr. James published several papers on botanical, paleontological and geological subjects, was a fellow of the American Association for the Advancement of Science and an original fellow of the Geological Society of America.

AMER

ART. XLII
IV. *Ph*
anatomic.

THE monition in the Nova Scotia strictly hydric borders of spite of the nevertheless, terest, which Although on is readily dis may be of so idea of its e intention to p of details, ob lect some dat. allinities of ti In regard t eally placed two-ranked b these genera the distinctly *Dalichium* b *Cyperus* and correct, as sha If we exam observe a rat ramification an