ART. XXVII.—*The Colors of Allotropic Silver*; by J. C. BLAKE.

[Contributions from the Kent Chemical Laboratory of Yale University—CXIX.]

A GREAT deal has been written concerning the allotropy of silver, perhaps the most remarkable phenomena described being the beautiful color effects obtained by Carey Lea.* No satisfactory explanation of such effects has ever been published, however. I have repeated most of the work described in the literature relating to "allotropic" silver, "colloidal" silver, and, to some extent, the so-called "sub-salts" of silver, and have arrived at the conclusion that all of the color effects observed may be explained by assuming the existence of three or possibly four allotropic forms of silver. Before describing these forms it will be necessary to point out specifically that each of them has a characteristic color in reflected light, and another, very nearly complementary color in transmitted light. In the case of mirrors transparent to certain wave-lengths of light, the colors of the reflected and transmitted light are commingled when such mirrors are viewed in ordinary light, to mutual obliteration. The confusion of colors resulting from the commingling of the various allotropic forms of silver among themselves, as well as the blending of colors due to the intermixture of allotropic silver and foreign colored substances, especially when such intermixtures are present in solution together, must be constantly borne in mind.

These four assumed allotropic forms of silver, together with their most pronounced characteristics and convenient modes of preparation, are as follows:

Form of silver, named after the color most readily observed.	Color in reflected light.	Color in transmitted light.
"White silver"	Nearly white	Nearly opaque, even in the thinnest films
"Blue silver"	Golden yellow	Blue
"Red silver"	Indigo-blue	Red
"Yellow silver"	Indigo-blue	Yellow

The transmitted colors are easily observable. They are the colors seen when the substances are in pseudo-solution—permanent suspension or colloidal solution,—and in mass, provided no mirror surface has been formed. The colors in reflected light, on the other hand, are observable only when a mirror surface has been formed, either by deposition on glass, by

* This Journal, xxxvii, 476, and many articles closely following. Phil. Mag., xxxi, 238, 320; xxxii, 337.

spreading on glass or other material, by undisturbed sedimentation from water, by burnishing, or by crystallization. In proportion as the mirror surface becomes more and more imperfect, the reflected light of "white silver" changes toward gray, the reflected light of "blue silver" changes to copper-colored, the substance finally appearing black. The light reflected by "yellow silver" has been observed only in the case of mirrors on glass, backed by bone-black. Indeed, "yellow silver" has been obtained satisfactorily in no other form. All four forms of silver have been obtained suspended in water, but suspensions of "blue silver" and "red silver" alone are permanent—the so-called colloidal solutions.

"White silver" is formed by treating "blue silver" and "red silver" with strong acids in considerable amount, and, consequently, whenever silver is thrown out by reduction in strongly acid solution. Roughly speaking, the greater the concentration of the acid present the more nearly white the silver will be. It is ordinarily gray, as noted by Lea in the transformation of his allotropic forms of silver to the "ordinary" form by treatment with acids. Silver nitrate reduced by ferrous sulphate in solutions sufficiently dilute gives a colloidal solution of "blue silver." In stronger solutions a gray, opaque precipitate is formed ("white silver"). If, however, a little sulphuric acid be first added to the ferrous sulphate solution, the product is plainly crystalline silver consisting of perfect and distorted microscopic octahedra; and the greater the dilution and the stronger the acid, within the limits tested, the more distinctly crystalline the silver will be and the more its color will approach to white. Such crystals are usually intermixed with grape-like clusters which, if crystalline, show no evidence of it in their external form.

"Blue silver" may readily be obtained in a great variety of ways, as indicated in Table I. It is, in fact, formed whenever silver is reduced in neutral or alkaline solution in the presence of small amounts of electrolytes and without the presence of too much organic matter. When electrolytes in sufficient amount are added to colloidal solutions of "blue silver" aggregation and subsequent sedimentation take place, the coagulum appearing blue or black when settled in mass according to its compactness and volume, the addition of salts and alkalis in sufficiently large amount tending to produce the black effect.

When such a blue or black precipitate of "blue silver" is spread upon glass while moist, the particles arrange themselves in mirror surfaces. If the preparation is made and handled in the dark, these mirrors reflect a very deep and rich golden color, transmitting blue light. No preparation was found which gave these mirrors in better form than those obtained

by following Lea's directions for the preparation of his "gold silver"; that is by the action of Rochelle salt and ferrous sulphate on a solution of silver nitrate. Drained and dried quietly in masses, these preparations give Lea's golden lumps.

Heat converts this blue silver to "white silver." Pressure does the same, and with great ease in the case of mirrors on glass. Exposure to light gradually brings about the same effect, the golden reflection slowly paling. If such mirrors of "blue silver" are originally prepared in the daylight, the surface reflection at first is pale yellow, which likewise fades into white by lapse of time. This partially converted yellow reflecting silver is Lea's "intermediate" form, scarcely sensitive to pressure. Its pale yellow color may reasonably be attributed to the dilution of the golden yellow surface-reflection of "blue silver" by the white light reflected by intermingled "white silver" formed by the exposure to daylight.

Mirrors of "red silver" and of "yellow silver" on glass may be conveniently prepared by the action of silver nitrate upon an ammoniacal solution of tannic acid, and mirrors of "red silver" may likewise be readily obtained by spreading on glass portions of the red-brown precipitate formed in the mixture. The mirrors of "yellow silver" thus formed tend to change into "red silver" spontaneously, and both, when gently heated, are transformed into "blue silver." These mirrors of both forms of silver are slowly soluble in water, but mirrors of "red silver" are stable for some weeks under atmospheric conditions, ultimately becoming dull gray and lusterless.

Colloidal solutions of "red silver" of approximate purity can be readily obtained by reducing a solution of silver nitrate with ferrous citrate (ferrous sulphate and sodium citrate) in the presence of a little free alkali, according to Lea's method of obtaining his "A" form of silver. The mother liquor should be withdrawn by suction through a porous cell, as recommended by Schneider, and the red precipitate suspended in water. If no free alkali is added the solution will be blue (experiment (19) of the table), a trace of free alkali in excess rendering most colloidal solutions more stable. On adding an electrolyte in sufficient amount to such a red solution, the silver is changed to "blue silver" and usually settles out. If the yellowish brown mother liquor has not been removed, the addition of an electrolyte will cause the solution to look green instead of blue, owing to the commingling of colors. To the intermixture of yellow sulphur is due the blue-green effect observed in experiments (39) and (48) of the table. "Red silver" may be looked for whenever silver is thrown out by reduction in the absence of electrolytes, or in the presence of electrolytes in small amount, accompanied by considerable amounts of organic

matter or typical colloids. This effect of typical colloids in rendering colloidal solutions of the metals more stable, discovered by Faraday, has been investigated at length by Zsigmondy* and others.

Mirrors formed by spreading on glass portions of a precipitate of "red silver" containing electrolytes, like that obtained by the action of ferrous citrate, transmit red light and reflect indigo-blue light only while moist. At the moment of drying, the substance suddenly changes over to "blue silver"—a change which undoubtedly served to prevent Lea from recognizing clearly the distinction between "red silver" and "blue silver," especially as he was accustomed to observe the "surface" and the "body" colors of these substances, instead of differentiating the colors of the reflected and transmitted light. When mirrors which show the color change are viewed in ordinary light after drying, the reflected (golden) and transmitted (blue) lights are commingled and the mirrors have a beautiful bright fluorescent green appearance. This effect was seen by Lea, who determined that the blue and the yellow colors were oppositely polarized.

Another variety of green effect, noted by Gutbier† in the action of hydrazine hydrate on a solution of silver nitrate, is still more deceptive. The green in this case is due to an intermixture of "blue silver" with "yellow silver" formed simultaneously. In order to see this it is only necessary to act with hydrazine hydrate on a solution of silver nitrate at considerable dilution. No action takes place for some minutes; then an orange-yellow color appears in the liquid and a yellow mirror forms on the sides of the containing vessel. Such yellow mirrors may even form in the more concentrated green solutions. In solutions still more concentrated pure blue effects may be readily obtained. The same sequence of colors was observed less clearly in other cases.

The detailed observations are collected in the following table. It is to be understood that the solutions used, both of the silver compounds and of the reducing mixtures, were in no case very strong, those marked "concentrated" containing about five or ten grams of the material per liter, those marked "dilute" containing from a tenth to a hundredth part as much. Care was taken to avoid a local excess of any electrolytic reagents employed, and the reducing mixture was always finally added in excess of the silver compound. Except for the purpose of avoiding known precipitates, the order in which the

* *Zeitschr. anal. Chem.* xl, 697. Schulz and Zsigmondy, Hofmeister's Beiträge, iii, 137. Lettermorer and Meyer, *Jour. prakt. Chem.* lvi, 248.

† *Zeitschr. anorg. Chem.* xxxi, 448; xxxvii, 347.

TABLE I.

A. Water Solution of Silver Nitrate.

Reagents.	Opaque precipitate, color in reflected light.	Solutions, color in transmitted light.			
		Blue.	Red, dilute.	Red, concentrated.	Yellow.
1. Formalin	If large excess, gray	Hot or moderate excess. Mirror	On standing		
2. Formalin + NH_4OH					If little ammonia; mirror
3. Formalin + NaOH		+			
4. Hydrazine hydrate		+			If dilute, mirror
5. Hydrazine hydrate + ether ..		+			"
6. Hydrazine hydrate + alcohol ..		+			"
7. Hydroxylamine		+			
8. Hydroxylamine sulphate + NH_4OH		Hydroxyl-amin sulph. in excess, gray	+		If little ammonia; mirror
9. Phenylhydrazine		+			
10. Ether + FeSO_4 (trace)		Add ether first, mirror			
11. Chloroform + NH_4OH		+			
12. Chloroform + FeSO_4		Soon changes to AgCl			
13. Carbon bisulphide + FeSO_4 ..		+			
14. Hypophosphorus acid		+	Unstable		Unstable
15. Phosphorus acid		+	+		
16. Phosphorus trichloride + NH_4OH		+			
17. Phosphorus in ether					+
18. Phosphorus in ether + NH_4OH		+			
19. Sodium citrate + FeSO_4		+			
20. Rochelle salt + FeSO_4		+		If little FeSO_4 w. prec., turns red	
21. Rochelle salt + NaOH		+	Turbid, stable		
22. Sodium citrate + NaOH + FeSO_4				Stable if little FeSO_4	
23. Rochelle salt + NaOH + FeSO_4				"	
24. Tannic acid + NH_4OH or NaOH				Mirror, stable	Mirror, unstable
25. Tannic acid + NaOH + FeSO_4 ..				Solution, stable, mirror, unstable	
26. Sulphur dioxide			White prec., turns pink		

TABLE I (continued).

B. Ammoniacal Solution of Silver Nitrate.

Reagents.	Opaque precipitate, color in reflected light.	Solutions, color in transmitted light.			
		Blue.	Red. dilute.	Red, concentrated.	Yellow.
27. Formalin	If large excess, gray	+			
28. Phenylhydrazine		+			
29. Chloroform		+			
30. Chloroform + NaOH		+			
31. Methyl alcohol + NaOH		+			
32. Ethyl alcohol + NaOH		+			
33. Amyl alcohol		+			
34. Amyl alcohol + NaOH		+			
35. Hypophosphorus acid		+			
36. Phosphorus acid		+			
37. Phosphorus trichloride in NH ₄ OH		+			
38. Sulphur dioxide			Slowly, faint pink		
39. Acid sodium sulphite		Blue-green, unstable, contains sulphur		Unstable	Unstable

C. Ammoniacal Solution of Silver Oxide.

40. Formalin	If large excess, yellowish-gray Yellowish gray changes to purple solution	+	Stable		
41. Formalin poured into silver solution; dilute			Purple, stable		
42. Hydrazine hydrate		+	Stable		
43. Hydroxylamine sulphate		+	Stable		
44. Hypophosphorus acid		+	Stable		

D. Water Suspension of Silver Oxide, filtered after treatment.

45. Hydrazine hydrate		+			
46. Hydroxylamine			Turbid, stable		

E. Water Solution of Silver Nitrate, slightly acid, with Sulphuric or Nitric Acid.

47. Phenylhydrazine		+			
48. Acid sodium sulphite, solid or in concentrated solution		Blue-green, contains sulphur, turns black		Coagulated by shaking	Coagulated by shaking

reagents are added is usually immaterial, although if a non-electrolyte which alone does not cause reduction of the silver compound is to be added, it is best to mix it with the silver solution before adding the final reducer in order to take advantage of the power which non-electrolytes possess of inhibiting the action of electrolytes toward colloidal solutions, as already pointed out. The resulting colloidal solutions were generally clear in ordinary light, but all gave the Tyndall effect when the light was concentrated with a lens. Except when otherwise stated the colors refer to transmitted light. A + sign indicates that the phenomenon takes place without special characteristics or conditions.

In the light of the foregoing discussion most of these results will be readily understood. It will be noticed that the gray effects ("white silver") were obtained only in acid solutions. In solutions sufficiently acid such effects are always obtained. The tinge of yellow noted in experiments (40) and (41) was doubtless due to the golden reflection of intermixed "blue silver," formed while the solution was still alkaline, as in experiment (2). The blue solutions obtained in experiments (3) and (10) were especially stable. In most cases the blue color was preceded by a red, brown, green, or purple color. It was found impossible to prepare red silver solutions which were stable except in the presence of organic matter or typical inorganic colloids, as stannic acid. "Yellow silver" was never obtained in stable solution. Except for the fact that glass is colored yellow by silver and not red, this "yellow silver" might be regarded as a variety of "red silver." The other forms of silver—"white," "blue," "red"—seem sufficiently distinct to be regarded as allotropic forms until their exact properties can be investigated. So far as that work has progressed it fully bears out the idea that silver does exist in allotropic forms.* Grimm worked with silver mirrors which transmitted blue-gray light, and found that the increase in electrical conductivity induced in them by lapse of time, by heat, light, burnishing, and other agencies, all indicated a gradual change from "molecular" to "normal" silver, corresponding, in the terminology here used, to the change from "blue silver" to "white silver."

The kind advice and helpful assistance of Prof. F. A. Gooch, who suggested this subject for investigation, is gratefully acknowledged.

* Grimm, *Drude's Ann.* [4] v, 448.