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

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.

† Has since become so.

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 by 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.

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