ART. IX.—*On a Combination of Silver Chloride with Mercuric Iodide;* by M. CAREY LEA, Philadelphia.

IN the course of an extended examination of the compounds formed by mercuric iodide, I some time since obtained two which I believed to be new. After having studied their properties, I found that one of them, a compound of the iodides of silver and of mercury, had previously been obtained by Meusel. I shall therefore here describe only the compound which mercuric iodide forms with silver chloride.

If to a portion of recently precipitated and still moist silver chloride, a considerably less quantity of mercuric iodide, also freshly precipitated and still moist, be added, we shall find that, after stirring them thoroughly together, the scarlet color of the mercuric salt is still plainly visible through the mass, which is of a bright salmon color. By standing some hours or a day, a remarkable change takes place, the red color wholly disappears and the powder became pure lemon-yellow. Before this change took place, the separate particles of the mercuric iodide could be plainly distinguished with a lens; after it, the powder becomes perfectly homogeneous. Fresh portions of mercuric iodide added, gradually disappear in the same way, until an equivalent quantity has been used.

A better plan, however, for preparing the substance consists in adding to a solution of a weighed quantity of potassic iodide an exactly equivalent quantity of mercuric chloride, and then, after thoroughly agitating and allowing the precipitate to fall, adding an equivalent quantity of silver nitrate, also in solution. The potassic chloride formed by the first reaction is exactly sufficient to throw down the whole of the silver as chloride. When the silver salt is added, one may remark three precipitates visible in the liquid, irregularly blended, scarlet mercuric iodide, white silver chloride and the yellow substance resulting from their combination. The precipitates are then to be thoroughly stirred together to promote combination, which, however, is not complete for about twenty-four hours. Meantime the mixture is salmon colored from the presence of free mercuric iodide.

Obtained in this way, the substance appears as a heavy yellow powder, wholly free from any trace of red, and rather inclining to a greenish or lemon-yellow. This color it always exhibits, no matter how prepared, while still wet, even if left for weeks. Mixed, however, with gum arabic and spread on card-board, it dries to a full chrome yellow. It could not be obtained in a condition sufficiently pure for analysis, but there can be little doubt that its constitution is $AgCl HgI$.

The new substance exhibits remarkable properties with respect to heat. Even below 100° F. it begins to redden, and this change rapidly increases with the rising temperature until it reaches a maximum at about 140° F. At this temperature it has a bright scarlet color, differing, however, a good deal from that of mercuric iodide, and more resembling, if moist, that of chrome red; if dry, that of vermilion. As the temperature falls again, the pale yellow color returns. A striking experiment consists in placing a portion of the substance in a test tube under water, and warming it at a Bunsen's burner. The very instant that the flame touches the glass, the whole layer of substance in contact with it flashes to a bright red. If heated till it is changed throughout, a portion taken out with spatula and dropped on a cold porcelain dish, becomes yellow at the instant of contact.

If a portion of the substance be mixed with a solution of gum arabic and be spread on card-board, it exhibits the following properties:

Warmed gently at a lamp (best by holding it near the glass chimney of an Argand burner), it assumes a deep red color; then, when removed, it recovers its yellow shade. Both changes take place so rapidly that the alteration of color may be watched, and is complete in a few seconds or half a minute. If instead of gently warming, a strong heat be applied, just below what is sufficient to char the card, the portion thus strongly heated assumes a still deeper color, and returns to the yellow much more slowly, retaining an intermediate orange shade for some hours. This change is brought about by a sudden and momentary heat: if the heat be continued, the mercuric iodide volatilizes, and the portion so treated becomes permanently yellow.

If one of these cards be exposed to sunlight with a portion perfectly protected, the exposed part becomes slightly darkened. This effect takes place with an exposure of half an hour or less and is scarcely increased if the exposure be prolonged for many hours. By keeping for a few days in the dark, the deepening of color gradually fades out until the exposed parts are not to be distinguished from the rest. This effect may be repeated several times with the same card.

In reference to the compound of silver iodide with mercuric iodide, I feel constrained to differ from Meusel, who considers it only a mixture and not a combination. I take it to be a compound, though an extremely loose one, and for the following reasons, which apply equally to the silver chloride compound.

So long as the substances are only mixed, and before they have united, the characteristic color of the mercuric iodide is always conspicuously observable, and no mechanical mixing, however thorough, is capable of concealing it. The eventual disappearance of this color seems to be a proof of combination. This view is farther strengthened by what takes place in the case of *silver bromide.* When HgI is placed in contact with AgBr, no combination takes place as in the case of AgCl and AgI under similar conditions. Even after many days the color of the mercuric salt is conspicuously visible. In one case I kept HgI in contact with excess of AgBr, both freshly precipitated, for several weeks under water, at the end of which time the particles of HgI could be distinguished under a lens with perfect facility. At the end of weeks, the mixture of AgBr and HgI retains exactly the appearance which it presents when first mixed (supposing, of course, that it has been protected from the light). AgCl and AgI, when mixed with HgI, present at first the same appearance, which, however, subsequently changes completely, and a substance with new properties is the result. This seems clearly to indicate a combination.

The striking fact that the thermochromic properties of mercuric iodide are inverted in the new compound, which passes from yellow to red by heat, instead of from red to yellow, and the far greater sensitiveness to heat of the new substance, are strong arguments of combination.

Meusel's explanation of the change of color, in his view of mere mechanical mixture, makes it depend on a diminished power of absorbing red rays when warmed, which he ascribes to silver iodide. But the experiment which I have described with the substance spread on card-board disproves this explanation in two distinct manners.

At a temperature about 30° or 40° of Fahrenheit above the boiling point of water, mercuric iodide becomes yellow. If, therefore, the new substances were mere mixtures on being heated to that temperature the red color previously acquired should disappear completely, since there could be no possible cause for its continuance. The mere mechanical mixture of two yellow substances (in the case of AgI and HgI), or of a white and a yellow (in the case of AgCl and HgI), could by no possibility produce a red one. This single argument would seem to be sufficient in itself.

The peculiar persistency, after applying momentarily a high heat, seems also inconsistent with the hypothesis of a mechanical mixture. Let us follow the phenomena which present themselves and consider them in the light of this hypothesis of a mechanical mixture. The substance is at ordinary temperatures yellow; it is difficult to suppose that white and scarlet mechanically mixed can form yellow. At 140° F., it is deep red; now this rise of temperature makes no visible change in the color of either constituent, taken separately; if the mixture be merely mechanical, it is difficult to see why the color should change. At a still higher temperature, let us say for example 300° F., mercuric iodide is yellow, but the substance in question is deep red. And, whereas before we had white and red mechanically mixed forming yellow, now we have white and yellow forming red. Even the phenomena of persistence are reversed, for whilst mercuric iodide after cooling retains for a time its yellow color, and then passes to its normal red, this substance, after a strong momentary heating, retains for sometime after cooling its red shade, and eventually recovers its normal yellow.

These properties seem to be irreconcileable with the view of mechanical mixture. The behavior of the substance when exposed to sunlight also affords a strong argument. The very faint darkening caused, and the gradual recovery of the original color, seem inconsistent with the hypothesis of the presence of free silver chloride. There is no doubt that the combination is a loose one. By repeated boiling with a considerable quantity of water, most of the mercuric iodide can be dissolved out, and this may be still more easily done with alcohol, in which mercuric iodide is more soluble than in water. This, however, is, of course, no proof of absence of combination, as many compounds can be broken up in a similar way. Even after repeated boiling with water, a portion of the mercuric iodide is held back, and it is curious that the abstraction of the mercuric salt does not change the color of the residue. The silver chloride does not recover its whiteness, the yellow color remains unchanged, but the property of reddening by heat disappears with the removal of the mercuric iodide.

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