

CLXXIV.—*The Doubtful Existence of Aurous Oxide.*

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It has been found that mercurous nitrate and chloroauric acid react to form gold and a basic auric compound (this vol., p. 529), and not "aurous oxide" as claimed by Figuier (*Ann. Chim. Phys.*, 1844, 11, 339) and Krüss (*Annalen*, 1887, 237, 276). In consequence of this, "aurous oxide," prepared in other ways, has been examined to see if it might not consist of colloidal gold and auric hydroxide. Analogous substances are known, such as Purple of Cassius, in which metallic hydroxides function as protective colloids.

From the equation $3\text{Au}_2\text{O} = 4\text{Au} + \text{Au}_2\text{O}_3$ it is clear that the determination of gold and oxygen cannot show whether the substance is aurous oxide or a mixture of gold and auric oxide in these proportions. This possibility was overlooked by Krüss, whose analyses are therefore inconclusive. Krüss's claim is, moreover, unsupported by any chemical evidence showing that aurous compounds can be formed from "aurous oxide."

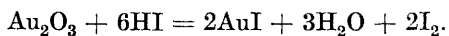
E X P E R I M E N T A L.

In attempts to prepare "aurous oxide" from potassium bromoaurate by Krüss's method, if an excess of potassium bromide was present, only metallic gold resulted. "Aurous oxide" was decomposed when heated with solutions of potassium bromide, but was much less decomposed by solutions of sodium chloride. As potassium bromide is a by-product in the formation of "aurous oxide," it is surprising that Krüss was able to obtain his substance in the proportions required by theory.

By the following slight modification it was found possible to work at room temperature. Gold (1.0 g.) was converted into chloroauric acid, made up to 1 litre with saturated sodium chloride solution, and reduced to the aurous state with sulphurous acid. The solution, now colourless, was made slightly alkaline with caustic soda. Very little precipitation occurred at first, but a black, colloidal substance separated on standing. Heat caused the precipitation to occur rapidly. The formation of the substance is therefore quite unlike that of metallic hydroxides, but is highly suggestive of the decomposition of aurous compounds.

The substance formed a dark blue, colloidal suspension when washed with cold water, but could generally be washed with hot water. With hydrochloric or hydrobromic acid it instantly formed metallic gold and chloroauric or bromoauric acid; the reaction did not suggest the slow decomposition which takes place in aurous

compounds. The addition of alkali metal chlorides or bromides to the corresponding acids failed to produce aurous compounds (Lenher, *J. Amer. Chem. Soc.*, 1913, **35**, 547). Hydriodic acid gave gold, aurous iodide, and iodine; with excess of the reagent, aurous iodide passed into solution. This reaction resembles that of hydriodic acid and auric oxide :



Although these reactions were known to earlier workers, no reason has been given to explain why iodine should be liberated by "aurous oxide."

With a solution of sodium sulphite, the substance formed sodium aurosulphite and left a residue of gold which had the same black colour as the original substance. With sodium thiosulphate, it formed sodium aurothiosulphate and left a residue of black gold. In both these cases an aurous compound is formed, but only a third of the gold takes part in the reaction and this has to undergo reduction.

When the substance was heated with strong nitric acid a residue of gold was left and a yellow solution was formed which, on dilution, hydrolysed with the separation of auric hydroxide.

When heated with potassium bromoaurate solution, gold dissolved and was deposited, on cooling, in shining crystals according to the equation $\text{AuBr}_3 + 2\text{Au} \rightleftharpoons 3\text{AuBr}$.

When the substance was heated with potassium bromide solution, a residue of brown gold was left and gold passed into the solution, which then became strongly alkaline. Potassium iodide behaved in the same way, but was more energetic in its action. Sodium chloride solutions were much less reactive. Although no previous reference could be found, auric hydroxide was shown to behave in exactly the same way, dissolving even in strong sodium chloride solution which thus became alkaline. The reaction, however, was most marked in the case of potassium iodide.

The substance was scarcely attacked by dilute caustic soda, but with strong solutions sodium aurate and metallic gold were formed. Auric oxide was slowly attacked by weak but rapidly attacked by strong solutions of caustic soda. This explains why Krüss found it necessary to employ "very weak potash" in the formation of his "aurous oxide," strong alkali preventing its formation just as strong hydrochloric acid prevents the formation of Purple of Cassius.

Although numerous reactions have been tried, in no case has any definite aurous reaction been discovered, the substance always behaving as a mixture of gold and auric hydroxide. As the sub-

stance is highly colloidal, any attempts at a mechanical separation into gold and auric hydroxide would present very great difficulty. Experiments were made, however, to see whether auric hydroxide could act as a protective colloid in the manner suggested.

Auric hydroxide prepared by the magnesia process was washed in a centrifuge with cold water until it began to pass into colloidal suspension just as Krüss's "aurous oxide" does. Portions were then taken, made alkaline with caustic soda, and partly reduced to gold by dilute solutions of various reducing agents. Little reaction occurred at first, but when the solutions were warmed or made more alkaline reduction set in. Further additions of reducing agent were made until the action was judged to have proceeded far enough; the precipitates were then separated in a centrifuge and washed. Black precipitates which appeared to be identical with Krüss's "aurous oxide" were thus obtained, with hydrazine, phenylhydrazine and formaldehyde as reducing agents. With sodium peroxide as reducing agent, a brown precipitate was obtained which transmitted red light but was otherwise identical with "aurous oxide."

No evidence has therefore been obtained to show that aurous oxide exists; its chemical and physical properties are those of a mixture of gold and auric hydroxide.

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