

XXVIII.—*Remarkable Molecular Change in a Silver Amalgam.*

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My attention was directed by Dr. Mallet, of the University of Virginia, to a curious swelling up, apparently attended with escape of gas, exhibited by a specimen of silver amalgam, when it was moderately heated over a lamp. The following experiments were made to determine, if possible, the nature of the change which takes place.

It was first ascertained by analysis that the amalgam originally used consisted of about 15 per cent. of silver and 85 per cent. of mercury. Having prepared a fresh specimen with the same proportions, but using both metals in a carefully purified state, it was found that this new material behaved in the same way as the old, so that the phenomenon did not depend on any foreign metals or other impurities which might have been present in the former specimen. In all subsequent experiments, the mercury used had been recently distilled with care in a vacuum, and the silver was brought to a pulverulent condition by dissolving chemically pure metal ("proof" silver from the United States Mint at Philadelphia) in pure nitric acid, precipitating as chloride, reducing the fresh precipitate by means of an ingot of very pure zinc, washing thoroughly first with dilute hydrochloric acid, and finally with water, and drying at a gentle heat.

When the proportions already mentioned were used, and the mercury was simply poured over the pulverulent silver, union took place at once, with very notable rise of temperature, so that any considerable mass of the amalgam became painfully hot to the hand. The product, when rubbed in a porcelain mortar, became a perfectly homogeneous, pasty mass. When this mass was shaken vigorously in a stoppered bottle, as also when rubbing in the mortar was continued, a small quantity of a black powder appeared upon the surface, sometimes rising in a dust-like cloud when the stopper was removed from the bottle. On heating it over a lamp, the amalgam showed very notable increase of volume, and the surface appeared as if a gas were being given off. After cooling, the amalgam retained its increased volume, was hard and crystalline in structure, a contrast to its former soft, pasty condition, and, on being broken across, was visibly porous throughout.

To ascertain with what proportions of mercury and silver the swelling would be greatest, a rough estimate was made by heating

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several amalgams of different composition in glass tubes closed at one end, marking on each tube the original volume and the increased volume after heating. The following results were obtained.

	Silver.	Mercury.	Expansion.
I	7.5	92.5	about 8 per cent.
II	15.0	85.0	„ 23 $\frac{1}{3}$ „
III	18.0	82.0	very slight.

Varying the proportions so as to represent the atomic ratio AgHg_4 , it was found that

Silver.	Mercury.	Expansion.
11.87	88.13	gave about 33 $\frac{1}{3}$ per cent.,

which seemed to be the maximum attainable. This amalgam, AgHg_4 , was used in all the remaining experiments. With it, the rise of temperature, on pouring the mercury over the pulverulent silver, and rapidly shaking the two together in a stout glass bottle of about $\frac{1}{4}$ -litre capacity, was, for a specimen of amalgam, weighing 220 grams, 40°C ., namely, from 25° to 65° . A second and more carefully made experiment gave for 156.64 grams a rise from 28.2° to $66.4^\circ = 38.2^\circ$. The amount of heat evolved in the act of combination was not, however, determined in a calorimeter.

The black powder which has been mentioned was examined. It was removed by means of a camel's hair pencil from the surface of the amalgam and of the bottle in which the latter had been shaken up, care being taken to reject all such minute globules of mercury as could be seen with the aid of a hand lens. The powder was digested with strong acetic acid, to dissolve any mercurous oxide which might be present, and, after filtration, the liquid was tested with a bit of copper wire, gently warming for some time, and adding a drop of hydrochloric acid; the copper became slightly coated, and, after drying, it gave, on being heated in a miniature glass tube, minute globules of mercury visible with a lens. The part of the powder undissolved by acetic acid was dried and heated in another small tube; it also gave a sublimate of mercury globules, and left a residue which, on being dissolved in a drop of nitric acid and precipitated by hydrochloric acid, gave chloride of silver, easily soluble in ammonia. Hence the black powder seems to consist of both metals in a state of fine subdivision, with a part of the mercury converted into mercurous oxide.

To determine more closely the amount of expansion, the sp. gr. of the amalgam under different conditions was examined, using large masses (50—80 grams), but weighing accurately on a good analytical balance.

I. The amalgam, AgHg_4 , in its original soft and pasty state, as

produced by rubbing the silver and mercury together in a mortar until the mass was entirely homogeneous, had the density 13.340 at about 24°/24°. The calculated density for this temperature, assuming no change of volume as the result of union between the metals, is about 13.216, so that some little contraction is indicated.

II. The density of the same amalgam after remaining at atmospheric temperature, about 22—27°, for several days was found to be 13.412. It was slightly crystalline, and harder than at first, but could be easily crushed between the fingers.

III. Two specimens of the amalgam, AgHg_4 , which had been heated (in a Sprengel vacuum), had swelled up and become quite crystalline, brittle, and too hard to be readily crushed in the fingers, after cooling to atmospheric temperature, gave $d = 9.229$ and 9.119 respectively. They were very porous, full of small cavities, so much so that it was not possible to avoid water entering the pores to some extent from the surface, and hence the sp. gr. of the porous mass as a whole could not be taken with great accuracy, but the approximate values thus found indicate the large increase of bulk resulting from the heating. When crushed in a mortar and rubbed sufficiently, this crystalline and swollen amalgam could be brought back to its original soft and pasty state.

The swelling up began at a temperature of about 240°, and continued until an immersed thermometer indicated 335°; the phenomenon seemed to be most marked at about 315° to 320°.

The appearance so closely resembled that of an escape of gas from the material heated, that the experiment, originally tried in the air, was repeated more than once in a vessel, made from Bohemian glass combustion tubing of large size, connected with a Sprengel pump, and well exhausted in advance of the heating. In a first attempt to collect any gas given off, 105.52 grams of amalgam consisting of 12 per cent. of silver and 88 per cent. of mercury, seemed to swell up more notably in the exhausted vessel than if heat had been applied under atmospheric pressure, but only a small bubble of gas was given off and collected. It proved to be oxygen, and probably came from some slight admixture of the black powder already mentioned. In another experiment, the amalgam AgHg_4 was used, and on heating 253.74 grams in a vacuum, a quantity of gas was obtained which would measure 1.62 c.c. at normal temperature and pressure (0° and 760 mm.); this also proved to be oxygen. It had been imagined as possible that silver in solution in mercury at common temperature might absorb gaseous oxygen as the former metal in the molten condition does, and might give it up on moderate heating, but it seems evident that this does not take place, at any rate to any considerable extent, and is not the cause of the phenomenon under examination,

which must be ascribed to molecular change involving only the two metals.

The marked development of heat which attended the union of the silver and mercury was suggestive of analogy to the similar but more striking effect of bringing together mercury and either of the alkali metals, and, therefore, sodium amalgam was prepared in pasty form, and heated, with the result that a similar swelling-up took place, though to a less extent than in the case of silver amalgam, and a similar hardening and assumption of crystalline structure appeared after cooling. Pasty copper amalgam was also tried, and showed something like the same behaviour, but the mass took a longer time to cool and settle to the crystalline state, and was not so porous as the amalgam of silver in the same condition.

This similarity of behaviour of silver to sodium and to copper in relation to mercury serves but to supply another bit of evidence in support of the positions assigned to the first three metals in classification based on the "periodic law."
