# CXXI.—*The Influence of Moisture on the Reaction between Sulphur and Silver.*

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It was observed by Lilienfeld and White (*J. Amer. Chem. Soc.*, 1930, **52**, 885) that when a test-tube containing silver and sulphur was sealed and kept at the ordinary temperature, the silver was blackened within one day, and after a week it was practically all converted into sulphide.

These authors had already confirmed the observations of Cabell (*Chem. News*, 1884, **50**, 208) and of Hahn (*Z. anorg. Chem.*, 1917, **99**, 118), respectively, that the presence of moisture and of oxygen is necessary for the reaction between hydrogen sulphide and silver to take place at ordinary temperatures and pressures, and had shown that in these circumstances the reaction yielded no trace of hydrogen. As an explanation for these phenomena, they suggested that hydrogen sulphide in the presence of moisture may be oxidised by contact with the oxygen atoms, molecules, or ions attached to the silver surface, yielding water and sulphur, and that the atoms of sulphur so formed combine instantaneously with the silver atoms to form the sulphide. Hence, since the supply of oxygen atoms, molecules, or ions on the silver surface is very small, air or some other suitable source of oxygen must be in contact with the metal in order that the reaction may proceed to any extent.

Lilienfeld and White also suggested that the reaction between polysulphides and silver in the absence of oxygen is not one of simple replacement, but is more probably due to the rupture of the loose sulphur–sulphur linkage in contact with silver, leading to formation of silver sulphide.

In view of these observations, it appeared to be of interest to investigate whether the presence of moisture is a necessary condition for the progress of the reaction between sulphur and silver.

## EXPERIMENTAL.

A small quantity of pure powdered sulphur was placed in a small thin-walled glass bulb, together with a little resublimed phosphoric oxide; the bulb was then sealed, and its contents mixed by shaking. The whole was now placed in a thick-walled glass tube, together with further phosphoric oxide and a strip of pure silver foil, and the tube in turn was sealed. After 3 days, this tube was shaken so as to break the inner bulb, and the silver was kept at room temperature in contact with the sulphur.

For comparative purposes, another tube was prepared in exactly the same manner, but without addition of phosphoric oxide in each case. The sulphur was again enclosed in a separate small bulb so as to prevent the possibility of the silver being heated in the presence of sulphur vapour. After the outer tube had been sealed and allowed to cool, the inner bulb was broken and the sulphur thus brought into contact with the silver strip.

Within 24 hours the silver in contact with the undried sulphur was appreciably tarnished, especially at the end in contact with and immediately above the sulphur, after a week it was completely blackened, and after a year it had almost disintegrated. On the other hand, the specimen in the tube containing phosphoric oxide has remained completely unchanged for a year.

Other specimens, treated in exactly the same manner, were placed in a bath at 100° : the " dry " specimen of silver was quite unchanged after a week, whereas the " moist " sample was definitely tarnished within an hour. At 120° a " moist " specimen was completely blackened in an hour, but the other showed no visible change whatever. The " dry " sample was then heated to 150—160°, so as to fuse the sulphur, and was maintained at this temperature for 3 hours ; no tarnishing was observable over the portion of the silver surface which was not immersed in the fused mass, but the other part seemed to have been attacked slightly.

Even calcium chloride drying is sufficient to inhibit the reaction between sulphur and silver considerably. A tube sealed in the same manner as before, but with the phosphoric oxide replaced in each case by freshly ignited calcium chloride, showed no perceptible tarnishing of the silver surface at first, but after a year a slight tarnish was visible. The reaction occurred rapidly, however, when the tube was warmed to about 50°.

That the reaction is not dependent on the presence of oxygen has been shown in two different ways. (1) The previous experiments were repeated, but with evacuated tubes ; the results were exactly similar to those obtained previously, but in the tube into which no phosphoric oxide had been introduced the rate of tarnishing seemed to be greater even than when the tubes were not evacuated. Again the phosphoric oxide-dried silver and sulphur showed no sign of reaction. (2) In another series of experiments a tube was arranged so that a stream of gas could be passed first over finely powdered sulphur and then over silver foil. In order to accelerate the reaction, this tube was immersed in a bath at 100°. In successive experiments, air, oxygen, carbon dioxide, and nitrogen were passed through the apparatus, but, so far as could be detected, each of the samples of silver was tarnished at about the same rate.

Various mechanisms might be suggested whereby water vapour may catalyse the reaction between sulphur and silver, but, since none of these seems to be capable of experimental confirmation, they are not discussed.

## *Summary.*

It has been shown that the removal of moisture causes the complete stoppage of the reaction between sulphur vapour and silver at temperatures up to about 150°. Even calcium chloride drying causes a marked diminution of reaction. The presence of oxygen is not essential to combination.

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