

## LII.—*Vapour Density of Dried Mercurous Chloride.*

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AMONG the large number of changes for which the presence of moisture is necessary, only one case of dissociation has been studied, that of ammonium chloride (Trans., 1894, 65, 615; 1898, 73, 422). Since this substance has a normal density when dried, it was thought that others, which have abnormal densities, might give interesting results if they were converted into vapour after careful drying.

Mercurous chloride was selected as a suitable substance, since its dissociation under ordinary circumstances is well established. It was obtained in a sufficiently pure condition by the following method.

Mercury was purified by shaking for 3 days with dilute nitric acid, then washed, boiled and distilled twice in a nitrogen vacuum. It was dissolved in cold nitric acid and precipitated with hydrochloric acid. The precipitated mercurous chloride was washed without contact with filter paper, until a large quantity of the wash-water gave, on evaporation, no opalescence with silver nitrate. It was dried at 110° and kept in a desiccator in a dark cupboard.

The vapour density determinations were made by Victor Meyer's method in an apparatus constructed of hard glass. A bent tube, in which plugs of phosphoric oxide were placed, was ground to fit the neck of the apparatus.

A small, hard glass tube containing a known weight of the substance rested on a glass spoon, the shaft of which was ground into a side tube fused to the neck of the apparatus. By turning the shaft of the spoon which projected from the side tube, the substance could be made to fall into the bulb of the apparatus. The whole apparatus was heated to low redness, while a current of nitrogen, dried by sulphuric acid, was passed through it, the delivery tube being then sealed. The tube containing mercurous chloride was then introduced, and the phosphoric oxide tube, previously filled with nitrogen, was put into position. No lubricators were used, mercury seals being placed over the two ground joints. The closed apparatus was left in the dark for three weeks. The bath used was an iron tube surrounded by a fireclay cylinder. In this, sulphur was boiled.\* The delivery

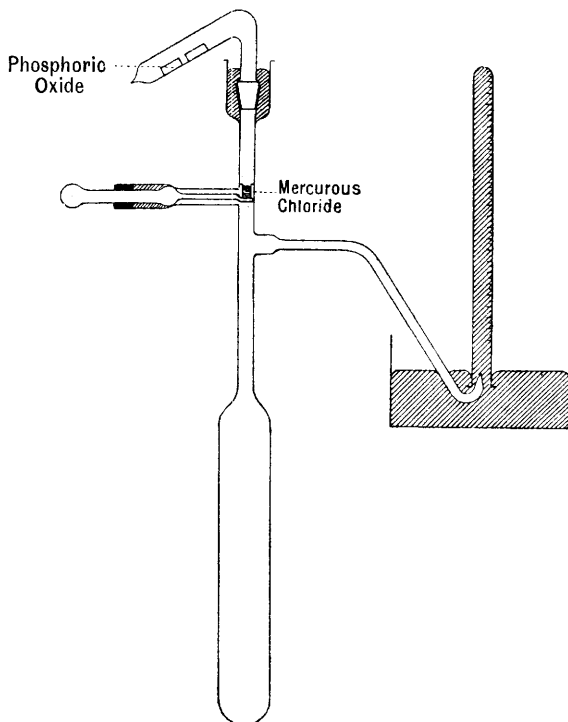
\* The actual determinations were performed almost in the dark, and this led to the observation of a phenomenon of which I can find no previous record. When the glass bulb was removed from the heated bath after the experiment, the sulphur burnt with a luminous, blue glow, very similar in character to the glow of phosphorus in air. If allowed to continue, this glow changes into the ordinary flame of sulphur. I have failed to reproduce this phenomenon in oxygen at the ordinary pressure, but it is distinctly seen in this gas at about half the atmospheric pressure.

tube dipped into a trough containing mercury which had just been boiled. The point of the delivery tube was not broken until there was a considerable excess of pressure in the apparatus, so as to diminish the chance of moisture diffusing from the dried mercury into the bulb.

The results of the determinations of the vapour density were :

I.	II.	III.	IV.	V.	Mean.
217·7	222·8	221·3	223·9	201·4	217·4
Calculated for no dissociation.....					235

A similar experiment, conducted in nitrogen which had been dried only by sulphuric acid, gave a vapour density of 118·4. Hence the



dissociation of mercurous chloride is much hindered by removing moisture as far as possible.

Some confirmation of this result was obtained by heating in the same air-bath the purified mercurous chloride in a nitrogen vacuum in two tubes containing gold leaf, one dried by phosphoric oxide, the other not specially dried. No amalgamation of the gold was seen in the dried tube, whilst in the other the gold had been freely attacked.

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Similar vapour density determinations were made with metallic mercury in order to find out if the vapour, which is under ordinary circumstances monatomic, is a product of the dissociation of a more complex molecular structure. These experiments were conducted at the boiling point of sulphur, the mercury used being a portion of that from which the mercurous chloride was prepared. The densities obtained were :

I.	II.	III.	Mean.
107·6	104·4	112·5	108·1

The vapour of dried mercury is therefore probably monatomic.

Many experiments have been made with phosphorus pentachloride, but very great difficulties have been experienced in obtaining it in a sufficiently pure state for the purpose. Until recently, all the results pointed to complete dissociation having taken place. The last determination, however, with a new specimen of the purified pentachloride, gave, at 440°, a density of 89·2, that calculated for no dissociation being 104·2. Phosphorus pentachloride may therefore be ultimately shown to undergo no dissociation when dried before heating, if it is obtained in a sufficiently pure condition.

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