XXXI.—*Preparing Phosphoric Anhydride free from the Lower Oxides of Phosphorus.*

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It is well known that even the best samples of phosphoric anhydride, as usually prepared, contain more or less of the lower oxides. These may be readily detected by the reactions of the substance with silver nitrate and mercuric chloride, or by its behaviour when a strong aqueous solution is evaporated and gently ignited.

During the past eight or nine months we have invented and tried several processes for preparing this important substance free from the lower oxides, and some months ago we had so far succeeded that we were able to state, at the last meeting of the British Association, that we had obtained it in the form of crystals, and without any reducing action whatever on the above reagents. Our method at that time was to heat commercial phosphoric anhydride to near its melting point in a current of dry oxygen until the red substance which is at first formed under this treatment in considerable quantities was completely oxidised, and then to fractionate the product of this operation by subliming it in a current of dry oxygen. The first fractions were usually not quite pure. Although there was considerable loss, in consequence of the oxide acting on the glass, the yield was fairly good. This process, however, was rather tedious, because the preliminary treatment of the oxide with oxygen not only took much time, but a good deal of special skill was required for the operation; for whilst, on the one hand, it was important to heat the oxide nearly to its melting point, on the other, it was equally important that the melting point should not actually be reached, for if the substance was even superficially melted, its further oxidation was either stopped or very greatly retarded.

In December last, we decided to try a more simple method, namely, to pass the vapour of phosphoric anhydride, together with excess of oxygen, slowly over platinum sponge. This process almost at once succeeded; and we were about to employ it on a larger scale, in order to obtain a small stock of the purified material, when, on January 28th, one of us found, in a memoir on the preparation of pure nitrogen (*Phil. Mag.*, January, 1893), that Professor Threlfall had also recently employed a similar method of oxidising commercial phosphoric anhydride, in order to prepare a trustworthy drying agent. After reading this paper, we decided to publish our method at once, although there were one or two points, such as the length of life, so

to speak, of the platinum sponge and the possibility of constructing larger and more permanent apparatus, which we intended to have worked out. We feel all the more justified in following this course, because the exact process described by Professor Threlfall is one which we have tried and abandoned as not perfectly satisfactory.

Threlfall passes the vapour of phosphoric anhydride through a tube packed for a considerable length with platinised porcelain and asbestos. Now the exposure of the anhydride to asbestos at a high temperature is very undesirable as the asbestos absorbs phosphoric anhydride very freely, which not only reduces the yield of the purified product, but also, we think, would soon remove the platinum from the sphere of action by enveloping it with a coat of the fusible products of the action. In one of our experiments, a column of platinised asbestos, 150 mm. in length, completely prevented the passage of the anhydride when a quantity of the latter was sublimed in oxygen at a moderate rate. We do not deny that the vapour of the phosphoric anhydride may partly escape the action of the asbestos, especially if it is rapidly sublimed; but the use of asbestos may lead to failure, and in any case its employment in quantity must result in a diminished yield of the pure anhydride, whilst it seems likely, from the character of the products of the action of the anhydride on asbestos, that the platinum would soon be prevented from acting.

The process we recommend, is as follows :—

Divide a piece of combustion tube, about 900 mm. long and about 20 mm. in diameter, into two chambers, A and B, by a constriction at C; join a side tube D at C; pack the tube from C to E with small

fragments of platinum sponge; compress some phosphoric anhydride, of good commercial quality, in a glass tube, exposing it as little as possible to the air; place the compressed mass in a large boat of platinum,* and introduce it quickly into the chamber A; fix the glass plug G into the tube at F, and connect L with a supply of oxygen.

* To keep the fluid phosphoric anhydride from contact with the glass as much as possible.

G may be secured by an india-rubber collar or by enlarging the end F of the tube, and tightly packing the joint with asbestos (Threlfall recommends glass wool and phosphoric oxide for the purpose). Also connect D with the same supply of oxygen, but with stopcocks, so that the admission of the gas can be separately regulated at L and D. Place in the other end B of the tube a slightly smaller tube K, which fits B closely, and secure it in its place by a collar of india-rubber, or by asbestos, as may be preferable.

Place the tube in a combustion furnace, with its ends well projecting from the furnace, heat it to redness from C to E, admit oxygen by D, and when the apparatus is full of oxygen heat the phosphoric anhydride and pass a slow stream of oxygen through L. The excess of oxygen can be received in a gasholder, and can be used again; if this be done, the consumption of oxygen will be very small. Possibly the double stream of oxygen might be dispensed with, in which case the side tube D would not be required. It is, however, easy to join on D with the oxy-hydrogen blowpipe, and it is convenient to be able to regulate the rate at which the phosphoric anhydride sublimes without reducing the supply of oxygen.

We have not yet experienced any trouble from the platinum adhering to the glass. We have used about 35 grams of platinum sponge.* The character of the product depends on the temperature of the condenser. If the tube K be kept rather hot, a finely crystalline and rather dense mass is obtained, which adheres somewhat firmly to the glass. If the tube be kept cool, the vapour condenses as a light crystalline powder, which rapidly fills the tube; if this be suddenly heated, it appears, to the eye, to change to the familiar amorphous form, and then volatilises. In every form it is intensely hygroscopic.

As K can be removed and replaced, and as fresh supplies of phosphoric anhydride can also be introduced almost without stopping the operation, the process is practically a continuous one. Unless great precautions be taken in preserving the substance, it is wiser to prepare small quantities at a time, and to employ it fresh. Perhaps the best plan is to distil it into the experimental apparatus whenever this is possible.

The best way to secure the sublimate is to place one end of K in a well-dried bottle, and to push down the phosphoric anhydride with a metal scoop, made rather smaller than the tube, and fitted with a long handle of stiff wire.

Tests for the Purity of Phosphoric Anhydride.

The best specimens of this substance that we have been able to

* It has not been difficult to transfer this from tube to tube. It might, however, be convenient to introduce it in a gauze cage.

obtain by purchase have all exhibited, in a marked degree, the following qualities :—

1. They reduce a 10 per cent. solution of silver nitrate very freely, when warmed.
2. They reduce a solution of mercuric chloride when boiled with it.
3. When an aqueous solution of the anhydride is evaporated and ignited moderately, the odour of phosphine becomes evident, and the ignited substance frequently shows signs of spontaneous ignition, such as may be observed on igniting phosphorous acid, only in a much smaller degree.

Phosphoric anhydride, carefully prepared by our method, gives no evidence of the presence of the lower oxides when it is examined by the above tests.

Professor Threlfall regards the presence or absence of the odour of phosphorus (phosphine?), when a few grams of the anhydride are thrown on to water, as the most delicate test of its purity. We are disposed to consider that tests 1 and 2 above are decidedly more satisfactory.

Doubtless the product obtained as we have described contains a little metaphosphoric acid. If pure phosphoric anhydride be required, the products of the combustion of the purest obtainable phosphorus in pure air might be conducted into A, and then resublimed, as above described, into receivers, previously prepared for sealing before the blowpipe when full.

The question has sometimes been asked whether the presence of the lower oxides of phosphorus is really objectionable in phosphoric anhydride which is to be employed as a drying agent. It is possible that in some cases their presence may do no harm. But there are others in which it would be very desirable to employ the fully oxidised product. And in any case, owing to our limited knowledge of the conditions of chemical change, no possible source of error can be safely neglected.

In concluding, we may add that, in our experience, the roasting of phosphoric anhydride in oxygen never removes the last traces of the lower oxides; on some occasions we have roasted it for weeks at a temperature not far below its melting point, but without success.

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