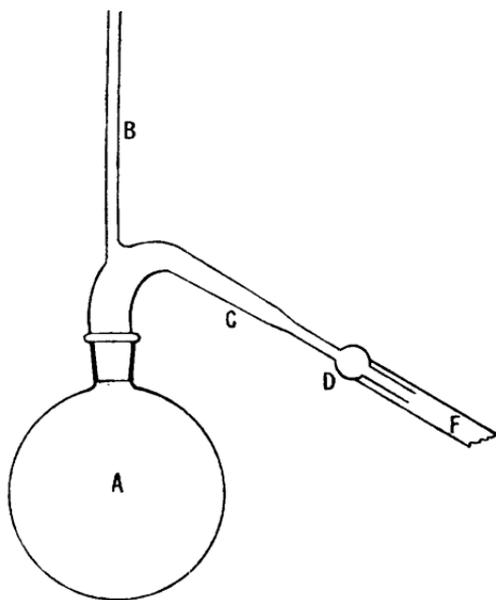


LIII.—*Preparation of Pure Hydrobromic Acid.*

By ALEXANDER SCOTT.

THE process for preparing pure hydrobromic acid "destiné aux essais des matieres d'argent," recommended by Stas (*Œuvres*, 1, 839), depends on the use of amorphous phosphorus as the agent for transforming the pure bromine into hydrobromic acid. Stas gives minute directions as to testing the phosphorus to be employed so as to ensure its entire freedom from the chlorides apt to be introduced with the alkali used in getting rid of any ordinary phosphorus. He has, however, quite overlooked an impurity in the phosphorus itself, one, indeed, which may be termed a normal impurity in all samples of phosphorus in the manufacture of which arsenical sulphuric acid has been employed. A moment's consideration shows that in the ordinary process of manufacturing phosphorus from phosphates, all the arsenic in the sulphuric acid employed will probably be found in the phosphorus obtained. When such phosphorus is treated with bromine, the arsenic is converted into arsenious bromide, which distils over with the hydrobromic acid, supposed to be of a very high degree of purity, and all bromides prepared with such acid are almost certain to be contaminated with arsenites and arsenates.

In preparing, some time ago, a fairly large quantity of hydrobromic acid, the phosphorus employed contained an extremely large amount of arsenic (over 1 per cent.); it was selected because it was a very old sample, and in a pasty (almost syrupy) condition from oxidation, and therefore very easily and satisfactorily washed free from chlorides. The hydrobromic acid when tested was found to give a very large precipitate of arsenious sulphide on treatment with hydrogen sulphide, and had to be diluted, treated with pure hydrogen sulphide (from zinc sulphide and dilute sulphuric acid), filtered, concentrated, and redistilled. No doubt in many cases the acid, after one or two distillations, would lose most of the arsenious bromide which it might contain, as this comes over largely in the first portions of the distillate, that is,



with water containing only small quantities of hydrobromic acid. But if the purest hydrobromic acid be desired, it is obviously much better to use materials as free from impurities as possible, rather than to trust to the purification of the acid afterwards.

An extremely convenient and satisfactory reducing agent to replace the phosphorus is found in liquid sulphur dioxide, which may be procured in glass syphons. This gives rise to no volatile bromides, and the hydrobromic acid is easily separated by distillation from the sulphuric acid produced at the same time. The apparatus required and its manipulation are of the simplest nature, and are almost sufficiently explained by the figure.

The bolt head with ground-in neck, or the distillation flask *A* has

sealed to its neck a glass tube, B, of such length and diameter that it will allow the thermometers usually employed to pass easily down into the wider part of the neck, and also to admit a tube through which the sulphur dioxide is to be passed. This tube or the thermometer employed is held air-tight in its place by a small piece of indiarubber tubing. The exit tube, C, has on it a bulb, D, of such a diameter that it is a little too large to pass into the inner tube, F, of a Liebig's condenser. If this inner tube has its end cut off quite square, and the sharp edges carefully taken off and nicely rounded by grinding it on a piece of not too rough emery paper held flat in the palm of the hand, we have, by bringing the bulb D into contact with the rounded edge, a joint which will allow of the distillation of litres of constant boiling point hydrobromic acid without any fuming, and with perfect security from any contamination by organic matter. The sulphuric acid obtained as a bye-product in the preparation of two or three kilograms of hydrobromic acid was distilled through a long tube simply air-cooled by means of this apparatus, without any inconvenience whatever from fumes.

To prepare a kilogram of real hydrogen bromide in solution, 350 c.c. of pure bromine are placed in A along with 2 litres of water, and a rapid current of sulphur dioxide washed first through a strong solution of sodium sulphite and then through water, is led *into the water* about 5 to 10 mm. above the surface of the bromine until the whole is transformed into a pale yellow, homogeneous liquid. Should the liquid become colourless, the yellow colour must be restored before distillation by the cautious addition of bromine or bromine water. This prevents any possible contamination of the hydrobromic acid with sulphurous acid, besides being a further security against traces of iodine or hydriodic acid occurring in the final product.

The acid is distilled from the vessel in which it is formed, and it is advantageous to keep a gentle current of air bubbling through the liquid throughout the distillation, as the troublesome bumping of the liquid is thus obviated. Practically the whole of the hydrogen bromide will have passed over when the residual sulphuric acid reaches the density 1.7. On redistilling, water comes over first, bringing with it all the free halogen, but only traces of acid.

When the acid begins to come over, the receiver is changed, and the acid should be once more redistilled from a small quantity of barium bromide to guarantee its freedom from every trace of sulphuric acid. This last distillation is best carried out with a very gentle current of hydrogen, which cannot be safely employed as long as the liquid to be distilled contains free sulphuric acid.

The purity of a sample of the acid prepared in this way was tested by preparing from it some potassium bromide, and titrating it against

silver with all the precautions described by Stas ; the equivalent of this bromide was found to be 119·099 ($Ag = 107·93$). A sample of bromide from the same specimen of pure potassium carbonate, and from the hydrobromic acid above referred to prepared by Stas's process, after being carefully freed from compounds of arsenic, gave an identical value 119·099, whilst another specimen of bromide, prepared from pure hydrobromic acid, made by Squibb's process, as recommended by J. P. Cooke (*Proc. Amer. Acad.*, 1881, 17, 31) gave the value 119·102.

The acid from which this last sample was prepared contained traces of platinum from having been distilled through a platinum condenser. This cannot be done with safety with hydrobromic acid in presence of atmospheric oxygen. Stas (*Œuvres*, 1, 748) gives the value 119·095 as the mean of 14 determinations of the equivalent of potassium bromide.

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