

LIV.—*A New Sulphide of Arsenic.*

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WHEN phosphoric acid is prepared by the oxidation of phosphorus by means of nitric acid, as is well known, the action takes place in two stages, which are more or less distinct according to the concentration of the nitric acid employed. Phosphorous acid is first produced, and if sufficient nitric acid be present, on boiling down the liquid, a point is reached when these react with some energy, giving rise to phosphoric acid with the production of torrents of red fumes. If, however, the nitric acid be not present in sufficient excess, the liquid almost invariably becomes brown in colour, and black flakes may even separate out. This is not due to the charring of any organic matter, but to the arsenic usually present in the phosphorus, which has been oxidised first to arsenic acid, and this, in turn, on concentration, is reduced again by the phosphorous acid present to arsenic. If sulphur dioxide be passed into the liquid before the second stage be reached and the solution warmed, a bright yellow precipitate of arsenious sulphide is obtained if arsenic be present, due to the reduction of the sulphurous acid to hydrogen sulphide, which then reacts with the arsenic or arsenious acid present. This reaction may be applied to the detection of arsenates or arsenites in solution, a solution containing 0.1 per cent. of arsenic acid giving an abundant precipitate of arsenious

sulphide, but if the solution of arsenic be very dilute, the reaction is apt to be masked by the simultaneous precipitation of sulphur. The easiest way to apply the test is to add about 1 c.c. of phosphorus trichloride to the solution to be tested, and warm after adding some sulphurous acid.

If, instead of heating the mixed solutions, they be allowed to stand at the ordinary temperature for some time, the solution becomes brown, and after about a day practically the whole of the arsenic is found as a dark brown precipitate. It was at first thought that this might be pure arsenic or arsenic mixed with sulphur, or with some sulphide of arsenic, or perhaps the brown or black substance obtained by Berzelius on treating realgar with potash solution and described by him as a sulphide of arsenic.

Analysis showed that it could not be this substance, as it contains about 13 per cent. of sulphur, whilst the black sulphide, according to Berzelius, contains only 3.44 per cent., corresponding to the formula As_2S_3 .

The new sulphide is insoluble in solutions of either ammonia or colourless ammonium sulphide, but dissolves readily in yellow ammonium sulphide, which is at the same time decolorised, and from the solution arsenious sulphide is precipitated on the addition of excess of hydrochloric acid. Carbon disulphide removes no sulphur from it on treatment for many hours in a Soxhlet's extraction apparatus.

Analyses of samples prepared at various times and with varying quantities of the reagents gave the following results :

	I.	II.	III.	IV.	V.
Sulphur.....	12.7	13.09 (mean of four)	13.62	13.6	13.3
Arsenic.....	—	87.06* (mean of two)	—	86.1†	—

The percentage of sulphur is usually rather higher than 12.45, which is required by the formula As_3S_5 , owing to the great difficulty of removing every trace of arsenious sulphide, which always accompanies it in small quantity. A quantity of sample II. above mentioned was treated with dilute ammonia solution on the water-bath, then a little hydrogen sulphide passed in and the digestion continued for some time, the liquid poured off, and the treatment repeated until the solution of ammonium sulphide thus prepared gave no yellow precipitate with excess of hydrochloric acid. On now analysing the residue, it was found to contain 12.3 per cent. of sulphur. A portion of this residue was now taken and treated with ammonia solution and hydrogen sulphide passed in, and one-eighth part of the sulphur required to

* Estimated gravimetrically as magnesium pyroarsenate.

† Estimated volumetrically as arsenious acid with standard iodine solution (Szarvasy, *Ber.*, 1897, **29**, 2900).

transform the sulphide into arsenious sulphide was added in fine powder, and, after digestion, the residue was collected and analysed, when it was found to contain 12·5 per cent. of sulphur; another portion was taken and similarly treated, but with twice the quantity of sulphur, and the residue from this analysed; it contained 12·3 per cent. of sulphur. This seems to prove conclusively that the substance behaves chemically as a single substance and not as a mixture. Heat resolves it into realgar, which sublimes, and arsenic, which remains behind. It is acted upon by potash solution, which leaves a substance of a darker colour containing 2·34 per cent. of sulphur.

Realgar was treated with potash in order to obtain the substance described by Berzelius. Commercial realgar containing 32·9 per cent. of sulphur (As_2S_2 contains 30 per cent.) gave a dark-brown residue containing 4·33 per cent. of sulphur. Native realgar was distilled, and the dark brown residue remaining after treatment with potash of the realgar thus purified contained exactly 1·0 per cent. of sulphur.

Convenient quantities of materials for the preparation of the new sulphide are: 200 grams of crystallised sodium arsenate dissolved in $3\frac{1}{2}$ litres of water, and then 150 c.c. of phosphorus trichloride added and allowed to stand till quite cold, the solution filtered and sulphur dioxide passed in and allowed to stand for a day or two. The supernatant liquid is then poured off and the precipitate washed first with water, then with dilute ammonia solution, then warmed with stronger solution of ammonia, and into this hydrogen sulphide is passed and the digestion continued for an hour or two; the precipitate is then well washed with water by decantation, and finally with alcohol, and dried in a vacuum. The same sulphide is obtained from arsenites, but the yield is much smaller in proportion, owing to the precipitation of much arsenious oxide from the strongly acid solution.

As solutions of antimony react but slightly with the solution of phosphorous and sulphurous acids, especially when warmed, and in presence of hydrochloric acid, it was hoped that conditions would be discovered under which arsenic and antimony might be quantitatively separated, but so far without success. The precipitates from the mixed solutions always contained notable quantities of antimony.

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