

CCCVIII.—*Germanium. Part VIII. The Sulphides of Germanium.*

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THE object of the present investigation was to prepare germanium monosulphide in order to determine its behaviour towards certain reagents, which will form the subject of a further communication.

Germanium monosulphide was prepared from the disulphide by Winkler (*J. pr. Chem.*, 1886, **34**, 215) by heating it with the metal in a stream of carbon dioxide, and also by reducing it with hydrogen. Dennis and Joseph (*J. Physical Chem.*, 1927, **31**, 1716) examined the latter method and found the optimum temperature to be 480°. The author has confirmed this observation: volatilisation of germanium disulphide does not commence below 480°.

Both these methods, however, involve the preliminary preparation of the disulphide, which, according to the methods hitherto described, is tedious. Dennis and Joseph (*loc. cit.*) prepared it by precipitating strongly acid solutions of germanium dioxide with hydrogen sulphide.

In this method, a high concentration of acid is essential and the washing process is very troublesome because the cake forms channels on the filter. In view of this, and of the fact that the dioxide is the usual final product obtained during the extraction of germanium, attempts were made to prepare these sulphides direct from the dioxide.

*Crystalline Germanium Disulphide. The Action of Sulphur Vapour on Germanium Dioxide.*—Preliminary experiments showed that germanium dioxide is only very slowly affected by sulphur below its boiling point. In one experiment, a weighed quantity of germanium dioxide was heated in a Rose crucible, with an excess of pure sulphur, in a current of carbon dioxide, and at least three lots of sulphur were required to convert half of the dioxide into disulphide. In another series of experiments, germanium dioxide was heated in a porcelain boat in a combustion tube and a slow stream of sulphur vapour was carried over it by means of carbon dioxide. At 400° a faint test for sulphur dioxide was obtained and the surface of the oxide turned yellow. At about 530° a faint yellowish-white sublimate appeared on the cool part of the tube above the boat, but the reaction was extremely slow. At 850° a much stronger test for sulphur dioxide was obtained and sublimation was much faster, but still very slow, about 4 hours being required to convert 1 g. of dioxide into disulphide. At this temperature, germanium disulphide volatilises rapidly. By maintaining the cooler parts of the tube above the boiling point of sulphur, the disulphide was obtained pure and uncontaminated with sulphur. In most of these experiments, the sublimate was seen to consist of two types of material, both of which, however, analysed as pure germanium disulphide. The portion deposited just outside the hottest part of the tube was yellowish, hard, and coherent, and it seemed to have been partially fused: indeed, in some of the experiments it had been completely fused and was obtained as an amber-coloured, transparent glass. The portion deposited on the cooler parts consisted of white, pearly, iridescent scales, recalling the appearance of tinsel. In some of the experiments, where a rapid current of carbon dioxide was employed to carry the vapour away from the hot regions, the whole of the sublimate consisted of these lustrous scales. For analysis, they were treated with dilute ammoniacal hydrogen peroxide, in which they dissolved without separation of sulphur (Found: S, 46.80. Calc. for  $\text{GeS}_2$ : S, 46.90%).

*Volatilisation of Germanium Disulphide.*—It is stated that germanium disulphide shows but little tendency to crystallise or volatilise (Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 274), but this is contrary to the

author's experience. Both the crystalline disulphide, prepared as described, and the amorphous disulphide prepared by precipitation were heated in an electric furnace in a current of carbon dioxide. At 480°, no trace of sublimate had appeared in 2 hours; at 500°, a faint white film appeared on the cool parts in the course of 2 hours, and at 800—850°, sublimation became very rapid. Many such experiments were carried out, and in all cases it was found that the disulphide volatilised readily at 800°. The mass turned yellow below a dull red heat and melted in the neighbourhood of 800° to a dark liquid.

*The Action of Hydrogen Sulphide on Germanium Dioxide.*—When germanium dioxide was similarly heated in a current of hydrogen sulphide, the first evidence of reaction appeared at about 420°, a black metallic glint appearing on the cool parts of the tube and the surface of the oxide becoming dark grey. Since the disulphide does not volatilise at this temperature, the sublimate probably consists of pure germanium monosulphide, but this was not investigated because the rate of reaction was too slow. At 700—800°, the reaction became quite rapid but the product was invariably a mixture. The sublimate on the hotter parts of the tube was practically pure white, crystalline germanium disulphide, as already described, and that on the cooler parts consisted of black lustrous crystals of almost pure monosulphide. The great bulk of the material was a mixture of the two, the disulphide forming about 90% of the total. By carrying out this operation in the presence of sulphur vapour, the formation of the monosulphide was prevented and the pure crystalline disulphide was obtained. This method of preparing germanium disulphide is simpler than that already described because reduction with hydrogen sulphide proceeds more readily than with sulphur vapour. The best method of all, however, consists in preparing germanium monosulphide, as described below, and subliming this in sulphur vapour.

*Germanium Monosulphide. The Action of a Mixture of Hydrogen Sulphide and Hydrogen on Germanium Dioxide.*—The action of hydrogen sulphide alone on germanium dioxide yields essentially germanium disulphide, which, however, is readily reduced by hydrogen to the monosulphide. A mixture of the two gases would, therefore, be expected to afford a convenient way of preparing the monosulphide from the dioxide. This has been found to be the case. The proportion of hydrogen in the mixed gases was varied between 1 and 3 vols. per vol. of hydrogen sulphide, but there was no appreciable alteration in the composition of the ultimate product; in the majority of the experiments the volume of hydrogen was in the ratio 2 : 1. At 500°, the reaction is too slow, very little sublim-

ation occurring in several hours; at  $600^{\circ}$ , it is fairly rapid, the dioxide turns black, and at a slightly higher temperature it melts to a dark liquid. Volatilisation is rapid at  $700^{\circ}$  and about 10 g. of dioxide may be volatilised as monosulphide in a few hours. The sublimate obtained was in all cases free from visible traces of white germanium disulphide. It consisted of black, lustrous, opaque crystals adhering firmly to the sides of the tube, with, in some cases, a very small proportion of reddish-brown powder deposited in the cooler parts. A typical analysis of the black material as withdrawn from the tube was Ge, 68.9; S, 31.0 (Calc. for GeS : Ge, 69.34; S, 30.66%). Evidently, the material contained a trace of germanium disulphide. The whole product was, therefore, pulverised and digested over-night with cold dilute ammonia. About 5% of the material dissolved, and the dried residue was shown by analysis to be pure germanium monosulphide (Found : Ge, 69.33; S, 30.52%).

Dennis and Joseph (*loc. cit.*) found difficulty in analysing this substance because of its resistance to the action of solvents. This is certainly true of the crystalline mass; the finely powdered material, however, is readily soluble in strongly alkaline liquids, and, although it is not appreciably soluble in ammonia, it is dissolved vigorously by ammoniacal hydrogen peroxide without separation of sulphur. Furthermore, the presence of germanium in the resulting liquid, according to the results of numerous analyses, does not appear to have any appreciable influence on the accuracy of the estimation of sulphur as barium sulphate.

The method just described forms, therefore, a very convenient way of preparing germanium monosulphide, in quantity, direct from the dioxide. According to Winkler (*loc. cit.*), even germanium monosulphide is reduced by hydrogen at high temperatures, and there is some confirmation of this in the results of one of the runs made with the mixture of gases used in the present work. In this run, the temperature of the furnace was about  $750^{\circ}$ , and the product, after the treatment already described, contained Ge, 69.50 (Calc. for GeS : 69.34%).

*The Properties of Germanium Monosulphide.*—The product obtained by this method of preparation corresponds in every respect with that described by Dennis and Joseph. It consists of heavy, black, glistening, opaque crystals, with a high lustre and resembling molybdenite or iodine. The crystals are of different habits, most of them being in the form of thin plates and needles, but occasionally large, fern-like growths occur. The monosulphide was insoluble in water, alcohol, benzene, or xylene. It had  $d_{4}^{20}$ : 4.012. It just scratched aluminium, but it was uncertain whether it scratched, or

was scratched by, rock-salt; its hardness is therefore 2 on Moh's scale. It melted in the neighbourhood of  $530^{\circ}$  to a black liquid, and volatilised rapidly above  $650^{\circ}$ . The coarse, crystalline material was only with difficulty attacked by acids and alkalis, even on boiling, but the finely powdered material dissolved readily in hot dilute caustic alkalis and in moderately concentrated hydrochloric acid. Hydrogen sulphide was liberated with the latter. From the solutions in caustic alkalis, acids reprecipitated amorphous, reddish-brown germanium monosulphide. It was difficultly soluble in ammonium hydroxide and in ammonium sulphide, but rather more so in yellow ammonium sulphide, from which the white disulphide was precipitated by acids. Dilute nitric acid dissolved it slowly when hot, and the concentrated acid attacked it vigorously, sulphur and germanium dioxide separating. It reacted with chlorine and bromine in the cold with evolution of much heat.

*The Properties of Germanium Disulphide.*—Crystalline germanium disulphide forms white, pearly scales and arborescent growths, of  $d_{14}^{20}$  2.942. It is only with difficulty wetted by water and is remarkably resistant to attack even by boiling concentrated acids. Concentrated nitric acid attacks it slowly on boiling, but it dissolves readily in hot caustic alkalis, and slowly on digestion with ammonium hydroxide in the cold. It melts at about  $800^{\circ}$  to a dark liquid, which solidifies to an amber-coloured transparent glass,  $d$  5.81.

#### *Summary.*

1. The behaviour of germanium dioxide towards sulphur and hydrogen sulphide has been studied.
2. Crystalline germanium disulphide has been prepared by heating the dioxide in hydrogen sulphide carrying sulphur vapour.
3. Germanium monosulphide is easily prepared by heating the dioxide in a mixture of hydrogen and hydrogen sulphide.
4. Some of the properties of these substances are described.

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