CCCXXXVIII.—*Germanium. Part VI. An Improved Method of extracting Germanium from Germanite.*

By WILLIAM PUGH.

IN the process for extracting germanium and gallium from germanite previously described (J., 1924, **125**, 816), the ore was roasted to remove as much of the arsenic as possible, and subsequently distilled with concentrated hydrochloric acid in a current of chlorine. Germanium tetrachloride passed over, carrying with it a small amount of arsenic chloride, and the last traces of this impurity were removed by redistilling, in the same manner, the germanium dioxide finally obtained. The process is somewhat tedious, for, apart from the necessity for redistillation and the separation of masses of sulphur when the distillate is saturated with hydrogen sulphide, 4 hours are required to drive over all the germanium from 100 g. of the ore. This slow distillation is due to two causes. (1) Germanium sulphide is not easily attacked by concentrated hydrochloric acid, and hence, when the ore is distilled directly with this acid, only 25% of the germanium distils in 3 hours. Even after 3 hours' roasting, a considerable portion of the germanium remains as sulphide, as shown by the fact that when 0·400 g. of pure germanium sulphide was heated in a crucible, gently at first, and finally to dull redness for 2 hours, it lost only 0·045 g., corresponding approximately to 50% conversion into oxide; during the initial stages, traces of yellow fume were evolved and, while the contents of the crucible were still comparatively cool, the sulphide became incandescent on the surface, but no further fuming then occurred, and as subsequent oxidation with nitric acid gave 0·303 g. of germanium dioxide (calc., 0·306 g.), there was no sensible loss of germanium during the roasting. (2) The hydrochloric acid in the distilling flask is partly neutralised by the large amount of copper oxide (some 70%) in the roasted ore, and therefore cannot be maintained at the high concentration which has been shown (J., 1926, 1051) to be required for the rapid attack of germanium dioxide.

A method was therefore developed in which the copper was removed and the germanium sulphide converted into oxide before the actual distillation; this had the further advantage that far larger germanium concentrates could be distilled together. The method depends upon the author's observation (this vol., p. 1994) that germanium dioxide is almost insoluble in acids at moderately high concentrations. The minimum quantity of nitric acid is employed to extract the copper, and this treatment also serves to oxidise the remainder of the arsenic to arsenic acid, which passes into solution with the copper.

Procedure.—The finely powdered ore is spread in thin layers on sheet iron and heated (under a hood) at about 300°. Fumes of arsenious oxide cease to be evolved in the course of ½ hour, and at this stage the loss in weight is 16—18%. The material is then raised to dull redness for 2½ hours, during which the ore increases in weight, so that the final loss is only 10—11%. Portions of 90 g. are then digested on a hot plate with water (50 c.c.) and concentrated nitric acid (125 c.c.). Action ceases in about 2 hours, the volume is then made up to 200 c.c., and the solution filtered. The filtrate deposits copper nitrate on cooling and the mother-liquor is employed for digesting the next portion of ore, with the addition of the necessary quantity of nitric acid. The insoluble residue is washed with small volumes of dilute nitric acid, the washings also being used for digesting the ore. In this way, the minimum amount of germanium dioxide passes into solution. The small residues (approximately 20% of the weight of the ore) consist chiefly of ferric oxide and germanium dioxide and contain rather more than 90% of the total germanium. The residues from 500 g. of ore are then heated with 600 c.c. of concentrated hydrochloric acid in a 1-litre Pyrex distilling flask and a fairly rapid stream of hydrogen chloride is bubbled through the liquid. If the liquid is maintained just below its boiling point, germanium tetrachloride distils rapidly as tiny oily drops. These are received in a flask containing 500 c.c. of 2*N*-sulphuric acid, where they are almost completely hydrolysed to germanium dioxide; the last traces of germanium chloride vapour are recovered in a trap attached to the flask. Practically the whole of the germanium distils in 1½ hours, and when the rate of distillation falls considerably, the receiver is changed, the stream of hydrogen chloride discontinued, and the liquid boiled vigorously for 2 hours. The first distillate is kept over-night in a tightly stoppered vessel to allow the germanium dioxide to settle, and the clear liquid is decanted. The solid is collected on a filter, washed free from hydrochloric acid, and ignited. The germanium dioxide obtained is entirely free from arsenic and represents 65—70% of the total element in the ore.

The decanted liquid is made 6*N* with respect to sulphuric acid and saturated with hydrogen sulphide; the pure white germanium sulphide obtained yields another 15% of the germanium. The second distillate yields about 5% of the element, but this is contaminated with a small amount of arsenic. The precipitated sulphides so obtained are separated by fractional precipitation from ammonia by Winkler's method (*J. pr. Chem.*, 1886, **33**, 142, 194), and the arsenic fraction, containing a trace of germanium, is added to a fresh portion of ore for digestion with nitric acid. The remaining 10% of germanium is found with the copper nitrate and is recovered by igniting it to the oxide and distilling it in the same manner. The gallium in the ore (0·5%) is recovered from the distillation residues in the manner already described (J., 1924, **125**, 816).

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THE UNIVERSITY, CAPE TOWN.

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