281. *Gallium. Part II. The Extraction of Gallium and Germanium from Germanite.*

By F. Sebba and W. Pugh.

Of the methods previously described for the extraction of germanium and gallium from germanite, none yields gallium in a reasonable time. All the methods make use of acid to decompose the ore, and the gallium must subsequently be separated from very large amounts of copper, iron, lead, and zinc. There is reason to believe, too, that these methods fail to extract gallium completely. The expectation that alkali digestion should extract the two rare elements has been fully realised, and by the method now described it is shown that both germanium and gallium can be easily extracted from the mineral and separated from each other and from arsenic. The method is quick, can be employed on a large scale, and, moreover, gives much larger yields of gallium than have ever been reported in germanite. Analysis of the mineral by this method showed it to contain 1·2% of gallium. The yield in practice is 10 g. per kg. The germanium is obtained as crude oxide, free from arsenic, and needs only simple distillation with hydrochloric acid to yield pure germanium dioxide.

Since the discovery of germanite (Schneiderhohn, *Met. Erz*, 1920, **17**, 364) many methods have been described for extracting the rare elements germanium and gallium therefrom. In the first method (Thomas and Pugh, J., 1924, **125**, 816), the roasted ore was distilled with hydrochloric acid, the volatile germanium tetrachloride being collected, and the distillation residues were treated for recovery of gallium. In a modified method, Pugh (J., 1929, 2540) decomposed the ore with nitric acid, thereby concentrating the germanium as the insoluble oxide, which was subsequently distilled with hydrochloric acid. Although this method worked well so far as the recovery of germanium was concerned, yet the yield of gallium from the soluble fractions was very low. It is now known, from work on the arsenates of gallium, shortly to be published, that the loss was undoubtedly due to the presence of arsenic acid: all the arsenic in the ore was concentrated by this method as arsenic acid in the soluble fractions, and it has since been shown that this acid peptises gallium arsenate under certain conditions. The presence of the large amounts of copper and iron also made the recovery of gallium a tedious process.

Keil (*Z. anorg. Chem.*, 1926, **152**, 103) decomposed the ore with nitric–sulphuric acid mixture, distilled off the germanium tetrachloride, and concentrated the gallium as ferrocyanide. Keil and Berg (*ibid.*, 1932, **209**, 383) modified the process by extracting gallium and ferric chlorides with ether saturated with hydrochloric acid.

The foregoing methods are not entirely satisfactory because they can deal with only small quantities of ore at a time. Patnode and Work (*Ind. Eng. Chem.*, 1935, **23**, 204) have described a semi-large-scale method for recovering germanium, but they have not yet described the recovery of gallium from the residues. Finally, Foster, Johnson, and Krauss (*J. Amer. Chem. Soc.*, 1935, **57**, 1828, 1832) distilled germanium monosulphide in ammonia gas and extracted gallium from the residue by methods similar to those described by earlier workers.

All these methods require for the extraction of gallium an acid decomposition of the ore or ore residues, and the large amounts of copper, iron, lead, zinc, and other metals go into solution with the gallium. This makes the recovery of gallium tedious. However, since both germanium and gallium form soluble alkali salts, and since the ore is a sulphide ore in which germanium is present probably as thiogermanate, it was expected that both elements would be extracted by alkali digestion. This expectation has been fully realised. The effect of this modification is to concentrate in a single operation both of the rare elements, free from even traces of copper, iron, and zinc, which remain as insoluble sulphides. This simplifies the extraction of both to an enormous degree, because their separation from arsenic and from each other is comparatively simple. Furthermore, the method can be adapted for large-scale use, and even on the laboratory scale it is possible to recover the gallium content of several kg. of ore within a week.

EXPERIMENTAL.

Alkaline Extraction.—1 Kg. of crushed germanite (180-mesh) is slowly dusted into an iron basin containing sodium hydroxide (500—600 g.) dissolved in its own weight of water; a vigorous reaction takes place, and it is best to cool the caustic liquor before adding the ore. By being thus dusted in, the ore is completely wetted and does not then tend to stick to the bottom of the basin. The mixture is heated over an air-bath, and the water allowed to evaporate. As the mass becomes pasty, it should be stirred to prevent caking. In the course of an hour the mass dries, and it is then scraped into about 1 l. of water. It is essential to dilute it immediately; otherwise, oxidation occurs, giving colloidal sulphides difficult to filter. The hot liquid is filtered through asbestos or paper (Whatman No. 5), and washed with hot water until the washings are pale yellow. The total volume at this stage is about 4 l. Sometimes, when the filtrate is allowed to cool before washing is commenced, white needle-like crystals separate, but they dissolve in the washings. These crystals gave all the tests quoted by Gutman for sodium trioxysulpharsenate (Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, 329). The insoluble ore residue is discarded, but it is necessary to guard against the risk of fire because the moist and finely divided material oxidises rapidly with great evolution of heat.

The filtrate contains germanium, arsenic, and a little molybdenum as thio-salts and gallium in anionic condition. Though germanium sulphide is not usually precipitated from neutral solution, it is not possible to separate the gallium and arsenic by neutralisation, for the arsenic sulphide carries down much of the germanium with it : in addition, the solution is highly coloured and neutralisation is difficult. The best plan at this stage is to oxidise the sulphides.

The liquid is partly neutralised with sulphuric acid, and then made acid with nitric acid. The reaction with nitric acid is vigorous and the liquid boils; the precipitated sulphides and hydroxides gradually disappear and give place to a brownish scum of arsenious sulphide and sulphur, which is filtered off.

From the filtrate, gallium is completely precipitated by neutralisation. At first, methyl-red was used as indicator, but it was then found that one-third of the gallium remained in solution. The reason for this remained obscure until gallium arsenate was studied, and the results of this investigation, shortly to be communicated, have shown that ammonium arsenate is able to peptise gallium arsenate at p_H values greater than 3 : at this p_H value, however, gallium arsenate is almost quantitatively precipitated. The most suitable indicator for use was found to be benzylanilineazobenzenesulphonic acid. With the gallium at this stage is co-precipitated about two-thirds of the germanium as hydrated oxide, and this fact makes filtration easier. The remainder of the germanium is recovered, again as hydrated oxide, by adding to the filtrate 10% by vol. of concentrated ammonia. A trace still remains, however, and this is recovered by adding magnesium sulphate to the filtrate (Muller, *J. Amer. Chem. Soc.*, 1922, **44**, 2496).

The germanium–gallium precipitate is next dehydrated by being heated to fuming with sulphuric acid : dehydrated germanium dioxide is almost insoluble in acids (Pugh, J., 1929, 1537) and is removed by filtration. Thus, about 90% of the germanium in the ore is concentrated in two fractions as oxide and hydrated oxide. Both fractions are almost free from arsenic, which is a great advantage, and pure germanium dioxide is obtained from them by simple distillation with hydrochloric acid, as described by Pugh (*loc. cit.*). There is no need for elaboration on this point because it has been amply described in the literature.

All the gallium is now in solution as sulphate, together with arsenic acid, a little molybdenum, and traces of germanium, lead, and tungsten. Considerable difficulty was experienced at first in removing the arsenic completely, and this was eventually traced to the presence of molybdenum, which forms rather stable complexes with arsenic acid; hydrogen sulphide in acid solution acts very slowly even after treatment with sulphur dioxide in boiling solution. Eventually, a simple and effective method was evolved. The solution is made alkaline, treated with excess of sodium sulphide, and acidified with hydrochloric acid. Arsenic, tungsten, and molybdenum are completely precipitated. The precipitate, however, adsorbs a trace of gallium, which is recovered by boiling with hydrochloric acid.

The filtrate now contains mere traces of germanium, lead, and molybdenum and the small amount of aluminium phosphate in the original ore. For removal of impurities from gallium solutions it is necessary frequently to concentrate the gallium by precipitation; the use of ammonium carbonate as described by Lecoq de Boisbaudran (*Ann. Chim. Phys.*, 1877, **10**, 119) is convenient in that it gives a more granular hydroxide than ammonia.

To remove germanium, the gallium is precipitated with ammonium carbonate and boiled with concentrated hydrochloric acid and a drop of bromine, to oxidise the sulphide; germanium tetrachloride volatilises. It is not possible, however, to remove the last trace of lead. Hydrogen sulphide in acid solution gives no precipitate because the acidity of the solution from hydrolysis of gallium sulphate is too high. The greater part of the lead can be removed by treating the alkaline solution with hydrogen sulphide and keeping it overnight. The last trace of molybdenum sulphide is precipitated when the solution is subsequently made faintly acid. Even so, a trace of lead goes through in colloidal solution and contaminates the crude gallium metal obtained. The isolation of the gallium by electrolysis and its subsequent purification are described in the following paper.

Analysis and Yield.—The sample of ore used in this investigation has given much larger yields of gallium than have ever been reported in the mineral, the highest hitherto being 0·74% (Berg and Keil, *loc. cit.*). All previous methods of analysis, however, have made use of acid to decompose the ore, and it is our opinion that considerable losses of gallium have occurred during its separation from the heavy metals, or, alternatively, that such methods do not extract the total gallium content of the ore. The following method of analysis has proved more satisfactory.

Finely powdered ore (5 g.) and sodium hydroxide (10 g.) are heated to quiet fusion in an iron crucible, and the cooled melt is extracted with water, the residue filtered off, and washed. The filtrate is acidified with hydrochloric acid so that the excess acidity is about 2*N*. The liquid is boiled to ensure complete solution of the gallium and to coagulate arsenic and molybdenum sulphide : there is sufficient sulphide in the fusion extract to remove all the arsenic at this stage. The sulphides are filtered off and the filtrate is neutralised (to methyl-red) with sodium hydroxide. The precipitated gallium hydroxide is evaporated to dryness with hydrochloric acid to volatilise traces of germanium and to dehydrate silicic and tungstic acids. The last traces of lead and molybdenum are removed by treatment with hydrogen sulphide in alkaline and in acid solution, as described above, and the gallium is finally precipitated with cupferron according to the method of Moser and Brukl (*Monatsh.*, 1929, **51**, 327). The germanium content was determined by methods already described (Thomas and Pugh, *loc. cit.*) (Found : Ga, 1·20, 1·20, 1·25; GeO_2, 7·9%). The actual yields per kg. of ore by the extraction process described above were : Ga, 10 g.; GeO_2, 70 g.

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