282. *Gallium. Part III. The Electrodeposition, Purification, and Dissolution of Gallium.*

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Though much work has been published on the electrodeposition of gallium, this has necessarily been accomplished with small amounts of the metal. The problem of dealing with larger amounts, such as are available from germanite, is quite different. Moreover, in spite of the work already published, there is little in the literature to indicate what degree of success may be expected under various conditions. For this reason, the conditions for the successful electrodeposition of quantities of the order of 10 g. of metal have been studied. The metal obtained in this way from germanite contains traces of lead, tin, and platinum, and it is shown that the last traces of these impurities are removed by simple washing with hydrochloric and nitric acids. The behaviour of the metal towards acids has also been studied.

Since Lecoq de Boisbaudran first isolated gallium by electrolysis (*Bull. Soc. chim.*, 1879, **31**, 50), this method has often been used. The earlier workers, Schucht (*Chem. News*, 1880, **41**, 280), Ehrlich (*Chem.-Ztg.*, 1885, **9**, 78), and Kunert (*ibid.*, p. 1826), followed the original method of electrolysing alkaline solutions, but gave only scanty details. Uhler and Browning (*Amer. J. Sci.*, 1916, **42**, 394) also employed alkaline solutions, and found

that the metal is deposited from cold solution in the form of trees, and from warm solution as globules which drop off the cathode.

More recent workers have preferred acid solutions. For instance, Richards and Boyer (*J. Amer. Chem. Soc.*, 1921, **43**, 274) and Richards and Craig (*ibid.*, 1923, **45**, 1157) were able to prepare pure gallium from sulphuric acid solutions provided the concentration of acid did not exceed $0.04N$; they were chiefly concerned, too, with the separation of zinc and indium impurities. Obviously, this method is not very suitable for dealing with large amounts of gallium which require a considerable concentration of free acid to maintain them in solution. The same applies to Reichel's method (*Z. anal. Chem.*, 1932, **87**, 322), who obtained quantitative yields from ammoniacal solution.

For dealing with amounts of the order of 10 g. at a time, such as were obtained from 1 kg. of germanite in the present work, the most obvious choice was electrolysis of alkaline solutions. Dennis and Bridgman (*J. Amer. Chem. Soc.*, 1918, **40**, 1537) made a few observations on this problem and stated that deposition was slow and that the metal probably contained alkali metal. Our experience is the reverse : current efficiencies of 25—30% are possible with concentrated solutions, and the metal obtained is quite free from sodium, at any rate after an acid wash.

Since so little information is available about the conditions necessary for successful electrodeposition from alkaline solution, our method is given in detail.

With regard to temperature, as Uhler and Browning (*loc. cit.*) have shown, cold solutions give gallium trees, which, although often very beautiful, are troublesome in practice. Fronds fully an inch long are often produced, connected to the cathode by a very thin neck : sooner or later they drop off under their own weight and then dissolve appreciably in the alkaline liquor. In hot solution, on the other hand, the metal melts, and provision must be made for collecting the molten metal and maintaining it permanently cathodic to prevent re-dissolution. Success depends largely on the design of the electrode.

It seems to be agreed that a high current density at the cathode is an advantage; for this reason most workers have used wire or rod.

With regard to the choice of cathode materials, platinum has been used by most workers, although it alloys slightly with gallium. Richards and Boyer (*loc. cit.*) used a gallium electrode for the preparation of the pure metal; in our experience, however, this type of electrode is slow, probably because of its small surface area. The only other cathode material that has been used is a tungsten wire (Willard and Fogg, *Trans. Amer. Electrochem. Soc.*, 1934, **66**, 110).

Experimental.

Nickel electrodes were first tried, but they were not adopted for regular work for the following reasons : A nickel anode is easily attacked by traces of anions which form soluble nickel salts, giving rise to a green deposit of nickel hydroxide in the bath; to avoid this would require prolonged washing of the gallium hydroxide. A nickel cathode has the same tendency as platinum to induce the formation of trees in the cold, and a suitable electrode to collect the molten metal could not be designed because of the difficulty of sealing nickel into glass. Apart from this, however, nickel appears to have some advantage over platinum, for gallium does not seem to alloy with it to the same extent. The surface of the cathode was blackened, but the coating was very adherent and gallium was easily melted off under water acidified with a drop of hydrochloric acid.

Platinum electrodes were therefore used. The anode was a piece of foil, 20 cm. long and 3 cm. wide, placed round the inside of a 250 c.c. beaker. The cathode (see fig.) was a piece of thick foil, 1.5 cm. by 1 cm., the lower edge of which, wedge-shaped, was sealed into a glass cup blown at one end of a U-tube. Contact was made by a platinum wire through the glass seal to mercury in the U-tube. The glass cup was 3 cm. in diameter, very shallow, but big enough to hold rather more than 10 g. of gallium. It was found advisable to give a thick edge to the platinum foil–glass junction, because the first electrode used was soon corroded at the wire–glass junction. The type described has shown no sign of corrosion after several hundred hours' use.

The molten gallium collected in the cup and remained cathodic; in fact, after a little use the electrode became essentially a gallium electrode of large surface, for the platinum was covered with a layer of gallium. Only the first lot of gallium collected was contaminated with platinum.

The chief advantage of the electrode was that it could be used for quantitative work : the metal was easily washed, dried, and weighed in it.

The gallium from 1 kg. of ore, after removal of impurities as described in the preceding paper, was concentrated by precipitation as hydroxide; this was then dissolved in the minimum of concentrated sodium hydroxide, diluted to 150 c.c., and electrolysed with a current of 1 amp. at 3—4 volts. The resistance of the electrolyte generated sufficient heat to maintain the temperature of the liquid above 30°, the m. p. of the metal. About 6 g. separated during the first 24 hours and 3·5 g. during the next period, but the efficiency then became very low and the recovery of the last 0·5 g. of gallium was tedious. The best plan was to reprecipitate the remaining metal as hydroxide and add it to a subsequent batch. When the aluminium content of the residue had increased appreciably, the remaining gallium was precipitated with cupferron, ignited to oxide, and fused with sodium hydroxide. In this connection it was noticed that the cupferron precipitate carried down with it some aluminium phosphate, which is of importance in relation to the work of Moser and Brukl on the separation of gallium and aluminium (*Monatsh.*, 1929, **51**, 327).

The gallium so obtained was quite free from aluminium. Usually, it was mobile and strongly reflecting, like mercury, but in some cases the metal was greyish and much of it in powder form. This phenomenon appears to be connected with the presence of sulphides, for when these were removed by treatment with peroxide, before electrolysis, globular metal was always produced. The grey metal was easily rendered silvery white and coalescible by one wash with a little nitric acid. The metal which adhered to the electrode was removed by pouring a little warm dilute hydrochloric acid over it, whereupon it immediately became spherical and was easily rubbed off. At no time was the red colloidal gallium solution described by Dennis and Bridgman (*loc. cit.*) observed.

Purification of the Metal.—The crude metal so obtained contained traces of lead, tin, and platinum, which were the only impurities detected spectroscopically. Dennis and Bridgman (*loc. cit.*) suggest that gallium obtained from alkaline solution contains alkali metal, and they find support for this view in the vigorous reaction which occurs when water is added to the metal. This may be true for metal obtained in the tree form, but when it is deposited from warm solution from an otherwise identical bath there is hardly any reaction with water. It would seem that the tree form is more reactive towards water, partly no doubt because of its larger surface area. Recently, Gilfillan and Bent (*J. Amer. Chem. Soc.*, 1934, **56**, 1662) have shown that the solubility of sodium in gallium at its m. p. is only 0·001%.

Various workers have used acids to remove impurities from gallium; Lecoq de Boisbaudran (*Compt. rend.*, 1876, **83**, 638), Richards and Craig (*loc. cit.*), and Dennis and Bridgman (*loc. cit.*) used nitric acid, but Fogg and James (*J. Amer. Chem. Soc.*, 1919, **41**, 949) and Berg and Keil (*Z. anorg. Chem.*, 1932, **209**, 383) used hydrochloric acid. Both acids were used to clean the metal obtained in this work.

All the gallium from the first 5 kg. of ore treated (45 g.) was melted under a little hot water, and an equal volume of concentrated hydrochloric acid added. The metal was rolled backwards and forwards under the acid for 5 minutes, and the acid then carefully washed out. A little concentrated nitric acid was next added; at first there was brisk effervescence and the metal broke up into numerous tiny globules. The reaction gradually abated, and after a few minutes the acid was diluted with water and allowed to react for 10 minutes more, after which it was carefully washed out. Because, after treatment with nitric acid, the metal did not have that clean reflecting surface so characteristic of gallium washed with dilute hydrochloric acid, it was given a final wash with this acid; the tiny globules immediately coalesced.

The action of hydrochloric acid in this respect is striking and has never been exactly described. When a little gallium is melted under water it remains shapeless, has a dull surface, and sticks to glass. This is probably due to a film of oxide on its surface. The addition of a single drop of hydrochloric acid to the water, however, causes the metal immediately to assume a perfectly spherical form. At first there is a brisk evolution of gas but this soon dies down; the metal reacts very slowly with dilute hydrochloric acid. Probably, there is a protective film of gas formed on the surface and, in the absence of edges to facilitate bubble formation, the film remains adherent. The metal so obtained had a perfect reflecting surface.

About 5% of the metal had dissolved during the washing. Tests showed that the wash liquid contained traces of lead, tin, and platinum. The presence of the last was unexpected, for mixtures of acids were not used at any stage. Further tests showed, too, that the whole of the
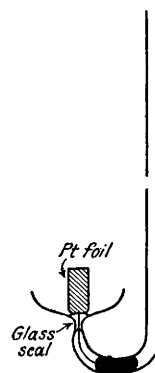
platinum had been removed. However, as it was naturally expected that some platinum still remained, the total yield (43 g.) was fractionally crystallised as described by Richards and Boyer (*loc. cit.*). Samples of the two extreme fractions and of two middle fractions were then converted into oxide and examined with a Hilger quartz spectrograph. All four samples were identical, and showed no evidence of lead, tin, or platinum. There were four faint lines which could not be identified as gallium lines : 2297·9 [2297·8, Fe(6)], 2624·7 [2625·5, Fe(4)], 2632·6 [2632·3 Fe(4)], and 2664·7 [Fe(3)]. The nearest line of the most likely impurity, with its intensity as given by Kayser ('' Tabelle der Hauptlinien der Linienspektra aller Elemente,'' Berlin, Springer, 1926), is shown in brackets. It would appear that a spectroscopic trace of iron is the only impurity in the metal, and that fractional crystallisation of the acid-washed metal is quite unnecessary.

Dissolution of Gallium in Acids.—The action of dilute hydrochloric, sulphuric, and nitric acids on gallium is very slow and is probably due to the protective action of a film of gas. This view is supported by the fact that reaction is much faster with oxidising acids.

The action of concentrated sulphuric acid has never been described. There is no action in the cold but, on heating, the metal dissolves vigorously. The gas liberated consists largely of hydrogen sulphide; some sulphur is also formed. In this respect, then, gallium resembles thallium (Ditte, *Ann. Chim. Phys.*, 1891, **19**, 68). After a short time, an insoluble white powder separates and stops further action. If this powder is dissolved by dilution with water, and the remaining metal treated with fresh acid, several g. of metal may be dissolved in an hour, whereas several days are needed by concentrated hydrochloric acid.

Hot concentrated nitric acid is the best solvent and, in this connection, some interesting phenomena have been observed. When the acid is kept just below its b. p. there is a continuous and vigorous evolution of gas, giving the impression that the metal is dissolving rapidly. However, about 10 hours are required to dissolve 5 g. Unlike hydrochloric acid, which induces the metal to coalesce, hot nitric acid disperses the metal into large numbers of tiny globules. If the acid is allowed to cool thoroughly, these globules break up into a dark grey powder, and if the acid is then warmed again this powder dissolves very rapidly, leaving some small globules. If this process of alternate warming and cooling is repeated a few times, large amounts of metal may be dissolved in a short time. The mechanism of the reaction is obscure, but it is possible that nitrous acid has much to do with it, because the cold acid in contact with the grey powder is markedly blue.