[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE TEXAS TECHNOLOGICAL COLLEGE]

Preparation and Properties of Gallium and Gallium Trichloride[1]

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In the commercial purification of zinc by redistillation at a low temperature a lead dross is left behind as a residue.[2] Fourteen kilograms of this dross were used as the source of gallium for the following research.

1. **Separation of Crude Gallium.**—The dross was treated in portions of about one kilogram weight. Each batch was melted in a porcelain evaporating dish and 80 g. of dry lead chloride was added. The temperature was then raised somewhat above 501°, the melting point of lead chloride, and the whole mass was stirred well for five minutes. Gallium, indium and zinc are all much more active than lead.[3] For this reason the chlorides of these three metals were formed by metathesis, and dissolved in the fused lead chloride.

After cooling, 2 separate 50-cc. portions of dilute hydrochloric acid were used to leach out the mass. Water was added and the suspended matter was filtered out; 30 cc. of nitric acid was added to the filtrate and the mixture was heated to oxidize the gallium from the divalent to the trivalent state. Dilute sulfuric acid was used to precipitate the major portion of lead left in solution. After filtering, 20 g. of sodium carbonate was added to neutralize partially the acid in the filtrate. Gallium hydroxide was then precipitated by the cautious addition of ammonium hydroxide, and the precipitate was filtered off; 24 g. of potassium hydroxide was then dissolved in water and added to the precipitate, and the resulting suspension was filtered. The filtrate, which contained gallium in basic solution, was electrolyzed to obtain crude metallic gallium.

2. **Purification of Gallium.**—This crude gallium was further purified by heating to 810° at a pressure of 0.5 mm. or less in a heavy iron pipe 90 cm. long and 4 cm. in diameter, which was securely capped at one end. Earlier experiments[4] had shown that all of the zinc and only part of the indium were removed by this treatment. For this reason the gallium was converted into the trichloride with chlorine, and was further purified by three fractional distillations in chlorine,[5] two in dry air, and two in partial vacuum. This treatment removed indium quantitatively.

3. **Boiling Point and Melting Point of Gallium Trichloride.**—This pure gallium trichloride was then distilled into a Pyrex flask fitted in its top with a deep thermometer well. Joined in series with this flask were a similar flask, a large test-tube with thermometer well sealed into its top, and a third flask which was added as a safety trap.

Four consecutive sets of boiling point determinations were made at four different pressures in the distillation train described above. The following average values were obtained.

TABLE I

BOILING POINTS OF GALLIUM TRICHLORIDE

Pressure, mm.	760	730	700	677
Av. b. p., °C.	199.6	197.9	196.3	195.1

The former value[6] obtained at 760 mm. pressure for the boiling point of gallium trichloride was 215–220°.

After making the boiling point determinations the gallium trichloride was distilled into the large test-tube. It was heated to a temperature just above its melting point and the test-tube was jacketed with a slightly larger test-tube to prevent too rapid cooling. In this way three time–temperature cooling curves were obtained, each of which showed a distinct hold at 76.65°. The former accepted value for this melting point was 75.5°.[6]

Spectrograms of the gallium were made at this point with a Hilger Constant Deviation Wave Length Spectrometer using a carbon arc as a light source. They showed no trace of zinc, cadmium or indium.

The chloride, which now represented our purest gallium salt, was dissolved in water and excess potassium hydroxide solution was added. The alkaline solution was electrolyzed by a current of 5 amperes and an e. m. f. of 25 volts, and the gallium was deposited on a short cathode of platinum wire. A second heating of the metal in a porcelain boat in an iron pipe under reduced pressure for four hours at 810° and etching with sulfuric acid completed the purification. Spectrograms of the metal were made as before, and no trace of zinc, cadmium, or indium was found.

4. **Determination of the Melting Point of Metallic Gallium.**—About fifteen grams of the pure crystals of metallic gallium was placed in a glass dilatometer[7] and water which had just been boiled and cooled was added. The open dilatome-

(1) Presented by G. Wilson Drake to the Faculty of the Texas Technological College in partial fulfilment of the requirements for the degree of Master of Arts.

(2) Hillebrand and Scherrer, *Ind. Eng. Chem.*, **8**, 225 (1916).

(3) Richards and Boyer, THIS JOURNAL, **43**, 275 (1921).

(4) (a) Browning and Uhler, *Am. J. Sci.*, [IV] **42**, 398 (1916); (b) Ref. 3, p. 281; (c) Richards and Craig, THIS JOURNAL, **45**, 1158 (1923).

(5) (a) Richards, Year Book No. 17, Carnegie Inst., 281 (1918); (b) Richards, Craig and Sameshima, THIS JOURNAL, **41**, 131 (1919); (c) Dennis and Bridgman, *ibid.*, **40**, 1540 (1918).

(6) Boisbaudran, *Compt. rend.*, **93**, 329 (1881).

(7) Ref. 3, p. 282.

ter was placed in a flask which was then evacuated to remove air bubbles. The ground glass end of the long capillary tube of the dilatometer was greased lightly before inserting and was held securely in place by means of rubber bands.

The thermostat used was capable of holding the temperature constant within three thousandths of a centigrade degree. An Emerson mercury-in-glass calorimeter thermometer graduated directly to hundredths of a degree was used. It had been calibrated by the Bureau of Standards to thousandths of a degree.

After twenty preliminary determinations had been carried out to perfect technique, six consecutive readings were made which showed that the water rose slowly in the capillary of the dilatometer when the thermostat was kept at a temperature of 29.750°. This indicated a temperature as low as or lower than the freezing point, as gallium expands during solidification.

At a temperature of 29.760° the water in the capillary gradually fell and indicated that the metal was melting. The average of these two temperatures, 29.755°, was taken as the true melting point of gallium. This temperature is 0.005° higher than the values determined by Richards and Boyer.[8] Browning and Uhler[4a] had previously found a melting point of 29.7°, and Lecoq de Boisbaudran[9] had reported as low as 29.5°. It was found that gallium when quite pure shows little of the tendency toward supercooling which is so characteristic of impure gallium.

5. Determination of the Density of Gallium.— The density of gallium was determined by the use of a small pycnometer of the usual form. It was weighed successively empty, with its charge of gallium and air, with gallium and water, and finally filled with water alone. A ground glass cap prevented loss by evaporation. The weights which were used were new and had been compared by the method of Richards.[10] Weighings were made by the method of substitution and all weights corrected to vacuum.

The seven consecutive determinations of the final series gave at 25° an average density of 5.903, with a maximum deviation of 0.003 and an average deviation of ±0.001. More than twenty-five preliminary determinations had been made to perfect technique, and three different batches of gallium, each obtained by different methods of treatment, were used in all. The preliminary determinations gave results agreeing closely with those of the final series.

Richards and Boyer[11] obtained in the two determinations of their final series an average density of 5.9037 at 29.65°. If corrected by means of their coefficient of cubic expansion, 0.000055, it becomes 5.905 at 25°.

When our density is divided into the latest accepted value of the atomic weight of gallium, 69.72,[12] a new value of 11.81 is obtained for the atomic volume. The old value was 11.85.

Summary

1. An easy and rapid method for the separation of traces of gallium from lead dross by means of fused lead chloride is described.

2. The boiling point of gallium trichloride at 760 mm. pressure was found to be 199.6°, and its melting point 76.65°.

3. The melting point of metallic gallium was found to be 29.755°.

4. The density of gallium was determined as 5.903 g. per cc. at 25°, and the atomic volume 11.81.

5. Pure gallium shows little tendency toward supercooling.

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(8) Ref. 3, p. 283.

(9) Boisbaudran, *Compt. rend.*, **83**, 611 (1876).

(10) Richards, THIS JOURNAL, **22**, 144 (1900).

(11) Ref. 3, p. 284.

(12) Richards and Craig, THIS JOURNAL, **45**, 1166 (1923).