ART. XXVI.—*On a Gallium-Indium Alloy*; by PHILIP E. BROWNING and HORACE S. UHLER.

[Contribution from the Kent Chemical and the Sloane Physical Laboratories of Yale University.]

A FEW months ago Mr. F. G. McCutcheon, chemist of the Bartlesville Zinc Company, observed some mercury-like globules upon the surface of a leady residue from the distillation of zinc. The appearance of these globules seemed to be due to the fact that the residue had been stored away in a warm place, and the phenomenon suggested to the observer the subjection of the residue to a sweating process. This treatment resulted in a more abundant separation of the peculiar material, which, from the character of its source and its low melting point, suggested the element gallium. It proved to be essentially an alloy of that element with indium.*

Through the kindness of the manager, Mr. K. Stock, and the chemist of the Company, we have been supplied with several grams of the alloy and a considerable amount of the leady residue. Rough analyses of these products show the gallium-indium alloy to contain about 10 per cent of indium, with small amounts of zinc and lead, and spectrographic traces of copper and silver. The leady residue contains about 95.6 per cent of lead, a fraction of 1 per cent of copper, about 3 per cent of gallium and indium together, and about 1.2 per cent of zinc.

The alloy is not very vigorously attacked by the common acids, especially by nitric acid, nor by potassium or sodium hydroxide, although all of these reagents act upon it more or less, especially upon warming. Aqua regia dissolves it very readily. From a solution of the alloy the hydroxides of gallium and indium may be precipitated together by ammonium hydroxide in the presence of ammonium chloride,—a method of separation from zinc first worked out by Lecoq de Boisbaudran.†

Other procedures suggested by him are the separation of gallium from indium by treating a solution containing them with potassium or sodium hydroxide in excess, which dissolves the gallium hydroxide,‡—a method followed by us with fair success; and the separation from aluminium, chromium and beryllium, elements which form a group with gallium because their hydroxides are not only precipitated by ammonium hydroxide in the presence of ammonium chloride, but are soluble in sodium or potassium hydroxide, the separation being accomplished by making the alkaline solution of the hydroxides

* Hillebrand and Scherrer, Jour. Indust. and Eng. Chem., viii, 225. (This article appeared after our paper had gone to press—authors.)

† Compt. rend. (Paris), xciv, 1628.

‡ Ibid., xciv, 410.

strongly acid with hydrochloric acid and precipitating as the ferrocyanide.*

Gallium may be precipitated electrolytically by passing a current through an alkaline solution containing the element.† By this method gallium may be separated from indium, as our experiments have shown, practically no spectrographic evidence of indium being found in the product.

A fractional crystallization of the ammonium-gallium and the ammonium-indium alums has resulted after six crystallizations in a marked separation, the ammonium-gallium, at the less soluble end of the series, giving no flame test for indium, while the ammonium-indium alum, at the more soluble end, gave abundant evidence of indium in the flame. This method will be studied more in detail with the substitution of other alkalies for ammonium. The fact that gallium and indium are alum-forming elements makes this method promising for the removal of the non alum-forming elements which may be associated with them, and this possibility also will be further investigated.

The results obtained by purely physical processes will now be presented. Since no data on the boiling point of gallium could be found the following experiments were performed. A transparent silica tube, of internal diameter 0.7^{cm} and about 30^{cm} long, was first sealed off round at one end by fusion in an oxygen-illuminating gas flame. After introducing about 0.4 cm³ of the alloy, the tube was joined by sealing-wax to a long glass tube which led to a Gaede rotary mercury pump. The fused end of the tube where the alloy was situated was heated red hot for three hours with an ordinary blast flame while the pump was kept in action and the sealing wax was cooled by running water. The silica tube was nearly horizontal and the pressure in the glass tube was less than 0.0005^{mm}. This process removed all the zinc and other elements of relatively low boiling points but the gallium-indium alloy showed no signs of boiling. A bulb made from a silica test-tube was then fused to the end of a new quartz tube and the liquid globule which had not distilled in the previous heating was dropped into the bulb. While the pump and ordinary blast flame were kept going the bulb was also heated very cautiously with an oxygen-illuminating gas flame. The alloy then disintegrated with violence, shooting very fine particles of the liquid and a gray powder for a distance of 15^{cm} along the axis of the tube. Even when the silica bulb was dazzling white and began to cave in there remained a globule of metal which

* Compt. rend., xciv, 1228, 1439.

† Schucht. Chem. Ztg. (1880), 292; Erlich, *ibid.* (1885), 78; Kunert, *ibid.* (1885), 1826.

did not appear to diminish in mass on continued, intense local heating. This globule was subsequently burned in the carbon arc and the spectrogram showed that it was nearly pure gallium. As might be expected from the tabulated boiling points (at 76^{cm} pressure) most of the copper (b. p. 2310° C.) had not been driven off. Not a trace of lead (b. p. 1525° C.) could be detected. The amount of indium remaining was very small. It seems safe to conclude that the boiling point *in vacuo* of pure gallium is greater than 1600° C. and that prolonged heating in a suitable furnace at a temperature of about 1800° C. would effect a complete separation of indium from the alloy.

The density of the specimen was found to be 5.91 grams per cubic centimeter at 20° C., the value given in the standard tables being 5.95. The smaller value cannot be accounted for on the ground of contamination with silicon from the walls of the tube because this hypothesis is not consistent with the spectroscopic evidence. The melting point of the globule was not absolutely sharp but the metal consistently fell through a platinum ring, of smaller diameter than the solid disc, at a temperature of 29.5° C. As recorded by other observers, the metal remained liquid at 0° C. and showed no signs of congealing at the expiration of several hours. It may be of interest to note that when, on different occasions, small globules of the fairly pure metal and very impure alloy were partially volatilized in the electric arc, there usually remained on the positive carbon a grayish white, vitreous mass having a definite crystalline structure.

Notwithstanding the fact that a thorough investigation of the spectroscopic properties of gallium is now in progress, it may not be premature to record the results already obtained in the process of general orientation. The alloy was volatilized in a direct current arc (110 volt mains) with regraphitized Acheson graphite electrodes. The spectrograph contains an excellent concave grating (by Anderson) of 1 meter radius of curvature and is an improved form of the instrument designed and made by one of us in the year 1904.* The dispersion is such that 1^{mm} includes, on the average, 25.25 Å in the first order. Since the camera covers the interval from 2000 Å to 7600 Å, the identification of ultra-violet lines is facilitated by the superposition on the first order of the second and third orders. The films used were made to order through the kindness of Dr. C. E. K. Mees, and they are easily sensitive from 2000 Å to 7500 Å. The wave-lengths given below are highly tentative. The first negative of the alloy (taken January 22, 1916) brought out the following facts which have been sub-

* See "Atlas of Absorption Spectra" by H. S. Uhler and R. W. Wood, Carnegie Institution of Washington, Publication No. 71, May, 1907.

sequently verified by numerous exposures with much purer material in the crater of the arc. There is a new band spectrum due either to gallium or to gallium oxide (but very probably due to the gallium molecule) the wave-lengths of the heads of which are roughly 3889, 3778, 3677, 3586 (?), 3495, and 3415. The head near 3586 is partially concealed by the 3590 band usually ascribed to cyanogen. The band commencing at 3889 is by far the strongest and has a very sharp, well-defined edge. The intensity of the successive bands decreases as the wave-length becomes smaller. Moreover, the heads of the fainter bands are not sharp, but this may be due to underexposure. On the other hand, the individual bands shade off toward the red. The dispersion and resolving power are so low that there seems to be no separation of the bands into fine lines. These bands extend a relatively long distance and appear, at first glance, to form a continuous background to the entire region from 3415 to 4000. The cyanogen bands, on the contrary, show fine line structure even in the first order.

A series of eleven lines occurs between 3890 and 4030. These lines are comparatively fine and close together, and separate more and more as the frequency increases. The group probably constitutes the heads of a set of fine bands which are narrow and shade off toward the less refrangible side. Various careful tests show that indium is not responsible for the production of any of the bands mentioned above. Both sets of bands seem to be best developed when the gallium is first heated in the arc and the metallic vapor is evolved copiously.

In addition to the lines recorded by earlier investigators, the negatives of the purest specimens of gallium which we have so far been able to produce contain lines at $\lambda\lambda$ 2259, 2294, 2338, 2371, and 2418. These lines have the character of the heretofore known gallium lines and they certainly do not pertain to any of the impurities such as copper, indium, lead, silver, tin, zinc, etc. An attempt to discover a hypothetical ultra-violet absorption spectrum of the vapor of gallium failed. It is highly probable that this negative result was due to the fact that it was not feasible to heat the large silica bulb used to a higher temperature than was produced by the flame of a Meker burner. As soon as possible the wave-lengths of the gallium lines will be accurately determined by means of a 21 ft. grating so that the constants of the series formula may be calculated independently of the analogous data for aluminum, thallium, indium, etc.

The authors wish to make acknowledgment to Dr. W. F. Hillebrand of the Bureau of Standards, who first called their attention to the existence of this alloy.

Yale University, New Haven, Conn., March, 1916.