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THE PURIFICATION OF GALLIUM BY ELECTROLYSIS, AND THE COMPRESSIBILITY AND DENSITY OF GALLIUM.

BY THEODORE W. RICHARDS AND SYLVESTER BOYER.

Received October 29, 1918.

The method of separating gallium from indium by means of the different solubilities of the hydroxides in caustic alkali, recommended by various authorities, was tested without success. The separation was found to be so incomplete that several per cent. of indium remained in the gallium at least under the conditions used in our work, and it seemed clear that this difference in solubility is not enough to effect a complete separation. Much more promising results were obtained by the electrolytic method. Gallium occupies a place in the electrolytic series between indium and zinc. It is far less easy to deposit than indium, but, on the other hand, much more easy to deposit than zinc. By carefully regulating the hydrogen-ion concentration and current density it was possible to deposit practically all of the indium with only a little gallium; and thereafter most of the gallium could be separated in a slightly acid solution without the appearance of an important amount of zinc. Gallium obtained in this way from material which had previously been purified by the hydroxide method, melted at a temperature as high as 30.8°, a higher melting point (indicating a purer substance) than is recorded anywhere in the literature. The metal obtained by the hydroxide process, without electrolysis, melted at a temperature as low as 26.9°. Time has as yet been lacking for making complete spectroscopic and other tests of this material in order to confirm its complete purity, but enough has been done to show that this method is a very satisfactory and convenient one. Because of its obvious advantages it must have been employed before by others, but no early mention has as yet been found of it. Simultaneously and independently it has been tested by Dennis and Bridgman and has just been published in their interesting article on gallium.[1]

Having thus prepared gallium of substantial purity, we proceeded to determine its compressibility, both in the solid and in the liquid condition. This was an interesting problem, since comparatively few substances have been measured in both states. Moreover, gallium has the remarkable and rare property of occupying more volume in the solid than in the liquid condition. The determination of the compressibility was desirable in order to add to the long list of elements already determined at Harvard under the auspices of the Carnegie Institution. The apparatus and principle of the method was essentially similar to that employed in other cases, but a new difficulty was encountered. As in the

[1] Dennis and Bridgman, THIS JOURNAL, 40, 1540 (1918).

case of other metals, the gallium could not, of course, be allowed to come in contact with the mercury in the piezometer, but, on the other hand, it could not be conveniently solidified in a glass tube under such an inert liquid as toluene without bursting the tube. After many more or less satisfactory devices had been tried, the best results were obtained by solidifying gallium in a glass mould, and then placing a cylinder of the solidified metal in a slightly larger short test-tube, just fitting it, and capping this with another similar still larger test-tube under the inert liquid. 23 g. of pure gallium were used in this work, and the compressibility was found to be 2.09×10^{-6}, placing gallium precisely on the curve joining the other compressibilities in the graph representing the periodic relation of this property to atomic weight. The compressibility of gallium containing several per cent. of indium as obtained by the hydroxide method was found to be somewhat less (1.97×10^{-6}). Liquid gallium was determined not only in this apparatus but also in one similar to that used for caesium.[1] The liquid was thus found to have a compressibility of 3.97×10^{-6}, a value almost exactly identical with that of mercury, and nearly twice as great as that of solid gallium, although its volume is less. The determination was made at 30°. This confirms the universal experience that solids have compressibilities distinctly less than the same substances as liquids, entirely irrespective of the volumes which they occupy. The most marked case of this kind thus far observed is that of ice.[2]

The densities also of solid and liquid gallium were determined—data which have especial interest because the expansion of gallium on freezing has been attributed by some investigators to impurity. In the first place careful determinations were made by means of a pycnometer for solids[3] of the density of the impure material (containing some indium) in the solid and liquid condition, the values found being, respectively, 5.975 and 6.166. Subsequently, when the purest material had been obtained, the determinations were repeated with equal care, giving values 5.885 and 6.081, respectively. Evidently indium had produced no essential effect upon the expansion on freezing; and even if the more carefully prepared gallium was not absolutely pure, it is evident from the outcome, by extrapolation, that the purest gallium must still possess this unusual property.

Cambridge, Massachusetts.

[1] *Carnegie Inst. Publication* **76**, 20.

[2] Richards and Speyers, This Journal, **36**, 491 (1914).

[3] Richards and Wadsworth, *Ibid.*, **38**, 222 (1916).