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PREPARATION OF PURE GALLIUM

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ABSTRACT

A method is described for the preparation of pure gallium. The principal opertions consist in (1) preparing a hydrochloric-acid solution of the metal and extracting the gallium, molybdenum, gold, iron, and thallium, together with small amounts of other elements, with ether; (2) precipitating antimony, arsenic, bismuth, cadmium, copper, germanium, gold, mercury, silver, and tin, and most of the lead, molybdenum, and rhenium, with hydrogen sulphide in an acid solution of the ether extract; (3) precipitating iron and thallium with sodium hydroxide and filtering; (4) depositing the gallium electrolytically from the alkaline filtrate; and (5) eliminating the remaining impurities by fractional crystallization of the metal. Indium and lead are the most persistent impurities, but the last traces can be removed by fractional crystallization.

Gallium (at least 99.999 percent pure) containing only very faint traces of iron, lead, and calcium, and having a melting point of 29.780 ± 0.005°C, was obtained.

CONTENTS

I. GENERAL CONSIDERATIONS AND EXPERIMENTS

To provide metallic gallium of the highest purity for use as an alloying element in the cadmium-vapor arc lamp[1] and for researches in spectroscopy, and also for a study of its physical properties, a quantity of crude gallium, containing 5 percent of indium, 0.1 percent of lead, and smaller amounts of silver, tin, and zinc, was carefully purified. In order that the method of purification devised might be of general use, the separations employed were so chosen that additional impurities, such as aluminum, antimony, arsenic, beryllium, bismuth, cadmium, calcium, chromium, copper, germanium, gold, magnesium, mercury, molybdenum, rhenium, thallium, tungsten, uranium, and vanadium would be eliminated.

For the preliminary separation of gallium from most of the other elements, extraction of the chloride with ether is quite satisfactory.

[1] F. J. Bates, BS Sci.Pap. **16**,45(1920);S371

Gallium, molybdenum, and tervalent gold, thallium, and iron in hydrochloric acid solution are almost quantitatively extracted by ether, together with small amounts of germanium, arsenic, and antimony. All of the other elements likely to be present remain almost quantitatively in the acid solution. If thallium and iron are reduced to the univalent and bivalent stages, respectively, they likewise remain in the acid solution, but their reduction is recommended only if they are present in large amount; small amounts are more easily eliminated by precipitating them in the tervalent form with sodium hydroxide. Silver (and some univalent thallium when present in large amount) is precipitated as chloride and must be removed by filtration in order to obtain a clear solution for the ether extraction. Germanium and arsenic can be removed by precipitating them as sulphides and filtering, or by distilling them as chlorides ($GeCl_4$ and $AsCl_3$). If these are not previously eliminated, they will probably be volatilized when the ether extract is evaporated. Precipitation as sulphides followed by filtration also serves to remove antimony, bismuth, cadmium, copper, gold, mercury, silver, and tin, and most of the lead, molybdenum, and rhenium.

In the method described, gallium is deposited electrolytically from a strongly alkaline solution (10 percent NaOH). Consequently, the possibility of partial purification by fractional deposition from such a solution was investigated. Solutions containing indium, lead, and gallium were electrolyzed with a current of 2 to 5 amperes at 4 to 5 volts, and the deposited metal obtained at various stages of the electrolysis was tested for impurities. There was so little difference in the amounts of indium and lead in the fractions that this means of purification was abandoned. Preliminary tests also showed that electrolysis in such solutions did not yield complete separations of silver, bismuth, indium, molybdenum, rhenium, lead, tin, thallium, iron, calcium, and magnesium. Calcium and magnesium were shown spectrochemically to be present in the deposited metal only in faint traces, no greater than those found in material obtained in a similar way when calcium and magnesium were not added to the electrolyte. It may be inferred, therefore, that calcium and magnesium were not deposited electrolytically, but that sufficient of these to give a spectrochemical test was derived from the dust of the air. Probably dust was also the source of the faint trace of iron found in nearly all of the samples of gallium that were tested spectrochemically.[2]

A more comprehensive test was then made to determine the efficacy of the precipitation of iron, thallium, etc., with sodium hydroxide followed by electrolysis of the alkaline filtrate. To a slightly acid solution of gallium chloride, containing 4 g of gallium, were added 10 mg each of aluminum, antimony, arsenic, beryllium, bismuth, cadmium, calcium, chromium, copper, germanium, gold, indium, lead, magnesium, mercury, molybdenum, rhenium, silver, thallium, tin, tungsten, uranium, vanadium, and zinc. These were added as solutions of the chlorides or sulphates because nitrates must be

[2] In an attempt to eliminate calcium and magnesium, a portion of metal was recrystallized 10 times in a small closed room that was entirely lined (floor, sides, and ceiling) with tinned steel. Spectrochemical tests showed that calcium and magnesium were eliminated but that there was a notable increase in the amount of iron. Close examination of the surface of the galvanized steel showed that it contained many small rust pits. Dust from these was probably responsible for the increase in the amount of iron. Chemical analysis showed that the iron content had increased from 0.00008 to 0. 00015 percent during the 10 crystallizations.

avoided in alkaline solutions from which gallium is to be electrolyzed.[3] Sodium hydroxide was then added until an excess of 10 g per 100 ml was present. After standing overnight, the solution was filtered and the clear filtrate electrolyzed. The deposited gallium was definitely contaminated by zinc, copper, silver, thallium, indium, tin, and lead, and showed traces of rhenium, bismuth, and molybdenum. Of these, copper, silver, tin, and bismuth can be completely removed by treatment with hydrogen sulphide prior to electrolysis, and the others can best be eliminated by fractional crystallization of the deposited metal.

Lecoq de Boisbaudran [4] obtained crystals of the metal, and later T. W. Richards and S. Boyer [5] made use of fractional crystallization for the final purification of gallium. Recently F. M. Jaeger, P. Terpstra, and H. E. K. Westenbrink [6] have made a study of the crystal structure of gallium. These authors have shown that rather large ditetragonal-bipyramidal crystals are formed from strongly undercooled molten metal, whereas smaller and very flat crystals are the rule when crystallization takes place slowly from metal that is only slightly undercooled. These two types of crystals were observed in this work, and a photograph of the largest and most perfect crystal of the first type is reproduced in figure 1.

In order to determine the efficacy of fractional crystallization, a portion of metallic gallium containing traces of indium and lead was recrystallized five times by the procedure given in section II–4, page 669. Spectrochemical tests showed a decided improvement in the purity, and 15 additional recrystallizations entirely freed the crystals from indium and lead. Further tests on a portion of gallium containing silver, gold, indium, lead, platinum, tin, thallium, and zinc showed that fractional crystallization tends to eliminate all of these, but that faint traces of platinum and gold, especially the latter, often are very difficult to remove. Fortunately, gold is easily removed by a preliminary precipitation with hydrogen sulphide, but platinum must be considered as a possible contaminating element in the deposited metal because of attack on the electrodes during electrolysis.

II. METHOD FOR THE PREPARATION OF PURE GALLIUM

1. OUTLINE OF THE PROCEDURE

On the basis of the foregoing considerations, the procedure outlined below has been adopted for the preparation of pure gallium. The steps and the effect of the various operations, if applied successively to a solution containing gallium, aluminum, antimony, arsenic, beryllium, bismuth, cadmium, calcium, chromium, copper, germanium, indium, iron, lead, magnesium, mercury, molybdenum, rhenium, silver, tin, tungsten, uranium, vanadium, zinc, and tervalent gold, iron, and thallium, are as follows: (1) The first ether separation concentrates gallium, molybdenum, and tervalent iron, thallium, and gold in the ether; small quantities of all of the others may also be expected to accompany the gallium. (2) Precipitation by hydrogen sulphide in acid solution followed by filtration removes all of the cadmium, copper, silver, tin, germanium, antimony, bismuth, arsenic,

[3] H. S. Uhler, Am. J. Sci. [4]43, 81(1917).
[4] Compt. rend. 83,1044(1876).
[5] J. Am. Chem. Soc. 43,281(1921).
[6] Koninklijke Akad. Wetenschappen Amsterdam, Proc. of Section of Sciences, 29,1193(1926).

mercury, gold, and most of the lead, molybdenum, and rhenium. The solution, in addition to gallium, may now contain small quantities of indium, iron, zinc, calcium, aluminum, magnesium, thallium, uranium, beryllium, chromium, vanadium, tungsten, lead, molybdenum, and rhenium. The last three may remain because of incomplete precipitation by hydrogen sulphide. (3) A second ether extraction more completely removes elements other than molybdenum and tervalent thallium and iron. (4) Precipitation by sodium hydroxide and filtration removes iron, thallium, and probably the traces of uranium and chromium which may still remain, and may leave the gallium associated with traces of indium, zinc, calcium, aluminum, magnesium, beryllium, vanadium, tungsten, lead, molybdenum, and rhenium. (5) Electrolysis in a 10 percent solution of sodium hydroxide deposits gallium, indium, zinc, lead, and possibly traces of molybdenum and rhenium. (6) Fractional crystallization of the metal frees it from the remaining impurities.

2. PREPARATION OF THE SOLUTION FOR ELECTROLYSIS

If a quantity of gallium other than that specified in the directions which follow is used at the start, corresponding changes in the volumes of solutions and quantities of reagents should be made.

Dissolve 60 g of the impure metal in a mixture of 200 ml of water and 100 ml of hydrochloric acid. Use a covered 1.5-liter beaker and set it in a vessel containing cold water to retard the rapid initial reaction. Add 100 ml of hydrochloric acid to the resulting solution and evaporate to a sirup. Again add 100 ml of hydrochloric acid and evaporate to a sirup. Transfer the sirupy solution of gallium chloride to a 2-liter separatory funnel with the aid of not more than 150 ml of diluted hydrochloric acid (1+1).[7] Add 1 liter of ether, cool, shake cautiously at first and then vigorously for 2 or 3 minutes. After the contents of the funnel have separated into two distinct layers, withdraw the acid solution, and wash the ether by adding 50 ml of cool diluted hydrochloric acid (1+1), shaking thoroughly, and withdrawing the acid layer. Repeat the washing 7 times, and reserve the combined washings and acid solution. Now withdraw the ether extract and allow it to stand in a warm place until most of the ether has evaporated. Concentrate this solution as far as possible on the steam bath and add an excess of hydrogen peroxide (30 percent) to oxidize organic compounds. Destroy the excess of hydrogen peroxide by heating on the steam bath for about 1 hour, and then dilute the solution to 3-liters with diluted hydrochloric acid (2+98).

Heat the solution nearly to boiling and treat it with a rapid stream of hydrogen sulphide. Allow it to stand overnight, filter through a paper of close texture, and wash the paper and precipitate with diluted hydrochloric acid (2+98) saturated with hydrogen sulphide. Add 400 ml of hydrochloric acid to the filtrate, and evaporate it to a volume of 1 liter. Treat the solution with hydrogen sulphide, and filter if a precipitate appears. Evaporate the filtrate to a sirup, oxidize with hydrogen peroxide, and heat to destroy the excess of peroxide. Repeat the ether extraction and washing of the ether as previously described.

[7] This denotes one volume of hydrochloric acid, specific gravity 1.18, diluted with 1 volume of water. Diluted hydrochloric acid (2+98) means 2 volumes of the acid, specific gravity 1.18, diluted with 98 volumes of water. If no dilution is specified, the concentrated acid is intended.

FIGURE 1.—*Crystal of gallium, weighing 2.2 grams.*
Approximately 4 times actual size.

Cautiously expel the ether from this second ether extract, and oxidize organic compounds by heating with hydrogen peroxide. Dilute the solution to about 500 ml, add a 50-percent solution of sodium hydroxide until the solution is just alkaline to litmus, and then 200 ml in excess. Adjust the volume of the solution to 1 liter, digest on the steam bath for ½ hour, and allow it to stand overnight at room temperature. Filter through a paper of close texture, wash with a 1-percent solution of sodium hydroxide, and nearly fill a 1-liter platinum dish with the filtrate. (The small portion of filtrate and washings remaining is reserved to be added to the dish later).

3. ELECTROLYSIS

Electrolyze at 2 to 5 amperes and 4 to 5 volts, using the platinum dish as the anode and a platinum helix as the cathode. Immerse a 25-ml beaker under the helix in the electrolyte to receive the globules of gallium as they drop from the cathode. After most of the gallium has been deposited (30 to 40 hours), discontinue the current, and evaporate the electrolyte in the platinum dish on the steam bath to such a volume as will permit the addition of the reserved alkaline filtrate. Add the reserved solution and continue the electrolysis until no more gallium is deposited (30 to 40 hours).

A no. 18 (B. & S. gage) platinum wire, twisted into a helix, serves satisfactorily as a cathode. The total length of wire immersed in the electrolyte should be from 8 to 10 cm, but may be less. The small amount of gallium that remains attached to the cathode is preferably dissolved in hydrochloric acid and combined with other residual gallium for further purification. (See sec. V.)

At the end of the electrolysis, transfer the gallium from the beaker to a small Erlenmeyer flask. To remove most of the alkali, wash the metal 10 times by shaking it in the small flask with hot water and then decanting the water. In a similar way wash 3 or 4 times with ethyl alcohol. Remove the last of the alcohol by drying over sulphuric acid in a desiccator or by drawing a stream of clean dry air through the flask. Stopper the flask and reserve the gallium for further purification by fractional crystallization.

4. FRACTIONAL CRYSTALLIZATION

To the gallium in the small flask add sufficient distilled water to cover the metal to a depth of about 0.5 cm, warm to about 50° C, and then add 5 to 10 drops of hydrochloric acid. Transfer the contents of the flask to a 50-ml beaker, set the beaker in ice water, and, when the crystals appear, pick them out of the molten metal with the aid of glass-tipped tweezers. Continue picking out the crystals until only a small globule (0.5 to 1.0 g) of metal remains. Combine and melt the crystals, and by the same process repeat the crystallization until crystals of the desired purity are obtained. Reserve the hydrochloric acid solution and the small globules of uncrystallized metal for further purification. During the last crystallization, drop the crystals into cold alcohol and wash two or three times with alcohol by decantation. Dry the crystals by drawing clean dry air over them or by placing them in a desiccator over sulphuric acid. Preserve the crystallized metal in a stoppered flask.

If economy of metal is no object and it is desired to obtain a small portion of very pure crystals, the metal may be crystallized in 4 approximately equal portions and only the first 2 portions taken for the next crystallization. If this process is repeated many times, the yield is small, but pure crystals are obtained in less time than by the method just outlined.

III. TEST OF THE PROCEDURE OUTLINED

The procedure was tested by applying it to a hydrochloric-acid solution of gallium to which had been added sufficient zinc and indium to correspond to an impurity of 1 percent of each, sufficient lead, cadmium, copper, thallium, tin, aluminum, calcium, magnesium, germanium, antimony, bismuth, arsenic, and molybdenum to correspond to an impurity of 0.1 percent of each, and sufficient gold, silver, mercury, rhenium, beryllium, chromium, vanadium, uranium, and tungsten to correspond to an impurity of 0.01 percent of each. The spectrochemical report on the metal as obtained by following all the steps of the procedure except fractional crystallization showed: calcium, trace; indium, trace; lead, trace; silver, faint trace?; magnesium, faint trace; and iron, faint trace. Ten crystallizations of this metal eliminated practically all indium, magnesium, lead, and silver, but 20 to 25 recrystallizations were necessary to eliminate indium and lead so completely that they could not be detected with the apparatus used by the spectroscopy section of the National Bureau of Standards.

IV. PURITY AND YIELD

Tests of the purity of the metal at the various stages were made spectrochemically by B. F. Scribner of the spectroscopy section. A stigmatic concave spectrograph was used,[8] and the spectra were examined for the sensitive lines of Ag, Al, As, Au, Ba, Be, Bi, Ca, Cb, Cd, Co, Cr, Fe, Ge, Hf, Hg, In, Ir, K, Li, Mg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Re, Rh, Ru, Sb, Si, Sn, Sr, Ta, Th, Ti, U, V, W, Zn, and Zr. In most cases the evidence for silver in the samples was questionable because of the presence of this element in the copper electrodes. In all cases the scale used in qualitatively designating the amounts of impurities is: *trace, very weak, weak, moderate, strong,* and *very strong.* The designation "*faint trace*" is used only when the most sensitive lines of the impurity appear near the limit of visibility.

Gallium originally containing 5 percent of indium, approximately 0.1 percent each of lead, zinc, and silver, and traces of calcium and tin was subjected to all of the treatments described in the foregoing procedure. Ten crystallizations of the electrolytically deposited metal yielded crystals which by spectrochemical tests showed only weak lines of indium and calcium and faint traces of lead and silver. Fifteen additional crystallizations yielded crystals in which *very faint traces* of only iron, lead, and calcium were detected. This metal showed a melting point[9] of $29.780 \pm 0.005°$ C.

The quantity of iron was determined chemically by treating a chloride solution of 3 g of this gallium with potassium thiocyanate,

[8] Described by W. F. Meggers, C. C. Kiess, and F. J. Stimson, BS Sci. Pap. 18, 244 (1922);S444, and by W. F. Meggers and Keivin Burns, BS Sci. Pap. 18, 191 (1922); S441.
[9] Determination described in J. Research, NBS 13,673(1934);RP735.

shaking with amyl alcohol, and comparing the color in the amyl alcohol with that obtained by treating a very dilute standard solution of iron in a similar way. Only 0.00009 percent of iron was found. No attempt was made to determine calcium because it was considered that the amount was too small for detection by chemical means. In order to eliminate the uncertainties concerning the presence of silver and copper and to get an approximation of the amount of platinum, 23 g of the metal was dissolved, and the resulting dilute-acid solution treated with hydrogen sulphide. After standing 3 days, more hydrogen sulphide was added, and the sulphides and sulphur were collected on a filter paper. This was gently ignited in a porcelain crucible, digested with hydrochloric acid, diluted to 25 ml, and treated with hydrogen sulphide as before. The small precipitate was collected on a filter paper, gently ignited, and weighed. The weight was only 0.2 mg more than that obtained on a blank on the reagents. This shows that the combined percentages of platinum, silver, and copper was less than 0.001. These tests indicate that the metal was at least 99.999 percent pure.

A lot of 53 g similarly prepared at a later time from impure metal from a different source was equally pure and had the same melting point (29.780° C).

By the procedure outlined it is not possible to obtain all of the gallium in the highest state of purity. An example will show approximately how the gallium is distributed. In the last preparation of pure gallium, 65 g of impure metal containing about 3 percent of indium was taken at the start. Of this 4.5 g passed into the acid extract and washings from the first ether extraction, 4.3 g passed into the acid extract and washings from the second ether extraction, and 2 g remained in the electrolyte. The metal obtained by electrolysis weighed 52 g. This was recrystallized 20 times and yielded 35 g of pure crystals and 17 g of uncrystallized metal. Even the latter was sufficiently pure for most purposes, as is shown by the fact that spectrochemically only the following impurities were reported: Indium, moderate; silver, trace; and faint traces of gold,[10] calcium, and lead.

V. RECOVERY OF RESIDUAL GALLIUM

As has already been stated, a certain amount of gallium remains in the acid during ether extractions, some remains in the electrolyte, and some remains as uncrystallized globules in the process of fractional crystallization. The procedure for the recovery of gallium from the acid solutions obtained in the ether separations depends upon the impurities in the original material. If considerable quantities of such elements as zinc, magnesium, manganese, nickel, or cobalt are present, precipitating the gallium with a slight excess of ammonium hydroxide and filtering will eliminate a large proportion of all of these. If elements such as gold, silver, copper, antimony, tin, etc., are present, these are removed by precipitating with hydrogen sulphide and filtering. If indium is the preponderant impurity (as is usually the case), most of it is eliminated by precipitating it with an excess of sodium hydroxide and filtering. If the amount of indium is large, the precipitate should be dissolved and the precipitation and filtration repeated. After the preliminary separations of the impurities

[10] Derived from the dish in which the electrolysis was made.

have been made as indicated, the gallium is converted to the chloride, which is then ready for purification by the procedure already described. The volumes of the solutions at the various stages are kept proportionately smaller in accordance with the quantity of gallium. Usually it is more convenient to set these solutions aside and add them to the hydrochloric acid solution of the next portion of gallium to be purified.

The gallium in the electrolyte is recovered by acidifying the solution, precipitating with a slight excess of ammonium hydroxide, and filtering. The precipitate is washed with hot water and dissolved in hydrochloric acid. The solution needs no further purification and may be electrolyzed as described in the procedure but in a correspondingly smaller volume. In practice, it is usually set aside and added to the next portion of solution that is to be electrolyzed.

The uncrystallized globules may be united and partially purified by fractional crystallization, or they may be dissolved and again put through the whole process of purification.

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