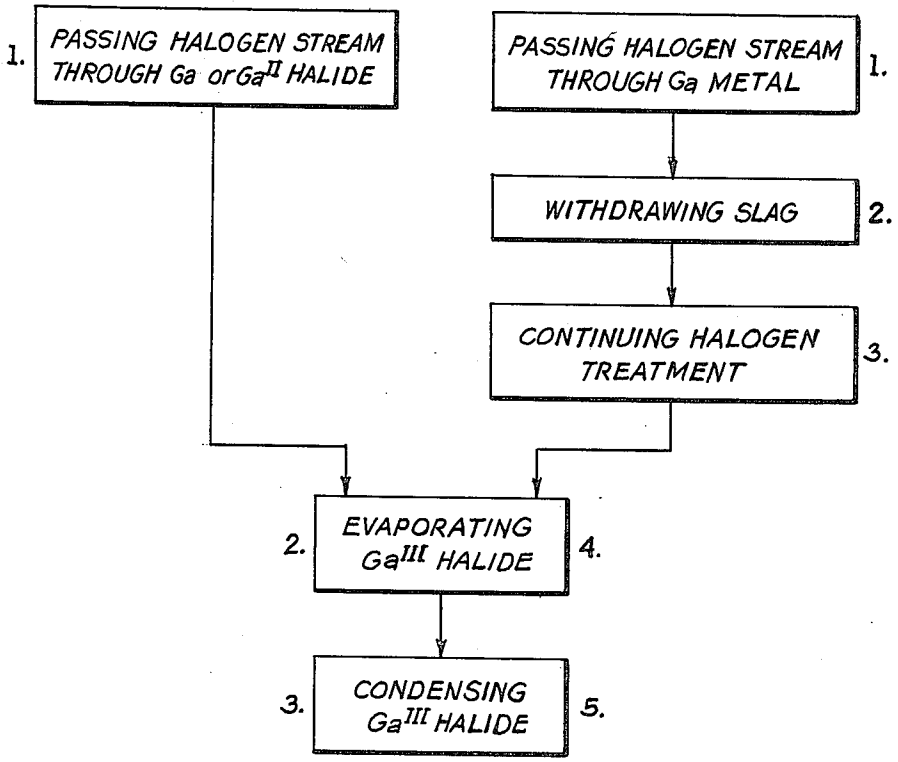
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PURIFICATION OF GALLIUM BY HALOGENATION AND ELECTROLYSIS

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Fig.1



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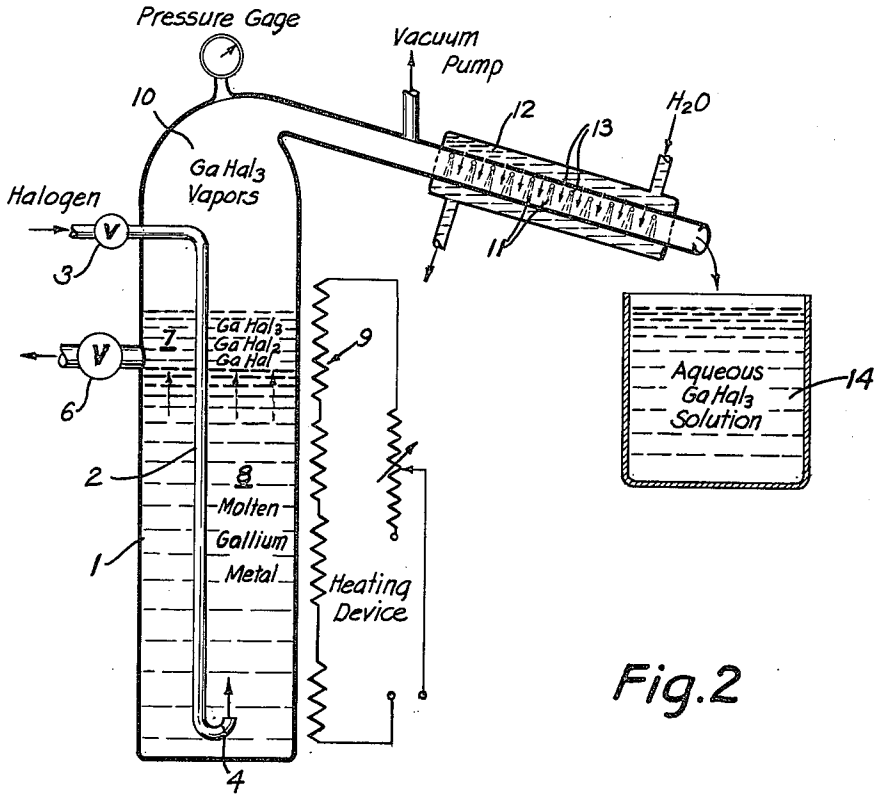


Fig.2

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PURIFICATION OF GALLIUM BY HALOGENATION AND ELECTROLYSIS

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This invention relates to the purification of gallium and, more particularly, to an improved process for producing very pure gallium metal via highly purified gallium halides.

Metallic gallium generally contains various impurities among which the principal ones are zinc and lead; other elements, such as aluminum, vanadium, copper, boron, sodium, iron, and silicon are often contained in gallium in varying proportions, as they accompany zinc and/or lead. Gallium metal produced by the known processes generally contains 99% of Ga, while a purity of 99.9% may be attained when the metal is produced by the electrolysis of aqueous solutions of alkali metal gallates, such as sodium gallate $NaGaO_2$ or Na_3GaO_3.

However, gallium is at present being used in the field of electronics, for instance, in intermetallic compounds, together with elements of Group V of the Periodic Table of Mendeleev, in the semi-conductior field which uses much higher degree of purity than have been attained with the known processes.

It is well known that, for example, intermetallic compounds, such as Ga_5Sb_3 and the like, constitute semiconductive materials the electro-conductive properties of which can be predetermined with the necessary accuracy only if the impurities contents of the components of this type of intermetallic compounds are in the order of 10^{-4} to 10^{-7} parts or even less for every part of intermetallic compound.

The known purification processes involving the repeated recrystallization of the metal or the distillation of an anhydrous gallium halide are cumbersome and permit the attainment of only relatively limited degrees of purity, the metal ultimately obtained by those known processes still containing impurities contents in the order of 10^{-3} parts in every part by weight of metallic gallium.

Thus, for instance, gallium of the last-mentioned relatively low degree of purity must be obtained by frequently repeated distillation of anhydrous gallium trichloride, as described in Gmelin's "Anorganische Chemie," vol. 36, 8th Edition, page 75.

It is, therefore, an object of our invention to provide an improved process of purifying a gallium halide to such a degree, and in a simple manner, that a highly pure metallic gallium suitable for uses of the above-mentioned type, in particular in the electronic field, can be obtained therefrom.

It is, more particularly, an object of our invention to produce metallic gallium having an impurity content of from 10^{-5} or only a few times of 10^{-6} down to 10^{-7} parts in every part by weight of gallium metal.

It is a further object of our invention to produce a gallium trihalide of a purity above 99.99% by weight, which constitutes an excellent starting material for the production of highly pure gallium for electronic uses therefrom.

The attached drawings assist in the explanation of the present invention, FIGURE 1 being a flowsheet, and FIGURE 2 being a schematic representation of suitable apparatus.

The objects are achieved by the process according to the invention, which permits first of all the production

of a highly pure gallium trihalide by the steps illustrated in the accompanying flowsheet, as follows:

(1) Passing a stream of a substantially anhydrous halogen through a reaction material consisting of at least one gallium halide in which gallium has a valence below three, so as to convert said halide to the corresponding gallium trihalide,

(2) Heating said reaction material sufficiently to evaporate said gallium trichloride from said material, and

(3) Condensing the evaporated gallium trihalide so as to obtain the latter with an impurity content below 0.01% by weight.

The gallium starting material which is to be purified may consist of gallium dichloride, gallium dibromide, gallium diiodide, or gallium fluoride, having an impurity content above 0.01% and often as high as 1% by weight, the impurities being of the nature mentioned further above.

The gallium halide material consisting of at least one gallium halide containing gallium of a valence below three, which material may also consist of mixtures of several gallium halides, is purified by distillation in a stream of anhydrous halogen at a temperature above the boiling or sublimation temperature of the respective gallium trihalide. The evaporation of the gallium trihalide formed during the reaction of the gallium material with the anhydrous halogen is facilitated by working under reduced pressure.

According to a preferred mode of operating the process according to our invention in practice, the gallium trihalide to be evaporated from the gallium material to be purified may be produced in the latter material by reacting a batch of liquefied gallium metal with the halogen.

This mode of operation comprises the steps of:

(1) Passing a stream of anhydrous gaseous halogen through a molten metallic gallium containing impurities up to about 1% by weight and higher, until about 1 to 15% by weight of the initial amount of metallic gallium have been converted to gallium halide in which gallium is of a valence below three, and which gallium halide forms a slag layer floating on the molten gallium and containing the major portion of the impurities contained in the initial gallium,

(2) Removing this slag layer from the molten gallium therebelow,

(3) Further passing said gaseous halogen through said molten metal so as to convert the latter gradually into the corresponding gallium trihalide, and

(4) Removing the latter from the reaction by transforming the same to the vapor phase and

(5) Condensing the gallium trihalide vapors, thereby obtaining a starting material for the production therefrom of highly pure gallium metal by conventional methods, which starting material has itself an impurity content in the order of less than 10^{-4} to 10^{-6} parts by weight for every part of gallium trihalide.

We have thus found that, in contrast to the difficulties of purification encountered in the known methods of distillation of a gallium halide, purification becomes unexpectedly easy to achieve and permits reaching the above-mentioned degree of purity when it is practiced in a halogen stream, preferably under a pressure below one atmosphere. Moreover, this purification becomes particularly effective when the gallium trihalide is formed in situ by the action of halogen on metallic gallium while the purification proceeds.

The starting halide used in carrying out the present invention may be a gallous and/or gallic fluoride, chloride, bromide or iodide; or if desired a mixture of several halides may be used. For economic reasons it is particularly advantageous to use gallium chloride.

The melting points of $GaCl_2$ and $GaCl_3$ are 164° C. and 75.5° C., respectively; their boiling points, under a pressure of 1 atmosphere, are 535° C. and 215° C. The distillation of gallium trichloride can thus take place at a temperature below 215° C., when carried out under reduced pressure. When the starting material is a molten gallium chloride in which the valence of gallium is below 3, and through which chlorine is passed, gallium trichloride distills as it forms, provided that pressure within the apparatus used is equal to or lower than the vapor pressure of $GaCl_3$ at the temperature of the bath of lower gallium chloride, which bath temperature must be higher than or equal to 164° C. Favorable industrial results are obtained at distillation temperatures comprised between 164° and 200° C.

In the case where the starting material is constituted by or contains a major portion of gallium trichloride, the distillation may be effected at lower temperatures between 75.5° C. and 215° C. under corresponding pressures sufficiently below and not exceeding 1 atmosphere, to ensure a satisfactory rate of evaporation of $GaCl_3$.

The above-mentioned preferred mode of carrying out the present invention comprises the steps of treating with chlorine the metallic gallium to be purified, so that the metal is transformed into gallium dichloride and then into gallium trichloride, and subsequetly distilling the latter, whereupon the resulting distillate of $GaCl_3$ is redissolved in pure water. The highly pure $GaCl_3$ solution thus obtained is then electrolyzed by a known method for producing very pure gallium. Such method is described by H. C. Fogg, Trans. Am. Electrochem. Soc. 66 (1934), 110.

It is an important step in this mode of operation to discard, at the beginning of the operation, the non-metallic slag which forms on the surface of the molten gallium as soon as a relatively small portion of the metal has been transformed into gallium dichloride. In fact, we have discovered that an important portion of the impurities, especially zinc, lead, and copper, are gathered in this slag.

According to the nature and proportion of impurities present in the starting gallium, the withdrawal of this slag should take place as soon as a fraction of from about 1 to 15% by weight of the metal has been transformed into the lower gallium halide. Usually, when the starting gallium metal is of a purity of 99% to 99.9% by weight, the proportion of halogenated metal—at the time when it becomes advantageous to withdraw the slag from the molten reaction material—is about 3 to 7%, and on an average in the vicinity of 5% by weight of the starting metal.

The amount of gallium dichloride formed can easily be determined by controlling the amount of consumed chloride. The percentage of chlorinated gallium can further be controlled by the decrease of the border level of the metallic phase and the slag which can be particularly well observed if the reaction apparatus is of glass.

During the treatment of the metallic gallium to be purified with a halogen, the exothermic reaction of forming lower gallium halides evolves generally sufficient heat to render heating of the reaction mixture unnecessary; thus in the case of chlorination of gallium to the dichloride, the temperature rises by itself up to about 200° C. However, as soon as the whole amount of gallium metal has been transformed into the dihalide, the formation of trihalide and the continuous distillation of the latter requires a supply of additional heat; therefore, in this step of the process, according to our invention, the reaction chamber must be heated.

The process, according to our invention, may be carried out in any suitable type of known apparatus for distillation under simultaneous passage of a gas or vapor stream. A particularly suitable apparatus comprises a reaction chamber constituted by a vertical tube, closed at its lower end. A pipe for introducing the gaseous halogen passes into the interior of the tubular chamber and opens near the bottom zone of the latter; the upper part of the reaction chamber is connected to a refrigerated or air-cooled condenser.

The preferred mode of operating the process according to our invention can be carried out, for instance, in the apparatus illustrated in FIGURE 2 of the drawings. In this figure, reference numeral 1 designates a tubular reactor provided with a halogen feeding tube **2** and valve means **3** for controlling the rate of halogen flow. The tube **2** opens in the bottom zone of reactor **1** at **4**. A tapping outlet **5** with pressure control valve **6** permits withdrawal of the initially formed first portion of slag **7** which forms on top of the molten gallium metal **8** and contains the larger portion of the impurities initially contained in the metal. The temperature in reactor **1** can be increased during the evaporation step by conventional heating means, an electrical heating device **9** being shown. In the dome **10**, gaseous gallium trihalide gathers and passes into the condenser **11** provided with cooling means **12** and water spraying means **13**.

The aqueous solution of gallium trihalide flows into vessel **14** in which it can be subjected to electrolysis in a manner known per se in order to obtain highly pure gallium metal.

In order to further illustrate our invention, there shall now be described hereunder a number of examples, which are, however, not to be considered as limitation of the scope of said invention.

Example I

One kilogram of gallium metal containing as impurities

	Grams
Zn	22.7
Pb	15.7
Al	0.06
Cu	0.02
V	0.007

is introduced into a glass-walled reactor **1** of the apparatus illustrated in FIGURE 2 and heated to 30° C., so as to melt the metal. Dry gaseous chlorine is then passed through the liquid metal at a flow rate of about 2 g. per minute, for about 25 minutes, at which rate the chlorine is almost completely absorbed. The flow rate can easily be adjusted by observing the escape of chlorine bubbles on the liquid surface. The temperature in the reactor rises to about 200° C. without external heating due to the exothermic reaction between gallium and chlorine under formation of $GaCl_2$.

As soon as about 5% (50 grams) of the metal has been converted to gallium dichloride, which can be determined by observing the lowering of the level of liquid metal below the slag being formed, the slag layer **7** is withdrawn from reactor **1** through trap **6**. The metallic liquid in the reactor still contains as impurities per kilogram of this partially purified gallium:

	Grams
Zn	0.007
PB	0.375
Al	0.06
Cu	0.005
V	<0.005

The introduction of chlorine gas via tube **2** is continuous until all gallium metal is converted to $GaCl_2$. Concurrently $GaCl_2$ is being converted to $GaCl_3$, and by reducing pressure in the reactor 1 to 100 torrs (1 torr=1 mm. of Hg.) and heating the reactor to maintain the temperature in its interior at about 180° C., the gallium trichloride is evaporated as it is formed in the reaction material. It distills via dome **10** into condenser **11** where it is deposited in small white needles. The

solid gallium trichloride still contains the following impurities:

Zn	Less than 0.001 gram or <1 p.p.m.
Pb	Less than 0.001 gram or <1 p.p.m.
Al	Less than 0.012 gram or <12 p.p.m.
Cu	Less than 0.001 gram or <1 p.p.m.
V	Less than 0.005 gram or <5 p.p.m.

By spraying the gallium trichloride with water, there is obtained an aqueous gallium trichloride solution which is then electrolyzed as described by H. C. Fogg in "Trans. Am. Electrochem. Soc." 86 (1934), page 110.

An aqueous solution of gallium trichloride containing about 200 garms of gallium per liter is electrolyzed with a voltage of 8 volts and a cathodic current density of 100 amperes per square decimeter.

Quantitative analyses of ultraviolet emission spectra reveal that the resulting highly pure gallium metal contains as impurities

	Parts per million
Zn	Less than 1
Pb	Less than 1
Al	Less than 5
Cu	Less than 1
V	Less than 5

and mass spectrographic analysis shows that none of these or any other impurities is contained in the thus obtained pure gallium metal in amounts above 10^{-7} parts (0.1 p.p.m.).

The gallium metal thus obtained is, therefore excellently suited for use in the electronic and semi-conductor art.

Example II

An excess of gallium metal containing about 99.3% by weight of Ga is brominated with the aid of a bromine-saturated stream of carbon dioxide as described in Helv. Phys. Acta 7 (1934), page 332. 1000 grams of the resulting gallium dibromide are charged into the reactor 1 of the apparatus shown in FIGURE 2.

A mixture of carbon dioxide laden with 10% by weilght of Br_2 is now passed through the liquid $GaBr_2$ at a rate of 250 g./h., while the temperature is held at 200° C., under a pressure of 100 torrs. $GaBr_3$ sublimates and deposits as $GaBr_3.3H_2O$ needles after the introduction of the necessary water through spray nozzles at 13.

The gallium tribromide is highly pure, with impurity contents similar to those given in Example I, and can be further processed to obtain highly pure gallium metal by electrolyzing its aqueous solution.

Example III

1000 grams of gallium metal having a total impurity content of about 1% and containing proportionately about the same ratios of impurities as in Example I are melted by heating to about 30° C. in the reactor 1 of the apparatus shown in FIGURE 2.

A current of iodine-laden carbon dioxide is passed through the liquid metal at a rate of 0.2 liter per minute, whereby a mixture of gallium mono- and diiodide is obtained which forms a red, viscid liquid on top of the molten gallium.

During this reaction, the temperature in the reactor is held at about 250° C.

After about 70 grams of the starting metal have been converted to the lower gallium iodides, as can be readily determined from the amount of iodine consumed, the layer of gallium iodides containing a major portion of the impurities is withdrawn.

Introduction of the iodine entrained in CO_2 is then continued at a flow rate of 0.2 liter per minute, while adjusting the temperature to 255° C. and pressure to 77 torrs. Gallium triiodide sublimates into condenser 11, where it gathers in the form of colorless needles.

This can be dissolved in water and further processed to obtain highly pure gallium metal in the manner described in Example I.

The degree of purity of the ultimately obtained gallium metal corresponds to that resulting from Example I.

Example IV

500 grams gallium trifluoride, GaF_3, are introduced into a reactor 1 of an apparatus similar to that shown in FIGURE 2, but having all walls in contact with the fluoride made of metallic copper or silver, which reactor has been charged with 500 grams of impure gallium metal and heated to 30° C. The suspension of GaF_3 in the gallium melt is then treated with a stream of fluorine gas at a flow rate of 2 g. per minute, while maintaining a temperature of 300° C. The passage of fluorine is interrupted and about 100 grams of the top layer of the melt, in which a considerable portion of the impurities of both the metal and the fluoride have gathered, is withdrawn.

Introduction of fluorine gas is then continued at a rate of 2 g. per minute, while adjusting the temperature to 350° C. and the pressure to 50 torrs. GaF_3 sublimates and is gathered in condenser 11, whereupon it is dissolved in diluted hydrochloric acid and electrolyzed to obtain a highly pure gallium metal therefrom. The impurity content of the final metal is in the same range as given in Example I.

Example V

Example I is repeated; however, a mixture of equal parts of gallium dichloride, gallium iodides, having an atomic ratio of gallium to iodine of about 1:1.5, and gallium tribromide is charged into the reactor. The mixture is treated with gaseous chlorine under the conditions described therein and a highly pure gallium trichloride is obtained, chlorine expelling bromine and iodine from the mixture.

The gallium trichloride is further processed as described in Example I.

Example VI

Example I is repeated; however, the stream of chlorine gas is replaced by a stream of nitrogen charged with bromine at a rate of 250 grams per hour. When about 5% of the liquid gallium metal has been brominated the gallium bromide step containing suspended therein the impurities is removed.

When the entire metal has been converted to gallium dibromide, the reaction vessel is heated while maintaining the flow of the bromine-containing gas, so as to maintain the temperature in the reaction zone at about 200° C. Pressure is reduced to 100 torrs. Gallium tribromide evaporates as it is formed out of the reaction zone and is deposited at room temperature as white crystals in the water-cooled condenser.

The gallium tribromide crystals are then dissolved in pure water and electrolyzed in the same manner as described in Example I.

The resulting gallium metal has a degree of purity similar to that stated in Example I.

It is understood that this invention is susceptible to modifications in order to adapt it to different usages and conditions, and, accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

What we claim is:

1. A process for producing highly pure gallium metal from impure gallium metal containing up to 1% of impurities comprised of zinc, lead, aluminum, copper and vanadium, said process comprising the steps of:

(*a*) passing a stream of an anhydrous gaseous halogen into a molten bath of the impure gallium metal, said gaseous halogen being added in sufficient amounts to convert impure gallium metal into a liquid gallium

dihalide, the amount of gallium dihalide converted being within the range of 1–15% of the initial impure gallium metal, whereby the major portion of the impurities present in said initial impure gallium metal is transferred to said liquid gallium dihalide;

(*b*) removing the impurity-laden liquid gallium dihalide from the remaining molten bath of gallium;

(*c*) passing sufficient gaseous halogen through the remaining molten gallium metal to convert all of said molten gallium into a purified gallium dihalide;

(*d*) passing additional and sufficient gaseous halogen into said purified gallium dihalide to convert all of the purified gallium halide into gallium trihalide;

(*e*) distilling said gallium trihalide under an halogen atmosphere to obtain further purified gaseous gallium trihalide; and

(*f*) condensing the further purified gaseous gallium trihalide, and converting the same to metallic gallium, thereby obtaining a metallic gallium, the impurity content of which is in the order of 10^{-5} to 10^{-7} parts by weight per part of gallium metal.

2. The process of claim 1, wherein the gaseous halogen is chlorine.

3. The process of claim 1, wherein steps (*c*) and (*d*) are effected substantially simultaneously at a temperature of 164–200° C. and at an absolute pressure of about 10 centimeters of mercury, the gallium trihalide being distilled as it is formed.

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