[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Extraction of Germanium and Gallium from Germanite. II. The Acid Extraction of Gallium

BY LAURENCE S. FOSTER, WARREN C. JOHNSON[1] AND CHARLES A. KRAUS

The methods of recovery of germanium from germanite developed by Thomas and Pugh[2] and Keil[3] involve the complete dissolution of the ore and the subsequent volatilization of germanium tetrachloride. The extraction of gallium from the residual germanium-free solution requires the handling of large volumes of liquids and the carrying out of numerous tedious separations of the remaining elements of the ore. A superior method was introduced by Berg and Keil,[4] who recover the gallium by extracting gallium trichloride from an acid solution by means of ether, but when this method is applied to kilogram lots of the ore, it has the disadvantage of being costly both in time and materials.

The pyrogenetic method of removal of germanium from germanite, described in the preceding article, leaves a black, partially-sintered residue, consisting chiefly of copper sulfide and amounting to about 75% by weight of the original ore. If these residues are boiled with hydrochloric acid, the gallium is removed completely, although only about 25% of the material is dissolved. The removal of the gallium from the extract is accomplished in six further operations involving neither special apparatus nor expensive chemicals. This method has the following advantages: (1) the necessity of completely dissolving the ore residue is eliminated; (2) the volumes of the solutions to be handled are markedly reduced; (3) the number of operations required to reach the final separation of metallic gallium is decreased; (4) loss of gallium through adsorption is minimized, eliminating reprecipitations; (5) the methods used in carrying out the precipitations lead to the formation of granular rather than flocculent and gelatinous masses, making it possible to use suction filtration in each step; and (6) all the gallium present is precipitated in one lot, making it unnecessary to recover traces of the element from many types of residues.

The Extraction Procedures

The Boiling Process.—The partially sintered residue, resulting from the removal of arsenic and germanium from germanite, is broken up and ground to pass a 100-mesh screen. One kilogram of the powder is placed in a 5-liter round-bottomed Pyrex flask, fitted with a rubber stopper carrying a small still-head. A water-cooled condenser and a large filter flask for the distillate are attached. One liter of 6 *N* hydrochloric acid is added to the flask and the mixture is refluxed for a total of twenty-two hours. Twice during this period, 150 cc. of concentrated hydrochloric acid is added to restore the acid concentration to approximately its original value. After heating for twenty-two hours, the rate of boiling is increased until distillation occurs and about 800 cc. of the acid is removed.[5] If during this process caking occurs, 500 cc. of water is added to the residue, the cake is loosened mechanically, and distillation continued until the amount of liquid left in the flask has again been reduced to a small volume.

The removal of hydrochloric acid by distillation minimizes the amount of alkali required for the subsequent neutralization, yet leaves the solution sufficiently acid to prevent hydrolysis of the dissolved salts. The cooled mixture, which contains some crystallized lead chloride, is suction-filtered. The sludge collected is washed by decantation at least five times with 200-cc. lots of 1% hydrochloric acid. The final volume of the filtrate, combined with the wash solution, need not be over 1500 cc.

The insoluble portion of the ore residue is returned to the boiling flask with 750 cc. of 6 *N* hydrochloric acid and refluxed again for five hours. After distilling off part of the acid, the mixture is filtered, the sludge is washed with a small amount of dilute acid, and the filtrate is added to the first extract. Besides gallium, the solution contains relatively large quantities of copper, lead, iron, aluminum and zinc, together with traces of many other elements.

The Efficiency of the Extraction.—The second hydrochloric acid extracts from two different lots of germanite were analyzed for gallium by a determination of the x-ray emission spectra, which gave $K\alpha_1$, $K\alpha_2$ and $K\beta_1$ lines.[6] A semi-quantitative check on the concentration of gallium was obtained by comparison with a known sample prepared to contain 0.5% of gallium oxide thoroughly mixed with ferric oxide. The intensities of the lines from the known and unknown samples showed the latter to contain about 1% of gallium in each case. Calculations made from these results indicate that the first hydrochloric acid extract contains between 99.0 and 99.8% of the total extractable gallium. Taking into account the amounts of

---

[1] Department of Chemistry, University of Chicago, Chicago, Illinois.

[2] Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924).

[3] Keil, *Z. anorg. allgem. Chem.*, **152**, 101 (1926).

[4] Berg and Keil, *ibid.*, **209**, 383 (1932).

[5] In case the germanium has not been removed completely in the earlier operations, much of the residuum will be found in the distillate.

[6] We are greatly indebted to Mr. C. M. Olson and Professor W. C. Pierce, of the University of Chicago, for these results. They carried out the experiments with an x-ray spectrograph constructed by them.

gallium reported in the ore by various workers,[7] which average around 0.5%, we may conclude further that the extraction process removes the gallium practically quantitatively. Since such a high percentage of the gallium does appear in the first extract, this conclusion appears reasonable, and certainly indicates that no more than two extractions are profitable.

Treatment of the Extract with Hydrogen Sulfide.—The combined extracts are first treated with strong sodium hydroxide solution until a small amount of a permanent green precipitate is observed (not to be confused with the crystals of lead chloride which appear as neutralization proceeds). Then enough hydrochloric acid is added to dissolve the green precipitate and to render the solution at least 0.2 *N* in excess acid. Hydrogen sulfide is introduced, the black precipitate which forms is allowed to settle and the mixture is suction-filtered. Finally, the precipitate is pressed dry with a spatula and then washed several times with small amounts of acidified water.

After the removal of the sulfides, the filtrate is tested for complete precipitation of the lead and copper. If shown necessary, the treatment with hydrogen sulfide is repeated, after the acidity of the solution has again been reduced to only 0.2 *N* in excess acid by the method outlined above.

If the acid concentration is kept at the recommended value, very little gallium is adsorbed on the sulfide precipitate, and, in general, reprecipitation is unnecessary.

The weight of the oven-dried sulfide is about 25 g. If the wash solution is concentrated by boiling before being mixed with the original filtrate, the volume of the combined solutions is kept below 2500 cc.

The Precipitation of Crude Hydrated Gallium Oxide.—As major components, the solution now contains between 4 and 8 g. of gallium, about 40 g. of iron, 30 g. of zinc, and 3–4 g. of aluminum. It is not feasible to precipitate the iron as hydroxide and the zinc as sulfide from an alkaline solution because in these processes a large percentage of the gallium is carried down by adsorption,[8] necessitating many reprecipitations. The extraction of gallium chloride by means of ether, as described by Berg and Keil,[4,9] is very convenient on a small scale, but when kilogram lots of ore residues are used, the method becomes very laborious and wasteful. A method was sought whereby gallium could be precipitated from solutions containing large quantities of iron and zinc. Thomas and Pugh[2] accomplished a similar separation by boiling the solution (containing gallium iron, copper and zinc) with a limited amount of ammonium hydroxide until a permanent precipitate was formed which contained the gallium, a small amount of iron and, in their case, all of the copper. The disadvantage of using ammonium hydroxide is that the precipitate formed is flocculent, making rapid filtration impossible. Dennis and Bridgman[10] found that a granular precipitate of hydrated gallium oxide is formed by boiling the gallium solution in the presence of sodium sulfite, sodium hydrogen sulfite or ammonium hydrogen sulfite. Porter and Browning[11] precipitated gallium quantitatively in the presence of zinc by this method. Following these suggestions it was found possible to separate the gallium and the aluminum from the iron as well as the zinc. The precipitate produced is readily filtered and washed. The small amount of iron present as impurity is subsequently removed without danger of adsorption.

Procedure.—The filtrate resulting from the removal of sulfides is boiled to expel hydrogen sulfide and treated while still warm with ammonium hydroxide until a small amount of permanent precipitate appears. The precipitate is redissolved by the addition of a few drops of hydrochloric acid. The solution is then brought to a boil and ammonium hydrogen sulfite solution, prepared by saturating 5 *N* ammonium hydroxide with sulfur dioxide, is slowly added. The amount of reagent must be determined by trial; if too large a quantity is used, the precipitate is contaminated with large quantities of basic ferrous sulfite. After the addition of the sulfite reagent, boiling is continued until sulfur dioxide is no longer being rapidly expelled. The granular precipitate settles rapidly and is removed by suction filtration and washed with hot water.

The process must be repeated to guard against incomplete precipitation. Before this is done, the film of gallium oxide, adhering to the walls of the beaker, is dissolved in a few drops of concentrated hydrochloric acid. The filtrate is returned to the beaker, 5 cc. of a 0.1% aqueous solution of sodium alizarin sulfonate added to serve as an indicator, and hydrochloric acid is added until the solution becomes distinctly yellow. The acidified solution is heated to boiling and a limited quantity of ammonium hydrogen sulfite solution is again introduced. During the evolution of sulfur dioxide which ensues, the color of the indicator turns from yellow to pink and, when the *p*H has become sufficiently high, the remaining traces of gallium and aluminum hydroxides are slowly precipitated. It may be necessary to repeat this process once more before only negligible quantities of precipitate are obtained. Gallium hydroxide is concentrated largely in the first two precipitations, since it is more acidic than aluminum hydroxide.[12]

Analyses.—In two instances, the combined precipitates prepared as described above from equal volumes of solution were analyzed. The results, reproduced in Table I,

TABLE I

ANALYSIS OF CRUDE GALLIUM OXIDE SEPARATED FROM GERMANITE

No.[a]	Vol. of soln., cc.	Ga_2O_3, g.	Al_2O_3, g.	Fe_2O_3, g.
A-1	1365	2.01	1.70	0.103
A-2	1365	2.02	1.60	.206
B-1	400	0.436	0.562	.021
B-2	400	.438	.590	.055

[a] The two solutions, A and B, do not contain comparable amounts of gallium. In case of solution A, the separation of gallium and aluminum was made by precipitating $AlCl_3 \cdot 6H_2O$; in case of solution B, by the extraction of $GaCl_3$ with ether.

---

[7] Kriesel, *Metall u. Erz.*, **20**, 357 (1923); *Chem.-Ztg.*. **48**, 961 (1924); Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924); Abrahams and Müller, THIS JOURNAL, **54**, 93 (1932).

[8] Wainer, *ibid.*, **56**, 348 (1934).

[9] It may be pointed out that if the oxidation of the iron, as recommended by Berg and Keil, is omitted, very little iron is dissolved by the ether and the subsequent purification of the gallium is facilitated.

[10] Dennis and Bridgman, THIS JOURNAL, **40**, 1531 (1918).

[11] Porter and Browning, *ibid.*, **41**, 1491 (1919).

[12] Fricke and Blencke, *Z. anorg. allgem. Chem.*, **143**, 183 (1925); Schwarz von Bergkampf, *Z. anal. Chem.*, **90**, 333 (1932).

show that the procedure outlined is capable of yielding quantities of gallium oxide in good agreement, while the amount of aluminum varies. The table shows, in addition, that the precipitate is contaminated with only a small amount of iron.

The Separation of Gallium and Aluminum.—Of the various methods proposed to separate gallium and aluminum, the most satisfactory is that used by Dennis and Bridgman[10] and Ato[13] in which aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, is precipitated from an ether–water mixture saturated with hydrogen chloride. In adapting it to the large scale extraction of gallium, the procedure described below was followed.

Procedure.—The precipitates containing the hydrated oxides of gallium, aluminum and iron are dissolved in concentrated hydrochloric acid. To the strongly acid solution produced, an equal volume of ether is added slowly with cooling and agitation. The resulting mixture, in two layers, is saturated with hydrogen chloride, care being exercised to keep the contents of the flask thoroughly mixed and cooled. During this process, the ether layer disappears and fine, white crystals of aluminum chloride hexahydrate settle out. The precipitate is filtered off, using a sintered glass Büchner type funnel (Jena 17, G-3), and is washed with a 50–50 mixture of ether and water saturated with hydrogen chloride. The filtrate is transferred to a large beaker and, after the addition of some dilute sulfuric acid, the ether and excess acid are removed by evaporation of the solution to a small volume. The residue is diluted with distilled water to make about 300 cc. of solution in preparation for the removal of traces of iron.

The aluminum precipitate is tested for gallium before being discarded. The separation is usually found to be very satisfactory.

The Separation of Gallium and Iron.—The gallium solution, containing a small amount of iron, but no aluminum, is brought to the boiling point and hydrogen peroxide is added to oxidize the iron. Sodium hydroxide solution, 6 *N*, is then added slowly to the boiling solution until the gallium hydroxide, which at first precipitates, is redissolved, leaving the brick-red hydrated ferric oxide suspended in a clear, colorless solution. Continuing the boiling, for a few minutes, dehydrates the ferric oxide more thoroughly and makes filtration easier. The hot solution is filtered on a suction filter, with only a slight difference in pressure, and the precipitate is washed thoroughly with hot water. The amount of iron oxide precipitated is usually so small that reprecipitation is unnecessary. The filtrate contains all the gallium but only traces of other metallic elements.

The Precipitation of Pure Gallium Hydroxide.—The alkaline filtrate from which the iron has been removed is neutralized and made slightly acid with hydrochloric acid; excess ammonium hydrogen sulfite is added and the solution is boiled vigorously to expel sulfur dioxide. A copious pure white precipitate of hydrated gallium oxide appears. When the evolution of sulfur dioxide is no longer rapid, boiling is discontinued, the precipitate is allowed to settle and is removed by suction filtration. The precipitate is washed with hot water until free from chloride ion. The filtrate may be reboiled to test for completeness of precipitation, but usually there is so little gallium left in solution that it may be collected conveniently by means of tannin, following the directions of Moser and Brukl.[14] The presence of sulfite does not interfere with this procedure.

To indicate the quantities of material that can be handled at one time, we cite an instance in which 10 g. of gallium oxide, dissolved in 1500 cc. of solution, contained in a 2-liter Pyrex beaker, was precipitated by this method so completely that only a few hundredths of a gram of gallium oxide was recovered through the treatment with tannin.

The Preparation of Pure Gallium.—To prepare pure gallium from the hydrated oxide obtained in the above procedure, the latter is dissolved, while still moist, in a slight excess of potassium hydroxide solution and then electrolyzed. The metal may be converted to the volatile chloride, $GaCl_3$, which is readily sublimed *in vacuo*.[15]

Gallium Content of Germanite.—Published analyses[7] of different lots of germanite show the gallium content to range from 0.3 to 0.8%. Table II summarizes the results of the extraction of germanium and gallium from several kilograms of germanite.

TABLE II

RECOVERY OF GERMANIUM AND GALLIUM FROM GERMANITE

Ore lot no.	3	4
Ge recovered, %	6.88	5.13
Ga recovered, %	0.59	0.34

Observations on a large number of different samples of germanite have shown that when the germanium content is high, the gallium content is likewise high. The amount of gallium found is in substantial agreement with the value given by previous workers,[7] but we have observed that the ore contains a much higher percentage of aluminum than is given in their analyses. (Table I shows that with our ores, the gallium and aluminum contents are approximately the same.) It is possible that some of the very high values for gallium which have been published were the result of the failure to effect a complete separation of these elements. The ore is, nevertheless, the richest source of gallium yet discovered.

Summary

Gallium, occurring in germanite, is extracted after the removal of arsenic and germanium, by boiling the residues with hydrochloric acid.

After the precipitation of the sulfides of the heavy metals, the gallium and aluminum are separated from large quantities of iron and zinc by boiling the solution containing them with am-

---

[13] Ato, *Sci. Papers, Inst. Phys. Chem. Research* (Tokyo), **14**, 35 (1930); *C. A.*, **24**, 4729 (1930).

[14] Moser and Brukl, *Monatsh.*, **50**, 181 (1928).

[15] Craig and Drake, THIS JOURNAL, **56**, 584 (1934); J. I. Hoffman *Bur. of Stand. Jour. of Research*, **13**, 665 (1934).

monium hydrogen sulfite, leaving the iron and zinc in solution.

Aluminum is separated as $AlCl_3 \cdot 6H_2O$ from a hydrogen chloride saturated ether–water mixture in which gallium and traces of iron remain dissolved.

After the remaining iron has been removed, the gallium is precipitated as the hydrated oxide. The metal is obtained by electrolysis from a solution of the oxide in potassium hydroxide solution.

PROVIDENCE, R. I. RECEIVED JULY 5, 1935

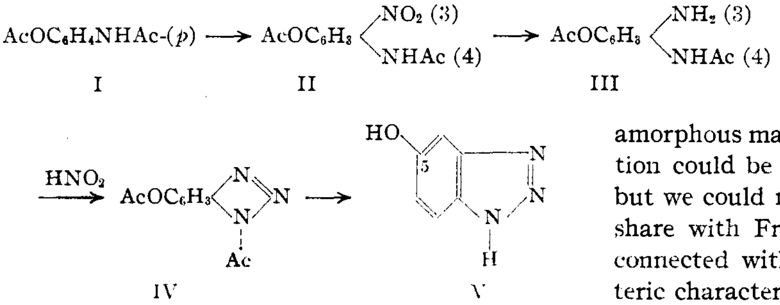
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Comparison of Heterocyclic Systems with Benzene. V. The Benzotriazole (Azimidobenzene) Series

BY LOUIS F. FIESER AND ELMORE L. MARTIN

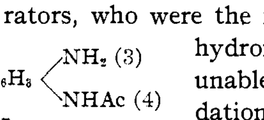
Since only one, rather unfavorable, example of a quinone containing the 1,2,3-triazole nucleus has been studied potentiometrically,[1] the synthesis of simple ortho or para quinones derived from benzotriazole was undertaken in order that a direct comparison might be made with the naphthoquinones. Although it was found that the benzotriazole quinones are unusually elusive substances, we were able to produce one member of the series in solution and to obtain from it the pure, crystalline hydroquinone. This was well suited to the purpose at hand.

The starting point for the preparation was 5-hydroxybenzotriazole, V, a compound which was unknown at the beginning of our investigation, but which has been described by Fries, Güterbock and Kühn[2] in a paper published since the completion of this part of our work. The Fries group prepared the hydroxy compound from the amine, the starting point for the preparation of which is 2,4-dinitroaniline. From the statements in the literature, supplemented by observations of our own, it is estimated that the over-all yield by this method is about 18%. We selected for the synthesis the series of transformations I → V.

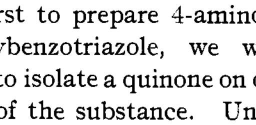


Reduction of the nitro compound II could not be accomplished with stannous chloride or sodium hydrosulfite without hydrolysis, but catalytic hydrogenation to the amine III proceeded smoothly, with a small amount of the hydrazo compound as the only by-product. The remaining steps were nearly quantitative, and the yield from p-aminophenol was 53%.

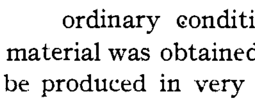
As a means of introducing an amino group in the 4-position, the reduction of the arylazo, nitro, and nitroso derivatives of 5-hydroxybenzotriazole was studied under various conditions. All of these substances gave the same reduction product, VI, but the only satisfactory preparative method consisted in the reduction of the nitroso compound with sodium hydrosulfite in a neutral, aqueous suspension. Like Fries and collaborators, who were the first to prepare 4-amino-5-hydroxybenzotriazole, we were unable to isolate a quinone on oxidation of the substance. Under ordinary conditions only black, amorphous material was obtained. A red coloration could be produced in very dilute solutions, but we could not isolate the red substance. We share with Fries the view that the difficulty is connected with the water solubility and amphoteric character of the unknown quinone.



VI



VII



VIII

From the 4-nitroso derivative we obtained with bisulfite 4-amino-5-hydroxy-7-sulfonic acid,

---

[1] Fieser and Ames, THIS JOURNAL, **49**, 2604 (1927).

[2] Fries, Güterbock and Kühn, *Ann.*, **511**, 213 (1934).