

ANALYTICAL CHEMISTRY OF
GALLIUM

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Translated by J. SCHMORAK



ANN ARBOR SCIENCE PUBLISHERS

ANN ARBOR · LONDON · 1970

ANN ARBOR SCIENCE PUBLISHERS INC.

Drawer No. 1425, 600 S. Wagner Road, Ann Arbor, Michigan 48106

ANN ARBOR SCIENCE PUBLISHERS LTD.

5 Great Russell Street London W.C. 1

© 1970 Ann Arbor Science Publishers Inc.

Library of Congress Catalog Card Number 74-104376

SBN 250 39927 X

This book is a translation of

ANALITICHESKAYA KHIMIYA GALLIYA

Izdatel'stvo "Nauka"

Moskva 1968

ANALYTICAL CHEMISTRY OF THE ELEMENTS
ANALYTICAL CHEMISTRY OF GALLIUM

Analytical Chemistry of the Elements

Series prepared by the Vernadskii Institute of Geochemistry and Analytical Chemistry
USSR Academy of Sciences

A. P. VINOGRADOV, *Editor*

English translation by ISRAEL PROGRAM FOR SCIENTIFIC TRANSLATIONS, Jerusalem

ANALYTICAL CHEMISTRY OF BERYLLIUM
ANALYTICAL CHEMISTRY OF BORON
ANALYTICAL CHEMISTRY OF COBALT
ANALYTICAL CHEMISTRY OF GALLIUM
ANALYTICAL CHEMISTRY OF MOLYBDENUM
ANALYTICAL CHEMISTRY OF NICKEL
ANALYTICAL CHEMISTRY OF NIOBIUM AND TANTALUM
ANALYTICAL CHEMISTRY OF PLUTONIUM
ANALYTICAL CHEMISTRY OF POTASSIUM
ANALYTICAL CHEMISTRY OF PROTACTINIUM
ANALYTICAL CHEMISTRY OF RUTHENIUM
ANALYTICAL CHEMISTRY OF TECHNETIUM, PROMETHIUM, ASTATINE
AND FRANCIUM
ANALYTICAL CHEMISTRY OF THALLIUM
ANALYTICAL CHEMISTRY OF THORIUM
ANALYTICAL CHEMISTRY OF URANIUM
ANALYTICAL CHEMISTRY OF YTTRIUM AND THE LANTHANIDE ELEMENTS
ANALYTICAL CHEMISTRY OF ZIRCONIUM AND HAFNIUM

FOREWORD

The Vernadskii Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences has begun the publication of a series of monographs on the analytical chemistry of individual elements. This series, *Analytical Chemistry of the Elements*, will include about fifty volumes, and it is planned to complete the publication during the coming five years. The necessity for such a project has been felt for a long time. We also have at our disposal the accumulated experience of numerous laboratories which now can (and should) be summarized. In this way the present series originated, the first of its kind. The analytical chemistry of any element with its different compounds is at present extremely varied; this is due to the complexity of the modern materials investigated and the wide range of concentrations determined, as well as to the variety of the methods employed.

With this in mind, a general plan has been worked out for the present series, both with respect to the contents and to the presentation of the material.

The monographs contain general information on the properties of the elements and their compounds, followed by a discussion of the chemical reactions which are the basis of the analytical work. The physical, physicochemical, and chemical methods for the quantitative determination of the element are given in the following order: first, the analysis of raw materials, next the analysis of the typical semi-manufactured products, and last, that of the finished products—metals or alloys, oxides, salts, and other compounds and materials. The underlying principles are always explained; whenever necessary, the exhaustive description of the entire analytical procedure is given. Due attention is paid to rapid analytical methods. A separate place is allotted to techniques for the determination of impurities in high purity materials.

Particular stress is placed on the accuracy and the sensitivity of the various methods, in view of the general tendency toward increased sensitivity of determination of traces of impurity elements.

The monographs contain an exhaustive and up-to-date bibliography. They are intended for a wide circle of chemists: in the first place, for the analysts of research institutes and industrial laboratories of various branches of the national economy, and also for teachers and students of chemistry in institutions of higher education.

Our most prominent experts participated in the preparation of the monographs, drawing upon their own extensive experience in the analytical chemistry of the element in question.

Each volume of the series will be published separately as soon as it has been made ready for publication. [A list of currently available volumes will be found facing the title page. Further titles are in preparation.]

We invite all our readers to send us their comments and criticisms on the monographs.

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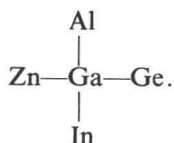
CHAPTER I

Physicochemical, Chemical and Analytical Properties of Gallium and Its Compounds

OCCURRENCE IN NATURE. ORES AND ORE PROCESSING. PREPARATION OF METALLIC GALLIUM

In 1870 D.I. Mendeleev forecast the existence and predicted the properties of a number of elements then unknown, including eka-aluminum—the nearest analog of aluminum. In 1875 a new element was discovered by a French chemist, Lecoq de Boisbaudran, as a result of a spectroscopic analysis of zinc blende from the Pyrenees, and was named *gallium* in honor of France; its properties coincided almost exactly with those postulated for eka-aluminum.

Gallium is a typical dispersed element [492, 975, 1318]; its average content in the Earth's crust is 15 grams per ton, or $1.5 \cdot 10^{-3}$ wt. % [117, 122, 134, 380, 563]. From the geochemical point of view, gallium mostly occurs together with its neighbors in the Periodic System, as is seen from the following "geochemical star":



Independent minerals of gallium are not known, except for gallite CuGaS_2 , found in 1958 in South-West Africa, which contains up to 35% Ga [119].

2 PROPERTIES OF GALLIUM AND ITS COMPOUNDS

Gallium does not appear as a major component in any mineral. The richest source of gallium is the very rare mineral germanite $\text{Cu}_3(\text{Fe,Ge})\text{S}_4$ which contains 0.3–1.85% Ga [468, 992, 993, 1062, 1314].

The bulk of gallium is found in the dispersed state as isomorphous impurities in bauxites ($2 \cdot 10^{-3}$ – $1 \cdot 10^{-2}$ %) and sphalerites ($1 \cdot 10^{-2}$ – $2 \cdot 10^{-2}$ %) [178], owing to the similarity in the chemical and crystallographic properties and in the atomic and ionic radii of gallium, aluminum and zinc. Table 1 shows the contents of gallium in different rocks, and their gallium:aluminum ratios [339]. Gallium is also a constituent of many other minerals and ores (iron, manganese, lead, copper) [80, 119] and is encountered in soils, micas and seawater [117, 468].

Table 1
OCCURRENCE OF GALLIUM IN IGNEOUS ROCKS

Rocks and minerals	Ga_2O_3 , %	$\text{Ga}_2\text{O}_3 : \text{Al}_2\text{O}_3$
Eclogites	$1 \cdot 10^{-3}$	1 : ($2 \cdot 10^4$)
Gabbro	$1 \cdot 10^{-3}$	1 : ($2 \cdot 10^4$)
Nepheline-syenites	$2 \cdot 10^{-3}$	1 : ($1 \cdot 10^4$)
Granites	$2 \cdot 10^{-3}$	1 : ($8 \cdot 10^3$)
Minerals of pegmatite veins	$1 \cdot 10^{-2}$	1 : ($3 \cdot 10^3$)

Gallium is often found together with germanium in coal ($1 \cdot 10^{-3}$ – $1 \cdot 10^{-2}$ %) [279, 280]. In the gasification and combustion of coal, gallium, together with germanium, becomes concentrated in smoke soot and in the volatile ash fractions [137, 339, 884]; such smoke may contain 1% Ga_2O_3 or more and constitutes the most important source of gallium in England [564].

Various processing schemes are available [177, 180, 280, 903, 1084, 1231, 1232, 1255, 1301, 1380, 1381] for the isolation of gallium from the products of coal combustion and coal processing, but gallium is more frequently obtained as a by-product in the combined processing of aluminum and sulfide ores, where it is present as an impurity [187, 225, 270, 286, 348, 550, 552, 553, 790, 1065, 1154, 1199, 1351]; more than 90% of the entire production of gallium is obtained from the products and wastes of the aluminum and alumina industries [178, 339].

The most promising sources of gallium are aluminate solutions obtained after alkali treatment of aluminum ores. The aluminum hydroxide, separated from the solutions contains gallates. Gallium may be obtained from aluminate solutions 1) by separation of gallium concentrate and isolation of the metal from it; 2) by electrolysis of solutions in vats with a mercury cathode, followed by decomposition of the amalgam and isolation of metallic gallium.

1. Gallium concentrates are obtained from the gallium-enriched hydrated precipitates formed during fractional (stagewise) carbonation of aluminate solutions based on the different values of the pH of precipitation for gallium and aluminum hydroxides. When the alkaline aluminate solution is slowly neutralized with carbonic acid, aluminum hydroxide containing very small amounts of gallium precipitates out first. The bulk of the gallium separates out at the final stage of the carbonation, together with the last fractions of aluminum hydroxide and alumocarbonate. A number of concentration techniques have been developed to extract gallium from the hydrated precipitate of the richer fractions.

Acid methods of preparation of gallium concentrates involve treatment of the hydrated precipitates with hydrochloric or sulfuric acids and extraction of gallium from the acid solutions with Cupferron [339, 421, 422] or else with ethers [178] or butyl acetate [598]. In the former case the precipitate is ignited, gallium oxide fused with sodium carbonate and the melt leached with water, while in the latter gallium is reextracted with water; in either procedure gallium is finally isolated by electrolysis [339, 1402]. The extraction method yields very pure solutions of gallium, and hence also a pure metal.

Alkaline methods of preparation of gallium concentrates involve the dissolution of the hydrated precipitates in alkali, with subsequent two-stage carbonation of the resulting solution. In the second stage a gallium concentrate separates out; it contains up to 10% Ga_2O_3 on the aluminum oxide. In this way gallium-rich concentrates can be obtained, but the degree of extraction is only low, since up to 30–40% Ga_2O_3 is lost with aluminum hydroxide in the first carbonation stage.

The simplest and most efficient method of preparing a gallium concentrate from the hydrated precipitates is the liming carbonation method [176, 421, 511, 656, 1302]. The hydrated precipitate is redispersed in water and treated with quicklime or with milk of lime. The solution of sodium gallate and sodium aluminate is separated from the calcium aluminate precipitate and gallium is then isolated together with residual aluminum by carbonating the solution. To obtain metallic gallium, the gallium concentrate is dissolved in hot alkali, the aluminate and gallate solution is purified from silicon with lime, and the solution is electrolyzed to separate the crude metal [48, 179, 1194].

2. The electrochemical method involves the isolation of gallium from aluminate solutions by electrolysis on mercury cathode [173, 179, 253, 566, 675, 803, 1009, 1197, 1198]. Decomposition of the amalgam yields a concentrated solution of sodium gallate (10–80 g Ga/liter), from which metallic gallium is isolated by electrolysis in vats with nonoxidizable cathode [188, 189, 676]. Gallium may also be isolated from aluminate solutions by cementation on sodium amalgam [329, 547, 548], metallic aluminum, [159, 549] or by electrolytic deposition of the metal on solid lead and copper cathodes [178]. When the cathode is treated with hot concentrated alkali, gallium passes into the alkaline solution, from which it can be isolated as metal on a stainless steel cathode.

A method of isolation of gallium from aluminate solutions by a chloroform solution of 8-hydroxyquinoline has been proposed [341]. When the aluminate solution is shaken with a solution of hydroxyquinoline in chloroform, gallium passes into the chloroform layer in the form of the hydroxyquinolate. This technique yields purer gallium than the methods described above, but is much more expensive.

Alkaline and acidic methods are employed to isolate gallium from the anodic alloy, i.e., the residue from the electrolytic refining of aluminum [136, 178, 339, 810].

Other industrial methods for the isolation of gallium from the melt use the Cupferron reaction [178] and the sorption of gallium on active manganese dioxide [421].

In the Cupferron method the alloy is dissolved in sodium hydroxide, after which gallium is solubilized in 1.5–2 *N* sulfuric acid. The gallium concentrate is precipitated by Cupferron and then ignited. In the adsorption method the alloy is decomposed by electrolytic dissolution in sulfuric acid, after which gallium is isolated

from solution by adsorption on active manganese dioxide. It is desorbed by treating the precipitate with a 10–12% solution of alkali.

Germanite ore is the only ore which serves as a direct source of gallium (which is produced together with germanium), and is obtained by extracting GaCl_3 with ether [423]. However, the occurrence of germanite is rare and the mineral cannot therefore be considered as an important source of gallium. The main sources of the metal are polymetallic lead–zinc sulfide ores. When these ores are worked up for the heavy nonferrous metals, gallium is extracted together with the other rare and dispersed elements: cadmium, germanium, indium, thallium, rhenium etc.

In the zinc industry, zinc and lead calcines and retort residues are the richest in gallium. The products of the lead industry contain much less gallium. Thus gallium is obtained only as a by-product together with other rare and scattered elements. One rational method of extraction of gallium from alkaline solutions obtained in the processing of wastes of the lead-zinc industry, in which it is separated from extraneous materials, is to coprecipitate Ga_2S_3 and ZnS by adding Na_2S [379].

The gallium-enriched products of the zinc industry are leached with sulfuric acid; gallium, zinc and iron dissolve, while lead remains in the sludge. The sludge is separated, and the solution is neutralized to pH 5 by adding zinc oxide, when gallium and iron precipitate out as hydroxides. Gallium is separated from iron by dissolving the precipitate in alkali. Repeated dissolution and precipitation yields concentrates containing up to 10% Ga_2O_3 . The concentrate is dissolved in alkali and gallium is separated by electrolysis [178, 234].

Thus, the last stage in gallium production is generally electrolysis of aqueous solutions. The electrolytic metal usually contains $1 \cdot 10^{-2}$ –3% impurities. Such metal is first treated with hot water to remove the residual electrolyte from the surface, and the liquid metal is then filtered to remove various occluded solid particles [178]. Washing and filtration of the crude metal yields gallium 98.0–99.0% pure. The metal is further purified by chemical methods (acids and alkalis) [1196, 1315], the nitride method [1098], mercury methods, distillation of gallium as an organic compound which is then decomposed by UV light [178], reduction of gallium trichloride by aluminum [751], chlorination method (fractional distillation of gallium chloride [178], the subhalide method [178]), electrochemical [1196] and physical [118, 754, 895, 1258] methods (fractional crystallization [392, 896, 999, 1444], crystal drawing from melt [441, 1444], zone melting [392, 441, 754, 1060, 1196, 1258, 1428], and thermal treatment in vacuo [1060, 1425]). Either the metal itself, or its salts may be purified. If a single method is employed alone, the result is an incomplete purification from only a small number of impurities. For more complete purification, a combination of methods must be applied [1211]. A combination of different refining methods yields a metal of any desired degree of purity, including semiconductor grade. The methods of zone melting and disproportionation of GaCl_2 , which yield 99.9999% pure gallium, should be given special mention.

USES OF GALLIUM

The industrial uses of gallium are still limited due to its high price, the small production volume, and the insufficient study of its potential applications. The metal, however, may be expected to find wide uses in the future because of its valuable physicochemical and semiconductor properties, and because the volume of gallium production could easily be increased [270, 442, 492, 665, 1065].

Gallium is the only metal which remains liquid in a wide temperature range (between 30 and 2300°C), while its vapor pressure at high temperatures is very low. It is thus suitable for use as high-temperature thermometric and manometric liquid, safety fuses, fire alarm devices, etc. [52, 779].

Gallium and gallium oxide are capable of increasing the refractive index of glass and are used in the manufacture of lenses and optical mirrors. Optical mirrors made of gallium have a high reflecting power and are stable at high temperatures [102, 131].

It was suggested that the volume expansion of gallium on solidification be employed to produce ultra-high pressures [314, 315] and in polygraphy [1409]. It has been suggested that liquid gallium be employed as heat carrier in nuclear reactors. However, owing to its chemical reactivity, it is not likely that it will find wide application in this field. At 600–800°C gallium reacts with most metals [665, 695, 1091, 1167].

Metallic gallium excites fluorescence in phosphors; it was accordingly proposed that it be used as an activator in phosphors [995, 1014], in fluorescent lamps and luminescent paints. The radioactive isotope Ga^{72} may be used in diagnosis and therapy of bone cancer [766]. Gallium oxide is used as catalyst [491], insulation material in indirectly heated cathodes [394] and in the spectroscopic determination of uranium [1167]; it is also used as an active component in the coatings of semiconductor instruments [822]. Gallium oxide may be used as a refractory material [493].

Gallium chloride is used as catalyst in the preparation of different polymers [563, 1167], its catalytic effect being stronger than that of aluminum chloride. Gallium sulfide is used to prepare luminescent materials [21].

Many gallium-based alloys are low-melting [380, 492, 665]. Addition of small amounts of gallium to magnesium alloys increases their mechanical strength and hardness, and enhances their resistance to corrosion [434, 665, 1107, 1300]. The addition of up to 3% gallium to Fe–Ni alloys increases their malleability and mechanical strength, but does not affect their plasticity [1167]. Such alloys are slower to become oxidized in the air.

Gallium is used in the doping of germanium and silicon and in the preparation of semiconductor compounds. Intermetallic gallium compounds (GaAs, GaSb and GaP) retain their semiconductor properties at elevated temperatures and can be used in high-temperature thermoelements [1116, 1117].

Certain semiconductor instruments [20] are made of compounds of the general composition MNX_2 , where M is Cu, Ag; N is Al, Ga, In, Tl; and X is Se, Te, S.

The ternary alloys Ga–Al–Sb and Ga–Al–As are semiconductors. They display anisotropic conductivity and are employed as rectifiers and transistors [1434]. The ternary alloys have a low melting point and are more resistant to corrosion than the binary alloys GaSb and AlSb.

Both metallic gallium and its low-melting alloys are used as high-temperature thermometric and manometric liquids [52, 665, 779].

The high wettability of liquid gallium and its low-melting alloys on solid materials is used in high vacuum technology. They are used as liquid seals in high vacuum instruments and diffusion pumps, and also in special electrovacuum instruments [665]. Gallium and its alloys with indium and tin are used as seals in gas systems, such as mass spectrographs for the analysis of hydrocarbons [1181], in which the gallium replaces the low-boiling mercury, so that these spectrographs can be used up to 400°C. These alloys are also used as lubricants and gaskets to join quartz, glass and earthenware parts under pressure, and also in sealing such parts together [677]. The alloy of gallium with indium is used as coating on bearings [178], and also as γ -carrier in radiation loops [255]. Liquid gallium and its alloys with indium, zinc,

tin and bismuth may be used to replace the toxic mercury in a number of electrical and radio instruments, e.g., in current rectifiers. Owing to the high boiling temperature and low vapor pressure of gallium and its alloys, such rectifiers can withstand a much higher charge and have a much higher output than mercury rectifiers [178]. The liquid Ga–Al alloy is used as a cathode in vacuum tubes; Ga–Cd–Sn alloys are used as additives in cathodes of vacuum tubes working at relatively low temperatures, using the ability of these alloys to emit electrons at low temperatures.

A gallium–cadmium alloy is used in cadmium arc lamps [825]. Low-melting Ga–Zn–Sn alloys, with gallium as the major component, are used as temperature clippers in thermoregulators [645].

Bismuth–tin–gallium alloys [393] and cobalt–gallium alloys [1329], as well as alloys of gallium with tin and silver [1409], nickel and silicon [695] and gold [665] are used in medicine. These alloys are non-toxic and their expansion on setting is insignificant; they are accordingly used in dentistry to make tooth fillings.

Various views have been advanced as regards the toxicity of gallium [405, 492]. It has been claimed [285] that gallium is about as toxic as mercury or bismuth; according to other workers [975], the toxicity of gallium compounds is very low and there is no need for any special safety measure.

PHYSICAL AND CHEMICAL PROPERTIES OF GALLIUM

Gallium is a fairly soft and brittle metal. It is silvery white in color, with a bluish tinge; it has a rhombic (pseudotetragonal) lattice, with $a = 4.5167 \text{ \AA}$, $b = 4.5107 \text{ \AA}$, $c = 7.6448 \text{ \AA}$ [178]. Its lattice does not consist of single atoms, as is usually the case in metals, but of diatomic molecules ($d = 2.44 \text{ \AA}$), which is a rare case of coexistence of molecular and metallic structures. A number of physical parameters of solid gallium are listed below:

Atomic number	31
Atomic weight	69.72
Atomic radius	1.39 \AA
Atomic volume	11.8 $\text{cm}^3/\text{g-atom}$
Density, d_4^{20}	5.907
Density of liquid Ga at 29.8°C	6.095
Mp, °C	29.78 \pm 0.02
Bp, °C	2300 [178]
	2516 [468]
	1983 [975]
Normal electrode potential, volt	$\left\{ \begin{array}{l} -0.52^* \text{ [651, 975]} \\ -0.56^* \text{ [178, 1281]} \\ -1.22 \text{ [563]} \end{array} \right.$
(for the electrode reaction $\text{Ga}^{3+} + 3e^- \rightleftharpoons \text{Ga}$)	
$\text{Ga} + 4\text{OH}^- = \text{H}_2\text{GaO}_3^- + \text{H}_2\text{O} + 3e^-$	

* Relative to hydrogen electrode.

Natural gallium has an atomic weight of 69.72 and is a mixture of two stable isotopes Ga^{69} and Ga^{71} (about 60.5% of the former and about 39.5% of the latter). Radioactive isotopes 64, 65, 66, 67, 68, 70, 72, 73 and 74 [48, 975] are also known (Table 2).

Table 2
DESCRIPTION OF RADIOACTIVE ISOTOPES OF GALLIUM

Isotope	Half-life period	Type of radiation*	Radiation energy, MeV	
			of particles	of γ -rays
64	48 min	β^+	—	—
65	15 min	K, e^-	—	0.54; 0.117
66	9.4 hours	β^+	3.1	—
67	83 hours [48]	K, e^-	—	0.09; 0.18; 0.30
	78 hours [975]	K, γ, e^-	—	—
68	68 min	β^+ [48]	1.9	—
		β^+, K, γ [975]	—	—
70**	20.3 min [48]	β^-, γ	1.68	—
	21 min [975]	β^-	—	—
72**	14.3 hours [48]	$4\beta^-, 7\gamma, 2e^-$	0.64–3.15	0.63–2.5
	14.2 hours [975]	β^-, γ	—	—
	14.1 hours [1095]	β^-, γ	0.7; 1.0	0.83†; 2.5†; 0.63†
			etc.	etc.
73	5 hours	β^- [48]	1.4	—
		β^- [975]	—	—
74	9 hours	β^-	8	—

* e^- internal conversion electrons; K electron capture; β^+ positrons; β^- negatrons.

** Isotopes of importance in analysis.

† Mixture of two or more γ -radiations.

Gallium displays a strong tendency to supercooling. Molten gallium may remain liquid for several months at temperatures below the solidification point. If, however, the supercooled solution is seeded with a crystal of solid gallium or stirred, crystallization occurs immediately and large, rhombic crystals are formed. Unlike other metals (except germanium and bismuth) the solidification of gallium is accompanied by a fairly strong force of expansion (by about 3%).

The highest valency of gallium is three, in accordance with its electronic structure $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$. Because they have similar ionic radii (0.62 Å for Ga and 0.57 Å for Al), gallium and aluminum can isomorphously substitute each other in different compounds, and they thus occur simultaneously in nature. Gallium(III) oxide may form corundum-type crystals, like aluminum oxide [423]. Gallium differs from aluminum in its low melting point, its softness and its capacity to be reduced to lower valency compounds.

The chemical properties of gallium depend on its purity: the purer the metal, the higher its chemical stability. Gallium is not oxidized in the air at room temperature, and the reaction with dry atmospheric oxygen only becomes significant above 260°C; this results in the formation of a dense oxide film, which protects the metal

from further oxidation. At high temperatures gallium is ignited to the oxide. The metal does not react with water not containing dissolved oxygen; in the presence of oxidants its surface becomes covered by an oxide film.

SIMPLE AND COMPLEX COMPOUNDS OF GALLIUM

Gallium forms three *oxides*, Ga_2O , GaO and Ga_2O_3 . The normal oxide Ga_2O_3 is the most stable at all temperatures; it is a white crystalline powder, m.p. 1900°C , which exists in five modifications (α , β , γ , δ , ϵ) [423, 1271]. Anhydrous Ga_2O_3 is obtained by dehydration of $\text{Ga}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ or by igniting gallium nitrate or gallium sulfate. Strongly ignited Ga_2O_3 is only sparingly soluble in acids and bases, similarly to aluminum oxide. When a mixture of the oxide with metallic gallium is heated in vacuo, the dark brown powder of Ga_2O is formed. The oxidation of metallic gallium yields GaO , which is a gray water-insoluble compound, soluble in acids. The oxide GaO may also be prepared by reducing Ga_2O_3 with hydrogen at $730\text{--}800^\circ\text{C}$. Both of the lower oxides are strong reducing agents ($E_0(\text{Ga}^{3+}/\text{Ga}^{2+}) = -0.65$ volt), and reduce sulfuric acid to hydrogen sulfide. GaO only achieves partial reduction.

Gallium hydroxide may be prepared by bubbling CO_2 through a solution of sodium gallate, by neutralizing a gallate solution with dilute HCl , or by neutralizing aqueous solutions of Ga(III) salts with NaOH , Na_2CO_3 and NH_4OH . Gallium hydroxide separates out of solutions as a white, gelatinous precipitate, which gives X-ray spectra indicating an amorphous structure [423] and which contains a variable amount of water ($\text{Ga}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) [1271]. Slow precipitation from alkaline or acid solution yields the microcrystalline precipitate of the metahydroxide of trivalent gallium GaO(OH) .

Gallium hydroxide precipitated out of solutions displays a considerable sorptive capacity for other cations. Thus, when it is precipitated with ammonia from a salt solution, Mg , Mn , Co , Ni , Cu , Zn , Cd and other metals are coprecipitated. Pure hydroxide is precipitated from solutions by pyridine in the presence of a large amount of NH_4Cl ($\text{pH} \approx 6.5$). Many metals react with pyridine to form soluble complexes of the type $[\text{MPy}_2]^{2+}$, which are not precipitated with the hydroxide. The precipitate of gallium hydroxide is soluble both in acids and in solutions of strong bases [902]. Unlike hydrated aluminum oxide, hydrated gallium oxide is soluble in large amounts of a concentrated ammonia solution. If the ammoniacal solution is boiled, the hydroxide again precipitates out. However, the solubility of the hydroxide in alkali, and especially in ammonia, considerably decreases as a result of aging [178]. The solubility is also a function of the amount of the precipitate. This indicates that gallium hydroxide exists in solution not only in the molecularly disperse, but also partly in the colloidal state [423].