

Gallium

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Gallium is a chemical element with symbol **Ga** and atomic number 31. It is in group 13 of the periodic table, and thus has similarities to the other metals of the group, aluminium, indium, and thallium. Gallium does not occur as a free element in nature, but as gallium(III) compounds in trace amounts in zinc ores and in bauxite. Elemental gallium is a soft, silvery blue metal at standard temperature and pressure, a brittle solid at low temperatures, and a liquid at temperatures greater than 29.76 °C (85.57 °F) (slightly above room temperature). The melting point of gallium is used as a temperature reference point. The alloy galinstan (68.5% gallium, 21.5% indium, and 10% tin) has an even lower melting point of −19 °C (−2 °F), well below the freezing point of water.

Since its discovery in 1875, gallium has been used to make alloys with low melting points. It is also used in semiconductors as a dopant in semiconductor substrates.

Gallium is predominantly used in electronics. Gallium arsenide, the primary chemical compound of gallium in electronics, is used in microwave circuits, high-speed switching circuits, and infrared circuits. Semiconductive gallium nitride and indium gallium nitride produce blue and violet light-emitting diodes (LEDs) and diode lasers. Gallium is also used in the production of artificial gadolinium gallium garnet for jewelry.

Gallium has no known natural role in biology. Gallium(III) behaves in a similar manner to ferric salts in biological systems, and has been used in some medical applications, including pharmaceuticals and radiopharmaceuticals. Gallium is used in thermometers as a non-toxic and environmentally friendly alternative to mercury and can withstand higher temperatures than mercury.

Physical properties

Elemental gallium is not found in nature, but it is easily obtained by smelting. Very pure gallium metal has a silvery color and its solid metal fractures conchoidally like glass. Gallium liquid expands by 3.1% when it solidifies; therefore, it should not be stored in glass or metal containers because the container may rupture when the

Gallium, ³¹Ga



General properties

Name, symbol	gallium, Ga
Appearance	silvery blue

Gallium in the periodic table

Atomic number (<i>Z</i>)	31
Group, block	group 13, p-block
Period	period 4
Element category	☐ post-transition metal
Standard atomic weight (\pm) (<i>A</i> _r)	69.723(1) ^[1]
Electron configuration	[Ar] 3d ¹⁰ 4s ² 4p ¹
per shell	2, 8, 18, 3

Physical properties

Phase	solid
Melting point	302.9146 K (29.7646 °C, 85.5763 °F)
Boiling point	2673 K (2400 °C,



Crystallization of gallium from the melt

gallium changes state. Gallium shares the higher-density liquid state with a short list of other materials that includes water, silicon, germanium, antimony, bismuth, and plutonium.^[4]

Gallium attacks most other metals by diffusing into the metal lattice. For example, it diffuses into the grain boundaries of aluminium-zinc alloys^[5] and steel,^[6] making them very brittle. Gallium easily alloys with many metals, and is used in small quantities in the plutonium-gallium alloy in the plutonium cores of nuclear bombs to stabilize the plutonium crystal structure.^[7]

The melting point of gallium, at 302.9146 K (29.7646 °C, 85.5763 °F), is just above room temperature, and is approximately the same as the average summer daytime temperatures in Earth's mid-latitudes. This melting point (mp) is one of the formal temperature reference points in the International Temperature Scale of 1990 (ITS-90) established by the International Bureau of Weights and Measures (BIPM).^{[8][9][10]} The triple point of gallium, 302.9166 K (29.7666 °C, 85.5799 °F), is used by the US National Institute of Standards and Technology (NIST) in preference to the melting point.^[11]

The unique melting point of gallium allows it to melt in the human hand, and then refreeze if removed. The liquid metal has a strong tendency to supercool below its melting point/freezing point. Seeding with a crystal helps to initiate freezing. Gallium is one of the four metals (with caesium, rubidium, and mercury) that are known to be liquid at, or near, normal room temperature. Of the four, gallium is the only one that is neither highly reactive nor highly toxic and can therefore be used in metal-in-glass high-temperature thermometers. It is also notable for having one of the largest liquid ranges for a metal, and for having (unlike mercury) a low vapor pressure at high temperatures. Gallium's boiling point, 2673 K, is more than eight times higher than its melting point on the absolute scale, the greatest ratio between melting point and boiling point of any element.^[12] Unlike mercury, liquid gallium metal wets glass and skin, along with most other materials (with the exceptions of quartz, graphite, and Teflon), making it mechanically more difficult to

	4352 °F) ^[2]
Density near r.t.	5.91 g/cm ³
when liquid, at m.p.	6.095 g/cm ³
Heat of fusion	5.59 kJ/mol
Heat of vaporization	256 kJ/mol ^[2]
Molar heat capacity	25.86 J/(mol·K)

Vapor pressure

P (Pa)	1	10	100	1 k	10 k	100 k
at T (K)	1310	1448	1620	1838	2125	2518

Atomic properties

Oxidation states 3, 2, 1, −1, −2, −4, −5^[3]
(an amphoteric oxide)

Electronegativity Pauling scale: 1.81

Ionization energies
1st: 578.8 kJ/mol
2nd: 1979.3 kJ/mol
3rd: 2963 kJ/mol
(more)

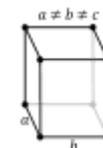
Atomic radius empirical: 135 pm

Covalent radius 122±3 pm

Van der Waals radius 187 pm

Miscellanea

Crystal structure orthorhombic



Speed of sound 2740 m/s (at 20 °C)
thin rod

Thermal expansion 18 μm/(m·K) (at 25 °C)

handle even though it is substantially less toxic and requires far fewer precautions. Gallium painted onto glass is a brilliant mirror.^[13] For this reason as well as the metal contamination and freezing-expansion problems, samples of gallium metal are usually supplied in polyethylene packets within other containers.

Gallium does not crystallize in any of the simple crystal structures. The stable phase under normal conditions is orthorhombic with 8 atoms in the conventional unit cell. Within a unit cell, each atom has only one nearest neighbor (at a distance of 244 pm). The remaining six unit cell neighbors are spaced 27, 30 and 39 pm farther away, and they are grouped in pairs with the same distance.^[15] Many stable and metastable phases are found as function of temperature and pressure.^[16]

The bonding between the two nearest neighbors is covalent; hence Ga₂ dimers are seen as the fundamental building blocks of the crystal. This explains the low melting point relative to the neighbor elements, aluminium and indium. This structure is strikingly similar to that of iodine and forms because of interactions between the single 4p electrons of gallium atoms, further away from the nucleus than the 4s electrons and the [Ar]3d¹⁰ core. This phenomenon recurs with mercury with its "pseudo-noble-gas" [Xe]4f¹⁴5d¹⁰6s² electron configuration, which is liquid at room temperature.^[17] The 3d¹⁰ electrons do not shield the outer electrons very well from the nucleus and hence the first ionisation energy of gallium is greater than that of aluminium.^[4]

The physical properties of gallium are highly anisotropic, i.e. have different values along the three major crystallographical axes *a*, *b*, and *c* (see table), producing a significant difference between the linear (α) and volume thermal expansion coefficients. The properties of gallium are strongly temperature-dependent, particularly near the melting point. For example, the coefficient of thermal expansion increases by several hundred percent upon melting.^[14]

Isotopes

Gallium has two stable isotopes: gallium-69 and gallium-73. The most commercially important radioisotopes are gallium-67 and gallium-68.

Thermal conductivity	40.6 W/(m·K)
Electrical resistivity	270 nΩ·m (at 20 °C)
Magnetic ordering	diamagnetic
Young's modulus	9.8 GPa
Poisson ratio	0.47
Mohs hardness	1.5
Brinell hardness	56.8–68.7 MPa
CAS Number	7440-55-3

History

Naming	after <i>Gallia</i> (Latin for: France), homeland of the discoverer
Prediction	Dmitri Mendeleev (1871)
Discovery and first isolation	Lecoq de Boisbaudran (1875)

Most stable isotopes of gallium

iso	NA	half-life	DM	DE (MeV)	DP
66Ga	syn	9.5 h	β+	4.153	⁶⁶ Zn
67Ga	syn	3.261 d	ε	1.001	⁶⁷ Zn
68Ga	syn	1.13 h	β+	1.899	⁶⁸ Zn
69Ga	60.11%	is stable with 38 neutrons			
70Ga	syn	21.1 min	β−	1.653	⁷⁰ Ge
			ε	0.655	⁷⁰ Zn
71Ga	39.89%	is stable with 40 neutrons			
72Ga	syn	14.10 h	β−	3.997	⁷² Ge
73Ga	syn	4.9 h	β−	1.598	⁷³ Ge

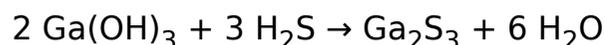
Chemical properties

Gallium is found primarily in the +3 oxidation state. The +1 oxidation is also found in some compounds. For example, the very stable GaCl₂ contains both gallium(I) and gallium(III) and can be formulated as Ga^IGa^{III}Cl₄; in contrast, the monochloride is unstable above 0 °C disproportionating into elemental gallium and gallium(III) chloride. Compounds containing gallium-gallium bonds are true gallium(II) compounds; for example, GaS can be formulated Ga₂⁴⁺(S²⁻)₂, and the dioxan complex Ga₂Cl₄(C₄H₈O₂)₂ contains a Ga-Ga bond.^[18]

Chalcogen compounds

Gallium reacts with the chalcogens only at relatively high temperatures. At room temperature, gallium metal is not reactive with air and water because it forms a passive, protective oxide layer. At higher temperatures, however, it reacts with atmospheric oxygen to form gallium(III) oxide, Ga₂O₃.^[19] Reducing Ga₂O₃ with elemental gallium in vacuum at 500 °C to 700 °C yields the dark brown gallium(I) oxide, Ga₂O.^{[20]:285} Ga₂O is a very strong reducing agent, capable of reducing H₂SO₄ to H₂S.^{[20]:207} It disproportionates at 800 °C back to gallium and Ga₂O₃.^[21]

Gallium(III) sulfide, Ga₂S₃, has 3 possible crystal modifications.^{[21]:104} It can be made by the reaction of gallium with hydrogen sulfide (H₂S) at 950 °C.^{[20]:162} Alternatively, Ga(OH)₃ can be used at 747 °C.^[22]



Reacting a mixture of alkali metal carbonates and Ga₂O₃ with H₂S leads to the formation of *thiogallates* containing the [Ga₂S₄]²⁻ anion. Strong acids decompose these salts, releasing H₂S in the process.^{[21]:104-105} The mercury salt, HgGa₂S₄, can be used as a phosphor.^[23]

Gallium also forms sulfides in lower oxidation states, such as gallium(II) sulfide and the green gallium(I) sulfide, the latter of which is produced from the former by heating to 1000 °C under a stream of nitrogen.^{[21]:94}

The other binary chalcogenides, Ga₂Se₃ and Ga₂Te₃, have zincblende structure. They are all semiconductors but are easily hydrolysed and have limited utility.^{[21]:104}

Aqueous chemistry

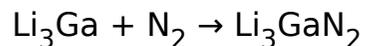
Strong acids dissolve gallium, forming gallium(III) salts such as $\text{Ga}_2(\text{SO}_4)_3$ (gallium sulfate) and $\text{Ga}(\text{NO}_3)_3$ (gallium nitrate). Aqueous solutions of gallium(III) salts contain the hydrated gallium ion, $[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$.^{[24]:1033} Gallium(III) hydroxide, $\text{Ga}(\text{OH})_3$, may be precipitated from gallium(III) solutions by adding ammonia. Dehydrating $\text{Ga}(\text{OH})_3$ at 100 °C produces gallium oxide hydroxide, $\text{GaO}(\text{OH})$.^{[20]:140-141}

Alkaline hydroxide solutions dissolve gallium, forming *gallate* salts containing the $\text{Ga}(\text{OH})_4^-$ anion.^{[19][24]:1033[25]} Gallium hydroxide, which is amphoteric, also dissolves in alkali to form gallate salts.^{[20]:141} Although earlier work suggested $\text{Ga}(\text{OH})_6^{3-}$ was another possible gallate anion,^[26] it was not found in later work.^[25]

Pnictogen compounds

Gallium reacts with ammonia at 1050 °C to form gallium nitride, GaN. Gallium also forms binary compounds with phosphorus, arsenic, and antimony: gallium phosphide (GaP), gallium arsenide (GaAs), and gallium antimonide (GaSb). These compounds have the same structure as ZnS, and have important semiconducting properties.^{[24]:1034} GaP, GaAs, and GaSb can be synthesized by the direct reaction of gallium with elemental phosphorus, arsenic, or antimony.^{[21]:99} They exhibit higher electrical conductivity than GaN.^{[21]:101} GaP can also be synthesized by reacting Ga_2O with phosphorus at low temperatures.^[27]

Gallium forms ternary nitrides; for example:^{[21]:99}



Similar compounds with phosphorus and arsenic are possible: Li_3GaP_2 and Li_3GaAs_2 . These compounds are easily hydrolyzed by dilute acids and water.^{[21]:101}

Halides

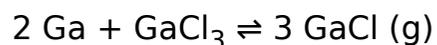
Gallium(III) oxide reacts with fluorinating agents such as HF or F_2 to form gallium(III) fluoride, GaF_3 . It is an ionic compound strongly insoluble in water. However, it dissolves in hydrofluoric acid, in which it forms an adduct with water, $\text{GaF}_3 \cdot 3\text{H}_2\text{O}$. Attempting to dehydrate this adduct forms $\text{GaF}_2\text{OH} \cdot n\text{H}_2\text{O}$. The adduct reacts with ammonia to form $\text{GaF}_3 \cdot 3\text{NH}_3$, which can then be heated to form anhydrous GaF_3 .^{[20]:128-129}



Gallium trichloride is formed by the reaction of gallium metal with chlorine gas.^[19] Unlike the trifluoride, gallium(III) chloride exists as dimeric molecules, Ga₂Cl₆, with a melting point of 78 °C. Equivalent compounds are formed with bromine and iodine, Ga₂Br₆ and Ga₂I₆.^{[20]:133}

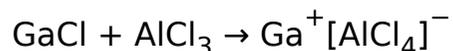
Like the other group 13 trihalides, gallium(III) halides are Lewis acids, reacting as halide acceptors with alkali metal halides to form salts containing GaX₄⁻ anions, where X is a halogen. They also react with alkyl halides to form carbocations and GaX₄⁻.^{[20]:136-137}

When heated to a high temperature, gallium(III) halides react with elemental gallium to form the respective gallium(I) halides. For example, GaCl₃ reacts with Ga to form GaCl:

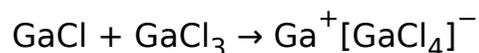


At lower temperatures, the equilibrium shifts toward the left and GaCl disproportionates back to elemental gallium and GaCl₃. GaCl can also be produced by reacting Ga with HCl at 950 °C; the product can be condensed as a red solid.^{[24]:1036}

Gallium(I) compounds can be stabilized by forming adducts with Lewis acids. For example:



The so-called "gallium(II) halides", GaX₂, are actually adducts of gallium(I) halides with the respective gallium(III) halides, having the structure Ga⁺[GaX₄]⁻. For example:^{[19][24]:1036[28]}



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