Gallium and its salts.

Gallium is a naturally occurring element that constitutes 0.0018 % of the Earth's crust. It is never found in its free state, but only as a trace element in conjunction with a variety of minerals, the most common of which are zinc ores such as sphalerite and bauxite (see Figure 1). It also occurs in minerals such as diaspore (an aluminium-based mineral) and germanite (a copper-iron-germanium sulphide mineral) and occasionally in coal, but this is not considered an economic source of gallium. It was discovered in 1875 by the French scientist Paul-Émile Lecoq de Boisbaudran, who initially identified it spectroscopically but later that year he managed to obtain a pure sample by electrolysis of gallium hydroxide in a solution of potassium hydroxide. He named it after the old name for France – Gaul. Gallium and its salts are considered as non-hazardous to humans and to have low toxicity.

Figure 1 Bauxite mine (Image: © horizonphoto / Adobe Stock)

Gallium is in Group 13 of the Periodic Table, along with boron, aluminium, indium and thallium. It has a density of 5,904 kg/m^3, an atomic number of 31 and it has 34 isotopes ranging between 56 to 86, of which 28 have known half-lives, with 3 being excited nuclear isomers. The only stable isotopes are 69 and 71 and occur in the ratio 60 %:40 %, giving it an atomic weight of 69.723.

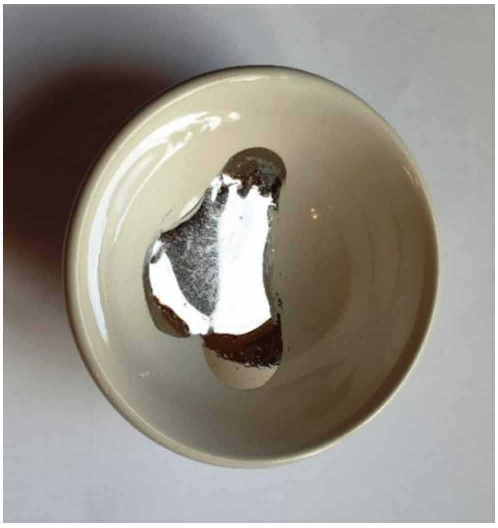

Figure 2 Pure gallium

Pure gallium metal (see Figure 2) is soft and bright silver in colour, but its solid form usually appears as bluish-grey due to a passive layer on its surface (see Figure 3); the solid has an orthorhombic crystal structure, with cell parameters off a= 4.52 Å, b= 67.66 Å and c=4.53 Å. For a metal, it has a very low melting point (29.8°C) but it has a very high boiling point (2,204°C), giving it the highest temperature range of any element in its liquid state (see Figure 4). The liquid metal has a very low surface tension (7.24 mNewtons/metre at room temperature) and it will wet glass, making it mechanically quite difficult to handle. Another unusual property of gallium is that it undergoes a 3.1% reduction in density when it solidifies; this characteristic is also seen with water, bismuth and germanium and, as a consequence, it should not be stored in glass or sealed containers. Gallium has a thermal expansion of 18 µm/(m.K) at 25°C and its thermal conductivity is 40.6 W/(m.K); its electrical conductivity is 7.1 x10^6 S/m.

Figure 3 Gallium in its solid form (Image: © Björn Wylezich / Adobe Stock)

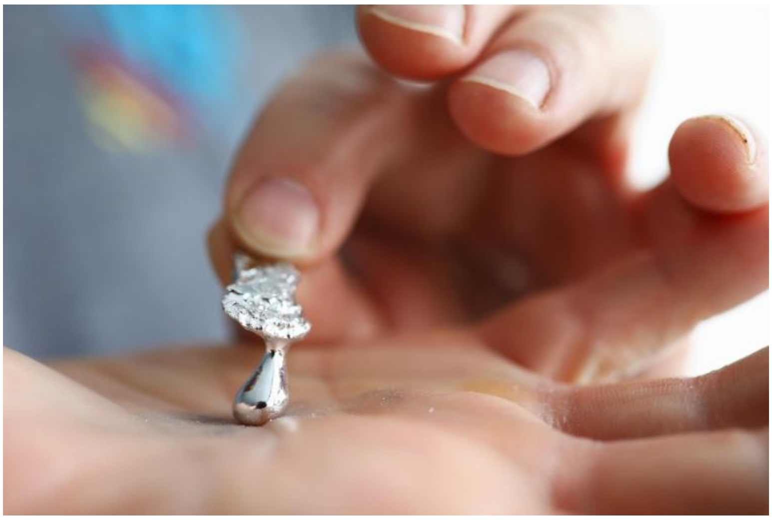

Figure 4 Gallium at room temperature (Image: © megaflopp / Adobe Stock)

Gallium is totally miscible with metals such as aluminium, tin, indium and zinc and does not form any compounds, but it reacts with most other metals by diffusing into the metal lattice to create intermetallic compounds along the grain boundaries. This usually results in embrittlement of the metal. Gallium salts are primary trivalent (Ga(III)), although there are a few monovalent salts (Ga(I)) known. There are also divalent salts such as $GaCl_2$, but these are actually mixed salts of Ga(I) and Ga(III) – Ga+Ga+++Cl_4. Gallium is an amphoteric element, reacting with both acids and alkalis. When it reacts with strong acids such as sulphuric and nitric acids it forms trivalent salts such as $Ga_2(SO_4)_3$ and $Ga(NO_3)_3$. When hydrated in aqueous solutions, the gallium ion has a coordination number of 6 - $[Ga(H_2O)_6]^{3+}$. When gallium, in the form of gallium hydroxide ($Ga(OH)_3$), is reacted with excess alkalis it forms the gallate ion - $(Ga(OH)_4)^-$.

Gallium reacts with the chalcogen group (Group 16) of the Periodic Table only at high temperatures as it is protected by a passivating layer. This group contains the elements oxygen, sulphur, tellurium and selenium. For instance, gallium will react with oxygen to form gallium oxide (Ga_2O_3), but if this oxide is heated to 500-700 °C under vacuum with excess gallium metal, it can form Ga_2O – a monovalent oxide of gallium:

$$Ga_2O_3 + 4Ga \rightarrow 3Ga_2O \qquad (1)$$

Gallium (I) oxide can also be formed by heating gallium with carbon dioxide, as well as reacting gallium with silica:

$$2Ga + CO_2 \rightarrow Ga_2O + CO \qquad (2)$$

$$4Ga + SiO_2 \rightarrow Ga_2O + Si \qquad (3)$$

Ga_2O is a very powerful reducing agent that can reduce sulphuric acid to hydrogen sulphide. If it is heated to over 800 °C it dissociates into Ga and Ga_2O_3.

Gallium will react in a similar way with sulphur to form sulphides:

$$2Ga + 3S \rightarrow Ga_2S_3 \qquad (4)$$

Gallium sulphide can also be produced by heating gallium in a stream of hydrogen sulphide gas at 950 °C:

$$2Ga + 3H_2S \rightarrow Ga_2S_3 + 3H_2 \qquad (5)$$

Alternatively, gallium oxide can be used by reacting it with hydrogen sulphide:

$$2Ga(OH)_3 + 3H_2S \rightarrow Ga_2S_3 + 6H_2O \qquad (6)$$

However, this reaction (6) can generate different polymorphic forms, depending on the reaction temperature. There are 4 polymorphs of gallium sulphide: hexagonal α, monoclinic α', hexagonal β and cubic γ. The α form is produced at 1020 °K, the β at 820 °K and γ at above 873 °K.

Gallium sulphide can also be prepared in the solid state by the reaction between gallium chloride and sodium sulphide:

$$GaCl_3 + Na_2S \rightarrow Ga_2S_3 + 3NaCl \qquad (7)$$

Gallium sulphide is a semiconductor and is very important in the electronics and photonics industries.

Ga_2S_3 disproportionates at high temperatures to form non-stoichiometric sulphides – Ga_4S_x, (where x = 4.8 to 5.2). It will also dissolve in aqueous acids to form the acid salt and hydrogen sulphide, whilst it also hydrolyses in moist air to produce gallium hydroxide and hydrogen sulphide.

Gallium sulphide can also be used to generate ternary sulphides by reacting it with other metal sulphides such as cadmium sulphide:

$$Ga_2S + CdS \rightarrow CdGa_2S_4 \qquad (8)$$

These ternary sulphides are also of particular interest as they have unusual electrical properties by way of their high optical absorption coefficients and their use in photovoltaics, linear and non-linear optical devices, superconducting materials, fluorescent materials and photocatalysts. Furthermore, gallium sulphide can be reacted with rare earth sulphides to form glasses, although gallium sulphide itself is not a glass former. However, its reaction with a rare earth sulphide such as lanthanum sulphide will produce gallium lanthanum sulphide glass, which is both a semiconductor and has potentially interesting optical properties, such as a strong dependence of its refractive index on its operating temperature. It also has a low thermal conductivity.