

Germanium

From Wikipedia, the free encyclopedia

Germanium is a chemical element with symbol **Ge** and atomic number 32. It is a lustrous, hard, grayish-white metalloid in the carbon group, chemically similar to its group neighbors tin and silicon. Pure germanium is a semiconductor with an appearance similar to elemental silicon. Like silicon, germanium naturally reacts and forms complexes with oxygen in nature. Unlike silicon, it is too reactive to be found naturally on Earth in the free (elemental) state.

Because it seldom appears in high concentration, germanium was discovered comparatively late in the history of chemistry. Germanium ranks near fiftieth in relative abundance of the elements in the Earth's crust. In 1869, Dmitri Mendeleev predicted its existence and some of its properties from its position on his periodic table, and called the element **ekasilicon**. Nearly two decades later, in 1886, Clemens Winkler found the new element along with silver and sulfur, in a rare mineral called argyrodite. Although the new element somewhat resembled arsenic and antimony in appearance, the combining ratios in compounds agreed with Mendeleev's predictions for a relative of silicon. Winkler named the element after his country, Germany. Today, germanium is mined primarily from sphalerite (the primary ore of zinc), though germanium is also recovered commercially from silver, lead, and copper ores.

Germanium "metal" (isolated germanium) is used as a semiconductor in transistors and various other electronic devices. Historically, the first decade of semiconductor electronics was based entirely on germanium. Today, the amount of germanium produced for semiconductor electronics is one fiftieth the amount of ultra-high purity silicon produced for the same. Presently, the major end uses are fibre-optic systems, infrared optics, solar cell applications, and light-emitting diodes (LEDs). Germanium compounds are also used for polymerization catalysts and have most recently found use in the production of nanowires. This element forms a large number of organometallic compounds, such as tetraethylgermane, useful in organometallic chemistry.

Germanium is not thought to be an essential element for any living organism. Some complex organic germanium compounds are being investigated as possible pharmaceuticals, though none have yet proven successful. Similar to

Germanium, $_{32}\text{Ge}$



A 12 gram (2×3 cm) polycrystalline block of germanium with uneven cleaved surfaces

General properties

| | |
|---------------------|---------------|
| Name, symbol | germanium, Ge |
| Appearance | grayish-white |

Germanium in the periodic table

| | |
|---|---|
| Atomic number (<i>Z</i>) | 32 |
| Group, block | group 14 (carbon group), p-block |
| Period | period 4 |
| Element category | ☐ metalloid |
| Standard atomic weight (\pm) (<i>A</i> _r) | 72.630(8) ^[1] |
| Electron configuration | [Ar] 3d ¹⁰ 4s ² 4p ² |
| per shell | 2, 8, 18, 4 |

silicon and aluminum, natural germanium compounds tend to be insoluble in water and thus have little oral toxicity. However, synthetic soluble germanium salts are nephrotoxic, and synthetic chemically reactive germanium compounds with halogens and hydrogen are irritants and toxins.

Characteristics

Under standard conditions, germanium is a brittle, silvery-white, semi-metallic element.^[26] This form constitutes an allotrope known as *α-germanium*, which has a metallic luster and a diamond cubic crystal structure, the same as diamond.^[24] At pressures above 120 kbar, it becomes the allotrope *β-germanium* with the same structure as β-tin.^[27] Like silicon, gallium, bismuth, antimony, and water, germanium is one of the few substances that expands as it solidifies (i.e. freezes) from the molten state.^[27]

Germanium is a semiconductor. Zone refining techniques have led to the production of crystalline germanium for semiconductors that has an impurity of only one part in 10^{10} ,^[28] making it one of the purest materials ever obtained.^[29] The first metallic material discovered (in 2005) to become a superconductor in the presence of an extremely strong electromagnetic field was an alloy of germanium, uranium, and rhodium.^[30]

Pure germanium spontaneously extrudes very long screw dislocations, and this is one of the primary reasons for the failure of older diodes and transistors made from germanium; depending on what they eventually touch, they may lead to an electrical short.

Chemistry

Elemental germanium oxidizes slowly to GeO_2 at 250 °C.^[31] Germanium is insoluble in dilute acids and alkalis but dissolves slowly in hot concentrated sulfuric and nitric acids and reacts violently with molten alkalis to produce germanates ($[\text{GeO}_3]^{2-}$). Germanium occurs mostly in the oxidation state +4 although many +2 compounds are known.^[32] Other oxidation states are rare: +3

Physical properties

| | |
|-----------------------------|-----------------------------------|
| Phase | solid |
| Melting point | 1211.40 K (938.25 °C, 1720.85 °F) |
| Boiling point | 3106 K (2833 °C, 5131 °F) |
| Density near r.t. | 5.323 g/cm ³ |
| when liquid, at m.p. | 5.60 g/cm ³ |
| Heat of fusion | 36.94 kJ/mol |
| Heat of vaporization | 334 kJ/mol |
| Molar heat capacity | 23.222 J/(mol·K) |

Vapor pressure

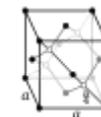
| P (Pa) | 1 | 10 | 100 | 1 k | 10 k | 100 k |
|----------|------|------|------|------|------|-------|
| at T (K) | 1644 | 1814 | 2023 | 2287 | 2633 | 3104 |

Atomic properties

| | |
|-----------------------------|---|
| Oxidation states | 4, 3, 2, 1, 0, −1, −2, −3, −4 (an amphoteric oxide) |
| Electronegativity | Pauling scale: 2.01 |
| Ionization energies | 1st: 762 kJ/mol 2nd: 1537.5 kJ/mol 3rd: 3302.1 kJ/mol |
| Atomic radius | empirical: 122 pm |
| Covalent radius | 122 pm |
| Van der Waals radius | 211 pm |

Miscellanea

| | |
|--------------------------|-----------------------------|
| Crystal structure | face-centered diamond-cubic |
|--------------------------|-----------------------------|



Speed of sound

is found in compounds such as Ge_2Cl_6 , and +3 and +1 are found on the surface of oxides,^[33] or negative oxidation states in germanes, such as -4 in GeH_4 . Germanium cluster anions (Zintl ions) such as Ge_4^{2-} , Ge_9^{4-} , Ge_9^{2-} , $[(\text{Ge}_9)_2]^{6-}$ have been prepared by the extraction from alloys containing alkali metals and germanium in liquid ammonia in the presence of ethylenediamine or a cryptand.^{[32][34]} The oxidation states of the element in these ions are not integers—similar to the ozonides O_3^- .

Two oxides of germanium are known: germanium dioxide (GeO_2 , germania) and germanium monoxide, (GeO).^[27] The dioxide, GeO_2 can be obtained by roasting germanium disulfide (GeS_2), and is a white powder that is only slightly soluble in water but reacts with alkalis to form germanates.^[27] The monoxide, germanous oxide, can be obtained by the high temperature reaction of GeO_2 with Ge metal.^[27] The dioxide (and the related oxides and germanates) exhibits the unusual property of having a high refractive index for visible light, but transparency to infrared light.^{[35][36]} Bismuth germanate, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$, (BGO) is used as a scintillator.^[37]

Binary compounds with other chalcogens are also known, such as the disulfide (GeS_2), diselenide (GeSe_2), and the monosulfide (GeS), selenide (GeSe), and telluride (GeTe).^[32] GeS_2 forms as a white precipitate when hydrogen sulfide is passed through strongly acid solutions containing Ge(IV).^[32] The disulfide is appreciably soluble in water and in solutions of caustic alkalis or alkaline sulfides. Nevertheless, it is not soluble in acidic water, which allowed Winkler to discover the element.^[38] By heating the disulfide in a current of hydrogen, the monosulfide (GeS) is formed, which sublimes in thin plates of a dark color and metallic luster, and is soluble in solutions of the caustic alkalis.^[27] Upon melting with alkaline carbonates and sulfur, germanium compounds form salts known as thiogermanates.^[39]

thin rod 5400 m/s (at 20 °C)

Thermal expansion 6.0 $\mu\text{m}/(\text{m}\cdot\text{K})$

Thermal conductivity 60.2 $\text{W}/(\text{m}\cdot\text{K})$

Electrical resistivity 1 $\Omega\cdot\text{m}$ (at 20 °C)

Band gap 0.67 eV (at 300 K)

Magnetic ordering diamagnetic^[2]

Young's modulus 103 GPa ^[3]

Shear modulus 41 GPa ^[3]

Bulk modulus 75 GPa ^[3]

Poisson ratio 0.26^[3]

Mohs hardness 6.0

CAS Number 7440-56-4

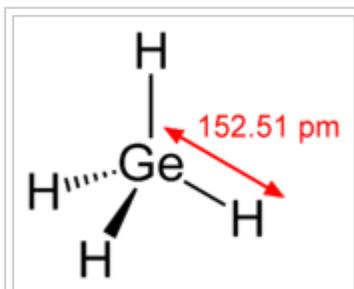
History

Naming after Germany, homeland of the discoverer

Prediction Dmitri Mendeleev (1871)

Discovery Clemens Winkler (1886)

Most stable isotopes of germanium



Germane is similar to methane.

Four tetrahalides are known. Under normal conditions GeI_4 is a solid, GeF_4 a gas and the others volatile liquids. For example, germanium tetrachloride, GeCl_4 , is obtained as a colorless fuming liquid boiling at $83.1\text{ }^\circ\text{C}$ by heating the metal with chlorine.^[27] All the tetrahalides are readily hydrolyzed to hydrated germanium dioxide.^[27] GeCl_4 is used in the production of organogermanium compounds.^[32] All four dihalides are known and in contrast to the tetrahalides are polymeric solids.^[32] Additionally Ge_2Cl_6 and some

higher compounds of formula $\text{Ge}_n\text{Cl}_{2n+2}$ are known.^[27] The unusual compound $\text{Ge}_6\text{Cl}_{16}$ has been prepared that contains the $\text{Ge}_5\text{Cl}_{12}$ unit with a neopentane structure.^[40]

Germane (GeH_4) is a compound similar in structure to methane. Polygermanes—compounds that are similar to alkanes—with formula $\text{Ge}_n\text{H}_{2n+2}$ containing up to five germanium atoms are known.^[32] The germanes are less volatile and less reactive than their corresponding silicon analogues.^[32] GeH_4 reacts with alkali metals in liquid ammonia to form white crystalline MGeH_3 which contain the GeH_3^- anion.^[32] The germanium hydrohalides with one, two and three halogen atoms are colorless reactive liquids.^[32]

The first organogermanium compound was synthesized by Winkler in 1887; the reaction of germanium tetrachloride with diethylzinc yielded tetraethylgermane ($\text{Ge}(\text{C}_2\text{H}_5)_4$).^[6] Organogermanes of the type R_4Ge (where R is an alkyl) such as tetramethylgermane ($\text{Ge}(\text{CH}_3)_4$) and tetraethylgermane are accessed through the cheapest available germanium precursor germanium tetrachloride and alkyl nucleophiles. Organic germanium hydrides such as isobutylgermane ($(\text{CH}_3)_2\text{CHCH}_2\text{GeH}_3$) were found to be less hazardous and may be used as a liquid substitute for toxic germane gas in semiconductor applications. Many germanium reactive intermediates are known: germyl free radicals, germynes (similar to carbenes), and germynes (similar to carbynes).^{[41][42]} The organogermanium compound 2-carboxyethylgermasquioxane was first reported in the 1970s, and for a while was used as a dietary supplement and thought to possibly have anti-tumor qualities.^[43]

Using a ligand called Eind (1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl) germanium is able to form a double bond with oxygen (germanone).^[44]

| iso | NA | half-life | DM | DE (MeV) | DP |
|------------------------|--------|----------------------------|-----------------|----------|------------------|
| ⁶⁸Ge | syn | 270.8 d | ϵ | - | ⁶⁸ Ga |
| ⁷⁰Ge | 20.52% | is stable with 38 neutrons | | | |
| ⁷¹Ge | syn | 11.26 d | ϵ | - | ⁷¹ Ga |
| ⁷²Ge | 27.45% | is stable with 40 neutrons | | | |
| ⁷³Ge | 7.76% | is stable with 41 neutrons | | | |
| ⁷⁴Ge | 36.52% | is stable with 42 neutrons | | | |
| ⁷⁶Ge | 7.75% | 1.78×10^{21} y | $\beta-\beta^-$ | 2.039 | ⁷⁶ Se |

Isotopes

Germanium occurs in 5 natural isotopes: ^{70}Ge , ^{72}Ge , ^{73}Ge , ^{74}Ge , and ^{76}Ge . Of these, ^{76}Ge is very slightly radioactive, decaying by double beta decay with a half-life of 1.78×10^{21} years. ^{74}Ge is the most common isotope, having a natural abundance of approximately 36%. ^{76}Ge is the least common with a natural abundance of approximately 7%.^[45] When bombarded with alpha particles, the isotope ^{72}Ge will generate stable ^{77}Se , releasing high energy electrons in the process.^[46] Because of this, it is used in combination with radon for nuclear batteries.^[46]

At least 27 radioisotopes have also been synthesized, ranging in atomic mass from 58 to 89. The most stable of these is ^{68}Ge , decaying by electron capture with a half-life of 270.95 days. The least stable is ^{60}Ge , with a half-life of 30 ms. While most of germanium's radioisotopes decay by beta decay, ^{61}Ge and ^{64}Ge decay by β^+ delayed proton emission.^[45] ^{84}Ge through ^{87}Ge isotopes also exhibit minor β^- delayed neutron emission decay paths.^[45]

Occurrence

Germanium is created by stellar nucleosynthesis, mostly by the s-process in asymptotic giant branch stars. The s-process is a slow neutron capture of lighter elements inside pulsating red giant stars.^[47] Germanium has been detected in some of the most distant stars^[48] and in the atmosphere of Jupiter.^[49]

Germanium's abundance in the Earth's crust is approximately 1.6 ppm.^[50] Only a few minerals like argyrodite, briartite, germanite, and renierite contain appreciable amounts of germanium, and none in mineable deposits.^{[24][51]} Some zinc-copper-lead ore bodies contain enough germanium to justify extraction from the final ore concentrate.^[50] An unusual natural enrichment process causes a high content of germanium in some coal seams, discovered by Victor Moritz Goldschmidt during a broad survey for germanium deposits.^{[52][53]} The highest concentration ever found was in Hartley coal ash with as much as 1.6% germanium.^{[52][53]} The coal deposits near Xilinhaote, Inner Mongolia, contain an estimated 1600 tonnes of germanium.^[50]

Source

- Wikipedia: Germanium (<https://en.wikipedia.org/wiki/Germanium>)