

= Germanium =

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 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 .

= = History = =

In his report on The Periodic Law of the Chemical Elements in 1869 , the Russian chemist Dmitri Ivanovich Mendeleev predicted the existence of several unknown chemical elements , including one that would fill a gap in the carbon family in his Periodic Table of the Elements , located between silicon and tin . Because of its position in his Periodic Table , Mendeleev called it ekasilicon (Es) , and he estimated its atomic weight to be about 72 @.@ 0 .

In mid @-@ 1885 , at a mine near Freiberg , Saxony , a new mineral was discovered and named argyrodite because of the high silver content . The chemist Clemens Winkler analyzed this new mineral , which proved to be a combination of silver , sulfur , and a new element . Winkler was able to isolate the new element in 1886 and found it similar to antimony . Before Winkler published his results on the new element , he decided that he would name his element neptunium , since the recent discovery of planet Neptune in 1846 had been preceded by mathematical predictions of its existence . However , the name " neptunium " had already been given to another proposed chemical element (though not the element that today bears the name neptunium , which was discovered in 1940) . So instead , Winkler named the new element germanium (from the Latin word , Germania , for Germany) in honor of his homeland . Argyrodite proved empirically to be Ag_8GeS_6 .

Because this new element showed some similarities with the elements arsenic and antimony , its proper place in the periodic table was under consideration , but its similarities with Dmitri Mendeleev 's predicted element " ekasilicon " confirmed that place on the periodic table . With further material

from 500 kg of ore from the mines in Saxony , Winkler confirmed the chemical properties of the new element in 1887 . He also determined an atomic weight of 72 @. @ 32 by analyzing pure germanium tetrachloride (GeCl_4)

4) , while Lecoq de Boisbaudran deduced 72 @. @ 3 by a comparison of the lines in the spark spectrum of the element .

Winkler was able to prepare several new compounds of germanium , including fluorides , chlorides , sulfides , dioxide , and tetraethylgermane ($\text{Ge}(\text{C}_2\text{H}_5)_4$) , the first organogermane . The physical data from those compounds ? which corresponded well with Mendeleev 's predictions ? made the discovery an important confirmation of Mendeleev 's idea of element periodicity . Here is a comparison between the prediction and Winkler 's data :

Until the late 1930s , germanium was thought to be a poorly conducting metal . Germanium did not become economically significant until after 1945 when its properties as an electronic semiconductor were recognized . During World War II , small amounts of germanium were used in some special electronic devices , mostly diodes . The first major use was the point @-@ contact Schottky diodes for radar pulse detection during the War . The first silicon @-@ germanium alloys were obtained in 1955 . Before 1945 , only a few hundred kilograms of germanium were produced in smelters each year , but by the end of the 1950s , the annual worldwide production had reached 40 metric tons .

The development of the germanium transistor in 1948 opened the door to countless applications of solid state electronics . From 1950 through the early 1970s , this area provided an increasing market for germanium , but then high @-@ purity silicon began replacing germanium in transistors , diodes , and rectifiers . For example , the company that became Fairchild Semiconductor was founded in 1957 with the express purpose of producing silicon transistors . Silicon has superior electrical properties , but it requires much greater purity that could not be commercially achieved in the early years of semiconductor electronics .

Meanwhile , the demand for germanium for fiber optic communication networks , infrared night vision systems , and polymerization catalysts increased dramatically . These end uses represented 85 % of worldwide germanium consumption in 2000 . The US government even designated germanium as a strategic and critical material , calling for a 146 ton (132 t) supply in the national defense stockpile in 1987 .

Germanium differs from silicon in that the supply is limited by the availability of exploitable sources , while the supply of silicon is limited only by production capacity since silicon comes from ordinary sand and quartz . While silicon could be bought in 1998 for less than \$ 10 per kg , the price of germanium was almost \$ 800 per kg .

= = Characteristics = =

Under standard conditions , germanium is a brittle , silvery @-@ white , semi @-@ metallic element . This form constitutes an allotrope known as ? @-@ germanium , which has a metallic luster and a diamond cubic crystal structure , the same as diamond . At pressures above 120 kbar , it becomes the allotrope ? @-@ germanium with the same structure as ? @-@ tin . 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 .

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} , making it one of the purest materials ever obtained . 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 .

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 . 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. Other oxidation states are rare: + 3 is found in compounds such as Ge_2Cl_6 , and + 3 and + 1 are found on the surface of oxides, or negative oxidation states in germanes, such as $-\frac{4}{3}$ in GeH_4 . Germanium cluster anions (Zintl ions) such as Ge_4^{2-} , Ge_9^{4-} , Ge_{10}^{4-} , $[\text{Ge}_9]^{2-}$ have been prepared by the extraction from alloys containing alkali metals and germanium in liquid ammonia in the presence of ethylenediamine or a cryptand. 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 (Ge_2O_3).

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.

The monoxide, germanous oxide, can be obtained by the high temperature reaction of GeO_2 with Ge metal. 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. Bismuth germanate, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) is used as a scintillator.

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).

GeS_2 forms as a white precipitate when hydrogen sulfide is passed through strongly acid solutions containing Ge (IV). 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. 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. Upon melting with alkaline carbonates and sulfur, germanium compounds form salts known as thiogermanates.

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 83.7°C by heating the metal with chlorine. All the tetrahalides are readily hydrolyzed to hydrated germanium dioxide. GeCl_4 is used in the production of organogermanium compounds. All four dihalides are known and in contrast to the tetrahalides are polymeric solids. Additionally Ge_2Cl_6 and some higher compounds of formula $\text{Ge}_n\text{Cl}_{2n+2}$ are known. 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.

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. The germanes are less volatile and less reactive than their corresponding silicon analogues. GeH_4 reacts with alkali metals in liquid ammonia to form white crystalline MGeH_3 which contain the GeH_3^- anion. The germanium hydrohalides with one, two and three halogen atoms are colorless reactive liquids.

The first organogermanium compound was synthesized by Winkler in 1887; the reaction of germanium tetrachloride with diethylzinc yielded tetraethylgermane ($\text{Ge}(\text{C}_2\text{H}_5)_4$).

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 ($(\text{CH}_3)_2\text{CHCH}_2\text{GeH}_3$)

and tetraethylgermane are accessed through the cheapest available germanium precursor germanium tetrachloride and alkyl nucleophiles. Organic germanium hydrides such as isobutylgermane ($(\text{CH}_3)_2\text{CHCH}_2\text{GeH}_3$)

2CHCH

2GeH

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) . The organogermanium compound 2 @-@ carboxyethylgermasesquioxane was first reported in the 1970s , and for a while was used as a dietary supplement and thought to possibly have anti @-@ tumor qualities .

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) .

= = = 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 $1 @.@ 78 \times 10^{21}$ 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 % . When bombarded with alpha particles , the isotope ^{72}Ge will generate stable ^{77}Se , releasing high energy electrons in the process . Because of this , it is used in combination with radon for nuclear batteries .

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 ? + delayed proton emission . ^{84}Ge through ^{87}Ge isotopes also exhibit minor ? ? delayed neutron emission decay paths .

= = = 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 . Germanium has been detected in some of the most distant stars and in the atmosphere of Jupiter .

Germanium 's abundance in the Earth 's crust is approximately $1 @.@ 6$ ppm . Only a few minerals like argyrodite , briartite , germanite , and renierite contain appreciable amounts of germanium , and none in mineable deposits . Some zinc @-@ copper @-@ lead ore bodies contain enough germanium to justify extraction from the final ore concentrate . 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 . The highest concentration ever found was in Hartley coal ash with as much as $1 @.@ 6$ % germanium . The coal deposits near Xilinhaote , Inner Mongolia , contain an estimated 1600 tonnes of germanium .

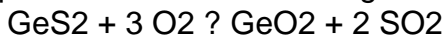
= = Production = =

About 118 tonnes of germanium was produced in 2011 worldwide , mostly in China (80 t) , Russia (5 t) and United States (3 t) . Germanium is recovered as a by @-@ product from sphalerite zinc ores where it is concentrated in amounts as great as $0 @.@ 3$ % , especially from low @-@ temperature sediment @-@ hosted , massive Zn ? Pb ? Cu (? Ba) deposits and carbonate @-@ hosted Zn ? Pb deposits . A recent study found that at least $10 @,@ 000$ t of extractable germanium is contained in known zinc reserves , particularly those hosted by Mississippi @-@ Valley type deposits , while at least $112 @,@ 000$ t will be found in coal reserves . In 2007 35 % of the demand was met by recycled germanium .

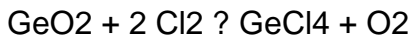
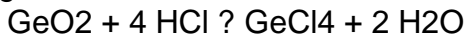
While it is produced mainly from sphalerite , it is also found in silver , lead , and copper ores . Another source of germanium is fly ash of power plants fueled from coal deposits that contain

germanium . Russia and China used this as a source for germanium . Russia 's deposits are located in the far east of Sakhalin Island , and northeast of Vladivostok . The deposits in China are located mainly in the lignite mines near Lincang , Yunnan ; coal is also mined near Xilinhaote , Inner Mongolia .

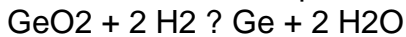
The ore concentrates are mostly sulfidic ; they are converted to the oxides by heating under air in a process known as roasting :



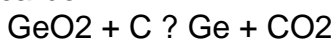
Some of the germanium is left in the dust produced , while the rest is converted to germanates , which are then leached (together with zinc) from the cinder by sulfuric acid . After neutralization , only the zinc stays in solution while germanium and other metals precipitate . After removing some of the zinc in the precipitate by the Waelz process , the residing Waelz oxide is leached a second time . The dioxide is obtained as precipitate and converted with chlorine gas or hydrochloric acid to germanium tetrachloride , which has a low boiling point and can be isolated by distillation :



Germanium tetrachloride is either hydrolyzed to the oxide (GeO_2) or purified by fractional distillation and then hydrolyzed . The highly pure GeO_2 is now suitable for the production of germanium glass . It is reduced to the element by reacting it with hydrogen , producing germanium suitable for infrared optics and semiconductor production :



The germanium for steel production and other industrial processes is normally reduced using carbon :



= = Applications = =

The major end uses for germanium in 2007 , worldwide , were estimated to be : 35 % for fiber @-@ optics , 30 % infrared optics , 15 % polymerization catalysts , and 15 % electronics and solar electric applications . The remaining 5 % went into such uses as phosphors , metallurgy , and chemotherapy .

= = = Optics = = =

The notable properties of germania (GeO_2) are its high index of refraction and its low optical dispersion . These make it especially useful for wide @-@ angle camera lenses , microscopy , and the core part of optical fibers . It has replaced titania as the dopant for silica fiber , eliminating the subsequent heat treatment that made the fibers brittle . At the end of 2002 , the fiber optics industry consumed 60 % of the annual germanium use in the United States , but this is less than 10 % of worldwide consumption . GeSbTe is a phase change material used for its optic properties , such as that used in rewritable DVDs .

Because germanium is transparent in the infrared wavelengths , it is an important infrared optical material that can be readily cut and polished into lenses and windows . It is especially used as the front optic in thermal imaging cameras working in the 8 to 14 micron range for passive thermal imaging and for hot @-@ spot detection in military , mobile night vision , and fire fighting applications . It is used in infrared spectrometers and other optical equipment that require extremely sensitive infrared detectors . It has a very high refractive index (4 @. @ 0) and must be coated with anti @-@ reflection agents . Particularly , a very hard special antireflection coating of diamond @-@ like carbon (DLC) , refractive index 2 @. @ 0 , is a good match and produces a diamond @-@ hard surface that can withstand much environmental abuse .

= = = Electronics = = =

Silicon @-@ germanium alloys are rapidly becoming an important semiconductor material for high

@-@ speed integrated circuits . Circuits utilizing the properties of Si @-@ SiGe junctions can be much faster than those using silicon alone . Silicon @-@ germanium is beginning to replace gallium arsenide (GaAs) in wireless communications devices . The SiGe chips , with high @-@ speed properties , can be made with low @-@ cost , well @-@ established production techniques of the silicon chip industry .

Solar panels are a major use of germanium . Germanium is the substrate of the wafers for high @-@ efficiency multijunction photovoltaic cells for space applications . High @-@ brightness LEDs , used for automobile headlights and to backlight LCD screens , are an important application .

Because germanium and gallium arsenide have very similar lattice constants , germanium substrates can be used to make gallium arsenide solar cells . The Mars Exploration Rovers and several satellites use triple junction gallium arsenide on germanium cells .

Germanium @-@ on @-@ insulator substrates are seen as a potential replacement for silicon on miniaturized chips . Other uses in electronics include phosphors in fluorescent lamps and solid @-@ state light @-@ emitting diodes (LEDs) . Germanium transistors are still used in some effects pedals by musicians who wish to reproduce the distinctive tonal character of the " fuzz " -tone from the early rock and roll era , most notably the Dallas Arbiter Fuzz Face .

= = = Other uses = = =

Germanium dioxide is also used in catalysts for polymerization in the production of polyethylene terephthalate (PET) . The high brilliance of this polyester is especially favored for PET bottles marketed in Japan . In the United States , germanium is not used for polymerization catalysts .

Due to the similarity between silica (SiO₂) and germanium dioxide (GeO₂) , the silica stationary phase in some gas chromatography columns can be replaced by GeO₂ .

In recent years germanium has seen increasing use in precious metal alloys . In sterling silver alloys , for instance , it reduces firescale , increases tarnish resistance , and improves precipitation hardening . A tarnish @-@ proof silver alloy trademarked Argentium contains 1 @-@ 2 % germanium .

Semiconductor detectors made of single crystal high @-@ purity germanium can precisely identify radiation sources ? for example in airport security . Germanium is useful for monochromators for beamlines used in single crystal neutron scattering and synchrotron X @-@ ray diffraction . The reflectivity has advantages over silicon in neutron and high energy X @-@ ray applications . Crystals of high purity germanium are used in detectors for gamma spectroscopy and the search for dark matter . Germanium crystals are also used in X @-@ ray spectrometers for the determination of phosphorus , chlorine and sulfur .

= = = Germanium and health = = =

Germanium is not considered essential to the health of plants or animals . Germanium in the environment has little or no health impact . This is primarily because it usually occurs only as a trace element in ores and carbonaceous materials , and the various industrial and electronic applications involve very small quantities that are not likely to be ingested . For similar reasons , end @-@ use germanium has little impact on the environment as a biohazard . Some reactive intermediate compounds of germanium are poisonous (see precautions , below) .

Germanium supplements , made from both organic and inorganic germanium , have been marketed as an alternative medicine capable of treating leukemia and lung cancer . There is , however , no medical evidence of benefit ; some evidence suggests that such supplements are actively harmful .

Some germanium compounds have been administered by alternative medical practitioners as non @-@ FDA @-@ allowed injectable solutions . Soluble inorganic forms of germanium used at first , notably the citrate @-@ lactate salt , resulted in some cases of renal dysfunction , hepatic steatosis , and peripheral neuropathy in individuals using them over a long term . Plasma and urine germanium concentrations in these individuals , several of whom died , were several orders of magnitude greater than endogenous levels . A more recent organic form , beta @-@

carboxyethylgermanium sesquioxide (propagermanium) , has not exhibited the same spectrum of toxic effects .

U.S. Food and Drug Administration research has concluded that inorganic germanium , when used as a nutritional supplement , " presents potential human health hazard " .

Certain compounds of germanium have low toxicity to mammals , but have toxic effects against certain bacteria .

= = Precautions for chemically reactive germanium compounds = =

Some of germanium 's artificially @-@ produced compounds are quite reactive and present an immediate hazard to human health on exposure . For example , germanium chloride and germane (GeH_4) are a liquid and gas , respectively , that can be very irritating to the eyes , skin , lungs , and throat .

= = Future = =

As of the year 2000 , about 15 % of United States consumption of germanium was used for infrared optics technology and 50 % for fiber @-@ optics . Over the past 20 years , infrared use has consistently decreased ; fiber optic demand , however , is slowly increasing . In America , 30 ? 50 % of fiber optic current lines in America are unused dark fiber , sparking discussion of over @-@ production and a future reduction in demand . Worldwide , demand is increasing dramatically as countries such as China are installing fiber optic telecommunication lines throughout the country .