

Boron

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Boron is a chemical element with symbol **B** and atomic number 5. Produced entirely by cosmic ray spallation and supernovae and not by stellar nucleosynthesis, it is a low-abundance element in the Solar system and in the Earth's crust.^[12] Boron is concentrated on Earth by the water-solubility of its more common naturally occurring compounds, the borate minerals. These are mined industrially as evaporites, such as borax and kernite. The largest known boron deposits are in Turkey, the largest producer of boron minerals.

Elemental boron is a metalloid that is found in small amounts in meteoroids but chemically uncombined boron is not otherwise found naturally on Earth. Industrially, very pure boron is produced with difficulty because of refractory contamination by carbon or other elements. Several allotropes of boron exist: amorphous boron is a brown powder; crystalline boron is silvery to black, extremely hard (about 9.5 on the Mohs scale), and a poor electrical conductor at room temperature. The primary use of elemental boron is as boron filaments with applications similar to carbon fibers in some high-strength materials.

Boron is primarily used in chemical compounds. About half of all consumption globally, boron is used as an additive in glass fibers of boron-containing fiberglass for insulation and structural materials. The next leading use is in polymers and ceramics in high-strength, lightweight structural and refractory materials. Borosilicate glass is desired for its greater strength and thermal shock resistance than ordinary soda lime glass. Boron compounds are used as fertilizers in agriculture and in sodium perborate bleaches. A small amount of boron is used as a dopant in semiconductors, and reagent intermediates in the synthesis of organic fine chemicals. A few boron-containing organic pharmaceuticals are used or are in study. Natural boron is composed of two stable isotopes, one of which (boron-10) has a number of uses as a neutron-capturing agent.

In biology, borates have low toxicity in mammals (similar to table salt), but are more toxic to arthropods and are used as insecticides. Boric acid is mildly antimicrobial, and several natural boron-containing organic antibiotics are known.^[13] Boron is essential to life. Small amounts of boron compounds play a strengthening role in the cell walls

Boron, ₅B



boron (β-rhombohedral)^[1]

General properties

| | |
|----------------------|--|
| Name, symbol | boron, B |
| Pronunciation | /ˈbɔːrən/ |
| Allotropes | α-, β-rhombohedral, β-tetragonal (and more) |
| Appearance | black-brown |

Boron in the periodic table

| | |
|---|---|
| Atomic number (<i>Z</i>) | 5 |
| Group, block | group 13, p-block |
| Period | period 2 |
| Element category | metalloid |
| Standard atomic weight (<i>A</i> _r) | 10.81 ^[2] (10.806–10.821) ^[3] |
| Electron configuration | [He] 2s ² 2p ¹ |
| per shell | 2, 3 |

of all plants, making boron a necessary plant nutrient. Boron is involved in the metabolism of calcium in both plants and animals. It is considered an essential nutrient for humans, and boron deficiency is implicated in osteoporosis.

Characteristics

Allotropes



Boron chunks

Boron is similar to carbon in its capability to form stable covalently bonded molecular networks. Even nominally disordered (amorphous) boron contains regular boron icosahedra which are, however, bonded randomly to each other without long-range order.^{[23][24]} Crystalline boron is a very hard, black material with a melting point of above 2000 °C. It forms four major polymorphs: α-rhombohedral and β-rhombohedral (α-R and β-R), γ and β-tetragonal (β-T); α-tetragonal phase also exists (α-T), but is very difficult to produce without significant contamination. Most of the phases are based on B₁₂ icosahedra, but the γ-phase can be described as a rocksalt-type arrangement of the icosahedra and B₂ atomic pairs.^[25] It can be produced by compressing other

boron phases to 12–20 GPa and heating to 1500–1800 °C; it remains stable after releasing the temperature and pressure. The T phase is produced at similar pressures, but higher temperatures of 1800–2200 °C. As to the α and β phases, they might both coexist at ambient conditions with the β phase being more stable.^{[25][26][27]} Compressing boron above 160 GPa produces a boron phase with an as yet unknown structure, and this phase is a superconductor at temperatures 6–12 K.^[28] Borospherene (fullerene-like B₄₀) molecules) and borophene (proposed graphene-like structure) have been described in 2014.

Chemistry of the element

Elemental boron is rare and poorly studied because the pure material is extremely difficult to prepare. Most studies of "boron" involve samples that contain small amounts of carbon. The chemical behavior of boron resembles that of silicon more than aluminium. Crystalline boron is chemically inert and resistant to attack by boiling

Physical properties

| | |
|--|---------------------------|
| Phase | solid |
| Melting point | 2349 K (2076 °C, 3769 °F) |
| Boiling point | 4200 K (3927 °C, 7101 °F) |
| Density when liquid, at m.p. | 2.08 g/cm ³ |
| Heat of fusion | 50.2 kJ/mol |
| Heat of vaporization | 508 kJ/mol |
| Molar heat capacity | 11.087 J/(mol·K) |

Vapor pressure

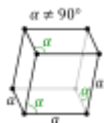
| P (Pa) | 1 | 10 | 100 | 1 k | 10 k | 100 k |
|----------|------|------|------|------|------|-------|
| at T (K) | 2348 | 2562 | 2822 | 3141 | 3545 | 4072 |

Atomic properties

| | |
|-----------------------------|---|
| Oxidation states | 3, 2, 1, −1, −5 ^{[4][5]} (a mildly acidic oxide) |
| Electronegativity | Pauling scale: 2.04 |
| Ionization energies | 1st: 800.6 kJ/mol 2nd: 2427.1 kJ/mol 3rd: 3659.7 kJ/mol (more) |
| Atomic radius | empirical: 90 pm |
| Covalent radius | 84±3 pm |
| Van der Waals radius | 192 pm |

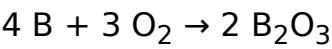
Miscellanea

| | |
|--------------------------|--------------|
| Crystal structure | rhombohedral |
|--------------------------|--------------|

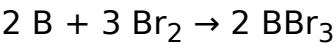


hydrofluoric or hydrochloric acid. When finely divided, it is attacked slowly by hot concentrated hydrogen peroxide, hot concentrated nitric acid, hot sulfuric acid or hot mixture of sulfuric and chromic acids.^[20]

The rate of oxidation of boron depends on the crystallinity, particle size, purity and temperature. Boron does not react with air at room temperature, but at higher temperatures it burns to form boron trioxide:^[37]



Boron undergoes halogenation to give trihalides; for example,



The trichloride in practice is usually made from the oxide.^[37]

Chemical compounds

In the most familiar compounds, boron has the formal oxidation state III. These include oxides, sulfides, nitrides, and halides.^[37]

The trihalides adopt a planar trigonal structure. These compounds are Lewis acids in that they readily form adducts with electron-pair donors, which are called Lewis bases. For example, fluoride (F[−]) and boron trifluoride (BF₃) combined to give the tetrafluoroborate anion, BF₄[−]. Boron trifluoride is used in the petrochemical industry as a catalyst. The halides react with water to form boric acid.^[37]

Boron is found in nature on Earth entirely as various oxides of B(III), often associated with other elements. More than one hundred borate minerals contain boron in oxidation state +3. These minerals resemble silicates in some respect, although boron is often found not only in a tetrahedral coordination with oxygen, but also in a trigonal planar configuration. Unlike silicates, the boron minerals never contain boron with coordination number greater than four. A typical motif is exemplified by the tetraborate anions of the common mineral borax, shown at left. The formal negative charge of the tetrahedral borate center is balanced by metal cations in the minerals, such as the sodium (Na⁺) in borax.^[37]

| | |
|-----------------------------------|---|
| Speed of sound thin rod | 16,200 m/s (at 20 °C) |
| Thermal expansion | β form: 5–7 μm/(m·K) (at 25 °C) ^[6] |
| Thermal conductivity | 27.4 W/(m·K) |
| Electrical resistivity | ~10 ⁶ Ω·m (at 20 °C) |
| Magnetic ordering | diamagnetic ^[7] |
| Mohs hardness | ~9.5 |
| CAS Number | 7440-42-8 |

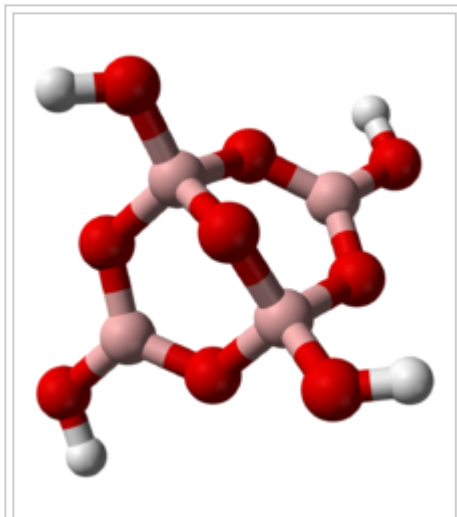
History

| | |
|------------------------|--|
| Discovery | Joseph Louis Gay-Lussac and Louis Jacques Thénard ^[8] (30 June 1808) |
| First isolation | Humphry Davy ^[9] (9 July 1808) |

Most stable isotopes of boron

| iso | NA | half-life | DM | DE (MeV) | DP |
|-----------------------|-----|---|----|----------|----|
| ¹⁰B | 20% | is stable with 5 neutrons ^[10] | | | |
| ¹¹B | 80% | is stable with 6 neutrons ^[10] | | | |

¹⁰B content may be as low as 19.1% and as high as 20.3% in natural samples. ¹¹B is the remainder in such cases.^[11]



Ball-and-stick model of tetraborate anion, $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$, as it occurs in crystalline borax, $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$. Boron atoms are pink, with bridging oxygens in red, and four hydroxyl hydrogens in white. Note two borons are trigonally bonded sp^2 with no formal charge, while the other two borons are tetrahedrally bonded sp^3 , each carrying a formal charge of -1 . The oxidation state of all borons is III. This mixture of boron coordination numbers and formal charges is characteristic of natural boron minerals.

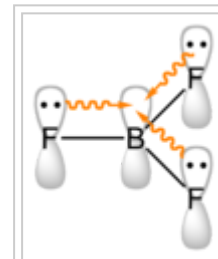
Boranes are chemical compounds of boron and hydrogen, with the generic formula of B_xH_y . These compounds do not occur in nature. Many of the boranes readily oxidise on contact with air, some violently. The parent member BH_3 is called borane, but it is known only in the gaseous state, and dimerises to form diborane, B_2H_6 . The larger boranes all consist of boron clusters that are polyhedral, some of which exist as isomers. For example, isomers of $\text{B}_{20}\text{H}_{26}$ are based on the fusion of two 10-atom clusters.

The most important boranes are diborane B_2H_6 and two of its pyrolysis products, pentaborane B_5H_9 and decaborane $\text{B}_{10}\text{H}_{14}$. A large number of anionic boron hydrides are known, e.g. $[\text{B}_{12}\text{H}_{12}]^{2-}$.

The formal oxidation number in boranes is positive, and is based on the assumption that hydrogen is counted as -1 as in active metal hydrides. The mean oxidation number for the borons is then simply the ratio of hydrogen to boron in the molecule. For example, in diborane B_2H_6 , the boron oxidation state is $+3$, but in decaborane $\text{B}_{10}\text{H}_{14}$, it is $7/5$ or $+1.4$. In these compounds the oxidation state of boron is often not a whole number.

The boron nitrides are notable for the variety of structures that they adopt. They exhibit structures analogous to various allotropes of carbon, including graphite, diamond, and nanotubes. In the diamond-like structure, called cubic boron nitride (tradename Borazon), boron atoms exist in the tetrahedral structure of carbons atoms in diamond, but one in every four B-N bonds can be viewed as a coordinate covalent bond, wherein two electrons are donated by the nitrogen atom which acts as the Lewis base to a bond to the Lewis acidic boron(III) centre. Cubic boron nitride, among other applications, is used as an abrasive, as it has a hardness comparable with diamond (the two substances are able to produce scratches on each other). In the BN compound analogue of graphite, hexagonal boron nitride (h-BN), the positively charged boron and negatively charged nitrogen atoms in each plane lie adjacent to the oppositely charged atom in the next plane. Consequently, graphite and h-BN have very different properties, although both are lubricants, as these planes slip past each other easily. However, h-BN is a relatively poor electrical and thermal conductor in the planar directions.^{[38][39]}

Organoboron chemistry



Boron (III) trifluoride structure, showing "empty" boron p orbital in pi-type coordinate covalent bonds

A large number of organoboron compounds are known and many are useful in organic synthesis. Many are produced from hydroboration, which employs diborane, B_2H_6 , a simple borane chemical. Organoboron(III) compounds are usually tetrahedral or trigonal planar, for example, tetraphenylborate, $[B(C_6H_5)_4]^-$ vs. triphenylborane, $B(C_6H_5)_3$. However, multiple boron atoms reacting with each other have a tendency to form novel dodecahedral (12-sided) and icosahedral (20-sided) structures composed completely of boron atoms, or with varying numbers of carbon heteroatoms.

Organoboron chemicals have been employed in uses as diverse as boron carbide (see below), a complex very hard ceramic composed of boron-carbon cluster anions and cations, to carboranes, carbon-boron cluster chemistry compounds that can be halogenated to form reactive structures including carborane acid, a superacid. As one example, carboranes form useful molecular moieties that add considerable amounts of boron to other biochemicals in order to synthesize boron-containing compounds for boron neutron capture therapy for cancer.

Compounds of B(I) and B(II)

Although these are not found on Earth naturally, boron forms a variety of stable compounds with formal oxidation state less than three. As for many covalent compounds, formal oxidation states are often of little meaning in boron hydrides and metal borides. The halides also form derivatives of B(I) and B(II). BF , isoelectronic with N_2 , cannot be isolated in condensed form, but B_2F_4 and B_4Cl_4 are well characterized.^[40]

Binary metal-boron compounds, the metal borides, contain boron in negative oxidation states. Illustrative is magnesium diboride (MgB_2). Each boron atom has a formal -1 charge and magnesium is assigned a formal charge of $+2$. In this material, the boron centers are trigonal planar with an extra double bond for each boron, forming sheets akin to the carbon in graphite. However, unlike hexagonal boron nitride, which lacks electrons in the plane of the covalent atoms, the delocalized electrons in magnesium diboride allow it to conduct electricity similar to isoelectronic graphite. In 2001, this material was found to be a high-temperature superconductor.^{[41][42]}

Certain other metal borides find specialized applications as hard materials for cutting tools.^[43] Often the boron in borides has fractional oxidation states, such as $-1/3$ in calcium hexaboride (CaB_6).

From the structural perspective, the most distinctive chemical compounds of boron are the hydrides. Included in this series are the cluster compounds dodecaborate ($B_{12}H_{12}^{2-}$), decaborane ($B_{10}H_{14}$), and the carboranes such as $C_2B_{10}H_{12}$. Characteristically such compounds contain boron with coordination numbers greater than four.^[37]

Isotopes

Boron has two naturally occurring and stable isotopes, ^{11}B (80.1%) and ^{10}B (19.9%). The mass difference results in a wide range of $\delta^{11}\text{B}$ values, which are defined as a fractional difference between the ^{11}B and ^{10}B and traditionally expressed in parts per thousand, in natural waters ranging from -16 to $+59$. There are 13 known isotopes of boron, the shortest-lived isotope is ^7B which decays through proton emission and alpha decay. It has a half-life of 3.5×10^{-22} s. Isotopic fractionation of boron is controlled by the exchange reactions of the boron species $\text{B}(\text{OH})_3$ and $[\text{B}(\text{OH})_4]^-$. Boron isotopes are also fractionated during mineral crystallization, during H_2O phase changes in hydrothermal systems, and during hydrothermal alteration of rock. The latter effect results in preferential removal of the $[\text{B}(\text{OH})_4]^-$ ion onto clays. It results in solutions enriched in $^{11}\text{B}(\text{OH})_3$ and therefore may be responsible for the large ^{11}B enrichment in seawater relative to both oceanic crust and continental crust; this difference may act as an isotopic signature.^[44]

The exotic ^{17}B exhibits a nuclear halo, i.e. its radius is appreciably larger than that predicted by the liquid drop model.^[45]

The ^{10}B isotope is useful for capturing thermal neutrons (see neutron cross section#Typical cross sections). The nuclear industry enriches natural boron to nearly pure ^{10}B . The less-valuable by-product, depleted boron, is nearly pure ^{11}B .

Commercial isotope enrichment

Because of its high neutron cross-section, boron-10 is often used to control fission in nuclear reactors as a neutron-capturing substance.^[46] Several industrial-scale enrichment processes have been developed; however, only the fractionated vacuum distillation of the dimethyl ether adduct of boron trifluoride (DME-BF_3) and column chromatography of borates are being used.^{[47][48]}

Enriched boron (boron-10)

Enriched boron or ^{10}B is used in both radiation shielding and is the primary nuclide used in neutron capture therapy of cancer. In the latter ("boron neutron capture therapy" or BNCT), a compound containing ^{10}B is incorporated into a pharmaceutical which is selectively taken up by a malignant tumor and tissues near it. The patient is then treated with a beam of low energy neutrons at a relatively low neutron radiation dose. The neutrons, however, trigger energetic and short-range secondary alpha particle and lithium-7 heavy ion radiation that are products of the boron + neutron nuclear reaction, and this ion radiation additionally bombards the tumor, especially from inside the tumor cells.^{[49][50][51][52]}

In nuclear reactors, ^{10}B is used for reactivity control and in emergency shutdown systems. It can serve either function in the form of borosilicate control rods or as boric acid. In pressurized water reactors, boric acid is added to the reactor coolant when the plant is shut down for refueling. It is then slowly filtered out over many months as fissile material is used up and the fuel becomes less reactive.^[53]

In future manned interplanetary spacecraft, ^{10}B has a theoretical role as structural material (as boron fibers or BN nanotube material) which would also serve a special role in the radiation shield. One of the difficulties in dealing with cosmic rays, which are mostly high energy protons, is that some secondary radiation from interaction of cosmic rays and spacecraft materials is high energy spallation neutrons. Such neutrons can be moderated by materials high in light elements such as polyethylene, but the moderated neutrons continue to be a radiation hazard unless actively absorbed in the shielding. Among light elements that absorb thermal neutrons, ^6Li and ^{10}B appear as potential spacecraft structural materials which serve both for mechanical reinforcement and radiation protection.^[54]

Depleted boron (boron-11)

Radiation-hardened semiconductors

Cosmic radiation will produce secondary neutrons if it hits spacecraft structures. Those neutrons will be captured in ^{10}B , if it is present in the spacecraft's semiconductors, producing a gamma ray, an alpha particle, and a lithium ion. Those resultant decay products may then irradiate nearby semiconductor "chip" structures, causing data loss (bit flipping, or single event upset). In radiation-hardened semiconductor designs, one countermeasure is to use *depleted boron*, which is greatly enriched in ^{11}B and contains almost no ^{10}B . This is useful because ^{11}B is largely immune to radiation damage. Depleted boron is a byproduct of the nuclear industry.^[53]

Proton-boron fusion

^{11}B is also a candidate as a fuel for aneutronic fusion. When struck by a proton with energy of about 500 keV, it produces three alpha particles and 8.7 MeV of energy. Most other fusion reactions involving hydrogen and helium produce penetrating neutron radiation, which weakens reactor structures and induces long-term radioactivity, thereby endangering operating personnel. However, the alpha particles from ^{11}B fusion can be turned directly into electric power, and all radiation stops as soon as the reactor is turned off.^[55]

NMR spectroscopy

Both ^{10}B and ^{11}B possess nuclear spin. The nuclear spin of ^{10}B is 3 and that of ^{11}B is $\frac{3}{2}$. These isotopes are, therefore, of use in nuclear magnetic resonance spectroscopy; and spectrometers specially adapted to detecting the boron-11 nuclei are available commercially. The ^{10}B and ^{11}B nuclei also cause splitting in the resonances of attached nuclei.^[56]

Occurrence



A fragment of ulexite

Boron is rare in the Universe and solar system due to trace formation in the Big Bang and in stars. It is formed in minor amounts in cosmic ray spallation nucleosynthesis and may be found uncombined in cosmic dust and meteoroid materials. In the high oxygen environment of Earth, boron is always found fully oxidized to borate. Boron does not appear on Earth in elemental form. Extremely tiny elemental boron was detected in Lunar regolith^{[57][58]}

Although boron is a relatively rare element in the Earth's crust, representing only 0.001% of the crust mass, it can be highly concentrated by the action of water, in which many borates are soluble. It is found naturally combined in compounds such as borax and boric acid (sometimes found in volcanic spring waters). About a hundred borate minerals are known.



Borax crystals

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