BORON, ELEMENTAL

1. Introduction

Boron [7440-42-8], B, is unique in that it is the only nonmetal in Group 13 (IIIA) of the Periodic Table. Boron, at wt 10.81, at no. 5, has more similarity to carbon and silicon than to the other elements in Group 13 (III A). There are two stable boron isotopes, ^{10}B and ^{11}B, which are naturally present at 19.10–20.31% and 79.69–80.90%, respectively. The range of the isotopic abundancies reflects a variability in naturally occurring deposits such as high ^{10}B ore from Turkey and low ^{10}B ore from California. Other boron isotopes, ^{8}B, ^{12}B, and ^{13}B, have half-lives of <1 s. The ^{10}B isotope has a very high cross-section for absorption of thermal neutrons, 3.835×10^{-25} m^2 (3835 barns). This neutron absorption produces alpha particles.

Table 1. **Boron Minerals of Commercial Importance**

Mineral[a]	Chemical composition	CAS Registry no.	Boron oxide, wt%
Boracite (stassfurite)	$Mg_6B_{14}O_{26}C_{12}$	[1318-33-8]	62.2
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	[12291-65-5]	50.8
Datolite	$CaBSiO_4 \cdot OH$	[1318-40-7]	24.9
Hydroboracite	$CaMgB_6O_{11} \cdot 6H_2O$	[12046-12-7]	50.5
Kernite (rasortie)	$Na_2B_4O_7 \cdot 4H_2O$	[12045-87-3]	51.0
Priceite (pandermite)	$CaB_{10}O_{19} \cdot 7H_2O$	[61583-61-7]	49.8
Probertite (kramerite)	$NaCaB_3O_9 \cdot 5H_2O$	[12229-14-0]	49.6
Sassolite (natural boric acid)	H_3BO_3	[10043-35-3]	56.3
Szaibelyite (ascharite)	$MgBO_2 \cdot 20H_2O$	[12447-04-0] [36564-04-2]	41.4
Tincal (natural borax)	$Na_2B_4O_7 \cdot 10H_2O$	[1303-96-4]	36.5
Tincalconite (mohavite)	$Na_2B_4O_7 \cdot 5H_2O$	[12045-88-4]	47.8
Ulexite (boronatrocalcite)	$NaCaB_5O_9 \cdot 8H_2O$	[1319-33-1]	43.0

[a] Parentheses include common names.

There is a very low cosmic abundance of boron, but its occurrence at all is surprising for two reasons. First, boron's isotopes are not involved in a star's normal chain of thermonuclear reactions, and second, boron should not survive a star's extreme thermal condition. The formation of boron has been proposed to arise predominantly from cosmic ray bombardment of interstellar gas in a process called spallation (1).

Boron is the 51st most common element present in the earth's crust at a concentration of three grams per metric ton. A widespread boron mineral is tourmaline [1317-93-7], a complex borosilicate of aluminum containing ~10% boron. However, the most common ores are alkali and alkaline-earth borates. Table 1 is a list of boron minerals of commercial importance (2). Borax is the most important ore of boron. Commercial deposits are rare; the two principal ones are in the Mojave desert in California and in Turkey (see BORON COMPOUNDS, BORON OXIDES).

2. Properties

Elemental boron has a diverse and complex chemistry, primarily influenced by three circumstances. First, boron has a high ionization energy, 8.296, 23.98, and 37.75 eV for first, second, and third ionization potentials, respectively. Second, boron has a small size. Third, the electronegativities of boron (2.0), carbon (2.5), and hydrogen (2.1) are all very similar resulting in extensive and unusual covalent chemistry.

Boron has electronic structure $1s^2 2s^2 2p$ and an expected valence of three. Because of the high ionization energies there is no formation of univalent compounds as for the other Group 13 elements. Boron forms planar tricovalent compounds, BX_3, $X =$ halides, alkyls, etc, having the expected 120° bonding angles. The empty p orbital makes these compounds electron-pair acceptors or Lewis acids. Alkyls and halides of aluminum dimerize to make up for the deficiency of electrons, but the boron atom is too small to coordinate strongly.

Boron also has a high affinity for oxygen-forming borates, polyborates, borosilicates, peroxoborates, etc. Boron reacts with water at temperatures above 100°C to form boric acid and other boron compounds (qv).

Boron is electron deficient relative to carbon. Therefore, small amounts of boron, replacing carbon in a diamond lattice, causes electron holes. As electrons move to fill these lattice vacancies, infrared light is absorbed causing the blue color of the Hope diamond and other blue diamonds.

Boron forms B–N compounds that are isoelectronic with graphite (see BORON COMPOUNDS, REFRACTORY BORON COMPOUNDS). The small size also has a significant role in the interstitial alloy-type metal borides boron forms. Boron forms borides with metals that are less electronegative than itself including titanium, zirconium, and hafnium.

Boron's electron deficiency does not permit conventional two-electron bonds. Boron can form multicenter bonds. Thus the boron hydrides have structures quite unlike hydrocarbons. The ^{11}B nucleus, which has a spin of 3/2, which has been employed in boron nuclear magnetic resonance (nmr) spectroscopy.

Crystalline boron is very inert. Low purity, higher temperatures, and changes in or lack of crystallinity all increase the chemical reactivity. Hot concentrated H_2SO_4–HNO_3 at 2:1 ratio can be used to dissolve boron for chemical analysis but boron is not soluble in boiling HF or HCl. Boron is also unreactive toward concentrated NaOH up to 500°C. At room temperature, boron reacts with F_2, but only superficially with O_2.

The physical properties of elemental boron are significantly affected by purity and crystal form. In addition to being an amorphous powder, boron has four crystalline forms: α-rhombohedral, β-rhombohedral, α-tetragonal, and β-tetragonal. The α-rhombohedral form has mp 2180°C, sublimes at ~3650°C, and has a density of 2.45 g/mL. Amorphous boron, by comparison, has mp 2300°C, sublimes at ~2550°C, and has a density of 2.35 g/mL.

Boron is an extremely hard refractory solid having a hardness of 9.3 on Mohs' scale and a very low ($1.5 \times 10^{-6}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) room temperature electrical conductivity so that boron is classified as a metalloid or semiconductor. These values are for the α-rhombohedral form.

The electron-deficient character of boron also affects its allotropic forms. The high ionization energies and small size prevent boron from adopting metallic bonding to compensate for its electron deficiency and that of other hypoelectronic elements. The structural unit dominating boron's covalent bonding is the B_{12} icosahedron.

The α-rhombohedral form of boron has the simplest crystal structure with slightly deformed cubic close packing. At 1200°C α-rhombohedral boron degrades, and at 1500°C converts to β-rhombohedral boron, which is the most thermodynamically stable form. The unit cell has 104 boron atoms, a central B_{12} icosahedron, and 12 pentagonal pyramids of boron atom directed outward. Twenty additional boron atoms complete a complex coordination (1).

The α-tetragonal form of boron has a unit cell $B_{50}C_2$ or $B_{50}N_2$; it always has a carbon or nitrogen in the crystal. The cell is centered: a single boron atom is coordinated to four icosahedrons ($4B_{12} + 2B$). The β-tetragonal form is believed to have a unit cell of 192 boron atoms.

3. Preparation

Amorphous boron, discovered and named by Sir Humphry Davy in 1807, was first made by electrolyzing boric acid. Then in 1808, boron was produced by using potassium to reduce boric acid. The initial reactions resulted in boron that was <50% pure. A process to produce boron of >90% purity was developed in 1892 by reducing boric oxide with magnesium, and by 1909, >99% boron was obtained by the decomposition of boron trichloride in hydrogen using an alternating current arc. These three methods, electrolytic reduction, chemical reduction, and thermal decomposition, are still used on a laboratory scale. A high purity (>99%) boron comes from the direct thermal decomposition of boron hydrides such as diborane [19287-45-7], B_2H_6. The kinetics of boron formation is discussed in an excellent review (3). Less pure boron from other methods can be purified by zone-refining (qv) or progressive recrystallization.

4. Production

The Moissan process, the reduction of boric oxide with magnesium, is the most widely used commercial process for producing boron. Although boric oxide can be reduced by many other agents, including calcium and potassium, the most efficient is magnesium. This process yields material from 90–92% pure. The boron is then leached with acid to separate it from the magnesium oxide formed in the process followed by multiple washes and final drying. Chemical processing can increase this purity to 95–97% pure. Boron is ground and made available in a particle size of about one micrometer. Multiple steps require an increase in handling of chemical waste, which must be recycled or disposed.

Another commercial process yields high purity boron of >99%. In this process boron hydrides, such as diborane, are thermally decomposed (4). Because only boron and hydrogen are present in the starting material, contamination is minimal, and a very uniform, submicrometer powder is formed by the gas nucleation process.

5. Health and Safety Factors

Boron is a trace element that is essential to human health and behavior. Evidence points to the fact that boron may reduce either the symptoms or incidence of arthritis. Researchers have discovered a relationship between the amount of boron in the soil and drinking water and the incidence of arthritis in an area. Postmenopausal women who were magnesium deficient, benefited from 3 mg/day of boron added to their diet, which resulted in calcium and magnesium retention and elevations in circulating serums of testosterone and a form of estrogen. Similar improvements were seen in Vitamin D deficient postmenopausal women. No recommended daily allowance has been set for humans, but females are recommended to take 2.0 mg/day (5).

There have been no reports of toxicity in humans. Since the element is very insoluble, the dust should be treated as such, with a respirable dust limit applied (6).

6. Uses

Elemental boron is used in very diverse industries from metallurgy (qv) to electronics. Other areas of application include ceramics (qv), propulsion, pyrotechnics, and nuclear chemistry.

Dispersed mixtures of boron and another metal are used as deoxidizing and degassing agents to harden steel (qv) (7,8), to increase the conductivity of copper (qv) in turbojet engines, and in the making of brass and bronze (see COPPER ALLOYS). Two examples are alloys of ferroboron and manganese boron.

Another metallurgical application is in amorphous magnetic alloys that are based on boron and iron, nickel, or cobalt (see MAGNETIC MATERIALS, BULK). The boron is used in power transformers as a soft magnet to convert from high to lower voltage; this material is commercially available from Allied-Signal, Inc. under the trademark METGLAS (see GLASSY METALS).

Another material that has permanent magnetic properties is neodymium–iron–boron, $Nd_2Fe_{14}B$. For an in-depth discussion see Ref. 9. Aimants Ugima, a member of the Pechiney Group, is a leading producer of rare-earth magnets in both the United States and Europe. Sumitomo Special Metals of Japan also produces these rare-earth magnets under the trade name of Neomax, and General Motors has commercial-scale production of a material called MAGNEQUENCH. The first World Solar Challenge Race, in 1987, was won using an electric motor fabricated using Nd–Fe–B. More mundane applications for cars include fuel pump motors, headlight door motors, starter motors, and heater motors. A patent has also been awarded for Nd–Fe–B bonded in polymer material that can be stamped and shaped easily for making electronic components for applications including stereo speakers and computer chip switches (10) (see MAGNETIC MATERIALS, THIN-FILMS AND PARTICLES).

The Federal Railroad Administration of the U.S. Department of Transportation intends to construct a magnetic levitation train (maglev). Maglev is an advanced transportation technology in which magnetic forces lift, propel, and guide a vehicle over a specially designed guide way. Boron is used in the superconducting and other high intensity magnets of this system. Maglev could reduce the need for many mechanical parts and thereby minimizing resistance permitting excellent acceleration and cruising speeds of 386 km/h (240 mi/h) (11).

The ceramic, polycrystalline silicon carbide [409-21-2], SiC, is processed using β-silicon carbide and boron (12). The boron is a sintering aid used at 0.3–3% by weight to densify the sintered body to at least 85% of theoretical. The increased density improves strength (see ADVANCED CERAMICS).

Boron filaments are formed by the chemical vapor deposition of boron trichloride on tungsten wire. High performance reinforcing boron fibers are available from 10 to 20 mm in diameter. These are used mainly in epoxy resins and aluminum and titanium. Commercial uses include golf club shafts, tennis and squash racquets, and fishing rods.The primary use is in the aerospace industry.

Boron has been studied as a possible fuel for solid fuel ramjets (13,14). Fine particle sized boron, where the average particle size is 0.3 μm, has been studied for use as a gas-generating agent for solid fuel ram rockets (15).

DaimlerChrysler AG's Natrium Town and Country minivan is powered by fuel technology using water, borax, and hydrogen. Hydrogen derived from sodium borohydride is the most promising of all energy carriers. It is entirely free of carbon monoxide, which can damage cells. It is efficient, clean, abundant, and renewable energy. The fuel cells were to be used in buses in 2002 and are expected to be used in passenger cars in 2004 (16).

Boron mixed with an oxidizer is used as a pyrotechnic. This ordnance application for missiles and rockets is predominantly military. However, boron is also used in air bags, placed in automobiles as safety devices, for initiating the sodium azide [26628-22-8] that fills the bag with nitrogen (17). Other boron compounds are also used in the air-bag pyrotechnic application.

Boron creates an electron deficiency in the silicon lattice resulting in a p-type semiconductor for $p{-}n$ junctions. Boron compounds are more commonly used as the dopant, however (see BORON HYDRIDES).

The high cross-section for thermal neutrons results in the use of boron and boron compounds for radiation shielding (18). The ease of detecting the α-particle produced when boron absorbs thermal neutrons results in the use of boron for neutron counters as well. The U.S. Department of Energy plans to store spent nuclear fuel encased in boron-containing glass inside stainless steel containers underground at Yucca Mountain in Nevada in 2009 (2).

The U.S. Department of Energy has studied boron–aluminum–magnesium alloys and found its hardness nearly equal to that of diamond. Diamond wears quickly when cutting steel. The new alloy cuts without getting hot because of its fine grain size and complex crystal structure (19).

Millenium Cell has patented a design for boron-based longer life batteries. The batteries are potentially several times better than zinc batteries and can last as long as traditional batteries (20).

Boron is one of 16 nutrients essential to all plants. It is essential to plant growth and can be applied as a spray and incorporated in fertilizers, herbicides, and irrigation water.

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