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BORON

and its **ISOTOPES**

Compiled for the U. S. ATOMIC ENERGY COMMISSION

by the HOOKER ELECTROCHEMICAL COMPANY, Niagara Falls, N. Y.

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TO HELP YOU

This guide will supply answers to your questions concerning boron isotopes of masses 10 and 11. You may save time and avoid expense by using the sections on "Uses of Boron Isotopes" as a source of possible solutions for your related problems. Scattered data on the physical, chemical and nuclear properties of boron and its isotopes have been brought together for your ready reference.

The boron isotope of mass 10 is being made available in increasing quantities by the U. S. Atomic Energy Commission for use in peace time application of Atomic Energy. This increased production is being carried on at government facilities operated by the Hooker Electrochemical Company. The facilities are located at Model City, New York.

Availability and prices of boron and boron compounds enriched in B^{10} are included. Inquiries concerning B^{10} as well as B^{11} should be addressed to:

Chief, Niagara Falls Branch
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P.O. Box 338
Niagara Falls, New York

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BORON AND ITS ISOTOPES

INTRODUCTION

Occurrence

Boron is found in the earth's crust to the extent of 0.001%. It occurs concentrated in deposits of Sassolite (H_3BO_3), Colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), Ulexite ($\text{CaNaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$) and Kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$). The primary deposit of boron compounds in the United States is found in California and consists of Kernite. Sodium borate is recovered from Kernite, which is approximately 75% sodium borate and 25% clay, by crystallization techniques.

Isotopes

Boron is classified as a metalloid in group 3 of the periodic table. The element, listed as #5 in the periodic system, has 5 protons in the nucleus. The two stable isotopes, 10 and 11, have 5 and 6 neutrons respectively. Isotopes having atomic weights of 8, 9, and 12 are known but have very short half lives. The normal ratio of the two stable isotopes as found in nature has been subject to question for some time. The presently accepted value is 19.57% B^{10} ; 80.43% B^{11} . Although the atomic weight of natural boron as calculated from the ratio of its isotopes should be taken as 10.81, the value of 10.82 as listed in the latest tables of atomic weights and determined on naturally occurring material should probably be taken as a preferred value.

The Element Boron

Elemental boron was first prepared by Sir Humphrey Davy in 1808 and shortly thereafter by Gay-Lussac and Thénard. Until recently, materials believed to be elemental boron were actually borides, boron carbides or aluminum borides. As a result of the questionable purity of some sources of boron, as well as variations in the methods and temperatures of reduction of boron compounds to the

elemental form, the literature shows considerable inconsistency in physical properties.

SEPARATION OF BORON ISOTOPES

The U. S. Atomic Energy Commission Plant at Model City, New York is operated for the AEC by the Hooker Electrochemical Company. The function of this plant is to separate the isotopes of boron and reduce the boron compounds to the elemental form. The separation of B^{10} from B^{11} as practiced at the Model City Plant is an association-dissociation process. The material used to effect the separation of boron isotopes is dimethyl ether-boron trifluoride complex. This complex is prepared by combining methyl ether and commercially available boron trifluoride containing the natural ratio of isotopes. The methyl ether is prepared at the plant site by the catalytic dehydration of methyl alcohol at 350°C.

The complex is fed into what is believed to be one of the most effective large-scale fractionation columns in the United States and Canada. This column has an effective height of 350 feet, having the equivalent of 380 theoretical plates. Since such a vertical height is impractical, the column is constructed as 5 columns, 20" in diameter by 65' high and one column 6" in diameter by 25' high. These units are connected in series by suitable pumps and controls so as to function as a single column. A reflux ratio of approximately 700:1 is used. Due to B^{10} being a slightly better electron acceptor than B^{11} , the B^{10}F_3 produced by dissociation of the complex, reassociates more rapidly than the B^{11}F_3 . The ultimate result is that there is a gradual build-up of B^{11} in the vapor phase and a build-up of B^{10} in the liquid phase. Thus, the heavier isotope is concentrated in the vapor phase and is removed from the top of the column while the B^{10} , or lighter isotope, is concentrated in the bottom of the column in the liquid phase. The product of these columns is

B¹⁰ enriched complex which is removed and then purified by distillation.

PRODUCTION OF ELEMENTAL BORON

The complex produced by the isotope separation portion of the plant is reacted with potassium fluoride to produce potassium fluoroborate. Potassium fluoroborate is reduced to elemental boron by fused-salt electrolysis using an electrolyte of potassium fluoride, potassium chloride and potassium fluoroborate. Electrolysis is accomplished at temperatures of approximately 800°C. A Hooker designed cell and a process modified by Hooker were used to achieve the high purity and yields necessitated by the high cost of the boron compounds produced by the isotope separation plant.

After suitable grinding, leaching and drying operations, the elemental boron product satisfies the following specifications:

1. B¹⁰ to total boron ratio — 92% ±0.5%
2. Total boron — 94% minimum
3. Particle size — 100% through 100 mesh screen, 90% through 200 mesh screen
4. Iron — less than 0.3%

Although this is the standard material produced, isotopic ratios from 30% B¹⁰ to 95% B¹⁰ as complex can be supplied. In addition, experimental quantities of KBF₄ and elemental boron containing various isotopic ratios, as well as B¹¹ enriched to an isotopic ratio of approximately 99% B¹¹, can be supplied. Other particle sizes can also be supplied.

PHYSICAL PROPERTIES OF ELEMENTAL BORON

The literature shows considerable inconsistency in the physical properties of elemental boron. This inconsistency appears to be a function of the purity, physical form and method of preparation.

Physical Properties of Elemental Boron

Atomic No.	5
Atomic Wt.	10.82
Valence (normal)	3
Color	Black
Density	2.33
Melting Point	2300°C
Boiling Point	2550°C
Heat of Combustion (with O ₂)	14 Kilocalories/gram
Heat of Vaporization	90,000 cal/mole
Heat Capacity	1.54 + 0.00440T Cal/mole/°C in 273° to 1174°K range.
Enthalpy	127°C — 300 cal/mole 327°C — 1,080 cal/mole 527°C — 2,040 cal/mole 727°C — 3,130 cal/mole
Entropy	25°C — 1.7 cal/mole/°C 127°C — 2.57 cal/mole/°C 327°C — 4.13 cal/mole/°C 527°C — 5.5 cal/mole/°C 727°C — 6.7 cal/mole/°C
Coef. of Linear Expansion	1.1 to 8.3 x 10 ⁻⁶ per °C in 20° to 750°C range
Crystallography	See Text
Hardness	9.3 (Mohs Scale)
Ductility	Very Brittle
Electrical Resistivity	Varies inversely and approximately exponentially with temperature. Value of resistivity varies widely with production conditions.

Crystallography

Crystallographic studies of single boron crystals, as reported in the literature, indicate boron lattices are stable over a wide range of lattice imperfections, including holes and defects in the framework. There is considerable evidence of the coexistence of two different crystal lattices of boron. X-ray diffraction data on boron enriched in B^{10} as produced at the plant, has shown some consistency with results reported in the literature. However, the data on B^{10} has shown an apparent distortion of the reported lattice as well as the probable coexistence of a second crystalline structure. One of the crystalline forms of boron (natural) is considered to be tetragonal with $a = 8.73$ and $c = 5.06$, approximately. Hexagonal and other orthogonal structures have been reported but apparently have not reached a point of general acceptance.

CHEMICAL PROPERTIES OF ELEMENTAL BORON

Elemental crystalline boron is resistant to aqueous alkali and most acids. Hot concentrated nitric acid will attack boron that has been finely ground (thru 200 mesh). Hot chromic acid, sulfuric acid and other strongly oxidizing agents will slowly attack boron. Oxy-gas flames will oxidize boron with an attendant brilliant emission of green-white light. Removal of the heat source results in rapid cessation of oxidation. It has been noted, however, that quantities of a pound or more of elemental boron in a finely divided or amorphous form, and with carbon present, have entered into sustained oxidation reactions with air at 115°C .

Some fused salts will attack elemental boron. Sodium hydroxide, sodium carbonate-potassium nitrate, and sodium peroxide are such salts. These salts do not attack boron in hot aqueous solution.

Boron's affinity for oxygen at elevated temperatures makes it valuable as a "getter" in vacuum tubes and in copper casting.

NUCLEAR PROPERTIES OF BORON

Neutron Cross Section

The most outstanding difference between the isotopes of boron is to be found in their absorption cross sections for thermal neutrons.

boron-11	<0.05 barns
boron-natural	755 barns
boron-10	3850 barns

Exposure of B-10 to neutrons results predominantly in a $B^{10} (n,\alpha) Li^7$ reaction. No radioactive products are formed nor is gamma radiation given off by neutron irradiated boron. No resonance peaks are evident, absorption cross section versus neutron energy being of the $1/v$ type.

Nuclear Reactions

	B^{10}	B^{11}
Neutron	$\alpha, {}^3_3Li^7$ $dn, 2\alpha$ $t, 2\alpha$	
Alpha	$n, {}^7_7N^{13}$	$n, {}^7_7N^{14}$
Proton	$\alpha, {}^4_4Be^7$	$\gamma\gamma, {}^6_6C^{12}$
Deuteron	$n, {}^6_6C^{11}$ $p, {}^5_5B^{11}$	$n, {}^6_6C^{12}$
Gamma	$d, 2\alpha$	$t, 2\alpha$

Nuclear Properties

	B^{10}	B^{11}
Natural Abundance	19.57%	80.43%
Spin	3	3/2
Quadrupole Moment (Q)	$0.06 \times 10^{-24} \text{cm}^2$	$0.03 \times 10^{-24} \text{cm}^2$
Magnetic Moment (nuclear magnetrons)	1.7984	2.7896
Resonance Parameters (Kev)		430 $\pm$ 10 1260 $\pm$ 20 1780 $\pm$ 20 2450 $\pm$ 20 2580 $\pm$ 20

CHEMICAL PROPERTIES OF DIMETHYL ETHER-BORON TRIFLUORIDE COMPLEX

The boron-10 enriched complex produced by the boron isotopes separation plant can be the

starting point for many boron-10 enriched compounds. The reaction of the complex with calcium carbonate solution yields boric acid almost quantitatively. The ether complex may be reacted with calcium fluoride to produce a $\text{CaF}_2\cdot\text{BF}_3$ complex. (This procedure is available upon request.) When the $\text{CaF}_2\cdot\text{BF}_3$ complex is heated above 155°C , BF_3 is liberated. Boron trifluoride is widely used in neutron counter tubes directly, as well as for the synthesis of many compounds. The reaction of dimethyl ether-boron trifluoride with potassium fluoride produces potassium fluoroborate. This reaction is used at the plant to prepare feed material for the elemental boron producing electrolytic cells.

PROPERTIES OF POTASSIUM FLUOROBORATE

Potassium fluoroborate is a moderately soluble salt (0.4% at 20°C ; 6% at 100°C). It is quite stable even in the presence of moisture, undergoing hydrolysis only slowly if not heated. If evaporated to dryness, the hydrolysis compounds recombine to produce KBF_4 . If heated above 600°C , KBF_4 decomposes to liberate BF_3 . KCl depresses this decomposition.

TOXICITY AND HAZARDS

There is not much information available concerning toxicity of boron compounds. Work with elemental boron has shown it to be non-toxic. Boron compounds such as boric acid and sodium borate have demonstrated some toxicity. See "Handbook of Toxicity," Volume 1 — by W. S. Spector.

Diboranes have shown toxic affects on animals in 4 hours at a concentration of 50 ppm. From these results it is concluded that diboranes have a relatively high order of toxicity. At 2ppm diboranes have not shown significant pathological pulmonary changes after 4 weeks exposure. Reference should be made to CMLEM-52 entitled "Toxicity and Health Hazards of Boron Hydrides" by E. H. Krackow and available from the Office of Technical Services in Washington, D. C. The complex of

dimethyl ether and boron trifluoride has shown toxic affects on laboratory animals at concentrations of 5 ppm or more. The safe exposure concentration, however, is not known at present. Work done on the use of canisters has shown that the Wilson Universal Canister and the Mine Safety Appliances Universal Canister reduce the concentration of dimethyl ether-boron trifluoride complex to 0.4 ppm from an atmosphere containing 120 to 133 ppm. (Reference: Technical Information Service Document #M-1555- "Tests of Efficiency of 5 Respiratory Protective Devices in Atmospheres of 890" by P. Dygert and R. Sanford.)

Boron trifluoride and its complexes are corrosive to the skin. The usual precautions should be followed when handling these compounds, namely rubber gloves and face protection. If boron trifluoride or its complexes do contact the skin, prompt flushing with water will decrease or avoid tissue destruction. This treatment may be followed with the standard treatment for hydrogen fluoride burns if necessary. If ingested, an emetic of sodium bicarbonate should be used as first aid treatment. Oxygen inhalation is recommended in cases of exposure to gases or vapors containing boron trifluoride. A physician should be summoned for any of the above exposures. Booth and Martin in their book entitled "Boron Trifluoride and Its Derivatives" published by John Wiley & Sons, Inc. may be referred to for additional data.

Boron trifluoride is very reactive with water, alcohol, ether, esters, etc. Due care must be exercised when adding BF_3 to such liquids to avoid "suck-backs," by the use of suitable traps or vacuum breaks. The fire hazard associated with dimethyl ether should be considered when handling the complex. The flash point of dimethyl ether is -41°C and its auto ignition temperature is 150°C .

USES OF BORON-10 ISOTOPES

The most singular property of the isotopes of boron is in their thermal nuclear cross section, the B^{10} isotope having a very high cross section

equivalent to 3850 barns and the B^{11} isotope having a very low cross section of less than 0.05 barns. The physical properties of elemental boron, combined with its nuclear properties, permit it to be used for the control of nuclear reactors, as a shield for nuclear radiation and for instruments for detecting neutrons. In addition, the difference in mass as well as the cross section permits boron isotopes to be used as tracers. The low cross section of B^{11} suggests its use for high temperature components of nuclear reactors where low neutron capture is essential, such as for fuel cladding and nuclear fuel components themselves.

B^{10} undergoes a ${}_5B^{10}(n,\alpha){}_3Li^7$ reaction upon irradiation. As a neutron absorber it may be compared with cadmium, which has a cross section of 3100 barns and undergoes a $Cd^X(n,\gamma)Cd^X$ reaction. Cadmium, however, does not have the $1/v$ relationship to neutron energy that boron-10 has. (See chart on Page 11). Boron should also be compared with hafnium and rare earths such as europium, gadolinium and samarium. Of these materials, hafnium has a cross section of only 115 barns and the rare earths, although in some cases possessing attractive cross sections, are very expensive, thus making B^{10} economically more practical. As an example of cost, a recently available price of about \$4.00 per gram of Eu_2O_3 is equivalent to about 7 times the cost of boron-10 for equivalent neutron absorption. In addition, the long half-life of products of neutron irradiation of some of these materials requires that irradiated control rods be permitted to cool for long periods before they can be handled or discarded. Although cadmium is now widely used as a reactor control material, it is subject to corrosion. This is a serious handicap as reactors approach higher design operating temperatures. Cadmium undergoes a neutron-gamma reaction, the gamma requiring additional shielding almost comparable to that required for the thermal neutrons.

For shielding purposes B^{10} has a great advantage in that it undergoes a neutron-alpha reaction, the alpha being readily absorbed by practically

any retaining vessel. The release of alpha particles (helium nuclei), however, tends to cause structural damage in alloys unless provision is made for the diffusion of helium out of the structure or relaxation of the structure by annealing. The ability of B^{10} to absorb thermal neutrons might be more readily visualized by making the following comparison. One inch of B^{10} will have the same absorption cross section for thermal neutrons as 5" of natural boron, 20" of lead or 500" of concrete.

Control rods and shielding materials have been investigated using B^{10} in the form of liquids, gases, compounds and alloys, as well as elemental boron. Crystalline boron formed into alloys, or metal dispersions utilizing boron carbide, have high densities and can be made into rigid shapes. For high strength, titanium borides as well as boron steels can be used. Elemental boron itself can be formed into high strength shapes by pressing and sintering techniques in which a very small amount of the oxide acts as the binder. With as little as 2% boron oxide, compressive strengths of 45,000 psi have been obtained. At 5% boron oxide, compressive strengths of 75,000 psi are realizable. For certain applications of reactor control, the extremely high temperature resistance (2200°F) and high strength (55,000 psi transverse rupture strength at 1800°F) of zirconium boride has been considered. This material is considered to have excellent corrosion resistance to molten aluminum, copper, tin and magnesium, as well as resistance to nitric and hydrochloric acids. Specific uses of enriched B^{10} in instruments will be found in the many references to neutron counting tubes. Either highly purified boron trifluoride gas, or a solid film prepared by the deposition of elemental boron or one of its alloys on the inside of a tube, is used in the application of B^{10} in instrumentation. Such equipment has been used for the detection of neutrons in cosmic rays, the study of neutron diffusion in hydrogenous matter and for monitoring purposes.

Methods for the production of boron carbide, zirconium boride, titanium boride, uranium boride, barium boride, boron steels, plastic bonded boron

powder, tungsten boride and boron nitride, as well as the preparation of high strength shapes from crystalline boron are available in the literature. The production of shapes of boron carbide sandwiched between aluminum sheets, known as "Boral" sheet, have been prepared for use as thermal neutron shields. These sheets can be machined, stamped, sawed and welded, punched and drilled for fabrication into almost unlimited shapes. The average tensile strength of "Boral" sheet is 5,000 psi, and after irradiation of 8 weeks in the Graphite Reactor at Oak Ridge, the strength actually increased to 7,500 lbs. per sq. inch. After 14 months of exposure in the Oak Ridge National Laboratory Graphite Reactor, the sheet showed no serious damage. The neutron absorbing function of "Boral" is due to the B^{10} content of the boron carbide used.

The use of boron in the treatment of tumor in the brain tissue has been a subject of considerable investigation. Work done at the University of California has indicated that for 15 grams of borax per 70 Kg. of body weight, an uptake of 50 micrograms of B^{10} per gram of tumorous tissue occurs in 15 to 30 minutes after injection. If this boron is then irradiated with thermal neutrons, the tumor might be destroyed without irreparable damage to the surrounding tissue. Although no reference has been found concerning the use of isotopically enriched boron for this purpose, it is recognized that increased concentrations of boron-10 in the tumor tissue permit the destruction of the tumor with less exposure to the thermal neutrons.

USES OF BORON-11 ISOTOPES

Boron-11 has been used to produce C^{10} , which information is important to the problem of the nuclear theory of the light elements. C^{11} enriched car-

bon monoxide produced by the $B^{10}(d,n)$ reaction has been used in studies of the distribution of carbon monoxide in the human body.

B-11 has not previously been available in high isotopic concentration and commercial quantities. Pilot plant operations now permit a limited supply of boron having an isotopic ratio of approximately 99% B^{11} , which has a cross section of approximately 38 barns. This material should conceivably be used as a moderator, reactor lining or fuel cladding. Boron-11 could find use in any application requiring the chemical and physical properties of boron, its compounds or alloys, but also requiring a low neutron cross section. Uranium boride enriched in B^{11} is a refractory material which has promise of being usable as a high temperature fuel element. B^{11} can be used as a neutron source by making use of its alpha-neutron reaction. Polonium is usually used as an alpha source. The neutrons emitted from a polonium-boron source are in the 0.7 Mev range but may be slowed to thermal neutrons by passage through hydrocarbons.

PRICES AND AVAILABILITY

Availability and prices of boron, potassium fluoroborate and dimethyl ether-boron trifluoride complex enriched in B^{10} are included in a detachable appendix to this brochure. B^{11} enriched compounds are being produced on a pilot plant scale, and therefore are not included in the price list. Inquiries are invited.

All inquiries should be addressed to:

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NUCLEAR CROSS SECTIONS IN THE LOW ENERGY RANGE

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