11.3.3. Physical Properties of Boron

Boron is an extremely hard, low density solid with a melting point greater than 2450K and low electrical conductivity. Boron exists in several different modifications (**allotropes**). At least four allotropes of boron are known under different conditions. All boron allotropes have structures built up of B_{12} icosahedral units shown is Fig. 11.3.

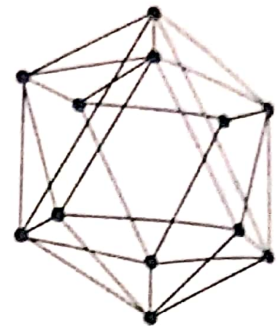

Figure 11.3 The B_{12} icosahedral unit, the basic building block of the structures of allotropes of boron. The icosahedron is a regular polyhedron having 20 faces.

11.3.4. Chemical Properties of Boron

(i) Reaction with air : Amorphous boron burns in air at 973 K forming boron trioxide (B_2O_3) and boron nitride (BN).

$$4B\,(s) + 3O_2\,(g) \xrightarrow{973\text{ K}} 2B_2O_3\,(s); \qquad 2B\,(s) + N_2\,(g) \xrightarrow{973\text{ K}} 2BN\,(s)$$

(ii) Action of water : Boron is inert towards water. It is not even attacked by steam.

(iii) Reaction with non-metals : At higher temperature, boron reacts with almost all non-metals except hydrogen and noble gases.

$$2B + 3X_2 \xrightarrow{\text{Heat}} 2BX_3\,(g) \qquad (X = F, Cl, Br, I)$$

BF_3 can also be prepared by heating B_2O_3 with CaF_2 and conc. H_2SO_4.

$$B_2O_3\,(s) + 3CaF_2\,(s) + 3H_2SO_4\,(l) \xrightarrow{\text{Heat}} 2BF_3\,(g) + 3CaSO_4\,(s) + 3H_2O\,(l)$$

All trihalides of boron are *electron deficient molecules and act as Lewis acids.*

(iv) Reaction with acids : Boron reacts with oxidising acids like conc. HNO_3, conc. H_2SO_4 but does not react with non-oxidizing acids like HCl.

$$B + 3HNO_3 \longrightarrow H_3BO_3\,(aq) + 3NO_2\,(g); \quad 2B + 3H_2SO_4 \longrightarrow 2H_3BO_3\,(aq) + 3SO_2\,(g)$$

It dissolves in a mixture of conc. H_2SO_4 and HNO_3 (2 : 1).

(v) Reaction with alkali : Boron dissolves in fused alkali (NaOH or KOH) forming borates and liberating dihydrogen gas :

$$2B\,(s) + 6KOH\,(s) \longrightarrow \underset{\text{Pot-borate.}}{2K_3BO_3\,(s)} + 3H_2$$

(vi) Reaction with metals : Boron reacts directly with almost all metals at higher temperatures except Ag, Au, Cd, Hg, Sn, Pb, Sb and Bi.

$$2B + 3Mg \longrightarrow \underset{\text{Magnesium boride}}{Mg_3B_2}; \qquad B + Cr \longrightarrow \underset{\text{Chromium boride}}{CrB\,(s)}$$

(vii) Reducing properties : It is a powerful reducing agent

$$3CO_2 + 4B \longrightarrow 2B_2O_3 + 3C; \qquad 3SiO_2 + 4B \longrightarrow 2B_2O_3 + 3Si$$

11.3.5 Anomalous Properties of Boron

Boron differs markedly from the rest of the members of group 13 and this abnormal behaviour is due to the following reasons:

(i) Boron has very small atomic radii, hence greater nuclear attraction on the outermost electrons.
(ii) It has very high ionization energy and as a result it forms covalent bonds.
(iii) It is non-metallic in nature.

The following properties of boron show its abnormal behaviour :

(a) Boron has a maximum covalency of four due to non-availability of d-orbitals while other members have mâximum covalency of six.
(b) Boron alone exhibits allotropy.
(c) The oxidation state of boron is +3 while others exhibit oxidation states of +1 and +3.
(d) Boron halides are monomeric (e.g. BCl_3) while the halides of other elements are dimeric (e.g. Al_2Cl_6).
(e) Boron forms a number of volatile hydrides which are electron deficient compounds. Other form only one polymeric hydride. Thallium does not form hydride.
(f) Boron does not decompose water or steam while others decompose hot water or steam.
(g) The oxide of boron, B_2O_3, is acidic in nature while the similar oxides of other members of the group are amphoteric or basic.
(h) Boron is not attacked by non-oxidising acids while others are attacked.
(i) Boron dissolves in conc. HNO_3 forming H_3BO_3. The other elements become passive specially Al and Ga.
(j) Boron combines with metals and form borides while other elements donot combine. They form alloys.

11.3.6. Boron Hydrides

Boron is trivalent but BH_3 does not exist. The simplest boron hydride known is diborane, B_2H_6. Besides diborane, boron forms a number of higher hydrides known as **BORANES;** most of them have molecular formulae corresponding to $B_n H_{n+4}$ **(nido-boranes)** and $B_n H_{n+6}$ **(arochno boranes).**

DIBORANE, B_2H_6

Preparation : 1. By treating boron trifluoride with $LiAlH_4$ in diethyl ether:

$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

2. Laboratory method : A convenient laboratory method for the preparation of diborane involves the oxidation of sodium borohydride with iodine.

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

3. Industrial preparation : Diborane is produced on an industrial scale by the reduction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF$$

The higher boranes are formed when diborane is heated at 373–523K.

Physical properties : Diborane is a colourless, highly toxic gas with a b.p. of 180 K. It catches fire spontaneously upon exposure to air.