

# 17

## Group IIIB (Group 13)\*. Boron, Aluminium, Gallium, Indium and Thallium

The five elements—boron, aluminium, gallium, indium and thallium comprise group IIIB (group 13) of the Periodic Table. The percent abundances of the elements in the earth's crust are : B(0.003%); Al(8.0%); Ga(0.0004%); In (0.00001%) and Tl (0.00001%).

Boron occurs in small amount due to its nucleus being disintegrated by natural bombardment reactions. Aluminium is very abundant and occupies the third position after oxygen (46.6%) and silicon (27.7%). The abundance of the other three elements is poor and falls from gallium to the other two.

### 17.1. COMPARATIVE STUDY OF THE GROUP IIIB (GROUP 13) ELEMENTS

**17.1.1. General Considerations :** Considerable changes occur on moving from group IIA (group 2) to group IIIB (group 13). All the elements have an outer quantum shell arrangement of  $s^2p^1$  (Table 17.1). Underneath this  $s^2p^1$  subshells boron and aluminium alone have noble gas electronic configurations but gallium, indium and thallium have filled  $d$ -subshells. This seems to influence the properties of the elements.

**Table 17.1. : Electronic Configurations and some Properties of Group IIIB- (Group 13) Elements**

Element	Atomic Number	Electronic Configuration	Ionisation Potential eV/atom (kJ/mole)	Electronegativity
B	5	[He] $2s^22p^1$	8.29, 25.15, 37.92 (800, 2426, 3685)	2.0
Al	13	[Ne] $3s^23p^1$	5.98, 18.82, 28.44 (577.5, 1816, 2744)	1.5

\* IUPAC recommendation

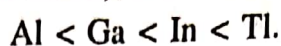
Element	Atomic Number	Electronic Configuration	Ionisation Potential eV/atom (kJ/mole)	Electronegativity
Ga	31	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>1</sup>	6.00, 20.51, 30.70 (579, 1979, 2962)	1.6
In	49	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup>	5.78, 18.86, 28.03 (558, 1820, 2704)	1.7
Tl	81	[Xe]4f <sup>14</sup> 5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>1</sup>	6.10, 20.42, 29.8 (589, 1970, 2875)	1.8

The first ionisation potentials are slightly lower than those of group IIA (group 2) possibly because the electron is lost from a 2p orbital in group IIIB (group 13) compared to the filled 2s orbital in group IIA (group 2). However the three successive ionisation potentials taken together (53.24 eV) (5136 kJ/mole) for Al make the energy too large to be compensated by lattice energy released in the formation of ionic crystals. Taking the case of boron, the charge/radius ratio is 15 whereas that for the preceding beryllium is only 6.4. Thus it is no wonder that boron chemistry is dominated by covalence. In fact small size, high ionisation potential and moderate electronegativity (being close to those of carbon and hydrogen) explain the existence of many exciting and unusual covalent compounds of boron. As we descend the group the ionisation potentials decrease in aluminium but the charge/radius ratio is still high (6.0). Aluminium has also a dominant covalent chemistry. The decrease in ionisation potentials from boron to aluminium may also be interpreted to mean that under favourable circumstances aluminium can form some ionic compounds as well. Unlike groups IA and IIA (groups 1 and 2) the ionisation potentials do not show a regular decrease from boron to thallium ; instead gallium, indium and thallium have very close potentials. The size of these three elements do not vary significantly. An explanation must be sought in the pseudo noble gas configurations underneath the outer valence shell. As we pass from Al (at. no. 13) to Ga (at. no. 31) there occurs a kind of d-block contraction and a higher effective nuclear charge. In Tl (at. no. 81) there are both d-block and f-block contractions and hence there is no increase in size from In to Tl.

In groups IA and IIA (groups 1 and 2) reduction potentials are increasingly more negative with increasing atomic number indicating increasing electropositive character. But in group IIIB (group 13) the trend is not maintained. With increasing atomic number reduction potentials ( $M^{3+} + 3e \rightleftharpoons M; E^0$ ) become less negative and in thallium it assumes even positive value (Table 17.2). This once again suggests that pseudo noble gas core is more deformable than a noble gas core. Fajans' rules predict that elements with pseudo noble gas core are more liable to deformation than those with noble gas configurations.



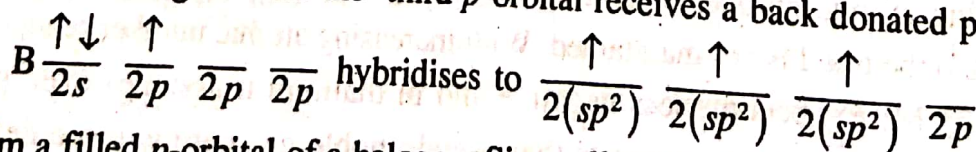
The trend of decreasing electronegativity with increasing atomic number, as observed with the elements of IA and IIA (1 and 2), is also reversed in this group :



**Table 17.2. : Some more Properties of Group IIIB (Group 13) Elements**

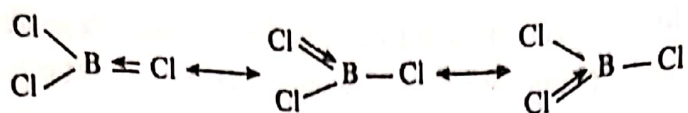
Element	Atomic Radius (A)(pm)	Ionic Radius $\text{M}^{3+}(\text{A})(\text{pm})$	M.P. ( $^{\circ}\text{C}$ )	B.P. ( $^{\circ}\text{C}$ )	Density (g/ml)	$E^{\circ}(\text{volt})$ $\text{M}^{3+} + 3e \rightleftharpoons \text{M}$
B	0.88 (88)	0.20 (20)	~ 2200	2550	2.31	—
Al	1.26 (126)	0.52 (52)	660	2270	2.7	-1.66
Ga	1.26 (126)	0.60 (60)	29.8	2030	5.93	-0.53
In	1.44 (144)	0.81 (81)	157	2100	7.29	-0.34
Tl	1.48 (148)	0.95 (95)	304	1460	11.85	+0.72

With two electrons in an  $s$ -orbital and one in a  $p$ -orbital, there is a case for showing monovalence in addition to the group valence. But boron never exhibits +1 (I) oxidation state but only a consistent + 3 (III) state. The trivalent state in boron is exemplified in non-electrolytic compounds of the form  $\text{BX}_3$ , the three covalent bonds involving the three equivalent  $sp^2$  hybrid orbitals at  $120^{\circ}$  to each other in the same plane. Three covalent bonds offer to boron a mere sextet, two electrons short of an octet. This makes boron an electron deficient element. The story of boron is, thus, the story of an electron deficient element. This character makes boron compounds very efficient Lewis acids, that is, electron acceptors (Chapter 8). A large number of stable adducts of boron halides with amines, ethers, sulphides, etc. are formed with evolution of large amount of heat. In these adducts boron attains a four covalent tetrahedral ( $sp^3$ ) structure. The triangular planar ( $sp^2$ )  $\text{BX}_3$  molecule gets distorted to a pyramid so that the empty  $p$ -orbital of boron now becomes an  $sp^3$ -orbital. This orbital then forms a bond with the lone pair from the donor amines, ethers etc. Electron deficiency makes boron form unique *hydrogen bridge bond with three centres but with two electrons* (Chapter 14). This unique character also explains its tendency to receive back coordinated electrons, to form  $\pi$ -bonds with elements like Cl, F etc. Boron in  $\text{BCl}_3$ ,  $\text{BF}_3$  etc. could have attained noble gas configuration through dimerisation (compare  $\text{Al}_2\text{Cl}_6$ ) (17-II) but it does not. The boron-halogen bonds are shorter than single bonds. The three  $sp^2$  hybrid orbitals form three electron-pair bonds with three halogens and the third  $p$ -orbital receives a back donated pair of



electrons from a filled  $p$ -orbital of a halogen. Since all the three boron-halogen distances are short and equivalent it can only mean that the real structure is a resonance hybrid of the following structures (17-I) :





(17-1)

The trend of multiple bond formation falls sharply in aluminium and other members. This is due to an increase in the size of the central element. Overlap of a larger aluminium orbital with a chlorine over a longer internuclear distance gives a weaker bond. Also both aluminium and chlorine have more filled inner orbitals, which tend to repel. This fall in multiple bond formation with increasing atomic number in a group is a general feature of the Periodic Table. As we move to aluminium there is still enough covalent trend which is reflected in dimeric covalent structures of the aluminium halides  $\text{Al}_2\text{X}_6$ . The ability to behave as Lewis acid falls off in the order  $\text{B} > \text{Al} > \text{Ga} > \text{In} \sim \text{Tl}$ . Halides of gallium, indium and thallium also show dimerisation. In contrast to boron there is a well-defined aqueous cationic chemistry of Al, Ga and In being exemplified by  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{In}(\text{H}_2\text{O})_6]^{3+}$ .

Although monovalence is not of importance in boron or aluminium it gains in importance down the group. With thallium + 1 (I) oxidation state becomes the dominating feature of its chemistry. The lower valence becomes increasingly important due to the so-called *inert pair effect*. The two *s* electrons of the  $s^2p^1$  outer shell become resistant to some chemical reagents and are neither easily lost nor do they easily participate in covalent bond formation. In this + 1 (I) oxidation state, too, gallium, indium and thallium do not show any gradation in properties. Their first ionisation potentials are nearly the same (5.79—6.11 eV) (558—589 kJ/mole) so that there is no spectacular enhancement in basic properties down the group. Thallium (III) solutions are not stable in the presence of metallic thallium. The equilibrium  $\text{Tl}^{3+} + 2\text{Tl} \rightleftharpoons 3\text{Tl}^+$  proceeds almost to completion.

The extremely high melting point of boron indicates very strong binding forces. Aluminium is comparatively soft. It has a true metallic lattice and has a high conductivity. Gallium is a liquid over a wide range  $\sim 2000^\circ\text{C}$ , which has made possible its use in high temperature thermometry.

**17.1.2. Chemical Behaviour :** The chemical behaviour will be discussed under two heads—trivalent state and the monovalent state.

**A. Trivalent State :** This is the group oxidation state and all the three electrons in the  $s^2p^1$  outer shell are utilised. A considerable covalent interaction between  $\text{M}^{3+}$  and  $\text{X}^-$  in  $\text{MX}_3$  is only expected. In boron the covalent state is important. The tendency to complexation is decidedly the highest in boron. This trend decreases in aluminium and the later members but not in a graded manner.

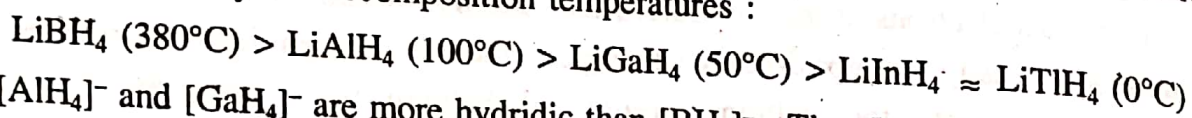
**Hydrides :** The boron hydrides are also called *boranes* and are designated usually by the number of boron atoms— $\text{B}_2\text{H}_6$  [diborane (6)],  $\text{B}_4\text{H}_{10}$  [tetraborane (10)],  $\text{B}_5\text{H}_9$  [pentaborane (9)],  $\text{B}_5\text{H}_{11}$  [pentaborane (11)] etc. The number of hydrogen atoms is indicated in parenthesis.



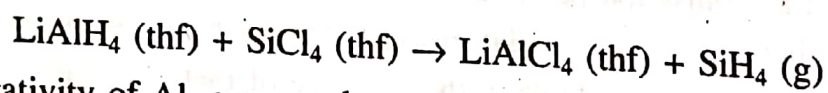
These are remarkable in their forming hydrogen bridge bond. The electron deficient character of boron leads to such special bonding (Chapter 14). These volatile, covalent hydrides were originally synthesised by Stock by the acid hydrolysis of magnesium boride which was obtained by heating boron and magnesium:  $Mg_3B_2 + \text{acid} \rightarrow$  a mixture of several boron hydrides.

The volatile hydrides were collected in liquid-air traps and then purified by fractional distillation. Thus the boron hydrides  $B_4H_{10}$ ,  $B_5H_9$ ,  $B_6H_{10}$  and  $B_{10}H_{14}$  were isolated. In these compounds there are *three-centred two electron bonds* along with usual two electron two-centred covalent bonds. For structure of diborane,  $B_2H_6$ , see Chapter 14.

The aluminium hydride *alane* is a polymeric species  $(AlH_3)_n$ . This also has hydrogen bridging. Evidences for *gallane* are not convincing. Great chemical reactivity of alane and gallane makes their syntheses by hydrolysis reactions difficult. They are made by subjecting a mixture of trialkyls  $[Al(CH_3)_3]$  and hydrogen to high voltage electric glow discharge. The group IIIB (Group 13) hydrides form many complex compounds with donor groups such as ammonia, amines, as also hydride ions. Complex anionic hydrides like lithium tetrahydroborate ( $LiBH_4$ ), lithium tetrahydridoaluminate ( $LiAlH_4$ ) and lithium tetrahydridogallate ( $LiGaH_4$ ) are well known. Thermal stability of these tetrahydro-complexes falls off from boron to thallium as shown by the decomposition temperatures :



The  $[AlH_4]^-$  and  $[GaH_4]^-$  are more hydridic than  $[BH_4]^-$ . Thus  $LiAlH_4$  reacts with  $SiCl_4$  in thf to give  $SiH_4$  :



Lower electronegativity of Al, compared to B, makes  $[AlH_4]^-$  a better hydride source than  $[BH_4]^-$ .  $[AlH_4]^-$  and  $[GaH_4]^-$  are stronger reducing agents than  $[BH_4]^-$ .

**Oxides and Hydroxides :** The hydroxide of boron,  $B(OH)_3$ , is a definite weak acid ( $H_3BO_3$ ) with no basic properties. Orthoboric acid,  $H_3BO_3$ , is a tribasic acid with  $K_A^I \sim 5.8 \times 10^{-10}$ ,  $K_A^{II} \sim 1.8 \times 10^{-13}$  and  $K_A^{III} \sim 3 \times 10^{-14}$ . Its acidity is greatly raised by the addition of certain polyhydroxy compounds like glycerol due to the formation of complex acids. On passing from boron to aluminium we find the hydroxide to be amphoteric and reacting in several ways : (1) as an acid ( $H[AlO_2]$  or  $H_3[Al(OH)_6]$ ) forming metallic aluminates ; (2) as a base  $Al(OH)_3$  giving ionised salts with aluminium as a hydrated cation ; (3) forming neutral, covalent derivatives  $AlBr_3$ ,  $Al(C_2H_5)_3$  etc. Gallic hydroxide is amphoteric but on the whole it is a weaker base but stronger acid than aluminium hydroxide, forming neutral gallates  $M^I GaO_2$ . Indium behaves in the same way giving indates  $M^I InO_2$ . But thallic hydroxide is not amphoteric but only basic, although only a weak one. The addition of alkali to solutions of gallic and indic salts first precipitate their hydroxides which dissolve on addition of more alkali but with thallic salt the hydroxide does not dissolve on addition of excess alkali.

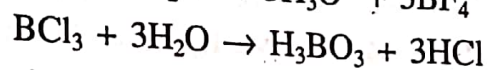
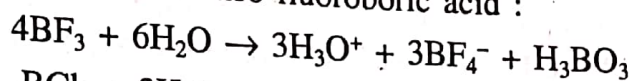


The boric oxide  $B_2O_3$  is obtained by fusing boric acid. With water it forms boric acid and it readily reacts with other metal oxides to give metal borates. The formation of some coloured metal borates is a common reaction employed in detection of some metal ions. Aluminium oxide,  $Al_2O_3$ , can assume different crystal structures depending on the mode of preparation. Gallium oxide also exists in more than one form and so also  $Tl_2O_3$ . Like boron, aluminium, gallium and thallium form mixed oxides, with other metal oxides.

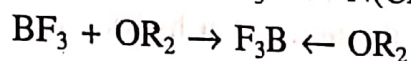
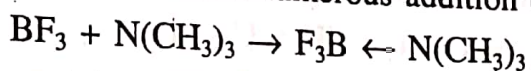
**Halides** : Boron halides are known for all the halogens. These are all covalent and monomeric. In keeping with the normal behaviour the boiling points increase with increasing molecular weights of the halides :

Halide	$BF_3$	$BCl_3$	$BBr_3$
B.P. ( $^{\circ}C$ )	-101	12.5	90

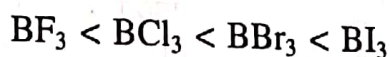
The triiodide,  $BI_3$ , is a white solid (M.P.  $43^{\circ}C$ ). These are readily hydrolysed by water-forming boric acids, and for the fluoride also fluoroboric acid :



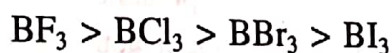
These are all strong Lewis acids, and form numerous addition compounds :



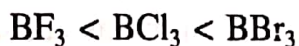
For a given Lewis base, L, the stability of the resulting adduct  $LBX_3$  follows the Lewis acidity order :



Consideration of the electronegativity of the halogens alone would indicate the reverse order of Lewis acidity *i.e.*



To cite one experimental result the heats of reaction of  $BX_3$  with Lewis base pyridine in nitrobenzene (*i.e.* the electron-acceptor strength of  $BX_3$ ) follow the order :

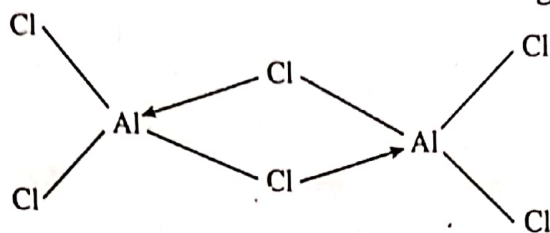


In order to change over from the  $\pi$ -bonded three-coordinate planar structure to four-coordinate tetrahedral, the  $\pi$ -bond has to be ruptured. By virtue of the smallest size of fluorine  $BF_3$  is the most strongly  $\pi$ -bonded and hence the adduct of  $BF_3$  is expected to be the least stable. Electronegativity effect is evidently less important (*cf.* problems, Chapter 8). For a given  $BX_3$ , the stability of  $LBX_3$  depends on several factors of which the chemical nature of the donor atom of L is the most important.

Among the halides of Al, Ga, In and Tl, the fluorides are all expected to be ionic with high melting points. However it has recently been shown that these have polymeric six-coordinated covalent structures with all the fluorine atoms being bridging in nature (*cf.* Part I, Chapter 5). The other halides are largely covalent, and attain octet through dimerisation (17-II). The dimeric structures are retained in non-polar solvents such as benzene

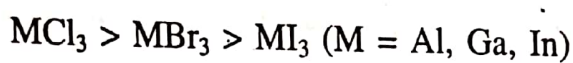


but in water they break down, being assisted by a large solvation energy, into the hexaaqua ions  $[M(H_2O)_6]^{3+}$ . The dimers also break down while reacting with other donor centres



(17-II)

(Lewis bases) forming adducts of the type  $(CH_3)_3N \rightarrow AlCl_3$ . These adducts widely vary in stability and in the mode of bonding, properties and structure. Towards amines, ethers and phosphanes (which are Lewis bases) the acceptor strengths of the metal halides follow the order :



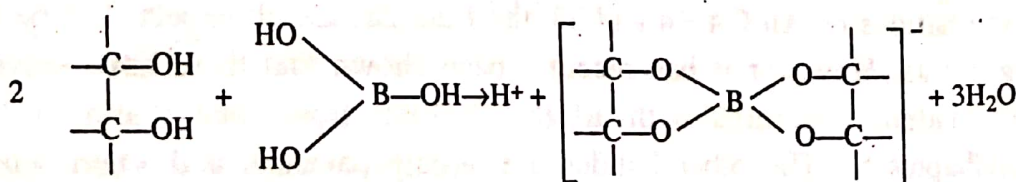
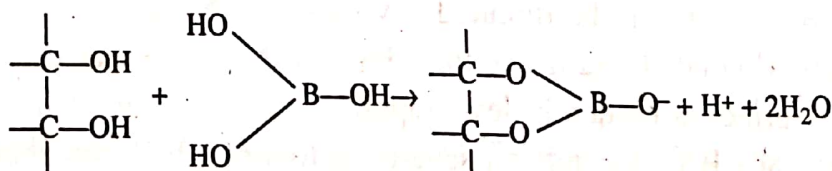
But for mild sulphur donors (soft bases)  $Me_2S$ ,  $Et_2S$  aluminium halides follow the same sequence as given above but for  $GaX_3$  and  $InX_3$  the sequence is reversed :



**Alums** : Aluminium, gallium, indium and thallium form double sulphates  $M^I M^{III}(SO_4)_2 \cdot 12H_2O$  where  $M^I$  is a univalent cation  $NH_4^+$ ,  $Cs^+$  etc.

**Complexes** : In addition to the tetrahedral hydride and halide complexes  $Li[AlH_4]$  and  $H[BF_4]$  already mentioned, many octahedral halocomplexes are known such as  $[GaCl_6]^{3-}$ ,  $[InCl_6]^{3-}$  and  $[TiCl_6]^{3-}$ . The increase in coordination number from four in boron to six in the later elements is due to increased size whereby more groups can be packed around the metal. The acceptor property of boron is noted in adduct formation of boron halides with Lewis bases. An interesting case of complexation tendency of boron is shown in the enhanced acid character of boric acid ( $K_A^I 5.8 \times 10^{-10}$ ) in the presence of polyhydroxy compounds. Addition of mannitol, glycerol, etc. makes it a far stronger acid. Mannitol group coordinates to boron (17-III), makes its weakly acidic  $H^+$  a strong acid and makes titration with sodium hydroxide possible to a phenolphthalein end point. The  $pK_A$  values of the polyhydric alcohols decrease from  $\sim 9.25$  to  $\sim 5.16$ , making these as strong as acetic acid.

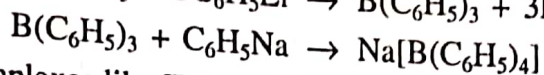
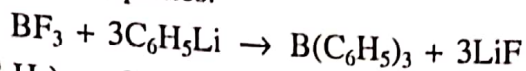
A mono-chelate or a dichelate may be formed ; in both cases one  $H^+$  is liberated.



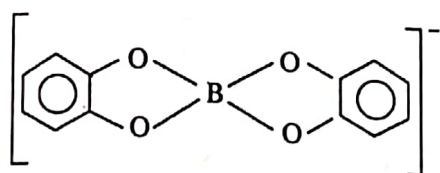
(17-III)



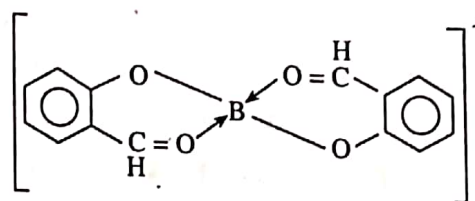
The tendency to chelation by boron is also revealed in the formation of complexes with catechol (17-IV), salicylaldehyde (17-V) etc. The former is an example of an anionic boron complex and the latter of a cationic boron complex. The boron salicylaldehyde complex has been resolved into optical isomers thus indicating a tetrahedral stereochemistry. Acetylacetonone (Hacac) reacts with boron halides to give cationic bis(acetylacetonato) complex  $[B(\text{acac})_2]X$ . An important and useful anionic complex is sodium tetraphenylborate,  $\text{Na}[B(\text{C}_6\text{H}_5)_4]$ . This anionic boron complex is an excellent precipitating agent for potassium ion and the heavier alkalis and for soluble cationic complexes.



Non-electrolytic complexes like  $[B(\text{acac})\text{F}_2]$  are also known. Note that in all its complexes boron is consistently four-coordinate tetrahedral. The other elements also form tris (chelate) complexes, for example with acetylacetonone, oxalate or with 8-hydroxyquinoline. The last named ligand is commonly utilised for gravimetric estimation of aluminium (Chapter 10).

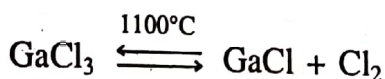


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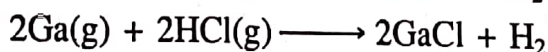
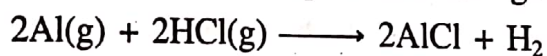


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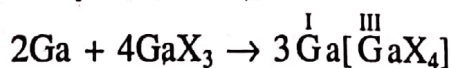
**B. Monovalent State :** This oxidation state gains importance only with the heavier elements of the group. The monovalent state of aluminium is suspected from the studies of anodic oxidation of aluminium. Hydrogen evolution at the cathode and the dissolution of aluminium at the anode are not in conformity with Faraday's law. Monovalent gallium compounds have been claimed to be formed by thermal dissociation of trivalent compounds :



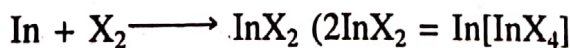
Aluminium monochloride and gallium monochloride have been obtained via high temperature ( $\sim 1200^\circ\text{K}$ ) reaction of the metal vapour and HCl gas :



Compounds of the empirical formula  $\text{GaX}_2$  ( $X = \text{halogen}$ ) indicating apparently an oxidation state of + 2 (II) for gallium are really  $\overset{\text{I}}{\text{Ga}}[\overset{\text{III}}{\text{Ga}}\text{X}_4]$ . These are obtained by the general reaction :



Mixed  $\text{In}^{\text{I}}/\text{In}^{\text{III}}$  halides,  $\text{In}^{\text{I}}[\text{In}^{\text{III}}\text{X}_4]$  have been prepared by refluxing indium metal with halogens in xylene :



With thallium the + 1 (I) oxidation state is well-characterised. The element is commercially available in  $\text{Tl}(\text{I})$  state. The low charge on the cation and comparatively large size confer on



the ion enough properties to make its chemistry resemble those of the alkalis and silver. The Tl(I) compounds are nearly all salts. Interestingly the ionic mobility is comparable to those of the alkalis and silver :

Ion	Tl <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Ag <sup>+</sup>
Ionic Radius M <sup>+</sup> (A)	1.44	1.33	1.48	1.69	1.26
(pm)	(144)	(133)	(148)	(169)	(126)
Ionic mobility × 10 <sup>5</sup>	65.6	64.2	67.2	68.0	54.3
(cm/sec/volt)					

The ionic nature of Tl(I) compounds is revealed by TlF having a distorted NaCl structure, and TlCl and TlBr having CsCl structure. The other similarities are : the ion is colourless, the hydroxide TlOH is very soluble in water and is highly ionised. The salts are nearly all anhydrous like those of ammonium, potassium, rubidium, caesium and silver. The Tl(I) halides are usually lower melting than the alkali halides. Resemblance to silver is particularly shown by the very slight solubility of the chloride, bromide and iodide and high solubility of the fluoride. But unlike silver, Tl(I) chloride does not form a soluble ammine complex. In conformity with general rules (Chapter 8) the oxide and the hydroxide in lower oxidation states are more basic while those in higher oxidation states are more acidic.

## 17.2. COMPARISON OF BORON AND SILICON : DIAGONAL RELATIONSHIP

The charge/radius ratios for boron and silicon are 15 and 10 indicating closeness in their behaviour although they are members of different groups of the Periodic Table.

Element	B	Si
Charge on the ion	+3	+4
Ionic Radius (A)	0.2	0.39
Charge/radius	15	10

The considerably high value of silicon must be taken as a suggestion that the chemistry of silicon will be dominated by covalence. The main points of resemblances between boron and silicon are the following :

1. The hydroxides of boron and silicon are weak but definite acids, H<sub>3</sub>BO<sub>3</sub> and H<sub>4</sub>SiO<sub>4</sub> ( $K_A^I, H_3BO_3 = 5.8 \times 10^{-10}$  ;  $K_A^I, H_4SiO_4 = \sim 10^{-10}$ ). These do not show any basic properties.
2. Boric acid reacts with alcohols in presence of H<sub>2</sub>SO<sub>4</sub> to form alkyl or aryl borates, B(OR)<sub>3</sub>. Orthosilicic acid also forms a series of volatile esters, Si(OR)<sub>4</sub>.
3. Halides of both boron and silicon are readily hydrolysed to boric acid and silicic acid.
4. Both boron and silicon form volatile hydrides, both being obtained by a common method of acid hydrolysis of magnesium boride and magnesium silicide. Due to electron-deficient character, the boron hydrides have unique hydrogen bridge bond, which is not necessary for the silicon hydrides.
5. Both B<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, being acidic oxides, are capable of reacting with basic oxides to form metal borates and metal silicates.



## 17.3. COMPOUNDS OF THE GROUP IIIB (GROUP 13) ELEMENTS

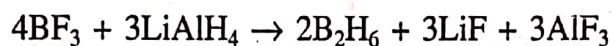
## 17.3.1. Boron Hydrides (Boranes), Carboranes and Borohydrides (Tetrahydroborates)

**Boron Hydrides (Boranes)** : In view of the complexities of formulae and structures of polyboron hydrides a nomenclature has been recommended by IUPAC in 1990. The recommendation puts the number of hydrogen atoms with arabic numerals in parentheses after the name 'borane'. The number of boron atoms in the molecule is indicated by appropriate numerical prefix di-, tri-, tetra-, penta- etc. before 'borane'. Thus the names of some boron hydrides are as given below :

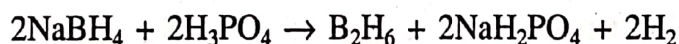
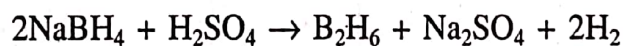
BH <sub>3</sub>	borane (3)	B <sub>5</sub> H <sub>9</sub>	pentaborane (9)
B <sub>2</sub> H <sub>6</sub>	diborane (6)	B <sub>6</sub> H <sub>10</sub>	hexaborane (10)
B <sub>4</sub> H <sub>10</sub>	tetraborane (10)	B <sub>10</sub> H <sub>14</sub>	decaborane (14)

Stock's original method of synthesis involved acid hydrolysis of metal borides like Mg<sub>3</sub>B<sub>2</sub>. By this procedure a mixture of B<sub>4</sub>H<sub>10</sub>, B<sub>5</sub>H<sub>9</sub>, B<sub>6</sub>H<sub>10</sub> and B<sub>10</sub>H<sub>14</sub> was obtained. No B<sub>2</sub>H<sub>6</sub> could be obtained by this procedure as it was readily decomposed by water. Nowadays Stock's method is hardly used ; instead, specialised methods are used for particular boron hydrides.

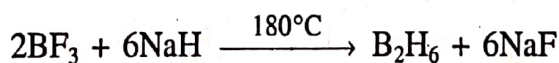
Diborane (6) is best made by adding slowly a solution of BF<sub>3</sub> in dry ether to an ethereal slurry of finely powdered LiAlH<sub>4</sub> :



The B<sub>2</sub>H<sub>6</sub> alongwith the ether is passed through a cold condenser whereby the ether is retained, and then the B<sub>2</sub>H<sub>6</sub> is collected in a trap cooled in liquid nitrogen. Diborane (6) is also obtained by reacting a tetrahydroborate with sulphuric acid or with phosphoric acid :



Gaseous BF<sub>3</sub> has been reduced to B<sub>2</sub>H<sub>6</sub> by NaH at 180°C :



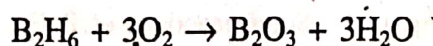
The B<sub>2</sub>H<sub>6</sub> is collected in cooled traps. This method forms the basis of its large-scale preparation.

Interaction of BCl<sub>3</sub> with H<sub>2</sub> over a Cu-Al catalyst at ~ 450°C also gives B<sub>2</sub>H<sub>6</sub>.

B<sub>2</sub>H<sub>6</sub> is a colourless gas (M.P -165°C ; B.P - 94°C)

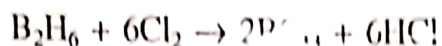
Pentaborane (9) (B<sub>5</sub>H<sub>9</sub>) is obtained in good yield on heating a mixture of B<sub>2</sub>H<sub>6</sub> and H<sub>2</sub> to ~ 250°C. B<sub>2</sub>H<sub>6</sub> gives a moderate yield of B<sub>5</sub>H<sub>11</sub> at 115°C. B<sub>5</sub>H<sub>11</sub> and H<sub>2</sub> give at 100°C a mixture of B<sub>2</sub>H<sub>6</sub> and B<sub>4</sub>H<sub>10</sub>.

All the boranes burn in air or oxygen, if ignition occurs, to give boric oxide and water :

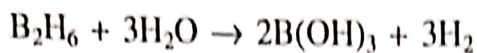




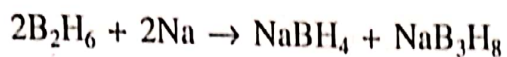
Diborane (6) reacts violently with halogens to form boron halides :



Boron hydrides are hydrolysed by water to boric acid and hydrogen :

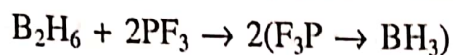
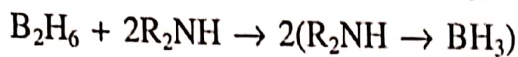
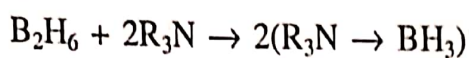


Diborane (6) undergoes slow reaction with active metals (Na, K, Ca) to give salts of tetrahydroborate :



With hydride ion  $\text{B}_2\text{H}_6$  gives tetrahydroborate.

Lewis acid character *i.e.* electron acceptor character of  $\text{B}_2\text{H}_6$  is evident from the many easy reactions with Lewis base (electron donors). Some Lewis bases break open the banana bond of  $\text{B}_2\text{H}_6$  to give addition compounds :



The structure of boron hydrides has already been discussed (Chapter 14).

Some reactions of  $\text{B}_2\text{H}_6$  are depicted in Fig 17.1.

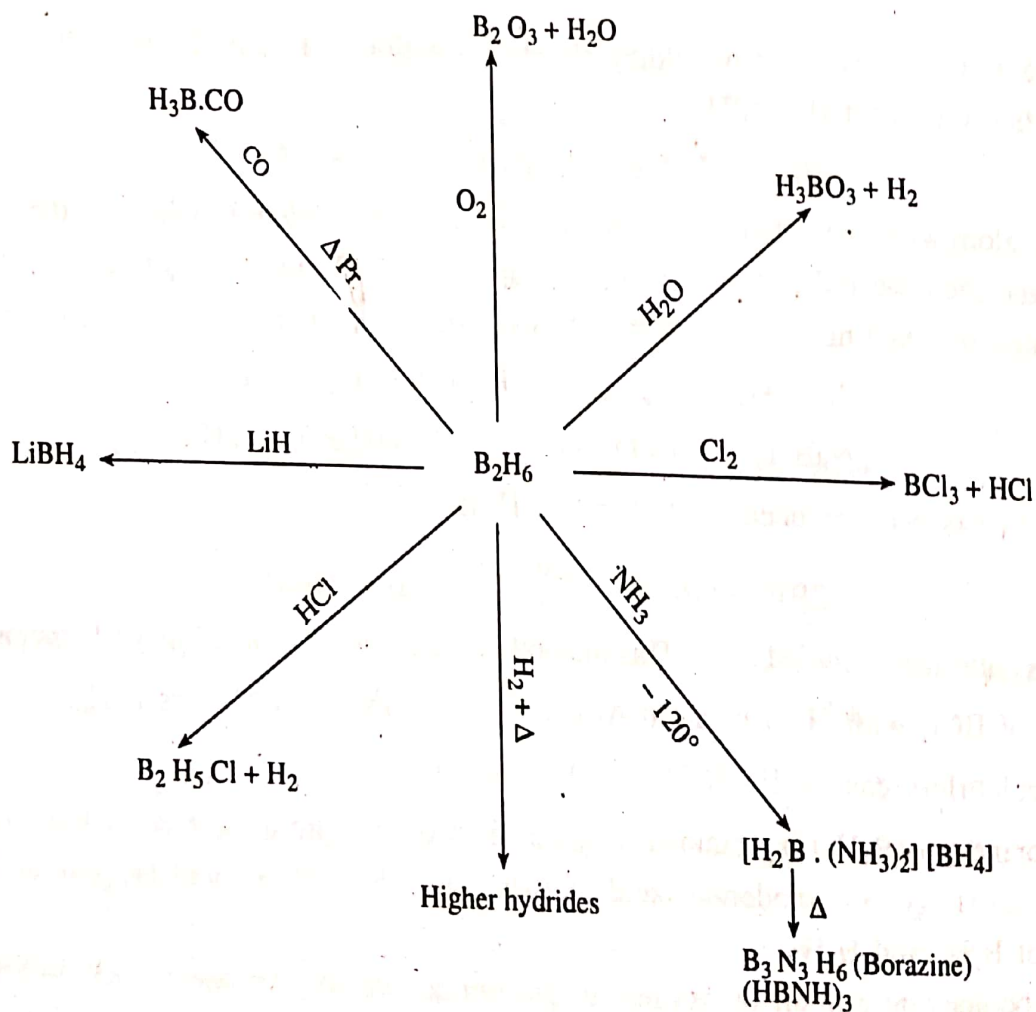
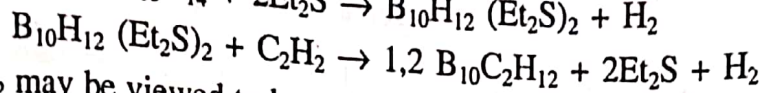
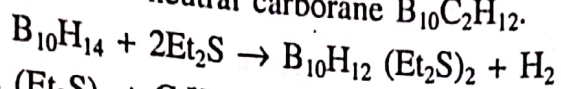


Fig 17.1 : Some reactions of  $\text{B}_2\text{H}_6$ .

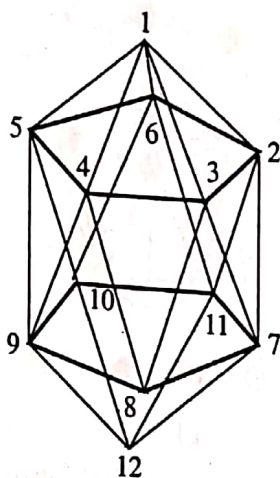


**Carboranes** : These are substituted boranes —BH<sup>-</sup> groups of boranes being substituted by CH groups. Note that BH<sup>-</sup> (with 5 electrons) is isoelectronic with CH (again with 5 electrons). Thus replacement of two BH<sup>-</sup> groups in B<sub>n</sub>H<sub>n</sub><sup>2-</sup> by two CH (again with 5 electrons) gives B<sub>n-2</sub>C<sub>2</sub>H<sub>n</sub>. Thus decaborane (14) B<sub>10</sub>H<sub>14</sub> reacts with Et<sub>2</sub>S to give B<sub>10</sub>H<sub>12</sub>(Et<sub>2</sub>S)<sub>2</sub> which reacts further with HC ≡ CH to give the neutral carborane B<sub>10</sub>C<sub>2</sub>H<sub>12</sub>.



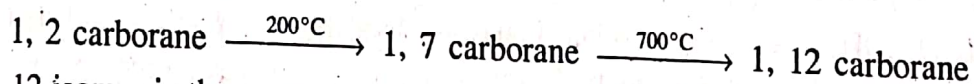
(1, 2 B<sub>10</sub>C<sub>2</sub>H<sub>12</sub> may be viewed to have been derived from B<sub>12</sub>H<sub>12</sub><sup>2-</sup> by substitution of two BH<sup>-</sup> units by two CH units.)

The carborane is built up on an icosahedral framework (17-VI) and is capable of generating three isomers (1, 2 ; 1, 7 ; and 1, 12) depending on the relative positions of the two carbon atoms.



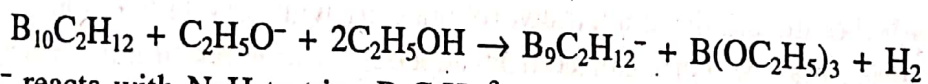
1, 2 dicarba-closo-dodecaborane (1 and 2 = CH ; 3 to 12 = BH)  
(17-VI)

The above reactions normally give the 1, 2 isomer. At 200°C this isomer gives the 1, 7 carborane and the latter at 700°C provides the most stable 1, 12 isomer.

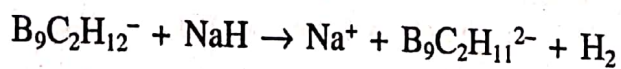


The 1, 12 isomer is the most stable because the two electron withdrawing carbon atoms (with δ<sup>-</sup> charge) are the most separated.

The 1, 2 B<sub>10</sub>C<sub>2</sub>H<sub>12</sub> reacts with base (ethoxide) to give degraded carborane anion B<sub>9</sub>C<sub>2</sub>H<sub>12</sub><sup>-</sup>;

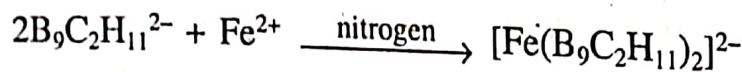


B<sub>9</sub>C<sub>2</sub>H<sub>12</sub><sup>-</sup> reacts with NaH to give B<sub>9</sub>C<sub>2</sub>H<sub>11</sub><sup>2-</sup> :

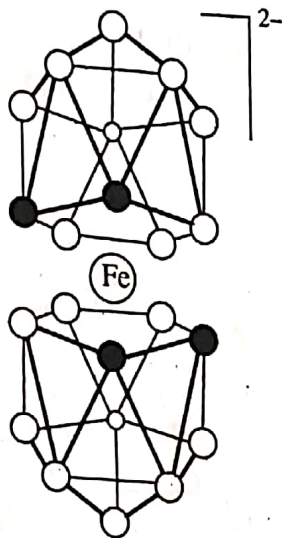


The removal of a BH<sup>2+</sup> from B<sub>10</sub>C<sub>2</sub>H<sub>12</sub> by strong bases like ethoxide C<sub>2</sub>H<sub>5</sub>O<sup>-</sup> and subsequent reaction with NaH may be viewed as a nucleophilic attack at the most electron deficient boron atoms (of the carborane) which are next to the electron withdrawing carbon atoms (cf: electronegativity : B, 2.0 ; C, 2.5).

The carborane  $B_9C_2H_{11}^{2-}$  is an incomplete icosahedron with an open pentagonal face which resembles the cyclopentadienyl anion. The latter forms well-established bis (cyclopentadienyl) metal complexes—the metallocenes. Hawthorne succeeded in synthesising complexes of  $B_9C_2H_{11}^{2-}$  with transition metal ions such as Fe(II) and Co(III) with  $d^6$  configuration giving  $[Fe(B_9C_2H_{11})_2]^{2-}$  (17-VII) and  $[Co(B_9C_2H_{11})_2]^-$ .



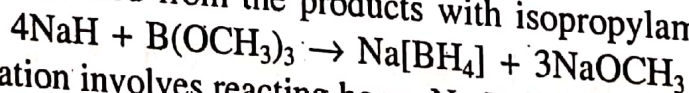
The  $B_9C_2H_{11}^{2-}$  acts as a 6-electron donor ligand (cf :  $C_5H_5^-$ ). The family name of such complexes is bis (dicarbollide) metal complexes.



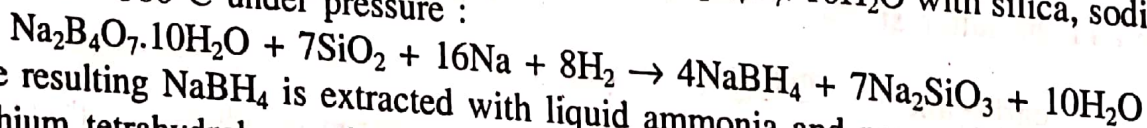
O = BH ; ● = CH

(17-VII)

**Borohydrides (Tetrahydroborates) :** The tetrahydroborate contains the complex  $[BH_4]^-$  ion. Sodium tetrahydroborate is formed out of the reaction of sodium hydride with boric ester at  $250^\circ C$ , and is extracted from the products with isopropylamine.

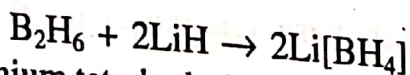


Large-scale preparation involves reacting borax  $Na_2B_4O_7 \cdot 10H_2O$  with silica, sodium and hydrogen at  $\sim 500^\circ C$  under pressure :

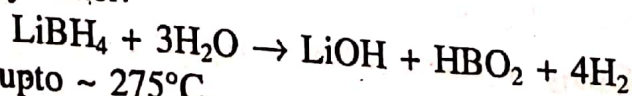


The resulting  $NaBH_4$  is extracted with liquid ammonia and recovered by evaporation.

Lithium tetrahydroborate is best obtained by the reaction of diborane with an ether solution of lithium hydride.

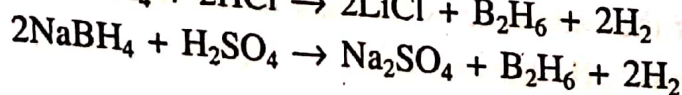
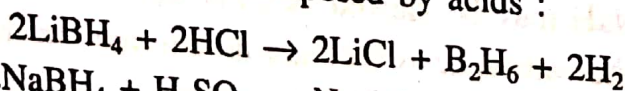


Sodium tetrahydroborate and lithium tetrahydroborate are white crystalline non-volatile solid. Sodium borohydride may be recrystallised from aqueous solution but lithium tetrahydroborate is rapidly decomposed by water.



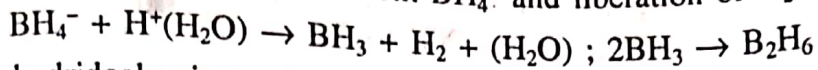
Both are stable to heat upto  $\sim 275^\circ C$ .

The tetrahydroborates are readily decomposed by acids :

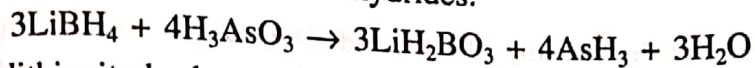




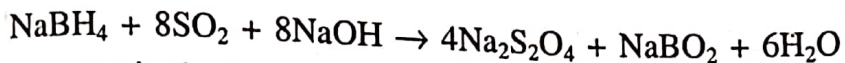
The sensitivity of  $\text{BH}_4^-$  towards aqueous  $\text{H}^+$  is due to the strong electron acceptor behaviour of  $\text{H}^+$ , which results in extraction of  $\text{H}^-$  from  $\text{BH}_4^-$  and liberation of  $\text{H}_2$  :



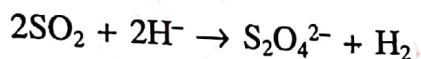
Like lithium tetrahydridoaluminate, the tetrahydroborate is also a formidable reducing agent, thus carbonyl compounds such as carboxylic acids, aldehydes, ketones are reduced to alcohols. It reduces arsenite and antimonite to their hydrides.



$\text{SO}_2$  is reduced to dithionite by borohydride. This reaction forms the basis of bleaching of wood pulp :

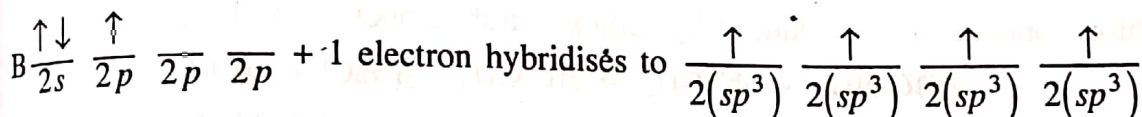


The real reducing agent is the hydride ion :



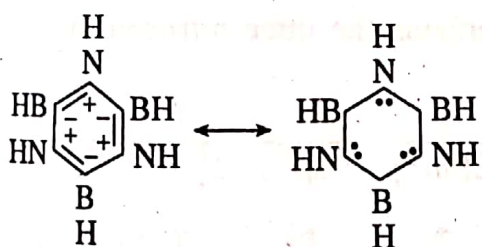
The  $[\text{BH}_4]^-$  ion is tetrahedral and the crystal structure of the sodium salt has been found to be ionic being composed of face-centred cubic lattice of sodium and  $[\text{BH}_4]^-$  ions. Each sodium ion is octahedrally surrounded by six  $\text{BH}_4^-$  ions and each  $\text{BH}_4^-$  ion by six sodium ions. Each boron in  $\text{BH}_4^-$  is tetrahedrally surrounded by four hydrogens.

In the  $[\text{BH}_4]^-$  ion, boron uses  $sp^3$  hybridisation :

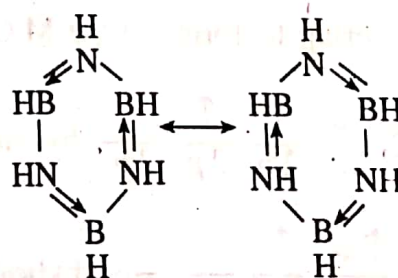


The four tetrahedral hybrid orbitals overlap with  $1s$  orbitals of four hydrogen atoms each containing one unpaired electron. Alternatively if we assume  $\text{BH}_4^-$  to be formed by the combination of  $\text{BH}_3$  and  $\text{H}^-$  then there will be three usual covalent bonds between boron and three hydrogens, and a coordinate link from  $\text{H}^-$  to boron.

**17.3.2. Borazine\* (Borazole). Inorganic Benzene :** The electron deficient character of boron is manifested in a number of compounds containing boron bound to N, P, S, etc. One such interesting compound is borazine (17-VIII)  $\text{B}_3\text{N}_3\text{H}_6$ , which has resemblance with benzene (17-IX) in having two resonating structures containing alternate NH and BH groups.

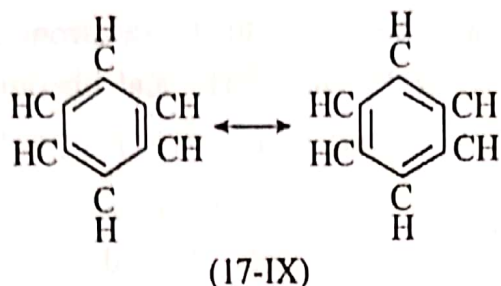


(17-VIII a)

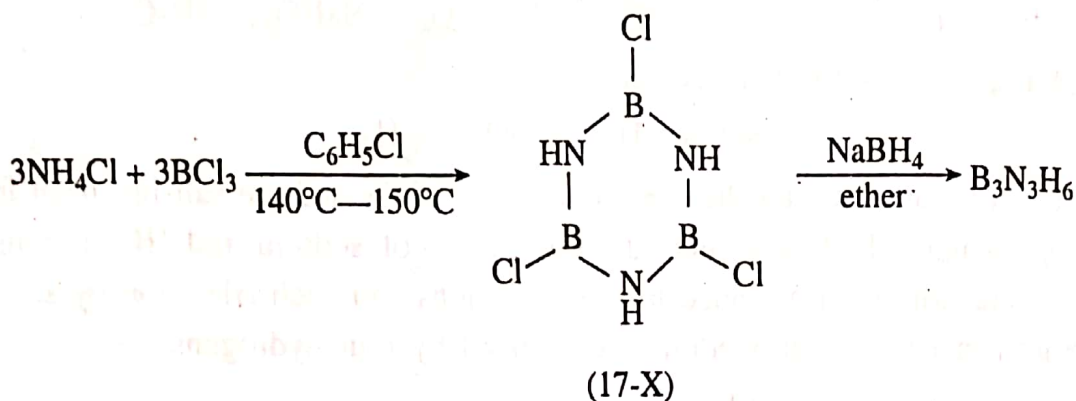


(17-VIII b)

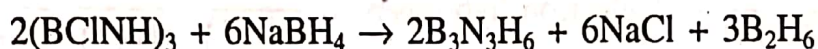
\* Systematic name is cyclotriborazane. The trivial name borazine (but not borazole) is allowed by IUPAC.



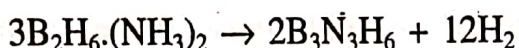
It is conveniently obtained by heating  $\text{NH}_4\text{Cl}$  and  $\text{BCl}_3$ , the product being chloroborazine,  $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ ,  $(\text{BClNH})_3$  (17-X)



The chloroborazine is next reduced by sodium tetrahydroborate in ether :

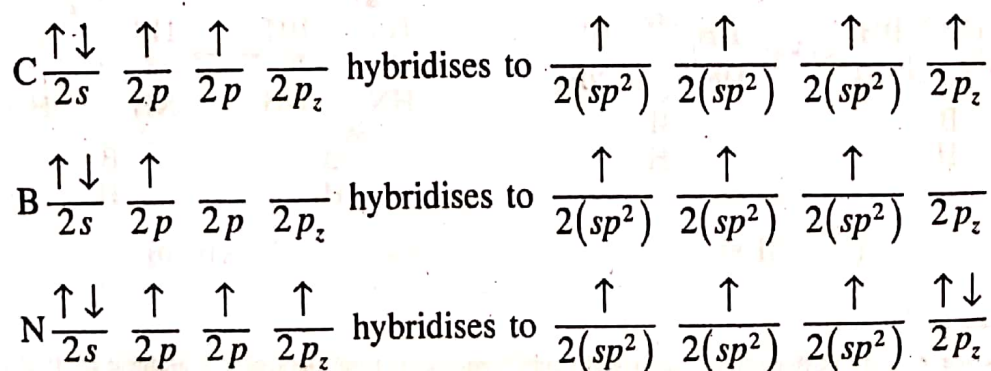


Borazine has also been prepared by the pyrolysis of diborane-diammoniate in a sealed tube at  $\sim 200^\circ\text{C}$  :



The so-called diborane-diammoniate is obtained as a white solid by the reaction of diborane and ammonia. Its structure shows that it is really  $[\text{H}_2\text{B}(\text{NH}_3)_2] [\text{BH}_4]$ .

In borazine the boron and the nitrogen atoms together are like the six carbon atoms in benzene. In benzene each carbon is  $sp^2$  hybridised and is bonded to two carbons and one hydrogen. The remaining  $p_z$  orbital can overlap with another  $p_z$  orbital of a neighbouring carbon to make a double bond. Alternatively all the  $p_z$  orbitals of six carbons may be assumed to overlap to form  $\pi$ -type M.O.'s. In borazine the three nitrogens and the three



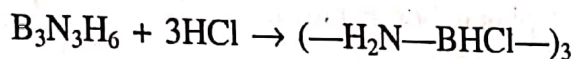


Borons are  $sp^2$  hybridised. Overlap of the  $sp^2$  orbitals gives three covalent bonds to nitrogen and boron while overlap of the  $p_z$  orbitals provides a  $\pi$ -bond from nitrogen to boron (17-VIIb). Resonance will lead to equivalent B-N distances. In effect a  $\pi$ -system comparable to that of benzene results. Many physical properties of borazine are similar to those of benzene (Table 17.3).

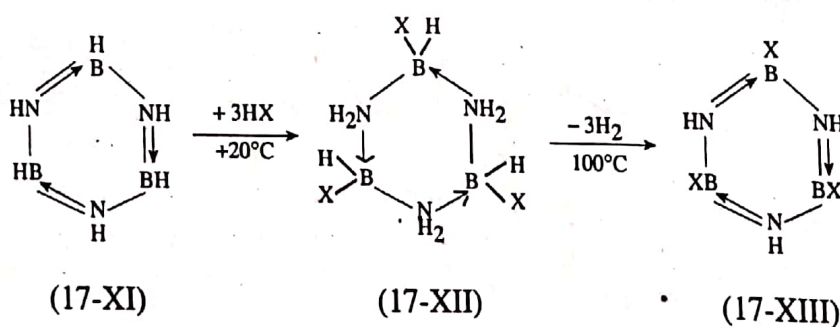
Table 17.3. : Comparison of Borazine and Benzene

Property	Borazine	Benzene
B-N distance	1.42 (142 pm)	—
C-C distance	—	1.41A (141 pm)
Molecular Weight	80.5	78
B.P. ( $^{\circ}\text{C}$ )	53	80
Critical temperature*	21.4	21.1
Heat of vaporisation kcal/mole (kJ/mole)	7(29)	7.4(31)
Density ( $\text{g}/\text{cm}^3$ )	1.00	1.01

Because of these similarities borazine has been nicknamed *inorganic benzene*. However borazine is more reactive than benzene. Unlike benzene, borazine undergoes addition reactions, say with HCl :



The HCl (or HBr) is added to the  $\pi$ -bond of borazine—the hydrogen of HCl (or HBr) migrates to the electronegative nitrogen and the chlorine (or Br) to the less electronegative boron. The products are saturated *inorganic cyclohexanes* (17-XII). At  $100^{\circ}\text{C}$  the halogen derivative eliminates 3 mol  $\text{H}_2$  forming a borazine with the hydrogen on the boron being substituted by halogen (17-XIII).

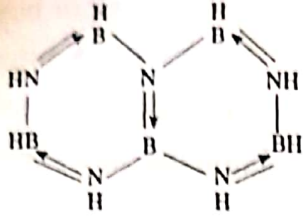


Prolonged heating of borazine at  $380^{\circ}\text{C}$  for five days gives :

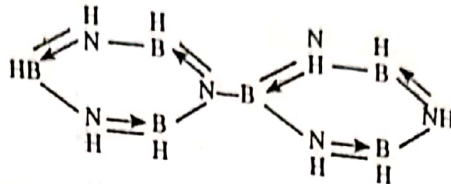
*inorganic naphthalene*,  $\text{B}_5\text{N}_5\text{H}_8$  (17-XIV) (M.P  $29^{\circ}\text{C}$ ) and

*inorganic biphenyl*,  $\text{B}_6\text{N}_6\text{H}_{10}$  (17-XV) (M.P  $60^{\circ}\text{C}$ ).

\* Critical temperature for a gas is that maximum temperature above which it cannot be liquefied at any applied pressure.



(17-XIV)

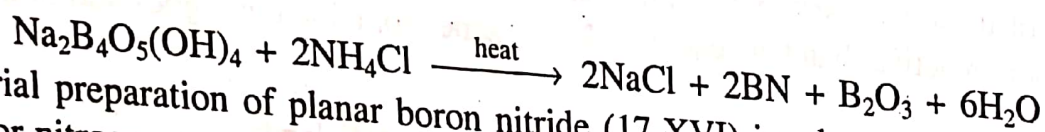


(17-XV)

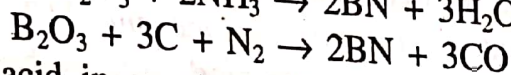
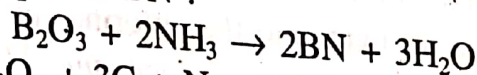
The closeness of  $B_3N_3H_6$  to  $C_6H_6$  is revealed in the formation of complexes  $(B_3N_3Me_6)Cr(CO)_3$  which is analogous to  $(C_6Me_6)Cr(CO)_3$ .  $B_3N_3Me_6$  behaves as a tridentate arene  $(C_6Me_6)$  ligand (Chapter 24). When bound in a complex the  $B_3N_3Me_6$  ligand is not quite planar. Free borazine or the  $C_6Me_6$ , however, is planar. The difference is attributed to the difference in atomic radii of boron and nitrogen (0.82 and 0.77Å) and to the weaker aromaticity of borazine.

**17.3.3. Boron Nitride : Inorganic Graphite and Diamond :** A count of the electrons of boron, carbon and nitrogen shows that a B-N unit is isoelectronic with a C-C unit. Furthermore electronegativity of carbon (2.5) is just the mean of those of boron (2.0) and nitrogen (3.0). It is small wonder that the binary compound boron nitride will be akin to graphite and diamond.

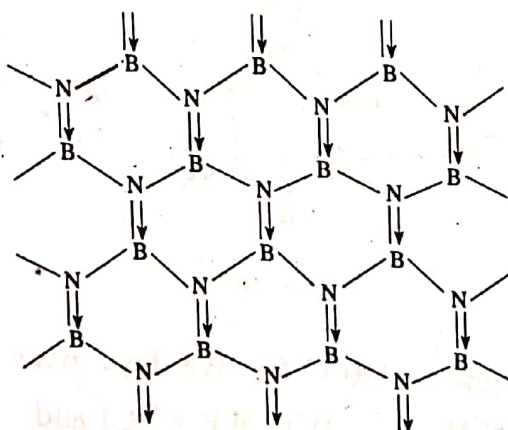
Boron reacts with nitrogen or ammonia on heating to form a binary nitride BN which is a white, refractory solid. The compound is also obtained by heating ammonium chloride and borax :



Industrial preparation of planar boron nitride (17-XVI) involves reaction of  $B_2O_3$  with ammonia or nitrogen at  $\sim 800 - 1200^\circ C$ . Reaction of  $B_2O_3$  with nitrogen in the presence of carbon at  $\sim 1800^\circ C$  gives pure planar BN :



Fusion of urea with boric acid in an atmosphere of ammonia in the temperature range  $500^\circ - 950^\circ C$  gives boron nitride. This form of boron nitride is similar to graphite in physical

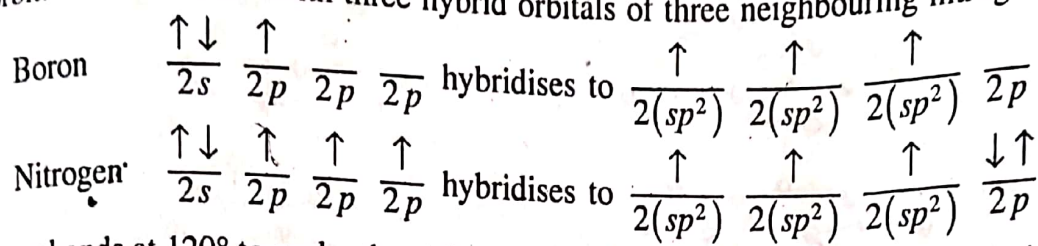


(17-XVI)

properties and has a graphite-like layer structure of alternate boron and nitrogen. The boron and nitrogen atoms are 1.45Å (145pm) from each other. The layers are at a distance of 3.34Å



(334pm). In boron nitride the atoms of one layer are directly above the atoms of the next layer but that a boron is above a nitrogen and a nitrogen is above a boron and so on. In graphite the carbon atoms of a particular layer are over the carbon atoms of alternate layers and not over the atoms of the adjacent layers. This form of boron nitride is often called *white graphite*. In this form each boron and nitrogen has  $sp^2$  hybridisation. The overlap of the hybrid orbitals of one boron with three hybrid orbitals of three neighbouring nitrogens give



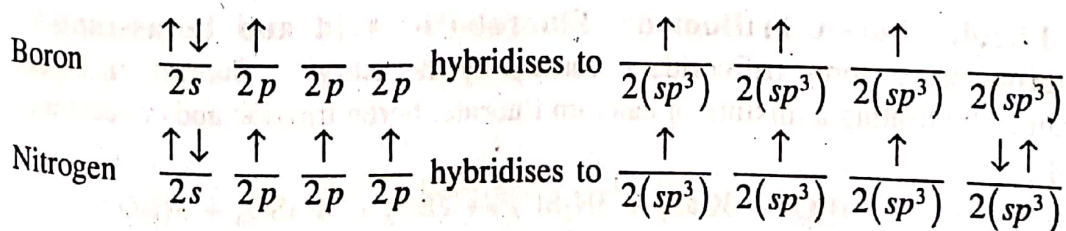
three planar bonds at  $120^\circ$  to each other. The lone pair in the remaining  $2p$  orbital of nitrogen then forms a  $\pi$ -bond with the vacant  $2p$  orbital of a boron. Note that  $(\text{BN})_3$  is isoelectronic with the  $\text{C}_6$  hexagonal structure in graphite. Through resonance all the B-N distance as also the bond order become equivalent. We can also say that the three lone pairs of the three nitrogen atoms of the hexagonal  $(\text{BN})_3$  overlap with the three empty  $p_z$  orbitals of the three borons giving  $\pi$ -type M.O.'s. However (like graphite) this variety of boron nitride does not conduct electricity at ordinary temperature. Evidently there are not enough mobile  $\pi$ -electrons. The  $\pi$ -electrons thus appear to be localised on the more electronegative nitrogen.

The graphite-like variety is used as an antisticking material in moulds in glass industry.

Table 17.4 : Comparison of Planar BN and Graphite

	Planar BN	Graphite
B-N distance, A (pm)	1.45 (145)	—
C-C distance, A (pm)	—	1.415 (141.5)
Layer spacing, A (pm)	3.34 (334)	3.35 (335)
Density ( $\text{g/cm}^3$ )	2.29	2.25

Like the conversion of graphite to diamond, the above layer structure of boron nitride can be converted to the tetrahedral non-ending diamond-like structure. High temperature ( $1800^\circ\text{C}$ ) and high pressure (85,000 atm.) and an alkali metal or alkaline earth metal catalyst are required to bring about this conversion. The diamond-like variety of BN is called *borazon*. In borazon each tetrahedral nitrogen is bonded covalently to four tetrahedral boron (and vice versa)—to three borons with usual shared pair covalent bond and to the fourth boron via a coordinate link from nitrogen to boron. Each boron is connected to three nitrogen through shared pair covalent bonds, and to the fourth nitrogen by a coordinate link from nitrogen to boron.



The crystal structure is that of zinc sulphide. (see section 6.1.1). B-N distance is 1.56Å (156 pm) (C—C distance in diamond is 1.54Å (154 pm). Single bond length in B—N is close to  $0.88 + 0.70 = 1.58\text{Å}$  (158 pm). Apart from diamond it is the hardest known (density,  $3.45\text{ g/cm}^3$ ).

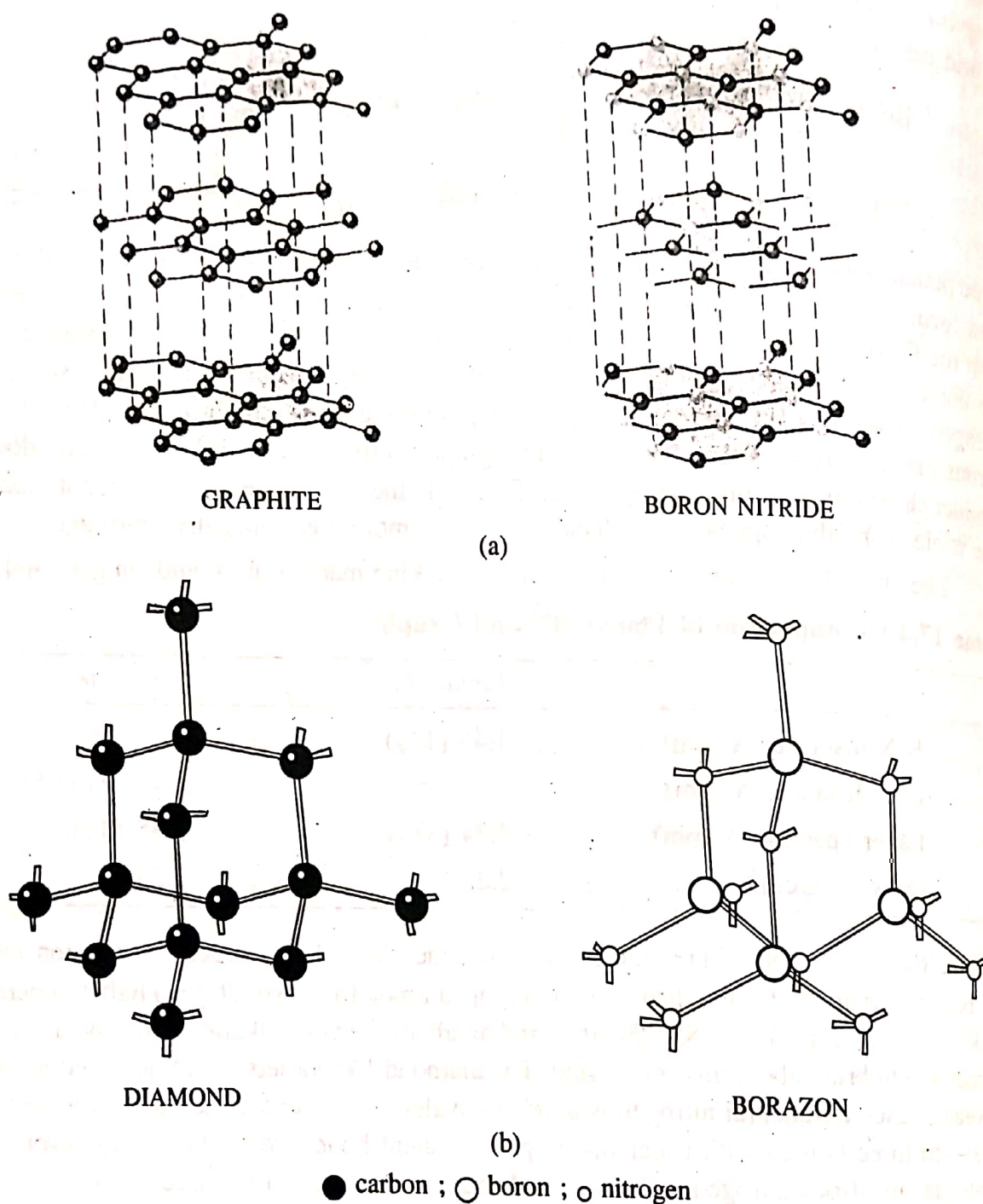
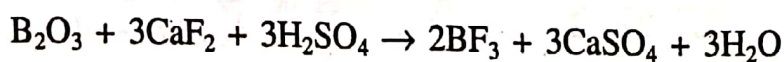


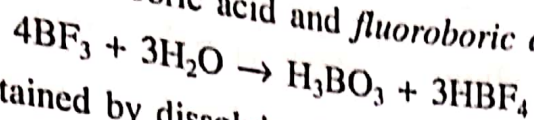
Fig. 17.2. Resemblance of (a) graphite and planar boron nitride (b) diamond and borazon.

**17.3.4. Boron Trifluoride, Fluoroboric Acid and Potassium/Ammonium Fluoroborate :** Boron trifluoride is formed by the action of fluorine on boron. It is also obtained by heating a mixture of calcium fluoride, boron trioxide and concentrated sulphuric acid :

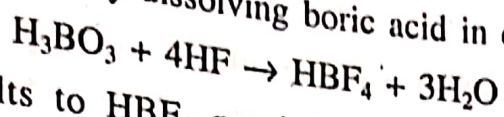




The gas reacts with water to form boric acid and fluoroboric acid :

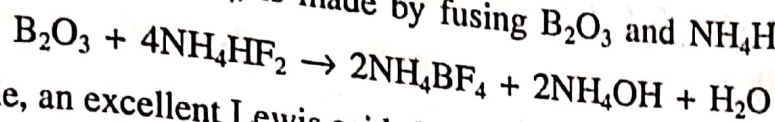


Fluoroboric acid is also obtained by dissolving boric acid in cooled 50% HF :

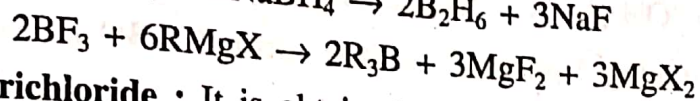
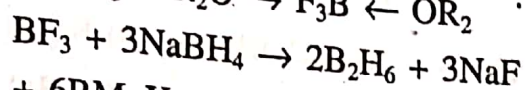
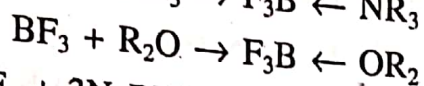
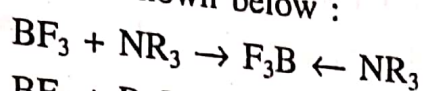


Addition of potassium salts to  $\text{HBF}_4$  precipitates potassium tetrafluoroborate. The tetrafluoroborate is tetrahedral ( $sp^3$  hybridisation) and  $\text{KBF}_4$  is isomorphous with  $\text{KClO}_4$ .

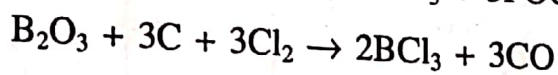
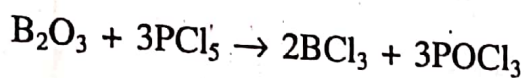
Ammonium fluoroborate,  $\text{NH}_4\text{BF}_4$ , is made by fusing  $\text{B}_2\text{O}_3$  and  $\text{NH}_4\text{HF}_2$  :



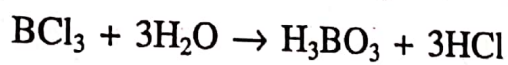
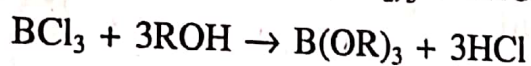
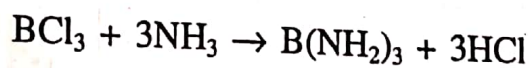
Boron trifluoride, an excellent Lewis acid, forms a number of stable addition compounds with Lewis bases. Some reactions are shown below :



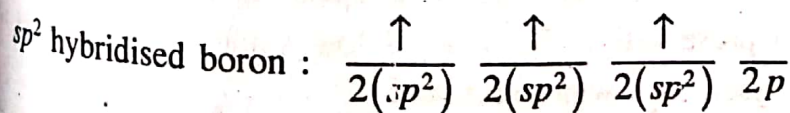
**17.3.5. Boron Trichloride :** It is obtained by burning boron in chlorine, by heating  $\text{B}_2\text{O}_3$  with  $\text{PCl}_5$  in a sealed tube or by passing dry chlorine gas over a heated mixture of  $\text{B}_2\text{O}_3$  and carbon. It is first condensed in a freezing mixture and then purified from chlorine by distillation over mercury.

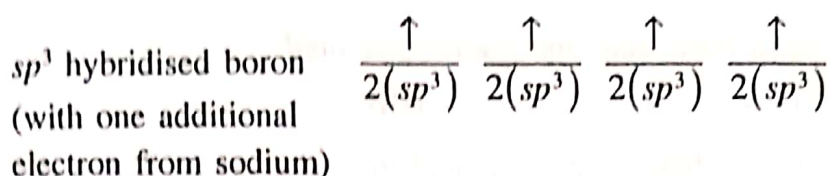


Some typical reactions of  $\text{BCl}_3$  are given below :



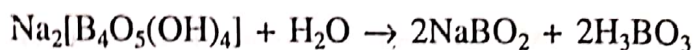
**17.3.6. Borates :** Recent studies indicate that borates have quite complicated stoichiometry and structure. Borax, commonly written as sodium tetraborate decahydrate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , has now been shown to be  $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ . The borax anion has two  $\text{BO}_4$  tetrahedra and two planar  $\text{BO}_3$  units. Each  $\text{BO}_4$  shares two oxygens with two planar  $\text{BO}_3$  and one oxygen with the second  $\text{BO}_4$  tetrahedron. The fourth oxygen is connected to the boron of  $\text{BO}_4$  unit and a hydrogen (17-XVII). The planar boron is  $sp^2$  hybridised and the tetrahedral boron  $sp^3$  hybridised.



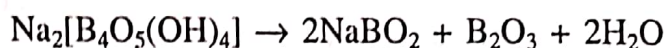


These hybrid orbitals then overlap suitable orbitals of oxygen with unpaired electrons.

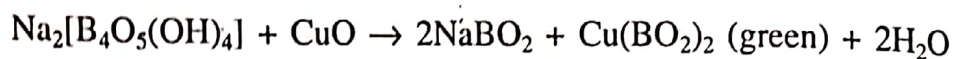
Borax gives a slightly alkaline reaction in aqueous solution because of hydrolysis, boric acid being only a weak acid :



On heating borax first swells due to losing the hydrate water. The anhydrous borax, on further heating, gives metaborate and boron trioxide :

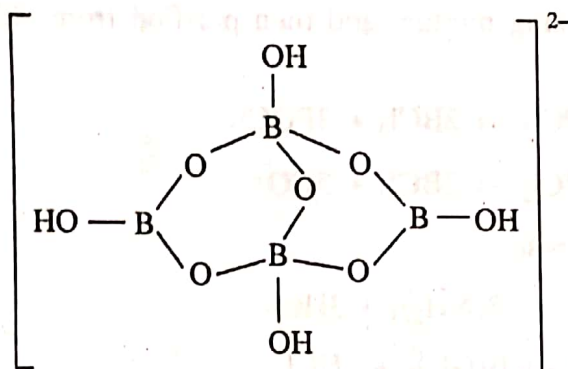


Fused borax can dissolve metal oxides to yield clear glasses with characteristic colours :

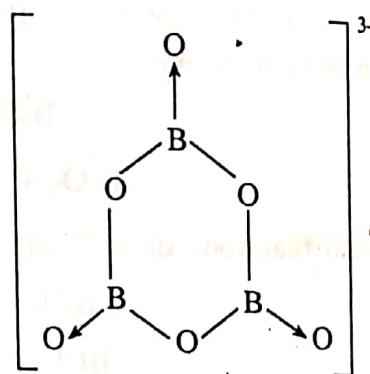


When heated in a reducing Bunsen flame the green  $\text{Cu}(\text{BO}_2)_2$  becomes dull red due to reduction to  $\text{CuBO}_2$ .

Such reactions form the basis of *borax-bead tests*. (Section 17.7)

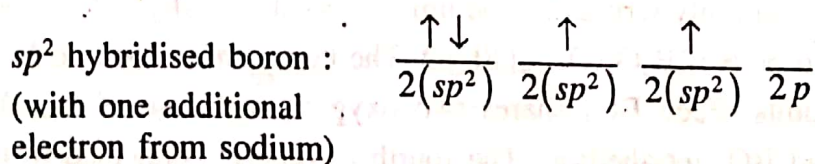


(17-XVII)



(17-XVIII)

The metaborate ion (eg.  $\text{NaBO}_2$ ) has a trinuclear cyclic structure (17-XVIII) and should better be written as  $[\text{B}_3\text{O}_6]^{3-}$  (as  $\text{Na}_3\text{B}_3\text{O}_6$ ). All the three borons are  $sp^2$  hybridised :

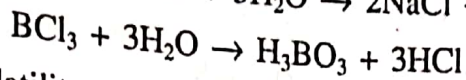
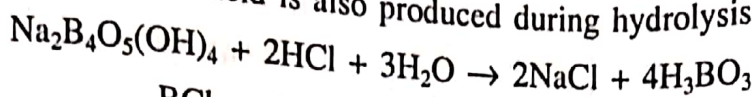


The  $sp^2$  orbital with paired spins forms the coordinate link to oxygen (17-XVIII).

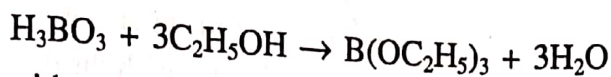
Borax finds extensive use in making optical and hard glass, as an antiseptic, in the manufacture of enamels, and as a preservative. Because of low solubility of calcium and magnesium borates, borax is also used as a water softener.



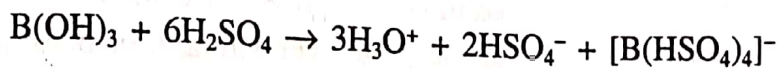
**17.3.7. Boric Acid :** Boric acid is obtained in the form of scales by boiling borax with acids and then crystallising. The acid is also produced during hydrolysis of boron halides :



The acid has distinct volatility and can be removed by repeated evaporation with HCl. Around 100°C the acid is changed to metaboric acid (HBO<sub>2</sub>), at 140°C to pyroboric acid (H<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) and finally at higher temperature to B<sub>2</sub>O<sub>3</sub> (Fig 17.3). With alcohols (in presence of sulphuric acid) alkyl borates are formed, this being the basis of detecting borates and boric acid in qualitative analysis.



The esters burn in air with a green flame. On fusion with metal oxides coloured borate glasses are formed. On fusion with NH<sub>4</sub>HF<sub>2</sub> ultimately BF<sub>3</sub> is obtained. Boric acid acts as a strong acid in anhydrous H<sub>2</sub>SO<sub>4</sub> :



Treatment of boric acid with sodium peroxide provides sodium peroxoborate which is now known to have the structure of [B<sub>2</sub>(O<sub>2</sub>)<sub>2</sub>(OH)<sub>4</sub>]<sup>2-</sup> in which two tetrahedral (sp<sup>3</sup> hybridised) borons are linked by bridging -μ peroxo groups (17-XIX).

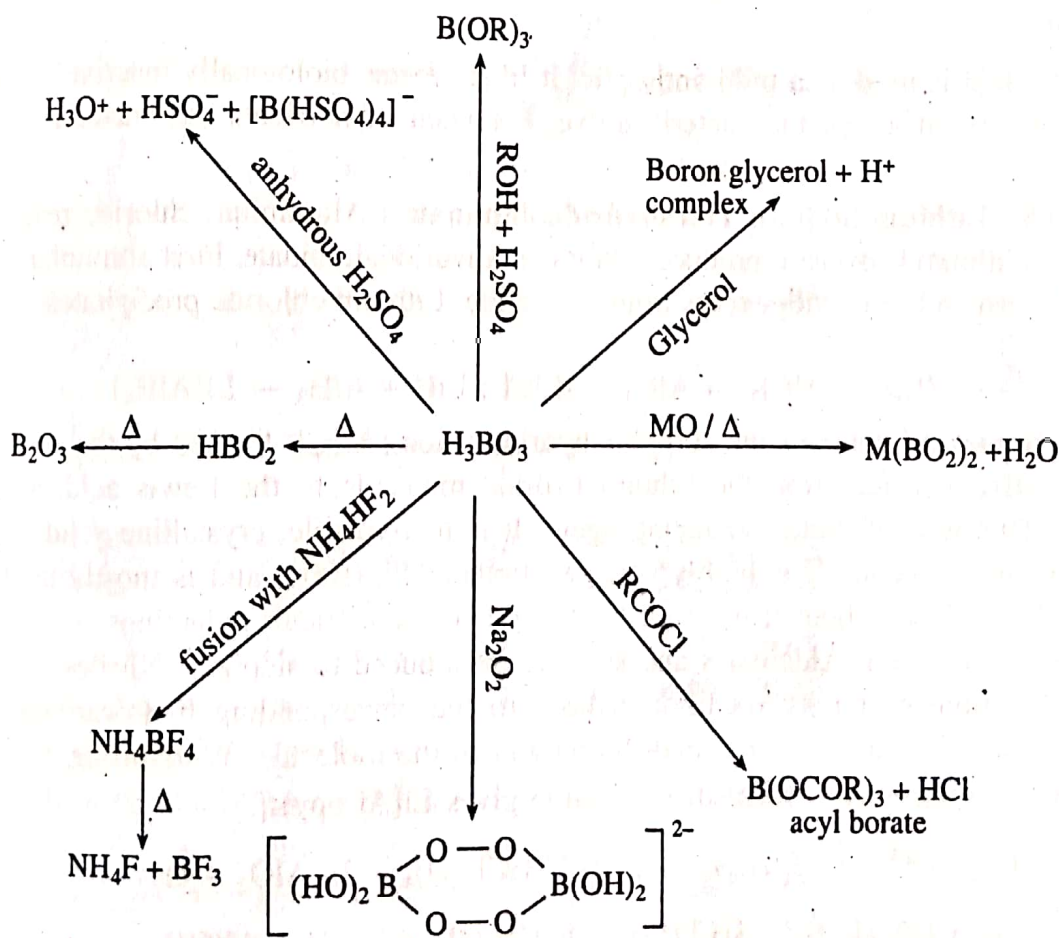


Fig 17.3 : Some reactions of H<sub>3</sub>BO<sub>3</sub>