p-BLOCK ELEMENTS
GROUP-IIIA (13) BORON FAMILY

The very word "experiment" refers to a situation where we can tell others what we have done and what we have learned

Niels Bohr

7.1 INTRODUCTION

The elements boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl) constitute Group III A or 13 of the periodic table. They belong to p-block elements. The electronic configuration in their outer most orbit is $ns^2 np^1$. These elements not only show marked similarities among them but also show a very wide variation in properties. Boron is a typical non-metal, aluminium is a metal but shows many chemical similarities to boron and the remaining elements are almost exclusively metallic in character. Although unipositive oxidation state is the characteristic one, for all the members of the group, the unipositive state occurs in compounds of all the elements except boron. In the case of thallium, the unipositive oxidation state is the stable one and in fact it shows similarities to so many elements such as alkali metals, silver and mercury. Hence, it is nick named as **duck-billed platypus** among the elements. A feature of the chemistry of boron is the existence of large number of electron-deficient species which pose formidable problems in valence bond theory. These include not only the hydrides but also organic and metallic derivatives of the hydrides, the metal borides etc.

7.2 ABUNDANCE

Boron and aluminium of this family are considered to be familiar elements whereas gallium, indium and thallium are less familiar elements. Particularly aluminium is abundant in nature. The elements occur in nature in the following proportions in the crust of the Earth.

Boron 3×10^{-4}%
Aluminium 8.13%
Gallium 1.5×10^{-3}%
Indium 1×10^{-5}%
Thallium 10^{-4} to 10^{-5}%

Aluminium is of course the most abundant of all the metals and the third most abundant of all the elements. The comparative scarcity of boron may be partially due to the ease with which the nuclei of its atoms are transmuted by natural bombardment process. Boron is well known, however, because of the existence of concentrated deposits of its compounds particularly in arid regions and because of the desirable properties of many of its compounds which have necessitated large-scale recovery of boron materials. Gallium, indium and thallium never found in concentrated deposits and until recently they were never recovered in sizable quantities.

7.3 OCCURRENCE

Borax $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2 [B_4O_5(OH)_4] \cdot 8H_2O$ is the principal source of boron. In India, it occurs in deserts and in the United States, at California. It occurs in hot springs and lakes in volcanic regions. Aluminium occurs mainly as bauxite (a hydrated oxide mineral), cryolite $Na_3[AlF_6]$ and also in the alumino silicate minerals such as mica and feldspar. Gallium, indium and thallium occur in traces in sulphide minerals. Gallium is also found in traces in bauxite.

7.4 ELECTRONIC CONFIGURATION

The electronic configuration of the elements of Group III A are listed in Table 7.1.

From Table 7.1, it follows that all the elements of Group III A have three electrons in their valence shell, two electrons in the s-orbital and one electron in the p-orbital, i.e., $ns^2 np^1$.

Owing to the similarity in electronic configuration of their outermost shell, they closely resemble in their physical and chemical properties. However, it is to be noted that the penultimate shell of those five elements differ in the configuration; the penultimate shell of boron is having s^2, aluminium is having $s^2 p^6$ and those of other three elements are having $s^2 p^6 d^{10}$ electrons. Thus, boron is expected to differ from aluminium and further boron and aluminium are

Table 7.1 Electronic configuration of Group III A elements

Element	Atomic number	Electronic configuration	Electronic configuration of valence shell
B	5	$1s^2\,2s^2\,2p^1$	$2s^2\,2p^1$
Al	13	$1s^2\,2s^2\,2p^6\,3s^2\,3p^1$	$3s^2\,3p^1$
Ga	31	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^1$	$4s^2\,4p^1$
In	49	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^1$	$5s^2\,5p^1$
Tl	81	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,4f^{14}\,5s^2\,5p^6\,5d^{10}\,6s^2\,6p^1$	$6s^2\,6p^1$

expected to have some similar properties because penultimate shell of the B and Al has noble gas kernel and are different from other three elements.

7.5 PHYSICAL PROPERTIES

1. Atomic and ionic radii: The atomic and ionic radii are given in Table 7.2. Atomic and ionic sizes of Group III A elements do not increase regularly. The greater difference in the atomic radius between boron and aluminium is due to the fact that boron has lesser number of electrons (i.e., two electrons) in its inner shell than aluminium (i.e., eight electrons). Thus, in boron, the outer most electrons experience lesser shielding effect and greater nuclear attraction.

Table 7.2 Atomic and ionic radii of Group III A elements

Element	Covalent radius (pm)	Metallic radius (pm)	Ionic radius (pm) M⁺	Ionic radius (pm) M³⁺
B	80	(88.5)	–	27
Al	125	143	–	53.5
Ga	125	135	120	62
In	150	167	140	80
Tl	155	170	150	88.5

2. Density: As we move down in Group III A, density increases. However, boron and aluminium have comparatively low density. This can be attributed to their lower atomic weights as compared to the remaining elements. Ga is unusual because the liquid expands when it forms solid. Therefore, solid Ga is not denser than liquid Ga.

3. Melting point: The elements of Group III A do not show a regular change in their melting points with increase in atomic number. The melting point of boron is very high because it has the structure of giant covalent polymer in both solid and liquid states. The melting points decrease from B to Ga and then increase. Low melting point of Ga (29.8°) is attributed to the fact that it consists of only Ga₂ molecules; it remains liquid up to 2000°C and hence used in high-temperature thermometry.

4. Boiling point: Boiling points of Group III A elements follow a regular decrease from boron to thallium. This

shows that the strength of bonds holding the atoms in their liquid state decreases from boron to thallium. Note that the boiling point of Ga is in regular order with others whereas the melting point is not. The very low melting point is due to the unusual crystal structure, but the structure no longer exists in the liquid.

5. Heat of sublimation: It decreases regularly on moving down the group.

6. Ionization energies: The ionization energies increase as expected, i.e, first ionization energy < second ionization energy < third ionization energy. The sum of the first three ionization energies for each element is very high.

As the *p*-electron is less tightly held as compared to the *s*-electrons, the first ionization energy has been rather low in each case. The second and third ionization energies have been considerably higher.

Ionization energy decreases from boron to aluminium but does not change appreciably as we move to gallium, indium and thallium. Decrease in ionization energy from boron to aluminium is attributed to the increased size. Further, penultimate shell in both boron and aluminium has inert gas configuration (He configuration in the case of B and Ne configuration in the case of Al) whereas the penultimate shell in all the three remaining elements, i.e., gallium, indium and thallium has 18 electrons [(n-1) $s^2 p^6 d^{10}$]. The extra *d*-electrons fail to shield the nuclear charge effectively because shielding by electrons present in various orbitals has been found to be in the order $s > p > d > f$. Therefore, the outer electrons in the case of gallium, indium and thallium are held more tightly by the nucleus. Consequently, their atoms become smaller and thus their ionization energies become higher than expected. The ionization energy of thallium is further affected because of the poor shielding of 14 f-electrons present in the anti penultimate shell, and it is even more than that of Al, Ga and In.

For gallium and indium, the electronic configuration of the species left after the removal of three electrons is [Ar]$3d^{10}$ and [Kr]$4d^{10}$, respectively whereas for thallium the species so formed has the configuration [Xe]$4f^{14}5d^{10}$. Thus, the fourth ionization energies of these three elements do not involve the removal of an electron from a noble gas

Element	Density (g cm⁻³)	Melting point (K)	Boiling point (K)	Heat of sublimation (kJ mol⁻¹)	Electro negativity
	2.35	2453	3923	564	2.0
	2.7	933	2740	324	1.5
	5.9	303	2676	273	1.6
	7.31	430	2353	241	1.7
	11.85	576	1730	179	1.8

Table 7.4 Ionization energies of Group III A elements

	Ionization energies kJ mol⁻¹			
	Ist	IInd	IIIrd	Sum of three
	801	2427	3659	6887
	577	1816	2744	5137
	579	1979	2962	5520
	558	1820	2704	5082
	589	1971	2877	5437

configuration and the difference between the fourth and the third ionization energies is not nearly so large as for boron and aluminium.

7. Electronegativity: Among the Group III A elements, boron has the maximum electronegativity. It decreases from boron to aluminium as expected. However, from aluminium to thallium, it increases instead of decreasing in contrary to the expectation. This is again attributed to the poor shielding of d-electrons in gallium and indium and d- and f-electrons in thallium (Table 7.3).

8. Oxidation states: The Group III A elements contain three more electrons in their outer most orbit than the stable inert gas (with B and Al) or pseudo inert gas (with Ga, In and Tl) structures. Hence, a uniform +3 oxidation state is expected. This state is characteristic of all the elements. The electronic arrangement in the outermost orbit of these elements $ns^2 np^1$ also suggests +1 oxidation states.

Outer electronic configuration

Ground state ns np +1
Excited state +3

In thallium, +1 oxidation state is well known. A few unipositive indium compounds mostly halides are known, in the solid state. In boron, there are no evidences for +1 oxidation state. Though aluminium and gallium compounds are prepared at elevated temperatures, they yield most unstable unipositive compounds and the +1 oxidation state of these elements is of least important.

The stability of +1 oxidation state increases more and more when we move down the group from B to Tl. Thus, Tl(I) compounds are more stable than Tl(III) compounds. This is attributed to the inert pair effect. **The two s-electrons in the outer shell tend to remain paired and are not participating in compound formation.** This pair of electrons is called **inert pair** and the effect is called **inert pair effect.** The inert pair effect increases gradually in gallium, indium and thallium compounds. For example, Ga⁺ compounds are unstable, In⁺ compounds are moderately stable, whereas Tl⁺ compounds are most stable. In fact, Tl(I) salts resemble alkali metals because thallium is having large size and low oxidation state. Some points of resemblance are as follows.

(i) TlOH is soluble in water yielding strong alkaline solution very similar to NaOH.

(ii) Tl (I) cyanide, perchlorate, sulphate, nitrate, phosphate and carbonate are stable and isomorphous with alkali metal salts.

(iii) TlF is having distorted NaCl-type structure whereas other thallous halides crystallize with CsCl structure.

(iv) Like alkali metals, thallium (I) is known to form alums, e.g., $Tl_2SO_4 \cdot Al_2(SO_4)_3 24H_2O$.
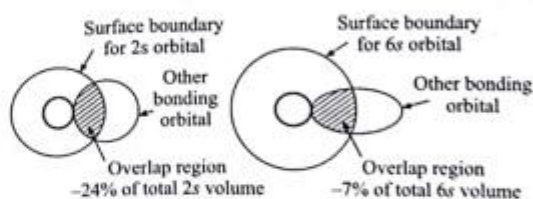

Fig. 7.1 Comparison of overlappings between small (2s) orbital and large (6s) orbital with the orbital of another atom

The stability of unipositive ions in aqueous solutions is consistent only in the case of thallium but for other elements the unipositive oxidation state disproportionates.

$$3M^+ \longrightarrow M^{3+} + 2M$$

Stability of +3 oxidation state decreases regularly as the atomic number increases from boron to thallium.

The stability of +1 oxidation state of Group III A elements should not be attributed strictly to inert pair effect. The inert pair effect explains what is happening, i.e., two electrons do not participate in bonding. The reason for not participating the two electrons in the outer most s-orbital in bonding can be explained basing on energy changes, i.e., excitation energy and the bond strength of the compound formed.

The small sized 2s orbital of boron overlaps sufficiently with the orbital of another element (X) to yield strong M-X bonds that impart stability to the molecule. However, when we move downwards, the larger orbital (5s or 6s) is involved because of which overlapping is poor giving rise to lower bond energy of the M-X bond.

As the small energy of the M-X bond is not sufficient to compensate for the excitation energy of s-electrons, it follows that the larger elements show increasing tendency to form univalent compounds.

Only boron is sufficiently electronegative to show any tendency towards a negative oxidation state. In the borides of the most highly electropositive elements, boron presumably exists in the −3 oxidation state.

9. Nature of bonding: Boron never forms B^{3+} cation because the sum of the three ionization energies is very large. Further because of the very small size of B^{3+} ion (20 pm) in its ionic compounds, the tripositive boron ion will have much polarizing power on the adjacent atoms which results in the covalent character (Fajans rules). Hence, in boron, +3 oxidation state is strictly covalent.

With other elements of Group III A, the +3 oxidation state is largely covalent. Tripositive cations are known in aqueous solutions for all the elements except boron. This is because of the fact that the hydration energies of tripositive cations overcome the ionization energies. Therefore, in aqueous solutions, they exist as hydrated cations and are greately hydrolysed in solution. For example, in the case of $AlCl_3$, the energy changes are as follows:

$\Delta H_{hydration}$ for Al^{3+} = −4665 kJ mol^{-1}

$\Delta H_{hydration}$ for Cl^- = −381 × 3 kJ mol^{-1}

Total hydration energy = −5808 kJ mol^{-1}

Sum of the first three ionization energies = 5137 kJ mol^{-1} for

$$Al \longrightarrow Al^{3+}$$

Thus, total hydration energy evolved (−5808 kJ mol^{-1}) more than offsets the ionization energy (5137 kJ mol^{-1}) required to convert Al to Al^{3+}.

The trivalent hydrated metal ions are having six molecules of water which are attached to them strongly giving an octahedral structure. These undergo hydrolysis to form acidic solutions. The strength of the metal oxygen bond in the hydrated ion would be able to weaken the O-H bonds. This causes some hydrolysis and protons get released giving acidic solution.

$$(H_2O)_5 M \leftarrow O \underset{H}{\overset{H}{\big<}} \longrightarrow [(H_2O)_5 M \leftarrow O]_H + H^+$$
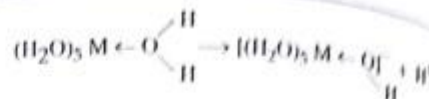
10. Electropositive character: Boron is a non-metal and its electropositive character is least. Aluminium is metal and is most electropositive. The remaining three elements gallium, indium and thallium are weakly metallic in nature and their electropositive character is less than that of aluminium and decreases from gallium to thallium.

The increase in electropositive character from boron to aluminium is ascribed to the increased size. The extra d electrons in case of gallium and indium whereas d and f electrons in the case of thallium do not shield the nuclear charge very effectively and these metals are, therefore, less electropositive. This is illustrated by the increase in ionization energy between aluminium and gallium even though the larger atom would be expected to have a lower value.

11. Electrode potentials: The standard electrode potentials E° for M^{3+}/M are given in Table 7.5.

Table 7.5 Standard electrode potentials E°

—	M^{3+}/M (volts)	M^+/M (volts)
B	− 0.87*	—
Al	− 1.66	+ 0.55
Ga	− 0.56	− 0.79**
In	− 0.34	− 0.18
Tl	+ 1.26	− 0.34

* For $H_3BO_3 + 3H^+ + 3e \longrightarrow B + 3H_2O$
** Value in acidic solution.

The standard electrode potentials E° for M^{3+}/M become less negative from Al to Ga to In. As the free energy change $\Delta G = nFE^\circ$ becomes more positive for the formation of the metal, the reaction $Al^{3+} + 3e \longrightarrow Al$ is not spontaneous. However, the reverse reaction $Al \longrightarrow Al^{3+} + 3e$ occurs spontaneously. As the standard potential becomes less negative down the group, so the reaction $M^{3+} \longrightarrow M$ occurs with less difficulty. Thus, the +3 oxidation state becomes less stable in aqueous solution on moving down the group. In a similar way, the increase in the stability of +1 oxidation state down the group is indicated by E° values for M^+/M. Thus, in thallium, +1 oxidation state is more stable than +3 oxidation state.

12. Complex formation: On account of their smaller size and greater charge, these elements have a much greater tendency to form complexes than the s-block elements. For example, the molecular trihalides or similar species of the elements of Group III A are still capable of accepting a pair of electrons and very large number of complexes such as $[BF_4]$, $[AlCl_4]$, $[GaCl_4]$ and $[InCl_4]$ are known. In boron, the second orbit is the outer most orbit and does not contain d-subshell but aluminium and other III A elements

...contain d-subshells in their outer most orbits. Hence, ...inium and the heavier elements are not restricted to an ... of electrons in their valence shells. Hence, for these ...ments, coordination numbers higher than four may be ...und, e.g., $[AlF_6]^{3-}$ and $[TlF_6]^{3-}$. Thus, the covalence of ...ron is restricted to 4 only while the other elements can ...how a covalence up to 6. Owing to this reason, boron ...bit a covalence up to 6. Owing to this reason, boron ...not form complexes such as $[BF_6]^{3-}$.

13. **Aqueous solution chemistry:** All the tripositive aquo ...ons of these elements are acidic, that of aluminium the least ...and that of thallium the most so. Thus, aqueous solutions ...of their salts are appreciably hydrolysed, and salts of weak ...acids (e.g., carbonates and cyanides) cannot exist in contact ...with water. In acidic solution, aluminium is present as the $[Al(H_2O)_6]^{3+}$ ion, as the acidity is decreased, polymeric ...hydrolysed species such as hydrated, $[Al_2(OH)_2]^{4+}$ and $[Al_6(OH)_{16}]^{2+}$ appear, then $Al(OH)_3$ is precipitated, and ...finally, in alkaline solutions, aluminate anions such as $[Al(OH)_6]^{3-}$ and $[Al(OH)_4]^-$ and polymeric species such ...as $[(HO)_3AlOAl(OH)_3]^{2-}$ are formed. The chemistry of ...gallium is broadly similar to that of aluminium in this ...respect. Indium and thallium(III) hydroxides, however, are ...not amphoteric.

Redox potential data show that Al^{3+} (aq) is much less ...readily reduced than the other tripositive cations in aque-...ous solution. This, doubtlessly, arises partly from a more ...negative hydration free energy of the smaller Al^{3+} ion, but ...another important contributory factor is the increase in ...ionization energies between aluminium and gallium and ...between indium and thallium; there is relatively little vari-...ation in atomization enthalpies, and the overall variation in E° is, therefore, quite different from that in two preceding ...groups.

The E° value of Tl^{3+}/Tl^+, +1.26 V indicates that it is a ...powerful oxidant. The value of E° is, however, very de-...pendent upon the anion present, because Tl (I) resembles ...an alkali metal ion by forming a few stable complexes in ...aqueous solution (e.g., TlCl, unlike AgCl is not soluble in ...aqueous ammonia or potassium cyanide), whereas Tl (III) ...is very strongly complexed by a variety of anions. Thus, ...at unit chloride ion concentration, although TlCl is fairly ...insoluble, E° for the system $[TlCl_4]^-/TlCl$ is only +0.9 V. ...Iodide forms a more stable complex than chloride (soft ...acid-soft base relation) and at high iodide concentrations $[TlI_4]^-$ is a stable species even though $E^\circ_{Tl^{3+}/Tl^+}$ is much high-...er than $E^\circ_{\frac{1}{2}I_2/I^-}$ (+0.54V) and TlI is sparingly soluble. Thus, $I_3^-(I^-+I_2)$ in solid TlI_3 can under these conditions oxidize Tl ...(I) and bring about the reaction.

$$TlI_3 + I^- \longrightarrow [Tl^{III} I_4]^-$$
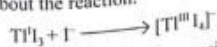
In alkaline media, Tl(I) is also easily oxidized, as ...TlOH is soluble in water and hydrated $Tl_2O_3 \cdot 3H_2O$ or 2 ...$Tl(OH)_3$ is very sparingly soluble, with K_{sp} about 10^{-45}.

7.8 ANOMALOUS BEHAVIOUR OF BORON

7.8.1 How Boron Differs from other Elements

As usual, the first element boron of the Group III A shows different properties from the rest of the elements because of the following.

(i) Small size and high charge make the ion B^{3-} highly polarizing power. Thus, it does not exist. Almost all boron compounds are covalent.

(ii) Boron does not have d-orbitals. Thus, its coordination number is limited to four, whereas the other elements can have a coordination number of six.

(iii) Boron does not exhibit the **"inert pair"** effect.

(iv) Boron combines with metals forming borides whereas other elements do not combine. They form alloys with other metals.

(v) Boron cannot be attacked by non-oxidizing acids such as HCl whereas others are attacked.

(vi) Boron does not decompose water or steam whereas other elements of Group III A decompose hot water or steam.

(vii) Boron is non-metal and bad conductor of electricity but other elements are metals and good conductors of electricity.

(viii) Boron exhibits allotropy but others elements do not exhibit allotropy.

(ix) Boron never forms B^{3+} ion, but other elements can form M^{3+} ions.

(x) Boron forms a large number of volatile hydrides which are electron-deficient compounds whereas other elements form only one polymeric hydride. Thallium does not form hydride.

(xi) Boron halides are monomeric whereas the halides of the other elements are dimeric.

7.8.2 Similarities between Boron and Aluminium

(i) **Electronic configuration:** Both boron and aluminium have the same outer electronic configuration $ns^2 np^1$.

(ii) Oxidation state: Both these elements exhibit +3 oxidation state. However, boron exhibits –3 oxidation state in metal borides.

(iii) Covalency: Both these elements form covalent compounds. However, aluminium may form electrovalent compounds with strong electron accepting groups or atoms.

(iv) Formation of oxides: Both these elements form similar sesquioxide of the type M_2O_3.

(v) Formation of chlorides: Both these elements form chlorides of the type MCl_3 when heated in a current of chlorine or by passing chlorine over the heated mixture of their oxides and charcoal.

$$2M + 3Cl_2 \longrightarrow 2MCl_3$$

$$M_2O_3 + 3C + 3Cl_2 \longrightarrow 2MCl_3 + 3CO$$

These chlorides are covalent and readily hydrolysed in water.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

(vi) Formation of nitrides: Both the elements when heated with nitrogen or ammonia form nitrides.

$$2M + N_2 \longrightarrow 2MN$$

$$2M + 2NH_3 \longrightarrow 2MN + 3H_2$$

These nitrides undergo decomposition when heated with steam or sodium hydroxide liberating ammonia gas.

$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$

$$BN + 3NaOH \longrightarrow Na_3BO_3 + NH_3$$

$$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$$

$$AlN + NaOH + H_2O \longrightarrow NaAlO_2 + NH_3$$

(vii) Formation of sulphides: Both these elements react with sulphur at high temperature to form sulphides which undergo hydrolysis by water.

$$B_2S_3 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$$

$$Al_2S_3 + 6H_2O \longrightarrow 2 Al(OH)_3 + 3H_2S$$

(viii) Formation of alkyl compounds: Both these elements form similar organic compounds with alkyl radicals.

(ix) Action with conc. H_2SO_4: Both these elements react with concentrated sulphuric acid to form sulphur dioxide

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2\uparrow$$

$$2Al + 6H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 6H_2O + 3SO_2\uparrow$$
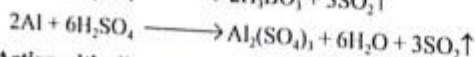
(x) Action with alkalis: They react with alkalis to evolve H_2.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2\uparrow$$

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2\uparrow$$
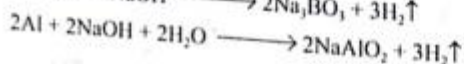
7.8.3 Dissimilarities of Boron and Aluminium

Boron and aluminium are more different than similar in their properties. This is due to the presence of two electrons in the penultimate shell of boron whereas there are eight electrons in the penultimate shell of aluminium. Boron differs from aluminium in the following respects.

(i) Boron is a typical non-metal whereas aluminium is a metal.

(ii) Boron exhibits allotropy whereas aluminium does not exhibit allotropy.

(iii) Crystalline boron is very hard whereas aluminium is sufficiently soft.

(iv) Aluminium is very good conductor of heat and electricity whereas boron is a bad conductor.

(v) Boron has very high melting point as compared with aluminium.

(vi) The maximum covalence shown by boron is 4 whereas as aluminium shows a maximum covalence of 6.

(vii) Boron is not attacked even by steam whereas aluminium decomposes steam liberating hydrogen.

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$

(viii) Dilute acids have no action on boron but concentrated. HNO_3 oxidizes it to boric acid. Aluminium evolves H_2 gas from dil. HCl and H_2SO_4 but concentrated. HNO_3 renders aluminium passive.

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2$$

(ix) Boron dissolves in fused alkalis evolving hydrogen whereas aluminium reacts with hot alkali solution.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

$$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$
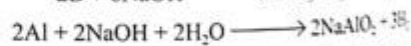
Borates are very stable as compared to the aluminates.

(x) Boron forms two types (B_nH_{n+4} and B_nH_{n+6}) hydrides whereas aluminium does not form such hydrides.

(xi) The halides of boron are covalent in nature and get hydrolysed by water giving boric acid. Aluminium chloride in solution gives Al^{3+} ions.

(xii) Oxide and hydroxide of boron are acidic whereas aluminium are amphoteric.

(xiii) Boron combines with metals to form borides like Mg_3B_2 but aluminium forms alloys only which are compounds.

(xiv) Boron forms many covalent compounds as compared with aluminium.

7.8.4 Resemblance between Boron and Silicon: Diagonal Relationship

Boron shows more resemblence to silicon because of diagonal relationship as shown below.

metallic character: Boron and silicon are typically non-metals. They both have high melting points and are bad conductors of electricity.

Allotropy: Both these elements exhibit allotropy (amorphous and crystalline) crystalline forms are

Density, atomic volume and electronegativity: Densities and the atomic volumes of both the elements are low. Their electronegativities are almost similar (B = 2.0; Si = 1.8)

Their ionization energies (kJ mol^{-1}) are also almost similar (B = 801; Si =786).

Oxides: Boron and silicon burn in air or oxygen to form stable and acidic oxides B_2O_3, SiO_2. These oxides in association with water yield corresponding acids, boric acid and silicic acid. Both are weak acids.

$$B_2O_3 + 3H_2O \longrightarrow 2H_3BO_3$$

$$SiO_2 + H_2O \longrightarrow H_2SiO_3$$

Extraction: Both these elements can be obtained by the reduction of their respective oxides with magnesium.

$$B_2O_3 + 3Mg \longrightarrow 2B + 3MgO$$

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO$$

Carbides: The oxides of both these elements when fused with carbon form carbides; B_4C and SiC. These are very hard substances and are used as abrasives.

$$2B_2O_3 + 7C \longrightarrow B_4C + 6CO$$

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Reaction with metals: Both combine with metals to form borides and silicides, which are decomposed by dilute acids to form volatile hydrides.

$$3Mg + 2B \longrightarrow Mg_3B_2$$

$$2Mg + Si \longrightarrow Mg_2Si$$

$$Mg_3B_2 + HCl \rightarrow 3MgCl_2 + \text{Mixture of boron hydrides}$$

$$Mg_2Si + 4HCl \longrightarrow 2MgCl_2 + SiH_4$$
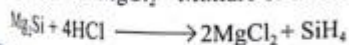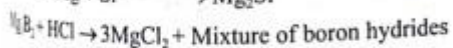
Reaction with halogens: Both boron and silicon form halides with halogens. Fluorides of both are colourless fuming gases. Chlorides BCl_3 and $SiCl_4$ are liquids, which are readily hydrolysed by water to acids.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$

$$SiCl_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HCl$$
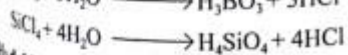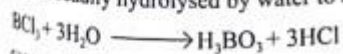
Hydrides: Both boron and silicon form a number of covalent hydrides.

$$BCl_3 + 3LiAlH_4 \longrightarrow 3LiCl + 3AlCl_3 + 2B_2H_6$$

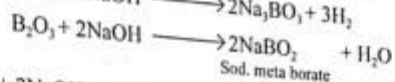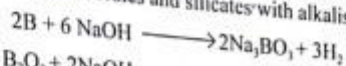$$SiCl_4 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + SiH_4$$
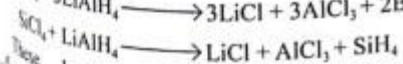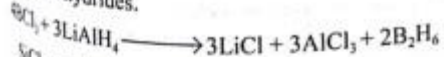
These hydrides are volatile, spontaneously inflammable and readily hydrolysed. These hydrides are known as boranes and silicoalkanes or silanes. Boron

appears to act as a tetra-covalent element such as silicon in these hydrides.

Boroethane B_2H_6 Borobutane B_4H_{10}

Silicoethane Si_2H_6 Silicobutane Si_4H_{10}
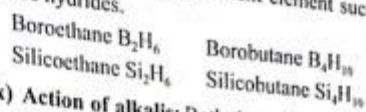
(x) Action of alkalis: Both these elements and their oxides form borates and silicates with alkalis.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

$$B_2O_3 + 2NaOH \longrightarrow 2NaBO_2 + H_2O$$
<div align="center">Sod. meta borate</div>

$$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$$

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$
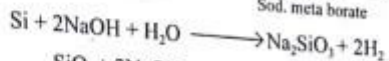
(xi) Formation of esters: Both these elements form volatile esters of the type $B(OR)_3$ and $Si(OR)_4$ with alcohols.

$$B(OH)_3 + 3ROH \longrightarrow B(OR)_3 + 3H_2O$$

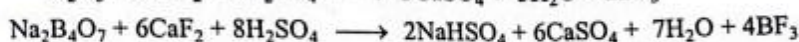$$Si(OH)_4 + 4ROH \longrightarrow Si(OR)_4 + 4H_2O$$

GROUP 13 HALIDES

3. Halides. The elements of Group 13 form a number of trihalides as well as lower halides. These are discussed below.

**Trihalides of Boron.** Boron trihalides, BX_3, are covalent compounds. They involve hybridisation of one s and two p orbitals (sp^2 hybridisation) of boron atom and have, therefore, trigonal planar structure.

All the four halides of boron, namely, boron trifluoride, BF_3, boron trichloride, BCl_3, boron tribromide, BBr_3 and boron triiodide, BI_3 are known. All of them are volatile, highly reactive and monomeric. BF_3 and BCl_3 are gases at room temperature ; BBr_3 is a volatile liquid while BI_3 is a solid.

Boron trifluoride, BF_3. This is the most important of the trihalides of boron. It is obtained by heating boron trioxide or borax with calcium fluoride and concentrated sulphuric acid.

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \longrightarrow 3CaSO_4 + 3H_2O + 2BF_3$$

$$Na_2B_4O_7 + 6CaF_2 + 8H_2SO_4 \longrightarrow 2NaHSO_4 + 6CaSO_4 + 7H_2O + 4BF_3$$

Pure BF_3 can be obtained by thermal decomposition of diazonium tetrafluoroborate.

$$C_6H_5N_2BF_4 \longrightarrow C_6H_5F + N_2 + BF_3$$
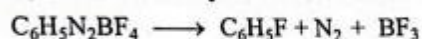
It is a colourless pungent gas (m.p. $-127 \cdot 1°C$ and b.p. $-99 \cdot 9°C$). It is exceedingly soluble in water and is, therefore, collected over mercury.

It combines with water forming two hydrates, $BF_3.H_2O$ and $BF_3.2H_2O$. The first hydrate melts at $10 \cdot 18°C$ and the second at $6 \cdot 36°C$.

It gets hydrolysed in aqueous solution yielding boric acid and hydrofluoric acid.

$$BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3HF$$

If boron trifluoride is passed in excess, it dissolves in the hydrofluoric acid formed, yielding hydrofluoboric acid, $H[BF_4]$.

$$BF_3 + HF \longrightarrow H[BF_4]$$

Boron trifluoride, being an electron-deficient compound, can accept a lone pair of electrons from ammonia, hydrogen sulphide and also a fluoride ion and thus behaves as a Lewis acid. It is this tendency to accept electrons which makes BF_3 useful as a catalyst in a number of reactions such as alkylation and acylation, in organic chemistry.

Boron trichloride, BCl_3. It is obtained by passing chlorine over a heated mixture of boron trioxide and powdered charcoal at about 500°C.

$$B_2O_3 + 3C + 3Cl_2 \xrightarrow{500°C} 2BCl_3 + 3CO$$
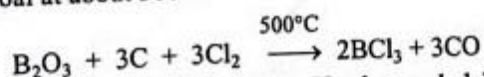
The gases evolved are passed through a U-tube cooled in a freezing mixture. Boron trichloride condenses as a colourless liquid while carbon monoxide and unreacted chlorine pass over.

It can also be prepared by heating boron trioxide with phosphorus pentachloride in a sealed tube at 15°C.

$$B_2O_3 + 3PCl_5 \xrightarrow{15°C} 2BCl_3 + 3POCl_3$$
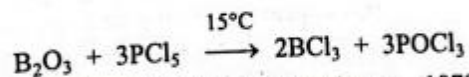
It is a colourless liquid boiling at $12 \cdot 5°C$ and freezing at $-107°C$. It fumes in moist air.

It is completely hydrolysed by water yielding boric acid and hydrochloric acid.

Relative Strengths of Trihalides as Lewis Acids. Effect of Back Bonding. The relative strengths of trihalides of boron to accept a pair of electrons and thus to act as Lewis acids have been determined by measuring their heats of formation as well as by studying their infra-red spectra. The power to accept an electron pair has been found to decrease in the order :

$$BF_3 < BCl_3 < BBr_3$$

This order is just the *reverse* of what should be expected normally from the electronegativites of the halogens. This *anomalous behaviour* can be explained on the basis of the *tendency of the halogen atom to* **back-donate** *its electrons to the boron atom*, as illustrated below.

In BF_3 molecule, while the $2p$ orbitals of each fluorine atom are fully filled, one of the $2p$ orbitals of the boron atom is *vacant* (Fig. 1). The two $2p$ orbitals involved in the formation of $B - F$ bond, therefore, overlap *laterally* resulting in the transference of the fluorine electrons into the vacant $2p$ orbital of the boron atom. An effective overlapping is easily possible because both the orbitals belong to the same energy level. In other words, an additional $p\pi - p\pi$ **bond** is established between boron and fluorine atoms. The $B - F$ bond, thus, acquires some double bond character. This type of bond formation is known as **back bonding**. This is illustrated in Fig. 1.
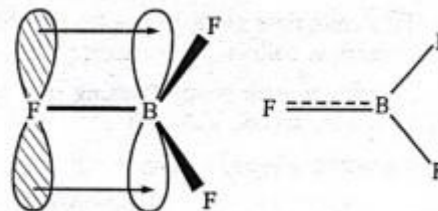
Fig. 1. The phenomenon of back bonding in BF_3 molecule.

Similar structures for the other two $B - F$ bonds are equally probable. The back bonding in BF_3 may, thus, be represented as in Fig. 2.
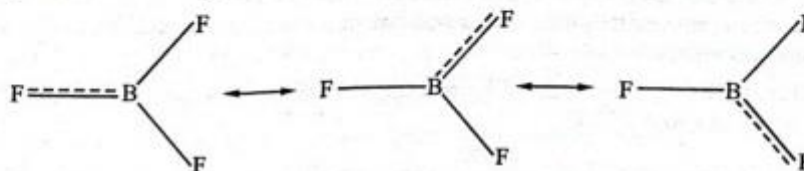
Fig.2. Various resonating structure of BF_3 molecule involving back bonding.

As a result of the **back donation** *of electrons from fluorine to boron, the electron deficiency of boron atom gets compensated and, therefore, the Lewis acid character of BF_3 decreases.*

The tendency to form $p\pi - p\pi$ bond is maximum in the case of BF_3 and falls rapidly as we move to BCl_3 and BBr_3. The probable reason for this appears to be the inability of the vacant $2p$ orbital of boron to overlap effectively with the $3p$ orbital of chlorine in $B - Cl$ bond and with the $4p$ orbital of bromine in $B - Br$ bond because of appreciable differences in the energies of the overlapping orbitals.

Structure of AlCl₃. The vapour density measurements show that $AlCl_3$ is *monomeric* above 800°C. The structure of the monomer is *planar triangular* and the bonding is predominantly *covalent*. The Al tom utilises three sp^2 hybrid orbitals to accommodate $3 + 3 \times 1 = 6$ electrons.

However, below 400°C it exists as a *dimer* with each Al atom utilizing four sp^3 hybrid orbitals to accommodate $3 + 3 \times 1 + 1 \times 2 = 8$ electrons (one of the chlorine atoms is coordinated to Al and donates two electrons). The structure of the dimer is as shown.
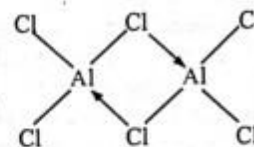
In the solid state also, aluminium chloride exists as a dimer and is non-conducting. Al_2Cl_6 is the species which exists when aluminium chloride is dissolved in non-polar or less polar solvents. Its solution in such solvents is also non-conducting.

However, when aluminium chloride is dissolved in a polar solvent like water, it dissociates into ions in the following manner and its solution becomes conducting :

$$2AlCl_3 + aq \longrightarrow [AlCl_2(H_2O)_4]^+ (aq) + [AlCl_4(H_2O)_2]^- (aq)$$
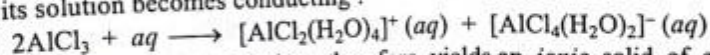
The crystallisation of $AlCl_3$ from aqueous solution, therefore, yields an *ionic* solid of composition $[AlCl_2(H_2O)_4]^+[AlCl_4(H_2O)_2]^- \cdot xH_2O$. This compound decomposes at about 190°C to give the *non-ionic* dimer Al_2Cl_6 :

$$[AlCl_2(H_2O)_4]^+[AlCl_4(H_2O)_2]^- \cdot xH_2O \xrightarrow[190°C]{\text{Heat}} Al_2Cl_6 + water$$
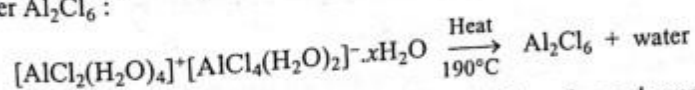
The thermal decomposition is accompanied by a *large decrease in density*. This is probably due to the fact that while there is considerable electrostatic attraction between the cations and the anions in the hydrated salt resulting in the decrease of interionic distance in the lattice of $[AlCl_2(H_2O)_4]^+[AlCl_4(H_2O)_2]^- \cdot xH_2O$ crystal, there is no such ionic attraction in the neutral Al_2Cl_6 units which, therefore, lie at a comparatively greater distance in the lattice of solid Al_2Cl_6.

Aluminium chloride is a strong Lewis acid and readily forms adducts with Lewis bases. It is, therefore, used as a catalyst in organic chemistry (Friedel-Crafts reaction). It is also used in the manufacture of dyes, drugs and pharmaceuticals.
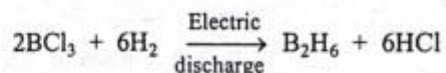
Diborane, B_2H_6

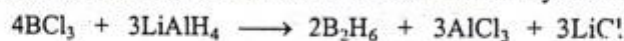**Preparation.** It is the simplest of the hydrides of boron and can be prepared by the following methods :

1. By the reaction of iodine on sodium borohydride in diglyme.

$$2NaBH_4 + I_2 \xrightarrow{\text{Diglyme}} B_2H_6 + 2NaI + H_2$$
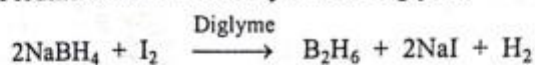
2. By passing silent electric discharge through a mixture of hydrogen and boron trichloride (vapour) at a low pressure.

$$2BCl_3 + 6H_2 \xrightarrow[\text{discharge}]{\text{Electric}} B_2H_6 + 6HCl$$

3. By the reduction of boron trichloride with lithium aluminium hydride.

$$4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

4. By reducing gaseous boron trifluoride with sodium hydride at 180°C.

$$2BF_3 + 6NaH \longrightarrow B_2H_6 + 6NaF$$

Properties. 1. Physical State. Diborane is a colourless gas with a foul smell.

2. Stability. It is stable only at low temperatures. When heated at temperatures between 100°C and 250°C in a closed vessel, it changes to a number of higher hydrides :

$$B_2H_6 \xrightarrow{\text{Heat}} B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12}, \text{etc.}$$
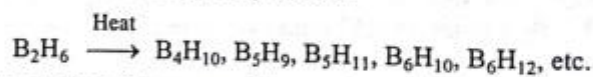
The process, evidently, involves a series of decompositions and polymerisations, the first step being decomposition of B_2H_6 into BH_3.

3. Action of oxygen. Diborane and other boranes have attracted the attention of technologists on account of a large amount of energy released during their combustion. For example,

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O ; \qquad\qquad \Delta H = -2165 \text{ kJ mol}^{-1}$$
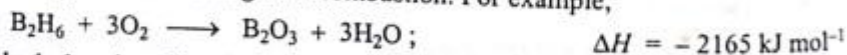
4. Hydrolysis. It gets hydrolysed readily yielding boric acid.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$
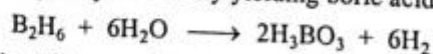
5. Action with alkalies. Diborane dissolves in strong alkali solutions giving metaborates and evolving hydrogen.

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$
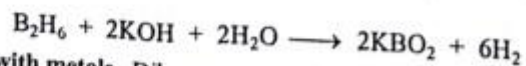
6. Action with metals. Diborane reacts slowly with active metals such as Na, K, Ca or their amalgams. However, the reaction becomes fast in the presence of ether.
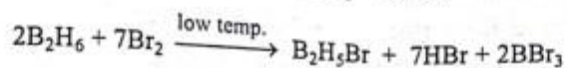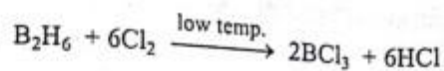
$$2B_2H_6 + 2Na \longrightarrow NaBH_4 + NaB_3H_8$$
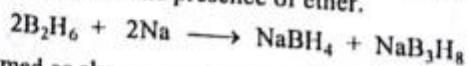
The anion $B_3H_8^-$ formed as above was the first known polyborane anion.

7. Action with carbon monoxide. It reacts with carbon monoxide at $100°C$ and 20 atm pressure to form the carbonyl H_3BCO.

$$B_2H_6 + 2CO \longrightarrow 2H_3BCO$$
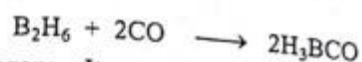
**8. Action with halogens.** It reacts with halogens under different conditions to form haloboranes and halodiboranes.

$$B_2H_6 + 6Cl_2 \xrightarrow{\text{low temp.}} 2BCl_3 + 6HCl$$

$$2B_2H_6 + 7Br_2 \xrightarrow{\text{low temp.}} B_2H_5Br + 7HBr + 2BBr_3$$

I_2 does not react with B_2H_6.

9. Action with halogen acids. Diborane reacts with halogen acids to give halodiboranes and evolving hydrogen.

$$B_2H_6 + HX \longrightarrow B_2H_5X + H_2$$

10. Action with hydrides. It combines with hydrides of alkali metals to form complex hydrides.
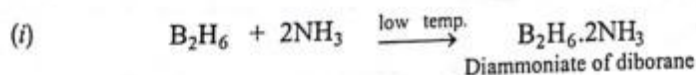
$$B_2H_6 + 2NaH \longrightarrow 2Na[BH_4]$$
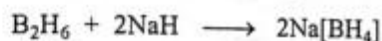
11. Addition to alkenes and alkynes. Diborane adds to alkenes and alkynes in ether at room temperature to form organoboranes.

$$6RCH=CH_2 + B_2H_6 \longrightarrow 2B(CH_2CH_2R)_3$$
$$\text{Organoborane}$$
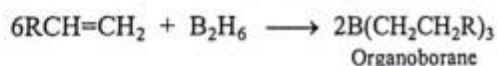
The reaction is known as hydroboration reaction and has been of great synthetic utility in organic chemistry.

12. Action with ammonia. Diborane reacts with ammonia, the products depending upon the conditions of experiment.

(i) $\qquad B_2H_6 + 2NH_3 \xrightarrow{\text{low temp.}} B_2H_6.2NH_3$
$$\text{Diammoniate of diborane}$$

(ii) $\qquad nB_2H_6 \xrightarrow[\text{high temp.}]{\text{Excess NH}_3} \underset{\text{Boron nitride}}{(BN)_n}$

(iii) $\qquad 3B_2H_6 + 6NH_3 \xrightarrow{200°C} 2B_3N_3H_6 + 12H_2$
$$\text{Borazine}$$
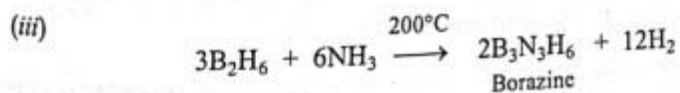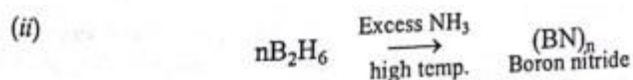
Structure of Diborane. Boranes provide interesting examples of **electron-deficient compounds**. We may consider the case of diborane, B_2H_6, as an example. Since boron atom in excited state has three half-filled orbitals, it has three electrons available for sharing. Therefore, it can link to itself three hydrogen atoms. Thus, while each boron atom in diborane can link to itself three hydrogen atoms, there are no electrons left to form a bond between the two boron atoms. Spectroscopic studies reveal that the structure of diborane is as shown in Fig. 4.

Fig. 4. Structure of diborane molecule.

The various bond distances and angles are as shown.

Four hydrogen atoms, two on the left and two on the right, known as terminal hydrogens, are in different environments from the other two hydrogen atoms which are known as the bridging atoms. The two boron atoms and the four terminal hydrogen atoms lie in the same plane while the two boron atoms and the two bridging hydrogen atoms, one above and the other below, lie in a plane perpendicular to this plane.

**Bonding in B_2H_6.** Valence orbitals of each boron atom in B_2H_6 are sp^3 hybridised. The two terminal BH_2 groups are present in one plane and the bridged B〈H H〉B part of the molecule is present in a plane perpendicular to the plane containing the two BH_2 groups. Since two valence electrons of each boron atom are used up in BH_2 bonding, the remaining valence electron of each boron atom is used in BHB bonding. Thus, each boron atom contributes one valence electron towards the $3c - 2e$ BHB bond. The nature of the $3c - 2e$ BHB bond has already been discussed above in details. The bonding molecular orbitals involved in B_2H_6 and the structure of the molecule are represented below.

B_2H_6(2002)

Bonding MOs in B_2H_6
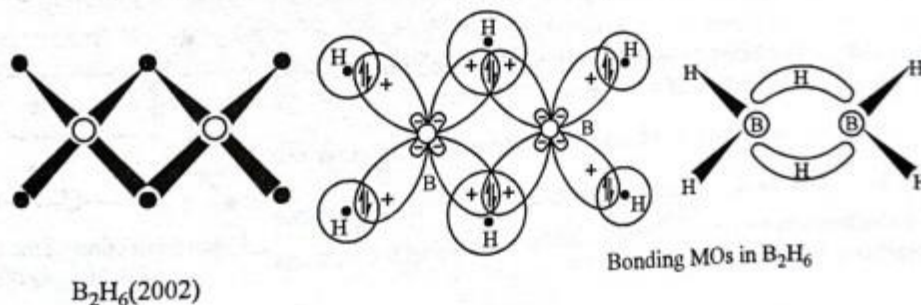
As already mentioned, the B〈H〉B bridges are considered as part of the B_2 framework. The valence electrons of the two boron atoms can thus be accounted for as follows :

Total number of valence electrons of two boron atoms = 6

Electrons used up in two B〈H〉B bridges = 2

Electrons used up in the four terminal B–H bonds = 4

Alternatively,

Total numbers of valence electrons of 2 boron and 6 hydrogen atoms $\Big]$ = 6 + 6 = 12

Electrons used up in the two B〈H〉B bridges = 4

Compounds of Boron with Nitrogen

Boron forms some interesting compounds with nitrogen, most significant of which are *boron nitride* and *borazine*.

Boron Nitride, BN. As already mentioned, boron nitride is obtained by the interaction of ammonia and diborane. Boron nitride is a white crystalline solid and resembles graphite in its structure, as shown in Fig. 5.

A boron atom bonded together with a nitrogen atom has 8 valence electrons, 3 from boron and 5 from nitrogen. This is the same number of electrons as are present in two adjacent carbon atoms in graphite. The structure of boron nitride, therefore, is very similar to that of graphite shown in Fig. 5(b). The B—N bonds in boron nitride are formed by the overlapping of sp^2 hybrid orbitals of boron and nitrogen atoms. The remaining electrons form pi bonds. Unlike graphite, where electrons are *completely delocalised* over all the carbon atoms of the lattice, the electrons in boron nitride are only *partially delocalised* over boron atoms leading to *unequal* B—N *bond lengths*. The layers are arranged in such a manner that boron atoms in one layer are immediately above the nitrogen atoms in the adjacent layer. On heating at 1800°C under a pressure of 85 atm, in the presence
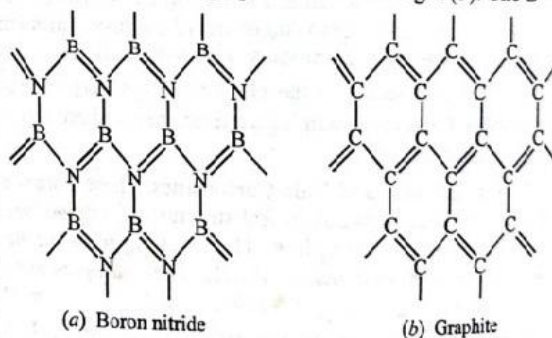

(a) Boron nitride (b) Graphite

Fig.5. Similarity in the structure of boron nitride and graphite.

Borazine or Borazole. Borazine can be prepared by heating together BCl_3 and NH_4Cl. The initial product formed is trichloroborazine which on reducing with $NaBH_4$ yields borazine. It can also be prepared by treating $NaBH_4$ with NH_4Cl.

The structure of borazine is similar to that of benzene (Fig. 6).

In this structure, the valence shell orbitals of both boron and nitrogen atoms are sp^2 hybridised. Each nitrogen atom has one lone pair of electrons while each boron atom has an empty p orbital. The bonding in borazine is dative and it arises from the sidewise overlapping of fully filled p orbitals of nitrogen and empty p orbitals of boron. Because of the similarity of the structures of borazine and benzene, borazine is also known as **inorganic benzene**.
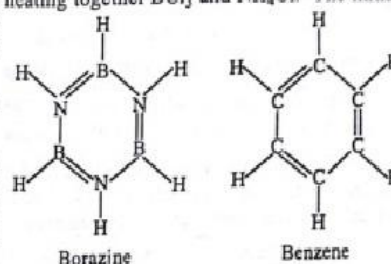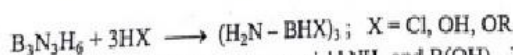

Borazine   Benzene

Fig.6. Similarity in the structure of borazine and benzene.

Molecular orbital calculations indicate that the electrons in borazine are only *partially delocalised* unlike benzene in which there is *complete delocalisation*. In fact, complete delocalisation in B_3N_3 ring is not expected either since N-π orbitals are of lower energy than the B-π orbitals. MO calculations indicate that the π electron-drift from N to B is less than the σ electron-drift from B to N due to greater electronegativity of N. These are thus the N atoms which are relatively more electronegative than B atoms in borazine. The π bonding stabilises the planar structure of borazine ring.

The retention of negative charge by nitrogen implies that chemically borazine would be different from benzene. It is thus much more reactive than benzene and readily undergoes addition reactions as, for example,
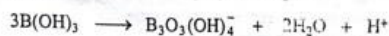
$$B_3N_3H_6 + 3HX \longrightarrow (H_2N - BHX)_3 ; \quad X = Cl, OH, OR$$

Borazine undergoes hydrolysis at high temperature to yield NH_3 and $B(OH)_3$. It decomposes slowly on storage.

Borazine resembles benzene in forming similar metal complexes, as illustrated below :

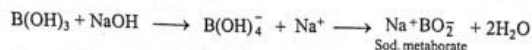

Borazine metal complex   Benzene metal complex
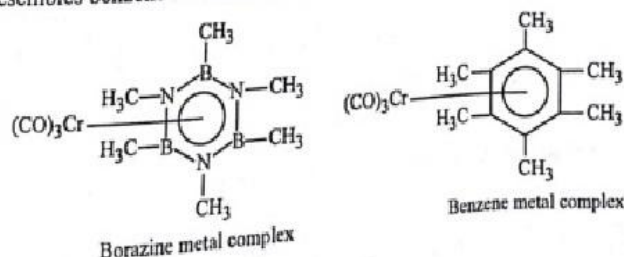
3. Boric acid is a very weak acid and ionises mainly as a monobasic acid and that, too, to a very limited extent. The dissociation constant of the acid is of the order of 1.0×10^{-9}. It is not a proton donor but behaves as a Lewis acid, *i.e.*, as an acceptor of a pair of electrons from an $.OH^-$ ion.

As the concentration of aqueous solution increases beyond 0.025 M, the acidity increases. This anomaly has been explained as due to the formation of a polymeric species.

$$3B(OH)_3 \longrightarrow B_3O_3(OH)_4^- + 2H_2O + H^+$$

With strong alkalies, it forms salts known as metaborates.

$$B(OH)_3 + NaOH \longrightarrow B(OH)_4^- + Na^+ \longrightarrow \underset{\text{Sod. metaborate}}{Na^+BO_2^-} + 2H_2O$$
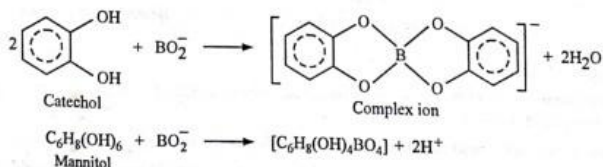
The end point in the titration of boric acid against sodium hydroxide is not sharp on account of excessive hydrolysis of sodium metaborate formed during titration.

$$NaBO_2 + H_2O \rightleftharpoons H_3BO_3 + NaOH$$
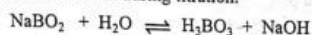
However, the addition of certain polyhydroxy compounds such as catechol, mannitol, glycerol or sugars to the titration solution checks the hydrolytic reaction and makes boric acid behave as a strong monobasic acid and the end point can thus be easily detected. The polyhydroxy compounds combine with the metaborate ion to form complex compounds, as illustrated below :
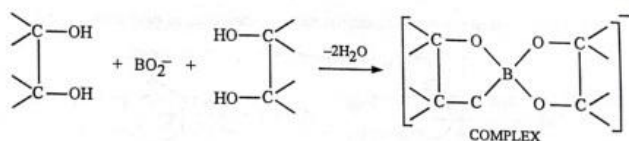

With catechol and mannitol, for instance, the complexation occurs as follows :

$$\underset{\text{Mannitol}}{C_6H_8(OH)_6} + BO_2^- \longrightarrow [C_6H_8(OH)_4BO_4] + 2H^+$$

The elimination of BO_2^- ion in the form of its complexes means no hydrolysis of the end product of the neutralisation reaction. As a result, boric acid ionises freely during titration against a strong alkali thus behaving as a strong acid.

4. On heating at 1000°C or a little above, orthoboric acid loses water to yield metaboric acid.

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$
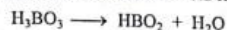
Structure of boric acid. In order to understand the structure of boric acid let us consider boron atom in ground state as well as in the excited state. It is evident that 3 singly occupied orbitals become available in the excited state which form bonds with three oxygen atoms. This, is, evidently, a case of sp^2 hybridisation.

Since only one electron from each oxygen atom enters into bond formation, the resulting unit is a trivalent ion, BO_3^{3-}, in which each boron atom is bonded to three oxygen atoms arranged at the corners of an equilateral triangle with boron atom lying in the centre.

The triangular BO_3^{3-} units are bonded together through hydrogen bonds into two-dimensional sheets, as shown in Fig. 7.

It is evident that each boron atom remains bonded to three oxygen atoms and each oxygen atom is bonded to a hydrogen atom. Thus, each unit now consists of H_3BO_3. The hydrogens provide the limbs (or bridges) between the oxygen atoms of different BO_3 units, as shown.

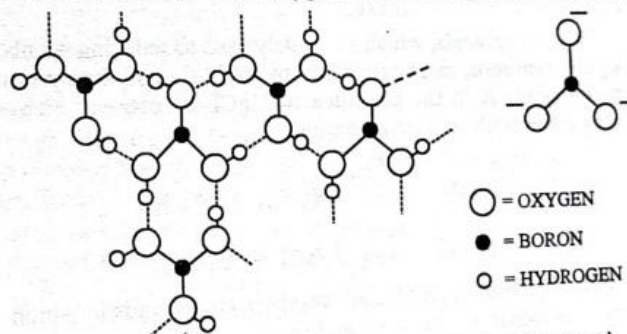$\bigcirc$ = OXYGEN
● = BORON
○ = HYDROGEN

Fig.7. Two-dimensional sheet structure of boric acid. Dotted lines represent hydrogen bonds.