## 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

#### 1.1 INTRODUCTION

The elements boron (B), aluminium (Al), gallium (Ga), infrom (ln) and thallium (T1) 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 ns2 np1. 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 elenents such as alkali metals, silver and mercury. Hence, it is tick named as duck-billed platypus among the elements. Afeature of the chemistry of boron is the existence of large mber 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.

#### 1.2 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<sup>-40</sup>% Aluminium 8.13% Gallium 1.5 × 10<sup>-30</sup>% Indium 1 × 10<sup>-50</sup>% Thallium 10<sup>-4</sup> to 10<sup>-5</sup>%

Aluminium is of course the most abundant of all the class 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, how ever, 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<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 10H<sub>2</sub>O or Na<sub>2</sub> [B<sub>4</sub>O<sub>3</sub>(OH)<sub>4</sub>] · 8H<sub>2</sub>O 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<sub>3</sub>[AIF<sub>6</sub>] and also in the alumino silicate minerals such as mica and feld-spar. 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<sup>2</sup> np<sup>1</sup>.

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  $s^2$ , configuration; the penultimate shell of boron is having  $s^2$  adminium is having  $s^2p^n$  and those of other three elements aluminium is having  $s^2p^n$  and those of other three elements are having  $s^2p^nd^n$  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 con
В	5	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>	yale
Al	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	
Ga	31	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{60} 4s^2 4p^4$	
In	49	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{60} 4s^2 4p^6 4d^{60} 5s^2 5p^6$	
T1	81	1s2 2s2 2p6 3s2 3p6 3d6 4s2 4p6 4d6 4f4 5s2 5p6 5d6 6s2 6p1	

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	Metallic	Ionic rad	ius (pm)
	radius (pm)	radius (pm)	M'	M3+
В	80	(88.5)	194001	-1
Al	125	143	-	27
Ga	125	10.000	-	53.5
In	150	135	120	62
TI		167	140	80
	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 (29.8°) is attributed to the fact that it consists of only Ga molecules; it remains liquid up to 2000°C and hence used
- 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 the liquid state decreases from boron to thallium, Note that boiling point of Ga is in regular order with others where the melting point is not. The very low melting point is to the unusual crystal structure, but the structure to know exists in the liquid.

- Heat of sublimation: It decreases regularly on more 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 that ionization energies for each element is very high.

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

Ionization energy decreases from boron to aluminate but does not change appreciably as we move to gallienindium and thallium. Decrease in ionization energy for boron to aluminium is attributed to the increased 525 Further, penultimate shell in both boron and aluminate has inert gas configuration (He configuration in the CAS of B and Ne configuration in the case of Al) whereas penultimate shell in all the three remaining elements i.e., gallium, indium and thallium has 18 electrons s<sup>2</sup>p<sup>6</sup>d<sup>10</sup>]. The extra d-electrons fail to shield the number charge effectively because shielding by electrons prosin various orbitals has been found to be in the order 577 d > f. Therefore, the outer electrons in the case of galling indium and thallium are held more tightly by the makes Consequently, their atoms become smaller and thus bell ionization. ionization energies become higher than expected ionization energies become higher than expected ionization energy of thallium is further affected being of the poor shielding of 14 f-electrons present in the penultimate shell, and it is even more than that of Al. (a) and In. and In.

For gallium and indium, the electronic configuration of the species left after the removal of three electrons [Ar]3d<sup>10</sup> and [Kr] 4d<sup>10</sup>, respectively whereas for thalling the species so formed has the configuration [Xe] 4f<sup>10</sup>. Thus, the fourth ionization energies of these three electrons do not involve the removal of an electron from a noble second

13 Density, melting point, boiling point, electronegativity and heat of sublimation of Group III A elements

elach			Heat of sublimation		
Density (g cm <sup>-3</sup> )	Melting point (K)	Boiling point (K)	(kJ mol <sup>-1</sup> )	Electr	o negativity
MANUAL SECTION	2453	3923	564		2.0
2.35	933	2740	324	- 2	1.5
2.7	303	2676	273		1.6
5.9	430	2353	241	*	1.7
7.31	576	1730	179		1.8

Table 7.4 Ionization energies of Group III A elements

	Ionizat	ion energies	kJ mol <sup>-t</sup>	
	lst	IInd	IIIrd	Sum of three
-	801	2427	3659	6887
ı.	577	1816	- 2744	5137
in the	579	1979	2962	5520
	558	1820	2704	5082
1	589	1971	2877	5437

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

Lectronegativity: Among the Group III A elements, boron has the maximum electronegativity. It decreases hum boron to aluminium as expected. However, from alutimum to thallium, it increases instead of decreasing in contrary to the expectation. This is again attributed to the Nor shielding of d-electrons in gallium and indium and 4 and f-electrons in thallium (Table 7.3).

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, and TI) structures. Hence, a uniform +3 oxidation state head..... Structures. Hence, a uniform of all the elements. The electronic arrangement in the outermost orbit of these elements ns2 np1 also suggests +1 oxidation states.

Outer electronic configuration

	Outer electr	np	+1
Ground state	$\uparrow\downarrow$	1	+3
Excited state	1		

In thallium, +1 oxidation state is well known. A few in the control oxidation state the state are individual to the state are no evidences for +1 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 host 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 TI\* 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) TIOH 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) TIF is having distorted NaCl-type structure whereas other thallous halides crystallize with CsCl structure.
- (iv) Like alkali metals, thallium (l) is known to form alums, e.g., Tl<sub>2</sub>SO<sub>4</sub> · Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> 24H<sub>2</sub>O.

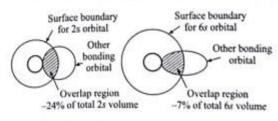


Fig. 7.1 Comparison of overlappings between small (2s) orbital and large (6s) orbital with the orbital of another atom

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.

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 x-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 B3 cation because the sum of the three ionization energies is very large. Further because of the very small size of B3+ 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 AlCl3, the energy changes are as follows:

$$\Delta H_{hydration}$$
 for Al<sup>3+</sup> = -4665 kJ mol<sup>-1</sup>  
 $\Delta H_{hydration}$  for Cl<sup>-</sup> = -381 × 3 kJ mol<sup>-1</sup>

Total hydration energy = -5808 kJ mol-Sum of the first three ionization energies = 5137 kJ mol-1 for

$$A1 \longrightarrow A1^{34}$$

Thus, total hydration energy evolved (-5808 kJ mol-1) more than offsets the ionization energy (5137 kJ mol 1) required to convert Al to Al3+

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.

$$(H_2O)_5\,M\leftarrow O \bigg\langle \frac{H}{H} \longrightarrow I(H_2O)_5\,M\leftarrow Q \int_{H^{\frac{1}{2}}H^{\frac{1}{2}}}$$

10. Electropositive character: Boton is a non-motal ag its electropositive character is least. Aluminium is negand is most electropositive. The remaining three elements gallium, indium and thallium are weakly metallic in today. and their electropositive character is less than that of  $\psi_0$ minium and decreases from gallium to thallium

The increase in electropositive character from being to aluminium is ascribed to the increased size. The extent electrons in case of gallium and indium whereas d'and p electrons in the case of thallium do not shield the trucker charge very effectively and these metals are, therefore, less electropositive. This is illustrated by the increase in indization energy between aluminium and gallium even through the larger atom would be expected to have a lower value

11. Electrode potentials: The standard electrode poten tials Eo for M31/M are given in Table 7.5.

Table 7.5 Standard electrode potentials E2

-	M"/M (volts)	M'/M (volts)	
В	-0.87*		
A1	-1.66	+ 0.55	
Ja .	-0.56	- 0.79**	
ln .	-0.34	-0.18	
TI	+ 1.26	-0.34	

For H<sub>1</sub>BO<sub>1</sub> + 3H<sup>4</sup> + 3e → B + 3H.O \*\* Value in acidic solution.

The standard electrode potentials Eo for Mo/M become less negative from Al to Ga to In. As the free etergy change  $\Delta G = nFE^{\alpha}$  becomes more positive for the is not spontaneous. However, the reverse reaction → Al<sup>37</sup> + 3e occurs spontaneously. As the stand ard potential becomes less negative down the group, so the → M occurs with less difficulty. Thus, reaction M31 --the +3 oxidation state becomes less stable in aqueous whi tion on moving down the group. In a similar way, the th crease in the stability of +1 oxidation state down the group is indicated by E° values for M'/M. Thus, in thallnum,

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, 1, 1A18]. as [BF<sub>4</sub>], [AlCl<sub>4</sub>], [GnCl<sub>4</sub>] and [InCl<sub>4</sub>] are known. In both the second state of ron, the second orbit is the outer most orbit and does not contain of orbit. contain d-subshell but aluminium and other III A elements

on and the heavier elements are not root. woman and the heavier elements are not restricted to an electrons in their valence shells. Hence, designation and their valence shells. Hence, for these coordination numbers higher than 6. of electron numbers higher than four may be [AlF<sub>a</sub>]<sup>L</sup> and [TlF<sub>a</sub>]<sup>L</sup>. Thus the [TIF<sub>6</sub>]<sup>1</sup>. Thus, the covalence of searcicled to 4 only while the other st ion is restricted to 4 only while the other elements can hold is resulted up to 6. Owing to this reason, boron the compound accordance such as IBF 13of the same form complexes such as [BF<sub>6</sub>]<sup>3</sup>.

BAqueous solution chemistry: All the tripositive aquo 15. Aqueon the seed of the see and that of thallium the most so. Thus, aqueous solutions when salts are appreciably hydrolysed, and salts of weak 15th (e.g., carbonates and cyanides) cannot exist in contact whwater. In acidic solution, aluminium is present as the [A][H,O], it ion, as the acidity is decreased, polymeric hardysed species such as hydrated, [Al<sub>2</sub>(OH)<sub>2</sub>]<sup>4+</sup> and [3](OH)<sub>16</sub>]<sup>3+</sup> appear, then Al(OH)<sub>3</sub> is precipitated, and mally, in alkaline solutions, aluminate anions such as [Al(OH)<sub>4</sub>] and [Al(OH)<sub>4</sub>] and polymeric species such s [(H0); AlOAl (OH)] are formed. The chemistry of glium is broadly similar to that of aluminium in this rspect. Indium and thallium(III) hydroxides, however, are

Redox potential data show that Al3+ (aq) is much less radily reduced than the other tripositive cations in aqueous solution. This, doubtlessly, arises partly from a more regative hydration free energy of the smaller Al3\* ion, but mother important contributory factor is the increase in inization energies between aluminium and gallium and between indium and thallium; there is relatively little variation in atomization enthalpies, and the overall variation in  $\mathcal{E}$  is, therefore, quite different from that in two preceding

The  $E^{\circ}$  value of  $TI^{3-}/TI^{*} + 1.26 \text{ V}$  indicates that it is a Joverful oxidant. The value of  $E^{\circ}$  is, however, very dependent upon the anion present, because TI (1) resembles an alkali metal ion by forming a few stable complexes in aqueous solution (e.g., TICl, unlike AgCl is not soluble in aqueous ammonia or potassium cyanide), whereas TI (III) is very strongly complexed by a variety of anions. Thus, a unit chloride ion concentration, although TICI is fairly hsoluble, Eo for the system [TICI4] /TICI is only +0.9 V. lodide forms a more stable complex than chloride (soft acid-soft base relation) and at high iodide concentrations [III] is a stable species even though  $E^{o}_{T^{b}/T^{b}}$  is much highthan E (+0.54V) and TII is sparingly soluble. Thus,  $\frac{1}{1}(\Gamma + \frac{1}{1})$  in solid TII<sub>3</sub> can under these conditions oxidize TI (1) and 1... (1) and bring about the reaction.

$$T_{I_1}^{I_1} + \Gamma \longrightarrow [T_{I_1}^{I_1}]$$

In alkaline media, TI(I) is also easily oxidized, as TiOH is soluble in water and hydrated TiO, 3H,O or 2 \(\hat{OH}\)\_1 is very sparingly soluble, with K, about 10.45.

#### 7.8 ANOMALOUS BEHAVIOUR OF BORON

#### 7.8. | 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 B3- 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
- (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 B3+ ion, but other elements can form M3+ 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 ns2 np1.

- (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 M2O3.
- (v) Formation of chlorides: Both these elements form chlorides of the type MCl, when heated in a current of chlorine or by passing chlorine over the heated mixture of their oxides and charcoal.

$$2M + 3Cl_2 \longrightarrow 2MCl_3$$
  
 $M_2O_1 + 3C + 3Cl_2 \longrightarrow 2MCl_3 + 3CO$ 

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.

$$BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$$
  
 $BN + 3NaOH \longrightarrow Na_3BO_3 + NH_3$   
 $AIN + 3H_2O \longrightarrow AI(OH)_3 + NH_3$   
 $AIN + NaOH + H_2O \longrightarrow NaAIO_2 + NH_3$ 

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

$$B_2S_1 + 6H_2O \longrightarrow 2H_3BO_3 + 3H_2S$$
  
 $Al_2S_1 + 6H_2O \longrightarrow 2 Al(OH)_1 + 3H_2S$ 

- (viii) Formation of alkyl compounds: Both these elements form similar organic compounds with alkyl
- (ix) Action with conc. H2SO4: Both these elements react with concentrated sulphuric acid to form sulphur di-

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2\uparrow$$
  
 $2AI + 6H_2SO_4 \longrightarrow AI_2(SO_4)_3 + 6H_2O + 3SO_2\uparrow$ 

(x) Action with alkalis: They react with alkalis to evolve

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2\uparrow$$
  
 $2AI + 2NaOH + 2H_2O \longrightarrow 2NaAIO_2 + 3H_2\uparrow$ 

# 7.8.3 Dissimilarities of Boron and Aluminium

Boron and aluminium are more different than timber Boron and anumation.

their properties. This is due to the presence of two electrons their properties. This is due to the presence of two electrons their properties. their properties. This their properties there shall of boron whereas there has been alternate shell of aluminium to the penultimate shell of alumi in the penultimate shell of aluminium, Born & fers from aluminium in the following respects.

- rs from and and an antique (i) Boron is a typical non-metal whereas aluminist (i)
- (ii) Boron exhibits allotropy whereas aluminium dogs to
- (iii) Crystalline boron is very hard whereas aluminium sufficiently soft.
- (iv) Aluminium is very good conductor of heat and the tricity whereas boron is a bad conductor.
- Boron has very high melting point as compared we aluminium.
- (vi) The maximum covalence shown by boron is 4 who as aluminium shows a maximum covalence of 6
- (vii) Boron is not attacked even by steam whereas alone ium decomposes steam liberating hydrogen.

$$2AI + 3H_2O \longrightarrow Al_2O_1 + 3H$$

(viii) Dilute acids have no action on boron but come trated. HNO3 oxidizes it to boric acid. Almine evolves H, gas from dil. HCl and H,SO, but cones trated. HNO, renders aluminium passive.

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$
  
 $2AI + 3H_2SO_4 \longrightarrow AI(SO_4)_3 + 3H_2$ 

(ix) Boron dissolves in fused alkalis evolving here whereas aluminium reacts with hot alkali solutes

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$
  
 $2AI + 2NaOH + 2H_2O \longrightarrow 2NaAIO_2 + 3B_3$ 

Borates are very stable as compared to the alimination

- (x) Boron forms two types (B,H,,, and B,H,,) hydrides whereas aluminium does not form
- (xi) The halides of boron are covalent in matter sol # hydrolysed by water giving boric acid Aleman (xii) Oxide and hydroxide of boron are acide where chloride in solution gives Al3+ ions.
- (xiii) Boron combines with metals to form Nocks Mg<sub>3</sub>B<sub>2</sub> but aluminium forms alloys only
- (xiv) Boron forms many covalent compounds as with adverse with aluminium.

## 7.8.4 Resemblance between Boron and Silicon: Diagonal Relationship

Boron shows more resemblence to silicent because agonal relational. agonal relationship as shown below.

sentialic character: Boron and silicon are typistreet like that the both have high melting points and conductors of electricity. are had conductors of electricity.

Both these elements exhibit allotropy and crystalline) crystalline forms are

atomic volume and electronegativity: and the atomic volumes of both the ele-Mostles and low. Their electronegativities are almost g = 2.0; Si = 1.8) (B = 2.0; Si = 1.8)

of ionization energies (kJ mol<sup>-1</sup>) are also almost on sol; Si = 786). slt (B = 801; Si = 786).

hiles: Boron and silicon burn in air or oxygen to on stable and acidic oxides B2O3, SiO2. These oxin succession with water yield corresponding bone acid and silicic acid. Both are weak acids.

$$_{B,0_3}^{\text{pik borne acts area}} \rightarrow 2H_3BO_3$$

$$80_1 + 310_2$$
  
 $80_2 + H_2O$   $\longrightarrow$   $H_2SiO_3$ 

furaction: Both these elements can be obtained by tenduction of their respective oxides with magne-

$$_{B,0}+3Mg \longrightarrow 2B+3MgO$$

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

(arbides: The oxides of both these elements when ised with carbon form carbides; B4C and SiC. These gevery hard substances and are used as abrasives.

$$2B_1O_1 + 7C \longrightarrow B_4C + 6CO$$

Reaction with metals: Both combine with metals to im brides and silicides, which are decomposed by thre acids to form volatile hydrides.

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

$$2Mg + Si \longrightarrow Mg_2Si$$

"EB;+HCl→3MgCl₂+ Mixture of boron hydrides

$$M_{g_1Si+4HC1} \longrightarrow 2MgCl_2 + SiH_4$$

Partion with halogens: Both boron and silicon form has with halogens. Fluorides of both are colourless saing gases. Chlorides BCl<sub>1</sub> and SiCl<sub>4</sub> are liquids, hich are readily hydrolysed by water to acids.

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

$$SiCl_4+4H_2O \longrightarrow H_4SiO_4+4HCI$$

drides: Both boron and silicon form a number of <sup>thalent</sup> hydrides.

$$\Theta(1_1+3\text{LiAlH}_4)$$
  $\longrightarrow$   $3\text{LiCl} + 3\text{AlCl}_3 + 2\text{B}_2\text{H}_6$ 

hydrides are volatile, spontaneously hydrides are volatile, spontantes are and readily hydrolysed. These hydrides are library Boron and readily hydrolysed. These nyunder boranes and silicoalkanes or silanes. Boron

7.13 Boron Family appears to act as a tetra-covalent element such as silicon

Boroethane B2H6

Borobutane B4H10 Silicoethane Si<sub>2</sub>H<sub>6</sub>

Silicobutane Si<sub>4</sub>H<sub>34</sub> (x) Action of alkalis: Both these elements and their oxides form borates and silicates with alkalis.

2B + 6 NaOH 
$$\longrightarrow$$
 2Na<sub>3</sub>BO<sub>3</sub> + 3H<sub>3</sub>

$$B_2O_3 + 2NaOH$$
  $\longrightarrow 2NaBO_2 + H_2O$   
Sod. meta borate

Si + 2NaOH + 
$$H_2O$$
  $\longrightarrow$  Na<sub>2</sub>SiO<sub>3</sub> + 2 $H_2$ 

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

(xi) Formation of esters: Both these elements form volatile esters of the type B(OR), and Si(OR), with alcohols.

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

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