Chapter 11

The p–Block Elements

The elements of group 13 to 18 in the long form periodic table form the p – block elements. They have the general outer electronic configuration ns^2np^{1-6}. The p–block is the only one which contains non–metallic elements. The maximum oxidation state given by p – block element is equal to the total number of valence electrons. In addition to this *group oxidation state*, p–block elements can show other oxidation states also.

In groups 13, 14 and 15, the group oxidation state is the most stable state for lighter elements of the group. However, the oxidation state two units less than the group oxidation state becomes progressively more stable down a group. For example, the group oxidation state of Group 13 elements is +3 but +1 oxidation state is the most stable state for the last member thallium *(Tl)*. *The occurence of oxidation state two units less than the group oxidation state in heavier members of certain p-block elements is due to* **inert pair effect.** The cause of inert pair effect is the tendency of ns^2 valence electrons of higher members to remain inert and do not participate in bond formation.

It is interesting to note that only p-block contains all types of elements: non-metals, metalloids and metals. The non-metals have higher ionisation enthalpies and higher electronegativities than metals. The non-metals oxides are acidic or neutral whereas metal oxides are generally basic or amphoteric.

The first member of each group (13 to 17) differs in many respects from the other members of the respective group This is due to (i) their small size (ii) high electronegativity and (iii) absence of d–orbitals in the valence shell. The first member of any of these groups shows greater ability to form $P\pi - P\pi$ multiple bonds to itself and to other elements (e.g., $C=C$, $C=O, N\equiv N, N=O$ etc). The higher elements can expand their covalency beyond four by the use of d orbitals whereas the first members (second period) of the groups cannot. For example, boron forms only BF_4^- while aluminium forms AlF_6^{3-}.

Group 13 Elements (BORON FAMILY)

The Group 13 of the periodic table consists of Boron, Aluminium, Gallium, Indium and Thalium.

Occurrence

Boron occurs as borax ($Na_2B_4O_7 10H_2O$), ortho boric acid (H_3BO_3) and Kernite ($Na_2B_4O_7 4H_2O$). Boron exists as two isotopic forms ^{10}B and ^{11}B. Aluminium is the most abundant metal in the earth's crust. It occurs mainly as bauxite ($Al_2O_3 . 2H_2O$) and cryolite (Na_3AlF_6) . Ga, In and Tl are less abundant in nature.

Metallic character

Boron is a typical non-metal while other elements are all metals. Metallic character increases down the family with increase in atomic mass.

Electronic configuration

The general outer electronic configuration is ns^2np^1. Boron and Al have 8 electron inner core while Ga and In have 18 electron inner core. Thalium has an inner core of 32 electrons. This difference in electronic structures affects the properties of the elements in the group.

Atomic radii

Down the group, atomic radii increase due to addition of newer shells. However, Ga is found to be smaller in size than Al due to poor screening effect of inner d–electrons which leads to greater attraction by the nucleus.

Ionisation enthalpy

Ionisation enthalpies of these elements do not decrease continuously down the group as expected. The ionisation enthalpy decreases from B to Al. But the value is slightly high for Ga. This trend in ionisation enthalpy is again attributed to the difference in the inner core structures of the elements. Tl has slightly higher ionisation enthalpy than In.

Electronegativity

Down the group, electronegativity decreases from B to Al and then increases. This is also due to anomalies in atomic size of the elements caused by inner core electronic structures.

Physical properties

Boron is a hard black non-metallic solid with very high melting point. The remaining members are soft metals with low melting points. The melting point of gallium is only 303K and so it exists in the liquid state in summer.

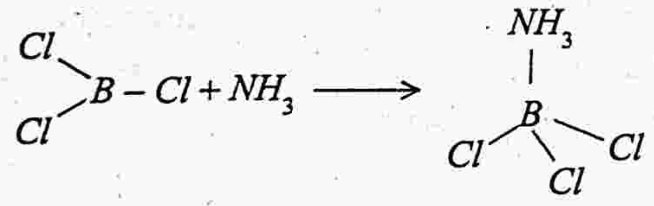
Oxidation state

Though the group oxidation state is +3, other oxidation state of +1 is possible in heavier elements due to inert pair effect. Down the group, due to poor shielding effect of inner *d* and *f* electrons, the increased nuclear charge holds ns^2 electrons tightly restricting their ability for bonding. So only the *p* electron is active in bond formation. In thalium, +1 oxidation state is more prominent than the +3 state.

Chemical properties

Due to the small size of boron atom, the sum of its first three ionisation enthalpies is very high. This prevents boron to form +3 ions and forces it to form only covalent compounds.

In the normal trivalent state, only six electrons are present around these atoms in their molecules (e.g., B has six electrons in BCl_3). As a result such molecules are **electron deficient** and are **Lewis acids** (electron pair acceptors). Thus BCl_3 readily accepts a lone pair of electrons from ammonia and forms the product, $BCl_3 . NH_3$



planar tetrahedral

The Lewis acid character decreases down the group as the size increases. Thus, Lewis acid character follows the order : $B X_3 > Al X_3 > Ga X_3 > In X_3$

(i) Reactivity towards air

Boron is unreactive in crystalline form. Aluminium forms a very thin oxide layer on the surface which protects the metal from further attack. Amorphous boron and aluminium on heating in air forms B_2O_3 and Al_2O_3 respectively.

$$4B + 3O_2 \xrightarrow{\Delta} 2B_2O_3$$

With nitrogen at high temperature, Al and B form nitrides.

$$2B_{(s)} + N_{2\,(g)} \rightarrow 2BN_{(s)}$$

$$2Al_{(s)} + N_{2\,(g)} \rightarrow 2AlN_{(s)}$$

on moving down the group, the acidic character of oxides decreases.

The decreasing order of acidic character of oxides is

$$\underset{\text{Acidic}}{B_2O_3} > \underset{\text{Amphoteric}}{Al_2O_3} > \underset{\text{Amphoteric}}{Ga_2O_3} > \underset{\text{Basic}}{In_2O_3} > \underset{\text{Basic}}{Tl_2O}$$

(ii) Reactivity towards acids and alkalies

Boron does not react with non-oxidising acids. Al dissolves in mineral acids and aqueous alkalies evolving hydrogen gas.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

$$2Al + 2NaOH + 6H_2O \longrightarrow 2Na^+ [Al(OH)_4]^- + 3H_2$$

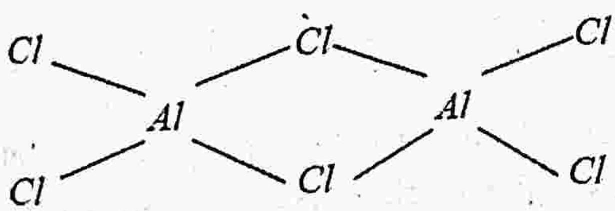
Con. HNO_3 renders Al inert or passive by forming an oxide layer on its surface (passivity).

(iii) Reactivity towards halogens

Group 13 elements form trihalides (MX_3) with halogens (But $Tl\,I_3$ is not known)

$$2M + 3X_2 \longrightarrow 2MX_3 \quad (X = F, Cl, Br, I)$$

Boron halides do not dimerise. But $AlCl_3$ exists as dimers



The trichlorides (MX_3) on hydrolysis in water forms $[M(OH)_4]^-$ ions in which the hybridisation of M is sp^3. Al_2Cl_6 in acidified aqueous solution gives $[Al(H_2O)_6]^{3+}$ ions

Anomalous properties of boron

Boron, the first member of Group 13, differs in many properties from the rest of the members of its family. The main reason for the difference are

(i) Small atomic size of boron

(ii) Its high ionisation enthalpy

(iii) Absence of d-orbitals in its valence shell

Some properties in which boron differs from the rest of the members of the group are given below:

(i) Boron is harder than other elements of the group

(ii) It has higher melting and boiling points

(iii) Due to the absence of *d*-orbitals, the maximum covalence of B is 4. But Al and other members can show higher maximum covalence.

(iv) The trihalides of boron (e.g., BCl_3, BF_3, etc.) are monomeric. The trihalides of Al and most other elements of the group exist as dimers (e.g., Al_2Cl_6)

Some important compounds of boron

1. Borax ($Na_2B_4O_7 \cdot 10H_2O$)

The correct formula of borax is

$Na_2[B_4O_5(OH)_4] . 8H_2O.$

Borax is a white crystalline solid. It dissolves in water and the solution is alkaline due to hydrolysis

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

Action of heat (Borax bead test): On heating borax loses its water of crystallization. On heating further, it melts into a clear liquid which solidifies to glass like beads which contain sodium metaborate($NaBO_2$) and boric anhydride (B_2O_3).

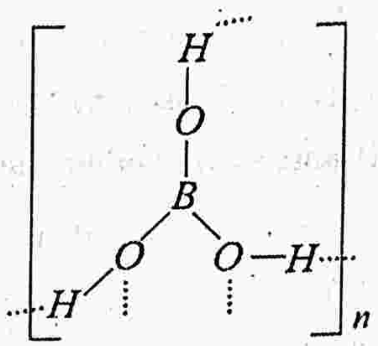
$$Na_2B_4O_7 . 10\,H_2O \xrightarrow[-10\,H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

When coloured salts of transition metals such as Ni^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+} etc are heated with borax bead, they form metaborates having characteristic colours. This is called *borax bead test* which is employed in the identification of these ions.

2. Boric Acid [H_3BO_3] or Orthoboric acid

It is prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow \underset{\text{orthoboric acid}}{4H_3BO_3} + 2NaCl$$



Boric acid is a white crystalline solid, sparingly soluble in cold water and fairly soluble in hot water. In boric acid, boron is sp^2 hybridised. Boric acid has a planar layer structure in which different $B(OH)_3$ units are joined by hydrogen bonds.

Boric acid is a weak monobasic acid. Unlike other acids, it does not act as proton donor but acts as a Lewis acid by accepting OH^- ion from water.

$$B(OH)_3 + HOH \longrightarrow [B(OH)_4]^- + H^+$$

When heated above 370K, it forms meta boric acid (HBO_2) which on further heating gives boric oxide.

$$H_3BO_3 \underset{-H_2O}{\overset{heat}{\rightleftharpoons}} HBO_2 \overset{heat}{\rightleftharpoons} B_2O_3$$