Chapter 2

p block part I

Day - 1

P BLOCK ELEMENTS

- In p-block elements the last electron enters the outermost p orbital. There are six groups of p–block elements in the periodic table numbering from 13 to 18. Their valence shell electronic configuration is ns^2np^{1-6}(except for He).
- P-block contains metals, non-metals and metalloids. The non-metal oxides are acidic, metal oxides are basic in nature whereas metalloid oxides are amphoteric.
- The first member of p-block differs from the remaining members of their corresponding group in two major respects. First is the size and second is their lack of the (d) orbital. This leads to following
- Second period elements of p-groups starting from boron are restricted to a maximum covalence of four (using 2s and three 2p orbitals). In contrast, the third period elements of p-groups have the vacant 3d orbitals and can expand their covalence above four. For example, while boron forms only $[BF_4]^-$, aluminium gives $[AlF_6]^{3-}$ ion.
- Reactivity: Elements of second period do not have d – orbitals and are less reactive as compared to elements of third period which have d – orbitals. For example tetrahalides of carbon are not hydrolysed by water whereas tetrahalides of other elements of group 14 are readily hydrolysed (for e.g. Si)
- The first member of a group differs from the heavier members in its ability to form pπ- pπ multiple bonds to itself (e.g., C = C, C ≡ C, N ≡ N) and to other second row elements (e.g., C = O, C = N, C ≡ N, N = O). Heavier elements of the group do not have strong tendency to form this type of pπ- pπ bonding. The heavier elements do form π - bonding but they but they involve d – orbitals and form dπ – pπ or dπ – dπ bonding
- General Electronic configuration and oxidation states of p-Block Elements.

Group	13	14	15	16	17	18
General electronic configuration	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6 (I s^2 for He)
First member of the group	B	C	N	O	F	He
Group oxidation state	+ 3	+ 4	+ 5	+ 6	+ 7	+ 8
Other oxidation states	+ 1	+ 2, - 4	+ 3, - 3	+ 4, + 2, - 2	+ 5, + 3, + 1, -1	+ 5, + 3, + 1, -1

GROUP 13 OR IIIA: THE BORON FAMILY

This group elements show a wide variation in properties. Boron is a typical non-metal; aluminium is a metal but shows many chemical similarities to boron, and gallium, indium and thallium are almost exclusively metallic in character. Boron is a fairly rare element, mainly occurs as orthoboric acid, (H_3BO_3), borax, $Na_2B_4O_7 \cdot 10H_2O$, and kernite, $Na_2B_4O_7 \cdot 4H_2O$. The abundance of boron in earth crust is less than 0.0001% by mass. Aluminium is the most abundant metal and the third most abundant element in the earth's crust (8.3% by mass) after oxygen (45.5%) and Si (27.7%).

ELECTRONIC CONFIGURATION

The outer electronic configuration of these elements is ns^2np^1. A close look at the electronic configuration suggests that while boron and aluminium have noble gas core, gallium and indium have noble gas plus 10 d-electrons, and thallium has noble gas plus 14 f- electrons plus 10 d-electrons cores. This difference in electronic structures affects the other properties and consequently the chemistry of all the elements of this group.

ATOMIC RADII

On moving down the group, for each successive member one extra shell of electrons is added and, therefore, atomic radius is expected to increase. However, Atomic radius of Ga is less than that of Al. This can be understood from the variation in the inner core of the electronic configuration. The presence of additional 10 d-electrons offer only poor screening effect for the outer electrons from the increased nuclear charge in gallium. Consequently, the atomic radius of gallium (135 pm) is less than that of aluminium (143 pm).

IONISATION ENTHALPY

The ionisation enthalpy values as expected from the general trends do not decrease smoothly down the group. It decreases from B to Al. The observed discontinuity in the ionisation enthalpy values between Al and Ga, and between In and Tl are due to inability of d- and f-electrons, which have low screening effect, to compensate the increase in nuclear charge. The sum of the first three ionisation enthalpies for each of the elements is very high. Effect of this will be apparent when you study their chemical properties.

ELECTRONEGATIVITY

Down the group, electronegativity first decreases from B to Al and then increases marginally. This is because of the discrepancies in atomic size of the elements.

PHYSICAL PROPERTIES

Boron is non-metallic in nature. It is extremely hard and black coloured solid. It exists in many allotropic forms. Due to very strong crystalline lattice, boron has unusually high melting point. Rest of the members are soft metals with low melting point and high electrical conductivity.

GROUP 13 ELEMENTS

Atomic and Physical Properties.

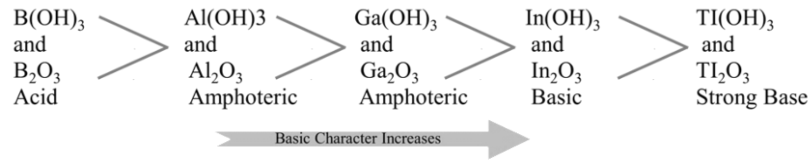
Property	Element				
	Boron B	Aluminium Al	Gallium Ga	indium In	Thallium Ti
Atomic number	5	13	31	49	81
Atomic mass(g mol ')	10.81	26.98	69.72	114.82	204.38
Electronic	-	-	120	140	150
Ionic radius WI/Pm'	(85)	143	135	167	170
Ionic radius WI/Pm'	(27)	53.5	62.0	80.0	88.5
Ionization Enthalpy (Kj mol^{-1}) $\Delta_t H_1$ $\Delta_t H_2$ $\Delta_t H_3$	801 2427 3659	577 1816 2744	579 1979 2962	558 1820 2704	589 1971 2877
Electronegativity	2.0	1.5	1.6	1.7	1.8
Density /g cm' at 298 K	2.35	2.70	5.90	7.31	11.85
Melting point / K	2453	933	303	430	576
Boiling point / K	3923	2740	2676	2353	1730
E / V for (M'/E9		-1.66	-0.56	-0.34	+1.26
E / V for (fir/MI		+0.55	-0.79(acid) -1.39(alkali)	-0.18	-0.34

CHEMICAL PROPERTIES OXIDATION STATE AND TRENDS IN CHEMICAL REACTIVITY

Due to small size of boron, the sum of its first three ionisation enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds. But as we move from B to Al, the sum of the first three ionisation enthalpies of Al considerably decreases, and is therefore able to form Al^{3+} ions. the same is true for other elements However, down the group, due to poor shielding effect of intervening d and f orbitals and the increased effective nuclear charge, these electrons are tightly bound and do not participate in bonding. The relative stability of +1 oxidation state progressively increases for heavier elements: Al < Ga < In < Tl. In thallium +1 oxidation state is more stable than the +3 oxidation state. This makes +3 oxidation states highly oxidising in character. This is attributed to inert pair effect.

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 metal on heating in air form B_2O_3 and Al_2O_3 respectively. The nature of these oxides varies down the group. Boron trioxide is acidic and reacts with basic (metallic) oxides forming metal borates. Aluminium and gallium oxides are amphoteric and those of indium and thallium are basic in their properties.



REACTIVITY TOWARDS ACIDS AND ALKALIS

Boron does not react with acids and alkalis even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalis and thus shows amphoteric character. Aluminium dissolves in dilute HCl and liberates hydrogen gas. However, concentrated nitric acid renders aluminium passive by forming a protective oxide layer on the surface. Aluminium also reacts with aqueous alkali and liberates hydrogen gas. This shows amphoteric nature of Al.

$2Al(s) + 6HCl(aq) \rightarrow 2Al^{3+}(aq) + 6Cl^{-}(aq) + 3H_2(g)$

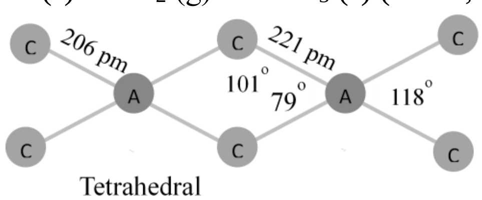
$2Al(s) + 2NaOH(aq) + 6H_2O(l) \rightarrow 2Na^{+} [Al(OH)_4] -$

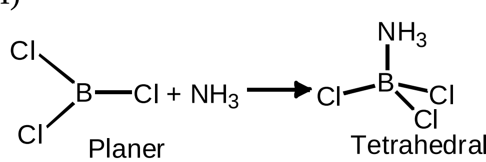
(aq) (Sodiumtetrahydroxoaluminate (III)) + $3H_2(g)$

REACTIVITY TOWARDS HALOGENS

These elements react with halogens to form trihalide (except TlI_3).

$2E(s) + 3X_2(g) \rightarrow 2EX_3(s)$ (X = F, Cl, Br, I)





ANOMALOUS PROPERTIES OF BORON

1. Boron is a non-metal whereas other elements are metalloids or metals.
2. Boron is a bad conductor of electricity whereas other elements are good conductor
3. Boron exists in two forms-crystalline and amorphous. Aluminium is a soft metal and does not exist in different forms.
4. The melting point and boiling point of boron are much higher than those of other elements.

5. Boron forms only covalent compounds whereas other elements form ionic compounds.
6. The hydroxides and oxides of boron are acidic in nature whereas those of aluminium are amphoteric.
7. The trihalides of boron (BX_3) exist as monomers. On the other hand, aluminium halides exist as dimers (Al_2X_6).
8. The hydrides of boron are quite stable while those of aluminium are unstable

DIAGONAL RESEMBLANCE OF BORON WITH SILICON

1. Boron and silicon exhibit the typical properties of non-metals. These do not form cations. Both exist in amorphous as well as crystalline forms.
2. Boron oxide (B_2O_3) and silica (SiO_2) both are acidic and dissolve in alkali solutions to form borates and silicates respectively.
$B_2O_3 + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2O$ and $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$
3. The chlorides of both B and Si get hydrolysed by water to boric acid and silicic acid respectively**.**
$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$ and $SiCl4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl$
4. The hydrides of Boron and Silicon are quite stable. Numerous volatile hydrides are also known which catch fire on exposure to air and are easily hydrolysed.
5. Both elements are semiconductors.

SOME IMPORTANT COMPOUNDS OF BORON

Borax is the most important compound of boron. It is a white crystalline solid of formula $Na_2B_4O_7 \cdot 10H_2O$**. {**Correct formula is $Na_2[B_4O_5(OH)_4].8H_2O$}. Borax dissolves in water to give an alkaline solution.

$Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$(Orthoboric acid).

Borax Bead Test:

On heating, borax first loses water molecules and forms Sodium metaborate. On further heating it turns into a transparent liquid, which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3.$$

The metaborates of many transition metals have characteristic colours and, therefore, borax bead test can be used to identify them in the laboratory. For example, when borax is heated in a Bunsen burner flame with CoO on a loop of platinum wire, a blue coloured $Co(BO_2)_2$ bead is formed.

ORTHOBORIC ACID OR BORIC ACID H_3BO_3

is a white crystalline solid, with soapy touch.

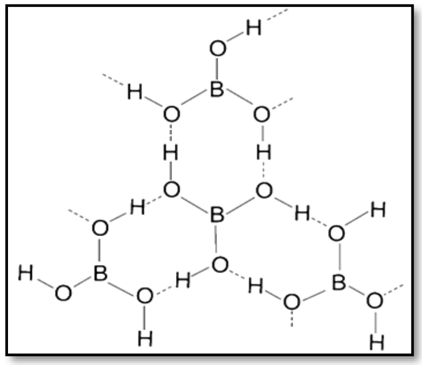
Preparation:

1. $Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4B(OH)_3$
2. $B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$

Physical Properties: It is a weak monobasic Lewis acid (not a protonic acid).

$B(OH)_3 + 2HOH \rightarrow [B(OH)_4]^- + H_3O^+$. Polyborate anions are formed at pH 7–10 if the boron concentration is higher than 0.025 mol/L. The best known of these is the tetraborate ion, found in the mineral borax: $4\ B(OH)^{-4} + 2H^+ \rightleftharpoons B_4O_2^{-7} + 9H_2O$ Chemical Properties: On heating above 370K it forms metaboric acid, HBO_2 which on further heating yields boric oxide, B_2O_3.

$$H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$$



Structure of boric acid: the dotted lines represent hydrogen bonds.

Diborane, B_2H_6

It is prepared by treating boron trifluoride with LiAlH4 in diethyl ether.

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

Lab. method: $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$ Industrial : $2BF_3+6NaH \xrightarrow{450K} B_2H6 + 6NaF$

Physical Properties: Diborane is a colourless, highly toxic gas with a b.p. of 180 K. Diborane catches fire spontaneously upon exposure to air. It burns in oxygen releasing an enormous amount of energy.

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$;

CHEMICAL REACTIONS

1. $B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$
2. $B_2H_6 + 2NMe_3 \rightarrow 2BH_3{\cdot}NMe_3$
3. $B_2H_6 + 2CO \rightarrow 2BH_3{\cdot}CO$
4. $3B_2H_6 + 6NH_3 \rightarrow 3[BH_2(NH_3)_2]^+[BH_4]^- \rightarrow 2B_3N_3H_6$ (inorganic benzene)$+12H_2$
5. $2MH + B_2H6 \rightarrow 2\ M+\ [BH_4]^-$ (M = Li or Na)