The p-Block Elements

Boron Family

ELECTRONIC CONFIGURATION :

The general outer electronic configuration is ns^2np^1. Hence these elements belong to p-block.

Elements	Configuration
Boron [B_5]	[He] $2s^2\ 2p^1$
Aluminium [Al_{13}]	[Ne] $3s^2$, $3p^1$
Gallium [Ga_{31}]	[Ar] $3d^{10}$, $4s^2\ 4p^1$
Indium [In_{49}]	[Kr] $4d^{10}$, $5s^2$, sp^1
Thalium [Tl_{81}]	[Xe] $4f^{14}$, $5d^{10}$, $6s^26s^26p^1$

* B is nonmetal due to its small size, high I.E. and high E.N.
* Al, Ga, In, Tl show typical metallic properties.
* Al is third most abundant element [7.4%]
* Tl is highly toxic.
* Compounds of Al are Al_2O_3, $AlCl_3.6H_2O$, alums, $LiAlH_4$, ultramarine etc.

CHEMICAL CHARACTERISTICS :

Boron	Aluminium
Oxidation state : [+3]	[+3]
B_2O_3, BCl_3, H_3BO_3, $Na_2B_4O_7$ [Boron also shows (–3) O.S. in metal borides]	Al_2O_3, $AlCl_3$, $Al(OH)_3$ $NaAlO_2$
Reaction with conc. H_2SO_4 :	
$2B + 3H_2SO_4 \rightarrow 2H_3BO_3 + 3SO_2$	$2Al+6H_2SO_4\rightarrow Al_2(SO_4) + 3SO_2 + 6H_2O$
Reaction with O_2.	
$4B + 3O_2 \xrightarrow{700°C} 2B_2O_3$	$4Al + 3O_2 \xrightarrow{800°C} 2Al_2O_3$
Formation of chlorides :	
$B_2O_3 + 3C + 3Cl_2 \rightarrow BCl_3 + 3CO$	$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$
Nature of Chlorides	
Lewis acids :	
$[H_3N \rightarrow BCl_3]$	$[H_3N \rightarrow AlCl_3]$
Hydrolysis :	
$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$	$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$

Formation of nitrides :

$2B + N_2 \rightarrow 2BN$	$2Al + N_2 \rightarrow 2AlN$
$2B + 2NH_3 \rightarrow 2BN + 3H_2$	$2Al+2NH_3 \rightarrow 2AlN+3H_2$
Hydrolysis of nitride :	
$BN + 3H_2O \rightarrow H_3BO_3 + NH_3$	$AlN+3H_2O \rightarrow Al(OH)_3+NH_3$
Reducing character :	
$4B + 3CO_2 \rightarrow 2B_2O_3 + 3C$	$2Al+3CO_2 \rightarrow 2Al_2O_3+3C$ $2Al+Cr_2O_3 \rightarrow Al_2O_3+2Cr$ $2Al+Fe_2O_3 \rightarrow Al_2O_3+2Fe$
Treatment with steam :	
$2B+2H_2O \xrightarrow{\text{Steam}} B_2O_3+H_2$	$2Al + 6H_2O \xrightarrow{\text{boiling water}} 2Al(OH)_3 + 3H_2$
Nonmetal	**Metal**
Boron forms hydrides $[B_2H_6, B_4H_{10}, B_{10}H_{14}$, etc]	Forms complex hydride: $LiAlH_4$
B_2O_3 is acidic; $B_2O_3 + 3H_2O \rightarrow 2H_3BO_3$	Al_2O_3 is amphoteric $Al_2O_3+NaOH \rightarrow NaAlO_2 +H_2O$ $Al_2O_3+6HCl \rightarrow 2AlCl_3 +3H_2O$
Borates are stable	Aluminates are less stable
Forms borides with other metals $3Mg + 2B \rightarrow Mg_3B_2$	Al forms alloys with other metals
Attacked by conc. HNO_3 $B + 3HNO_3 \rightarrow H_3BO_3 + 2NO_2$ Orthoboric acid	Becomes passive with conc. HNO_3 due to the formation of oxide layer Al_2O_3
Maximum covalency of four is observed in the compound $K[BF_4]$	Maximum covalency of six is observed in $Na_3[AlF_6]$
$B(OH)_3$ is acidic	$Al(OH)_3$ is basic
It forms covalent compounds only	It forms both covalent and electrovalent compounds
Forms of covalent carbide B_4C	Forms an ionic carbide Al_4C_3. $[Al_4C_3 \xrightarrow{H_2O} CH_4]$
Halides exist in monomeric form BX_3	$AlCl_3$ and $AlBr_3$ exist as dimer
It dissolves in fused alkalies	It dissolves in hot alkalies.

DIBORANE (B_2H_6)

1. **Preparations**

(i) $4BCl_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 2B_2H_6 + 3LiCl + 3AlCl_3$

(ii) $8BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiBF_4$

(iii) $2BCl_3 + 6H_2 \xrightarrow{\text{silent electric discharge}} B_2H_6 + 6HCl$

Reaction with O_2 :

$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 2H_2O$; $\Delta H = -2008$ kJ

[Thus boranes are useful as high energy fuels]

Reaction water :

$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3$ **(boric acid)** $+ 6H_2$

Reaction with ammonia :

$3B_2H_6 + 6NH_3 \xrightarrow{450K} B_3N_3H_6 + 12H_2$

[(borazol) inorganic benzene]

BORAX [$Na_2B_4O_7$. $10H_2O$]

1. **Preparation :**

(i) $Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow{\Delta} 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$

colemanite

[sod. metaborate]

A current of CO_2 is passed in the mother liquor, sodium metaborate is converted to borax.

$4NaBO_2 + CO_2 \rightarrow Na_2B_4O_7 + Na_2CO_3$

2. Properties :

Sparingly soluble in cold water.

Soluble in hot water.

Solution is alkaline

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

Action of heat :

$Na_2B_4O_7 . 10H_2O \xrightarrow[\Delta]{-10H_2O}$

$Na_2B_4O_7 \rightarrow B_2O_3 + 2NaBO_2$

boric anhydride sod. metaborate

transparent bead

Gives bead test with metal oxides :

$CuO + B_2O_3 \rightarrow Cu(BO_2)_2$ copper meta borate (blue)

$Mn(BO_2)_2$ -------------------- amethytst

$Co(BO_2)_2$ --------------------- blue

3. Uses :

(i) In borax bead test

(ii) Preservation for food stuffs

(iii) In making heat and shock resistance glass

(iv) Welding, soldering and in metallurgy

(v) Used in match and leather industries.

DIAGONAL RELATIONSHIP BETWEEN BORON AND SILICON :

Common characteristics :

B and Si do not occur in free state

B and Si are non metals

B and Si act as semi conductors

B and Si show two allotropic forms (crystalline and amorphous)

Hydrides : Both form hydrides :

	[B]	[Si]
B_2H_6	diborane – 6	SiH_4 silane
B_4H_{10}	tetraborane – 10	Si_2H_6 disilene

Oxides : Oxides of both the elements are acidic in nature :

$B_2O_3 + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2O$

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

Hydroxides : $B(OH)_3$ and $Si(OH)_4$ are weak acids

$H_3BO_3 + 3NaOH \rightarrow Na_3BO_3 + 3H_2O$

$H_4SiO_4 + 2NaOH \rightarrow Na_2SiO_3 + 3H_2O$

Halides : BF_3 and SiF_4 (colourless gases)

BCl_3 and $SiCl_4$ (volatile liquids

Undergoes hydrolysis :

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

boric acid

$SiCl_4 + 4H_2O \rightarrow H_4SiO_4 + 4HCl$

silicic acid

Carbides : B_4C and SiC are very hard substances and are used as abrasive.

ALUMINIUM CHLORIDE :

1. Preparation :

Anhydrous $AlCl_3$

(i) $2Al + 6HCl$ (dry gas) $\rightarrow 2AlCl_3 + 3H_2$

(ii) $2Al + 3Cl_2 \rightarrow 2AlCl_3$

(iii) $Al_2O_3 + 3C + 3Cl_2 \xrightarrow{1000^\circ C} 2AlCl_3 + 3CO$

Hydrated aluminium chloride [$AlCl_3 . 6H_2O$]

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

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

2. Properties

* $AlCl_3$ (anhydrous) is white, hygroscopic substance.
* Sublimes at 183° C under normal pressure. (at 100ºC in vacuum)
* V.D. corresponds to Al_2Cl_6 (at 350ºC) and $AlCl_3$ (at 750ºC)
* Soluble in organic solvents (C_6H_6, CS_2 etc)
* **Addition compounds :**

  Forms addition compounds with NH_3, PH_3, $COCl_2$ etc. [e.g. $AlCl_3 . 6NH_3$]
* **Hydrolysis :** It is highly soluble in water and undergoes hydrolysis.

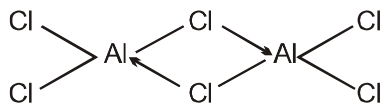
  $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$

* **Action of heat :** Hydrated form on heating gives Al_2O_3.

  $AlCl_3.6H_2O \rightarrow Al(OH)_3 + 3HCl + 3H_2O$

  $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

* **Structure :** (Halogen bridge dimer):



3. **Uses :** (i) Catalyst in the manufacture of petrol by cracking and in Friedel Crafts reactions. (ii) Reagent in the manufacture of dyes, drugs and perfumes.

ALUMS :

General formula :

$M_2SO_4.\ M_2^1(SO_4)_3.\ 24H_2O$

M = monovalent cation : Na^+, K^+, Rb^+ etc.

M_1 = Trivalent cation : Al^{3+}, Fe^{3+}, Mn^{3+} etc.

Examples : $M_2SO_4.\ M_2^1\ (SO_4)_3.\ 24H_2O$

M	M^1	Name of the alum
K^+	Al^{3+}	Potash alum
NH_4^+	Al^{3+}	Ammonium alum
K^+	Cr^{3+}	Chrome alum
NH_4^+	Fe^{3+}	Ferric alum

1. **Preparation :**

   Hot solution of equimolar amount of the constituent sulphates are mixed and the solution is left for crystallization.

* Alums are fairly soluble in cold water but soluble in hot water.
* Solutions of alums are acidic
* Alums are isomorphous and form mixed crystal
* Lose water of crystallization when heated and swells up (burnt alum)
* Solutions give the properties of ions of the constituent salts

2. **Uses :**

(i) Used as a mordant in dyeing and printing

(ii) In purification of water

(iii) In leather tanning

(iv) As antiseptic and in stopping bleeding from cuts.

Carbon Family

ELECTRONIC CONFIGURATION :

The general outer electronic configuration of elements of IV A group is ns^2np^2. Hence these elements belong to p-block.

Elements	Configuration
Carbon [C_6]	[He] $2s^2\ 2p^2$
Silicon [Si_{14}]	[Ne] $3s^2 3p^2$
Germanium [Ge_{32}]	[Ar] $3d^{10}, 4s^2 4p^2$
Tin [Sn_{50}]	[Kr] $4d^{10}, 5s^2 5p^2$
Lead [Pb_{82}]	[Xe] $4f^{14}, 5d^{10}, 6s^2\ 6p^2$

* C and Si are non metals.
* C occurs in free state as coal, diamond and graphite. In combined state it is found in tissues of plant and animal kingdom.
* Ge is metalloid.
* Sn and Pb are metals. Pb is the end product of the heavier radioactive elements.
* C is the 17th and Si is the 2nd most abundant element by mass in earth's crust.

CHEMICAL CHARACTERISTICS :

Oxides :

Group 14 elements form two types of oxides viz monoxide and dioxide.

1. **Monoxide [MO]**

   CO, SiO, GeO, SnO, PbO

   SiO (unstable) CO $\rightarrow$ neutral

   GeO $\rightarrow$ basic

   SnO, PbO $\rightarrow$ amphoteric

Carbon monoxide : It is a colour less toxic gas. It has the highest bond energy amongest monoxide of other members [1070 kJ mol^{-1}]. It forms carbonyls with transition metals $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$. These coordination compounds are also called organometallics. CO is found in exhaust fumes of automobiles.

2. **Dioxides [MO_2]**

CO_2, SiO_2, GeO_2, SnO_2 and PbO_2

$CO_2, SiO_2 \rightarrow$ acidic

$GeO_2, SnO_2, PbO_2 \rightarrow$ amphoteric

Reactions of CO_2, SiO_2 and SnO_2

Acidic:

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O$$

$$SiO_2 + 2NaOH \rightarrow \underset{\text{sodium silicate}}{Na_2SiO_3} + H_2O$$

Amphoteric:

$$SnO_2 + 4HCl \rightarrow SnCl_4 + 2H_2O$$

$$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O$$

3. **Oxidizing character of PbO_2 :**

PbO_2 is a powerful oxidant. The reaction with HNO_3 can be written as :

$$PbO_2 + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O + 0.5\ O_2$$

4. **CO_2 and SiO_2**

CO_2 :

* It is a gas at room temperature
* Solid CO_2 is called dry ice. It sublimes at –78ºC and at 1 atmospheric pressure.
* It is a linear, monomeric and nonpolar molecule.
* It is soluble in water and is used as fire extinguisher.
* On reduction with coke gives CO[$CO_2 + C \rightarrow 2CO$]
* It is a resonance hybrid of three non-equivalent structures.

$$[O = C = O \leftrightarrow \overset{+}{O} \equiv C - \overset{-}{O} \leftrightarrow -C \equiv \overset{+}{O}]$$

SiO_2 ;

* It is a solid at room temperature.
* It has a three dimensional net work solid.
* High m.p. (187 K) does not boil.
* Gives silicate when fused with NaOH.
* It is soluble in water.
* On reduction with coke gives SiC.

[$SiO_2 + 3C \rightarrow SiO + 2CO$]

CARBIDES :

Carbides are binary compounds of carbon with the elements of lower or about equal electronegativity.

Carbides

↓ Electrovalent carbides | ↓ Covalent carbide | ↓ Interstitial carbides

1. Electrovalent carbides :

They are formed by strong electropositive elements (I, IIA, IIIA group members) Zn, Cd etc.

(i) **Methanides (contain C^{4-} ion]**

* These carbides give methane on hydrolysis :

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$$

$$Al_4C_3\ \ 12H_2O \rightarrow 4\ Al(OH)_3 + 3CH_4$$

(ii) **Acetylides [contain $[C{\equiv}C]^{2-}$ ion]**

* These carbides give acetylene on hydrolysis.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

(iii) **Allylide : [contain C_3^{4-} ion]**

* These carbides give propyne or allylene on hydrolysis.

$$Mg_2C_3 + 4H_2O \rightarrow Mg(OH)_2 + CH_3C{\equiv}CH$$

2. **Covalent carbides :**

B_4C and SiC are covalent carbides.

SiC (carborundum) : It is extremely hard, non-fusible, thermally stable and chemically inert solid.

* The structure of SiC is similar to that of diamond.
* It has a better thermal conductivity at high temperature. Resistant to abrasion and corrosion.
* B_4C exhibit similarity with silicon carbide in proprieties.

3. **Interstital carbides (metallic carabids) :**

* Transition metals when combine with carbon or reduction of metallic oxide with carbon produces interstital carbides.

* Carbon atom being small occupy positions in the interstics of metal lattices. Formula of these carbides depend on the ratio of the number of metal atoms to the number of interstitial holes filled by carbon.
* These carbides [M_3C, where M = Fe, Co, Ni etc] are easily hydrolysed by water and dilute acids to give a mixture of hydrocarbons and hydrogen.

ANOMALOUS BEHAVIOUR OF CARBON :

Because of :

* Small size
* High electronegativity
* High ionization energy
* Non-availability of empty d-orbital carbon differs form the rest of the elements of group.

Points of differences :

(1) Carbon is hard. Diamond (allotropic form) is the hardest substance known with highest melting point. Other members of this group are relatively soft (Sn and Pb have low m.p.)

(2) Carbon form multiple bonds ($p\pi$ - $p\pi$ bonding) with itself and with N, O and S. Other members have very less tendency to form multiple bonds.

(3) Carbon cannot expand its covalency beyond 4 due to absence of d-orbitals. Thus do not form complexes.

(4) CO_2 is a gas a room temperature while dioxides of other elements are solids.

(5) Carbon exhibit the unique character of catenation while other members (except Si) do not show this character.

(6) CCl_4 does not hydrolyse while $SiCl_4$ undergoes hydrolysis.

SILICON :

Occurrence :

* 26% of silicon is found in earth's crust.
* As SiO_2 is found in sand, quartz etc.
* As silicates it is found in felspar ($KAl\,Si_2\,O_3$), mica $KH_2Al\,(SiO_4)_3$, clays etc.

1. Preparations

$$SiO_2 + Mg \xrightarrow{\Delta} Si + 2MgO$$

$$SiO_2 + 2C \xrightarrow{\Delta} Si + 2CO$$

2. Properties :

* It is a hard and brittle solid with a very high m.p. (1410ºC
* **Allotropic forms are :** (i) Brown amorphous powder (ii) Grey crystalline mass. Amorphous silicon is more active than crystalline variety.

Few reactions are :

$Si + 2H_2O \rightarrow SiO_2 + 2H_2$,

$Na_2CO_3 + Si \rightarrow Na_2SiO_3 + C$,

$2Mg + Si \rightarrow Mg_2\,Si$,

$Si + 2KOH + H_2O \rightarrow K_2SiO_3 + 2H_2$

GLASS :

* Glass is a hard, brittle, transparent, amorphous solid or supercooled liquid made up of silicates of Na, Ca and other metals like Pb, Zn etc.
* Being amorphous solid it has no sharp melting point and melts at high temperature
* Glass has no definite chemical formula, however it may be represented as :

$x\,M_2O\,.\,y\,M'O.6\,SiO_2$

where M = alkali metals Na, K.

M' = bivalent metals Ca, Pb, Zn etc.

x and y are integers.

Raw materials needed to manufacture glass are:

(a) Silica (SiO_2) (b) Alkali metal salts (Na_2CO_3, $NaNO_3$, Na_2SO_4, $NaNO_3$, K_2CO_3, KNO_3) (c) Heavy metal oxides (PbO, Pb_3O_4) (d) Alkaline earth metal salts ($CaCO_3$, $BaCO_3$, CaO)

2. Soft or soda or window glass :

It is ordinary glass-obtained by the fusion of the following material :

(i) Na_2CO_3 (ii) $CaCO_3$

(iii) Silica SiO_2 (sand or quartz)

Solid mixture after fusion should be cooled slowly. The process is known as annealing.

1. **Soft glass :** It is a common glass. The raw materials are SiO_2, $CaCO_3$ and Na_2CO_3.
2. **Hard glass :** It is a potash glass. The raw material are SiO_2, $CaCO_3$ and K_2CO_3.
3. **Flint glass :** It is a lead potash glass. The raw materials are SiO_2, red Pb, K_2CO_3. It is used in making prism, lenses and optical glass.
4. **Crook's glass :** It is a optical glass containing CeO_2 which prevents the entry of UV rays.
5. **Pyrex glass :** It is used to make lab applicances as it is resistant to heat, shock and common reagents. It is a mixture of zinc and barium boro silicates.
6. **Silica or quartz glass :** It is made by pure silica. It does not break even when put in water in red hot state.
7. **Ground glass :** Soft glass is grounded by turpentine oil and emery.
8. **Reinforced glass :** It has a network of wires embedded in the glass itself. Hence it resists ahocks and does not shatter easily.
9. **Laminated safety glass :** A layer of transparent plastic (vinyl acetate resin) between two layers of glass with the aid of suitable adhesive. It is used in making wind screen of automobiles. It breaks when subjected to heavy impact but particles are not harmful as they are plastic coated.

CEMENT :

* J. Aspdin introduced cement for the first time in England.
* It resembles with the famous Portland rock in England hence the name Portland cement was given.
* Composition of Portland cement Lime, CaO = 50–60%, Silica, SiO_2 = 20–25%, Alumina, Al_2O_3 = 5 – 10%, Ferric oxide, Fe_2O_3 = 1–2%, Sulphur trioxide, SO_3 = 1 – 2%, Magnesia MgO = 2–3% Sodium oxide Na_2O = 1%, Potassium oxide K_2O = 1%
* For a good quality cement the ratio of the oxide should be maintained as : [% SiO_2] : [%Al_2O_3] = 2.5 – 4.0

  [%CaO] : [%SiO_2 + %Al_2O_3 + %Fe_2O_3] = 1.9 – 2.1

* **Raw materials :**

1. Lime stone [$CaCO_3$] → it supplies CaO
2. Clay [Al_2O_3. SiO_3. Fe_2O_3. $2H_2O$] → it supplies SiO_2, Al_2O_3.
3. Gypsum, [$CaSO_4$. $2H_2O$] → it decreases the setting time of cement.

1. **Preparation of Slurry :**

* **Dry process :** When the raw materials i.e., lime stone and clay are hard dry process is used.
* **Wet process :** When the raw materials i.e., lime stone and clay are soft wet process is used.
* Burning of slurry in rotary kiln the maximum temperature zone is 1000–1500ºC.

  Reactions taking place in the kiln are :

  $2\ CaO + SiO_2 \rightarrow 2CaO\ .\ SiO_2$ (Dicalcium silicate)

  $3\ CaO + SiO_2 \rightarrow 3CaO.\ SiO_2$ (Tricalcium silicate)

  $2\ CaO + Al_2O_3 \rightarrow 2CaO.\ Al_2O_3$ (Dicalcium aluminate)

  $3\ CaO + Al_2O_3 \rightarrow 3\ CaO\ .\ Al_2O_3$ (Tricalcium aluminate)

  $4\ CaO + Al_2O_3 + Fe_2O_3 \rightarrow 4\ CaO.\ Al_2O_3.\ Fe_2O_3$ (Tetra calcium aluminoferrite)

  The resulting product of kiln is known as cement clinker it is collected in the cooler part. Obviously the composition of cement clinker is : $2CaO.\ SiO_2$, $3CaO\ .\ SiO_2$, $2CaOAl_2O_3$, $3CaO.\ Al_2O_3$, $4CaO,\ Al_2O_3.\ Fe_2O_3$.

Mixing of cement clinker with gypsum :

Clinker is powdered and 2 – 3% gypsum ($CaSO_4.\ 2H_2O$) is added to slow down the setting of cement. It assumes the form : $3CaO.\ Al_2O_3.\ 3CaSO_4.\ 2H_2O$ calcium sulphoaluminate.

Mortar : A mixture of Cement, sand [1 : 3] in water, used in binding bricks and plastering.