11. The *p*-Block Elements

- Six groups (13 – 18) of *p*-block elements
- Valence shell electronic configuration → ns^2np^{1-6} (except for He)
- Difference in inner core causes difference in physical and chemical properties.
- Have all types of elements – metals, non-metals, and metalloids
- In addition to group oxidation state, these elements show other oxidation states differing from the total number of valence electrons by unit of two.
- For lighter elements → Group oxidation state is the most stable.
  For heavier elements → Lower oxidation states are progressively more stable.
- Non-metals and metalloids are present only in *p*-block.
- Non-metallic character decreases on moving down the group.

Difference of the first member from the rest of the *p*-block elements of their corresponding groups:

- Size and properties based on size
- Unavailability of *d*-electrons in first member

Formation of π bonds:

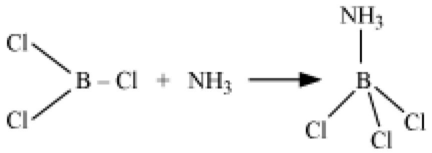
- Due to combined effect of size and availability of *d*-orbitals
- Lighter elements form $p\pi - p\pi$ bonds while heavier elements form $d\pi - p\pi$ or $d\pi - d\pi$ bonds.

Group 13 elements (The Boron family):

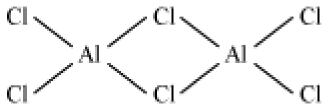
- Valence shell electronic configuration → ns^2np^1
- Atomic radius
  - increases on moving down the group
  - **Exception:** The atomic radius of Ga is less than that of Al. This is because of poor shielding of *d*-electrons in Ga.
- Ionisation enthalpy
  - $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3$
  - Decreases (not smoothly) on moving down the group
  - **Exceptions :** Al < Ga (Due to poor shielding by *d*-electron)
    In < Tl (Due to poor shielding by *f*-electrons)
- Electronegativity
  Decreases from B to Al and then increases on moving down the group
- Physical properties

- Ga has low melting point (303 K). Therefore, it can exist in liquid state during summer.

- Chemical properties
  - BCl_3, $AlCl_3 \rightarrow$ Electron deficient molecules
    BCl_3 behaves as Lewis acid.



AlCl$_3$ becomes stable by dimerisation.



Tetrahedral

  - Reactivity towards air

$$2E_{(s)} + 3O_{2(g)} \xrightarrow{\Delta} 2E_2O_{3(s)}$$
$$2E_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2EN_{(s)}$$

  - Reactivity towards acids and alkalies
    - Boron does not react.
    - Aluminium shows amphoteric character.

  - Reactivity towards halogens
    $2E_{(s)} + 3X_{2(g)} \rightarrow 2EX_{3(s)}$ (X = F, Cl, Br, I)

Some important compounds of boron:

- Borax ($Na_2B_4O_7 \cdot 10H_2O$)

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} \underset{\text{Sodium tetraborate}}{Na_2B_4O_7} \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

Mixture of sodium metaborate and boric anhydride $\rightarrow$ Borax bead
Borax bead is used in flame test.

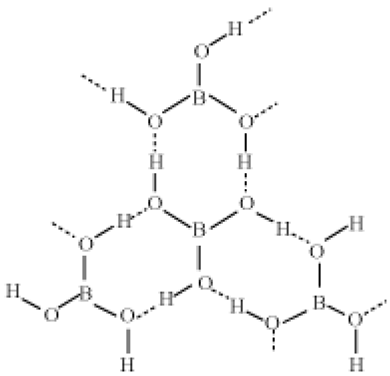
- Orthoboric acid (H_3BO_3)

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4B\ OH\ _3$$

Orthoboric acid

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

Metaboric acid — Boric oxide

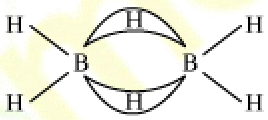


Structure of boric acid

- **Diborane, B_2H_6**
    - ❖ Prepared by treating boron trifluoride (BF_3) with $LiAlH_4$ in diethyl ether

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

    - ❖ It contains two bridging hydrogen atoms between two boron atoms.
    - ❖ The bridging bonds are three-centre, two-electron bonds.



- ❖ $3B_2H_6 + 6NH_3 \rightarrow 2B_3N_3H_6 + 12H_2$

Group 14 elements (The Carbon family):

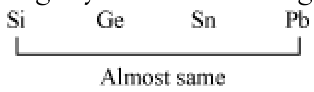
- Carbon is the most versatile element in the world.
- Valence shell electronic configuration $\rightarrow ns^2np^2$
- Covalent radius:
  Increases from C to Si, but small increase from Si to Pb (due to presence of completely filled *d*- and *f*-orbitals)
- Ionisation enthalpy
    - ➢ Higher than those of corresponding group 13 elements

Si → Ge → Sn → Pb

Small decrease (Si to Sn), Slight decrease (Sn to Pb)

(Due to poor shielding of d-and f-electrons)

- Electronegativity
    - Slightly more electronegative than corresponding group 13 elements



- Physical properties

  C, Si $\rightarrow$ Non-metals

  Ge $\rightarrow$ Metalloid

  Sn, Pb $\rightarrow$ Soft metals

- Chemical properties
    - Reactivity towards oxygen

      Two types of oxides – monoxide (MO) and dioxide (MO_2)

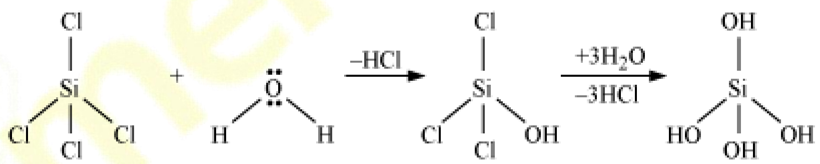
    - Reactivity towards water

      C, Si, Ge, Pb $\rightarrow$ Do not react

      $$Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$$

    - Reactivity towards halogen

    - Form halides of formula MX2 and MX4
    - PbI_4 does not exist
    - Except CCl_4, other tetrahalides are easily hydrolysed by water.



Anomalous behaviour of carbon:

- Due to smaller size,
  - $\rightarrow$ higher electronegativity
  - $\rightarrow$ higher ionisation enthalpy
  - $\rightarrow$ unavailability of *d* orbitals

- The order of catenation is

  C >> Si > Ge $\approx$ Sn

  (Pb does not undergo catenation)

Allotropes of carbon:

- Diamond
  - sp^3 hybridisation
  - Four directional covalent bonds
  - Used for sharpening tools, ornaments, making dyes, manufacturing tungsten filament, etc.

- Graphite
  - sp^2 hybridisation
  - three sigma bonds and one π bond
  - layered structure
  - conductor of electricity

- Fullerenes
  - Cage-like molecules
  - $C_{60} \rightarrow$ called Buckminsterfullerene
    - $\rightarrow$ 20 six-membered rings
    - $\rightarrow$ 12 five-membered rings
    - $\rightarrow$ sp^2 hybridisation

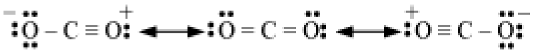
Some important compounds of carbon and silicon:

- Carbon monoxide (CO)
  - $2C_{s} + O_{2\,g} \xrightarrow{\Delta} 2CO_{g}$
  - $C_{(s)} + H_2O \xrightarrow{473\text{–}1273\text{K}} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas Or Synthesis gas}}$
  - $2C_{(s)} + O_{2(g)} + 4N_{2(g)} \xrightarrow{1273\text{K}} \underbrace{2CO_{(g)} + 4N_{2(g)}}_{\text{Producer gas}}$
  - CO is a highly poisonous gas as it forms a complex with haemoglobin. It prevents haemoglobin in the red blood corpuscles from carrying oxygen, leading to death.

- Carbon dioxide
  - Photosynthesis

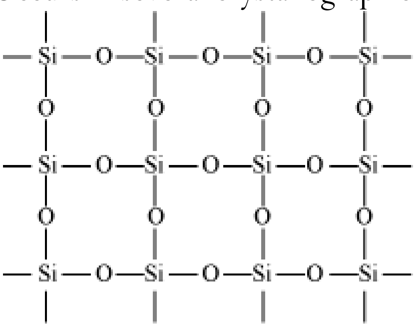
    $$6CO_2 + 12H_2O \xrightarrow[\text{Chlorophyll}]{h\upsilon} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

- Greenhouse gas
- Solid CO_2 is called dry ice.
- *sp* hybridisation
- Resonance structure



Some important compounds of silicon:

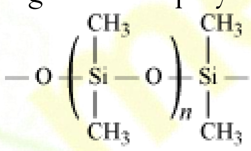
- Silicon dioxide (SiO_2)
  - Known as silica
  - Occurs in several crystallographic forms such quartz, cristobalite, tridymite



Three dimensional structure of SiO_2

  - Quartz is used as piezoelectric material.

- Silicones
  - Organosilicon polymer



- Silicates
  - The basic structural unit of silicate is SiO_4^{4-}.
  - Man made silicates – Glass and cement

- Zeolites
  - These are aluminosilicate minerals. E.g. ZSM–5
  - Widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation