11. *THE p-BLOCK ELEMENTS*

These are elements in which the last electron enters in the outer most p-subshell. They include elements of groups 13 to 18. Their general outer electronic configuration is ns^2np^{1-6} (except for He). They include metals, non-metals and metalloids.

Their maximum oxidation state = the total no. of valence electrons (i.e., the sum of the s- and p-electrons). But their common oxidation state may differ from the maximum oxidation state or group oxidation state. Generally, in the p-block elements, down the group, the common oxidation state is 2 less than the maximum oxidation state. This is due to the **Inert pair effect.** *It is the reluctance of s-electrons to participate in chemical bonding.* It is commonly seen in the elements of groups 13, 14 & 15. [Down the group, due to the poor shielding effect of inner d and f orbitals, the effective nuclear charge is greater, which holds the s-electrons tightly. So they cannot participate in bonding].

Due to the above reason, $TlCl$ is more stable than $TlCl_3$. Similarly lead mainly form $PbCl_2$ than $PbCl_4$. Or, Tl^+ is stabler than Tl^{3+} and Pb^{2+} is stabler than Pb^{4+}).

Group 13 Elements (Boron Family)

Group 13 include Boron (B(, Aluminium (Al), Gallium (Ga), Indium (In), Thalium (Tl) and Nihonium (Nh). Among these elements, Boron is a typical non-metal and the other elements are metals.

Atomic radii: Down the group, atomic radius increases. But atomic radius of gallium is less than that of aluminium. This is due to the presence of completely filled d-orbitals in Ga (Ga - [Ar] $3d^{10}$ $4s^2$ $4p^1$). The presence of 10 d-electrons offer only poor shielding effect for the outer electrons, from the increased nuclear charge.

Ionisation Enthalpy: The ionisation enthalpy values do not decrease smoothly down the group. This is due to the poor shielding effect of the completely filled inner d and f electrons.

Oxidation state: The common oxidation state of 13th group elements is +3. Due to high ionisation enthalpy, boron does not form +3 ions and it only forms covalent compounds. The stability of +3 oxidation state decreases and that of +1 oxidation state increases down the group. This is due to inert pair effect.

The trivalent compounds formed by 13th group elements are called electron deficient compounds. In these compounds, the number of electrons around the central atom of the molecule is only 6. In order to attain stable octet configuration, they accept a pair of electrons and so they behave as Lewis acids. e.g. BF_3, BCl_3, $AlCl_3$, B_2H_6 etc.

Chemical properties

Reactivity towards air: Boron is unreactive in crystalline form. Due to the presence of an oxide layer on the surface, Al does not react with air at normal temperature. But at high temperatures, they form oxide and nitride.

$2E + 3O_2 \longrightarrow 2\ E_2O_3$

$2E + N_2 \longrightarrow 2\ EN$ [E = Any 13th group element]

The oxide of boron (B_2O_3) is acidic, the oxides of Aluminium and Gallium are amphoteric and that of Indium and Thalium are basic.

Reactivity towards acids and alkalies: Boron does not react with acids and alkalies even at moderate temperatures. But aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric nature.

$2Al(s) + 6\,HCl(aq) \longrightarrow 2\,AlCl_3(aq) + 3H_2(g)$

$2Al(s) + 2NaOH(aq) + 6H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq) + 3H_2(g)$

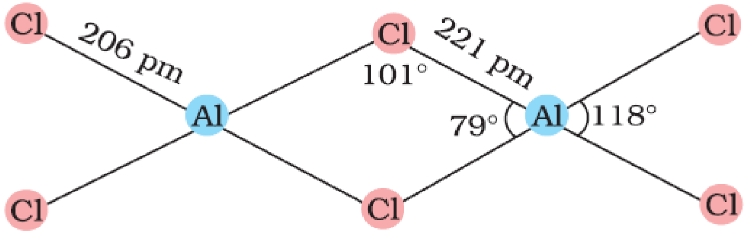
But it does not react with nitric acid due to the presence of the oxide layer on the surface.

Reactivity towards halogens: They react with halogens and form trihalides.

$2E(s) + 3X_2(g) \longrightarrow 2EX_3(s)$

$2Al(s) + 3Cl_2(g) \longrightarrow 2AlCl_3(s)$

$AlCl_3$ exists as dimer to attain stability.



Anhydrous aluminium chloride is partially hydrolysed with moisture to liberate fumes of HCl gas. So white fumes appears around the bottle of anhydrous $AlCl_3$.

Some important compounds of Boron

1. **Borax [$Na_2B_4O_7.10H_2O$]:** It is a white crystalline solid with formula $Na_2B_4O_7{\cdot}10H_2O$ (Sodium tetraborate decahydrate). It contains the tetranuclear units $[B_4O_5(OH)_4]^{2-}$ and hence its correct formula is $Na_2[B_4O_5(OH)_4].8H_2O$.

It dissolves in water to give NaOH and orthoboric acid. Since NaOH is a strong alkali and orthoboric acid is weak acid, the solution is basic in nature.

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

(Orthoboric acid)

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

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

(Sodium metaborate) (Boric anhydride)

The metaborates of many transition metals have characteristic colours and, therefore, ***borax bead test*** can be used to identify them in the laboratory.

2. **Ortho boric acid [H_3BO_3 or $B(OH)_3$]:** It is a white crystalline solid with soapy touch. It is prepared by acidifying an aqueous solution of borax.

$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$

It is also obtained by the hydrolysis of boron halides or hydrides.

It is a weak monobasic non-protic acid. It acts as a Lewis acid by accepting electrons from a hydroxyl ion.

$B(OH)_3 + 2H_2O \rightarrow [B(OH)_4]^- + H_3O^+$

On heating above 370K, it forms metaboric acid (HBO_2) which on further heating gives boric oxide (B_2O_3).

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

3. **Diborane (B_2H_6):** The simplest boron hydride is borane (BH_3), which exists as a dimer called Diborane (B_2H_6). It is prepared by treating BF_3 with Lithium aluminium hydride ($LiAlH_4$) in ether.

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

In the laboratory, it is prepared by the oxidation of sodium borohydride with iodine.

$$2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$$

Diborane is prepared industrially by the reaction of BF_3 with sodium hydride.

$$2BF_3 + 6NaH \xrightarrow{450K} 2B_2H_6 + 6NaF$$

Diborane is a colourless, highly toxic gas. It catches fire spontaneously on exposure to air. It burns in oxygen to form B_2O_3 and evolve large amount of heat.

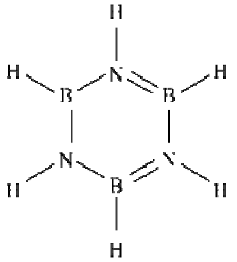
$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O\text{: } \Delta H = -1976\text{ kJ/mol}$$

It readily hydrolysed by water to give boric acid.

$$B_2H_6(g) + 6H_2O(l) \longrightarrow B(OH)_3(aq) + 6H_2(g)$$

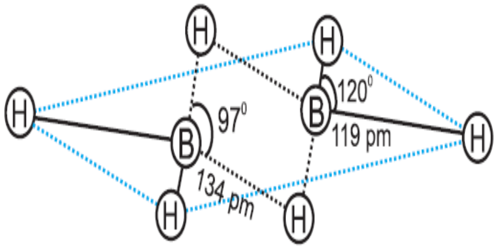
Diborane react with ammonia to form $B_2H_6.2NH_3$ which on further heating gives ***Borazine ($B_3N_3H_6$) which is commonly known as inorganic benzene.*** Its structure is similar to benzene with alternate BH and NH groups.

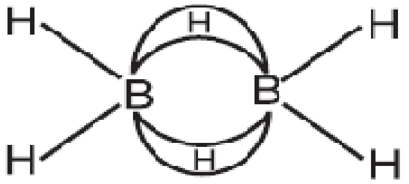
$$3B_2H_6 + 6NH_3 \rightarrow 3\,B_2H_6.2NH_3 \rightarrow 2\,B_3N_3H_6 + 12H_2$$



Structure of Diborane

In diborane, each boron atoms is in sp^3 hybridisation. The two boron atoms and 4 hydrogen atoms lie in one plane. These four H atoms are called *terminal hydrogen atoms*. The other two hydrogen atoms lie one above and one below this plane. These H atoms are called *bridging hydrogen atoms*. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds *are three centre- two electron (3c-2e) bonds or banana bonds*. Thus diborane is an *electron deficient compound*.





Uses of Boron and Aluminium

- Boron fibres are used in making bullet proof vest and light composite material for aircraft.
- Borax and boric acid are used in the manufacture of heat resistant glass.
- Borax is also used as a flux for soldering metals, for giving glazed coating to earthenware.
- It is also used in medicinal soaps.
- Orthoboric acid is used as a mild antiseptic.
- Aluminium is extensively used for making electrical cables.
- It is also used in packing, utensil making, construction, aeroplane and transportation industry.

Group 14 Elements (Carbon Family)

Group 14 includes Carbon (C), Silicon (Si), Germanium (Ge), Tin (Sn), lead (Pb) and Flerovium (Fl). Among these Carbon and silicon are non-metals, germanium is a metalloid and tin and lead are soft metals.

Oxidation states: These elements have 4 electrons in their valency shell. The common oxidation states exhibited by these elements are +2 and +4. Carbon also shows negative oxidation states. In +4 oxidation states, they mainly form covalent compounds. Down the group the stability of +2 oxidation state increases due to inert pair effect. The maximum covalency of carbon is 4 due to the absence of vacant d-orbitals.

Reactivity towards oxygen: They react with oxygen and form two types of oxides – MO and MO_2. MO_2 is more acidic than MO. Down the group, the acidity of oxides decreases. The dioxides CO_2, SiO_2 and GeO_2 are acidic, while SnO_2 and PbO_2 are amphoteric. Among monoxides CO is neutral, GeO is acidic and SnO and PbO are amphoteric.

Reactivity towards halogen: They form 2 types of halides – MX_2 and MX_4. Down the group, the stability of MX_2 increases. GeX_4 is more stable than GeX_2 while PbX_2 is stable than PbX_4. This is due to inert pair effect. Due to the absence of vacant d-orbitals CCl_4 cannot be hydrolysed. While $SiCl_4$ undergoes hydrolysis to give $Si(OH)_4$ [silicic acid].

Anomalous Properties of Carbon

C shows anomalous properties due to its smaller size, higher electronegativity, higher ionisation enthalpy and unavailability of d orbitals. some of the anomalous properties of C are:

1. The the maximum covalency of C is four. While other elements of group 14 can extend their covalency beyond 4 due to the presence of vacant d-orbitals.
2. Carbon has unique ability to form pπ– pπ multiple bonds with itself and with other atoms of small size and high electronegativity.
3. Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called ***catenation***. But other elements have less catenation property.
4. CCl_4 cannot be hydrolysed, but the tetrahalides of other elements can be hydrolysed.

Allotropes of Carbon

The existance of an element in two or more forms with same chemical properties but with different physical properties is known as allotropy. Carbon exists in crystalline and amorphous allotropes. The important crystalline allotropes of Carbon are diamond, graphite and fullerene.

a) **Diamond**: In diamond, each carbon atom is in sp^3 hybridisation and linked to four other carbon atoms in a tetrahedral manner. So it has a a rigid three dimensional network of carbon atoms. It is very difficult to break covalent bonds and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dies and in the manufacture of tungsten filaments for electric light bulbs.

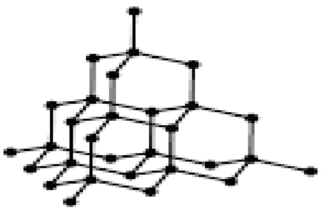
b) **Graphite**: Graphite has a layered structure. Different layers are held by weak van der Waals forces of attraction. Each layer contains planar hexagonal rings of carbon atoms. Here each carbon atom is in sp^2 hybridisation and makes three C-C sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. These electrons are delocalised and are mobile. Therefore graphite conducts electricity. Due to layered structure, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature.

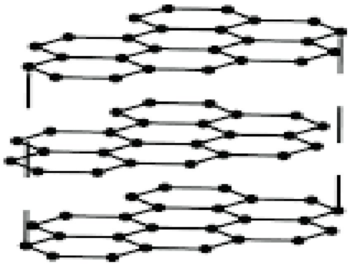
c) **Fullerenes**: These are the cage like spherical molecules of formula C_{60}, C_{70}, C_{76}, C_{84} etc. These are prepared by heating of graphite in an electric arc in the presence of inert gases like helium or argon.

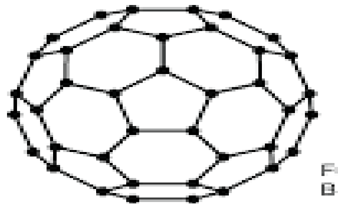
The most commonly known fullerene is C_{60}, which is known as Buckminster fullerene. It contains twenty six- membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals. This gives an aromatic character to the molecule.

Thermodynamically, graphite is the most stable allotrope of carbon.

Amorphous forms of carbon are charcoal, coke and carbon black. Carbon black is obtained by burning hydrocarbons in limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperature in the absence of air.


Diamond


Graphite


Fullerene
Bucky Ball

Uses of Carbon

- Graphite is used as electrodes in batteries and in electrolysis. It is also used for making tennis rackets, fishing rods, aircrafts etc.
- Activated charcoal is used to adsorb poisonous gases. It is also used in water filters and in air conditioners.
- Carbon black is used in black ink for printers and fillers in automobile tyres.
- Coke is used as a fuel and as a reducing agent in metallurgy.
- Diamond is used in jewellery.

Some important compounds of Carbon and Silicon

Oxides of Carbon**:** Two important oxides of carbon are carbon monoxide, CO and carbon dioxide, CO_2.

1. **Carbon Monoxide (CO):**

Preparation:

Carbon burns in limited supply of air to give CO.

$$2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$$

By the dehydration of formic acid with conc. H_2SO_4 at 373 K.

$$HCOOH \xrightarrow{\text{Conc. } H_2SO_4/\Delta} CO + H_2O$$

Commercially, it is prepared by passing steam over red hot coke.

$$C(s) + H_2O(g) \xrightarrow{473K - 1273K} CO(g) + H_2(g)$$

The mixture of CO and H_2 is known as *water gas or Syn gas*.

If instead of steam, air is passed over red hot coke, we get a mixture of CO and nitrogen commonly known as *producer gas*.

$C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} 2CO(g) + N_2(g)$

Both water gas and producer gas are used as industrial fuels.

Properties: CO is a colourless, odourless toxic gas and is insoluble in water. It is a powerful reducing agent. It reduces almost all metal oxides.

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

$ZnO(s) + CO(g) \longrightarrow Zn(s) + CO_2(g)$

Structure: In CO, there are one sigma and two pi bonds between carbon and oxygen ($:C \equiv O:$). Because of the presence of lone pair on carbon, CO molecule acts as an electron donor and reacts with metals to form metal carbonyls.

CO is highly poisonous in nature because it forms a highly stable complex with haemoglobin (carboxy haemoglobin). This prevents haemoglobin in RBC from carrying oxygen round the body. This will results in headache, weak eyesight, nervousness and even death.

2. Carbon Dioxide (CO_2)

Preparation: It is prepared by the complete combustion of carbon or hydrocarbons.

$C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$

It is also prepared by the action of dilute HCl on metal carbonates.

$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

Commercially it is obtained by heating lime stone ($CaCO_3$)

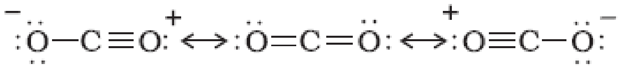
Properties: It is a colouless, odourless non-toxic gas which is slightly soluble in water. When dissolved in water it forms carbonic acid (H_2CO_3), which is a weak dibasic acid.

H_2CO_3/HCO_3^- buffer in our blood helps to maintain pH of blood between 7.26 and 7.43.

The excess CO_2 in the atmosphere is removed by green plants by the process of photosynthesis. If the concentration of CO_2 in the atmosphere increases, it will results in increase in temperature of the atmosphere (Green house effect).

Solid carbon dioxide is called Dry ice. It is obtained by cooling CO_2 under pressure. It sublimes directly to the vapour phase. It does not wet the surface on which it sublimes. So it is called dry ice. It is used as a refrigerant for ice-cream and frozen food.

Structure: In CO_2 molecule, C atom undergoes **sp** hybridisation. So it has a linear shape with no dipole moment. It exists as discrete (separate) molecules and there is only a weak attractive force between different CO_2 molecules. The resonance structures of CO_2 are:

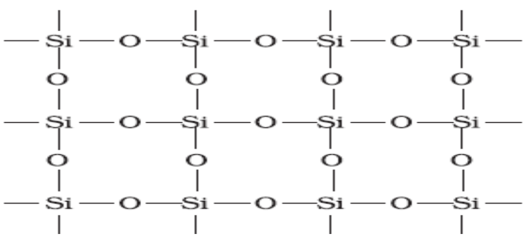


$$\overset{-}{:\ddot{\underset{..}{O}}}-C\equiv \overset{+}{O:} \leftrightarrow :\ddot{O}=C=\ddot{O}: \leftrightarrow \overset{+}{:O}\equiv C-\overset{-}{\ddot{\underset{..}{O}}:}$$

3. Silicon Dioxide (SiO_2)

Silicon dioxide is commonly known as silica. It exists in different crystalline forms like Quartz, Crystobalite, Tridymite etc.

Structure: In SiO_2, each silicon atom undergoes sp^3 hybridisation. Here each Si atom is tetrahedrally surrounded by 4 oxygen atoms. Each oxygen atom is covalently bonded to another silicon atom. So it has a three dimensional network structure and hence it is a solid.



Silica is almost unreactive because of very high Si – O bond enthalpy.

Uses:

- Quartz is used as a piezoelectric material. It is used to produce extremely accurate clocks, for radio and television broadcasting and mobile radio communications.
- Silica gel is used as a drying agent, in chromatography and as catalysts.
- Amorphous form of silica (Kieselghur) is used in filtration plants.

4. Silicones:

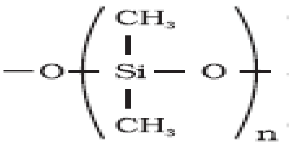
Silicones are a group of organosilicon polymers, which have (-R_2SiO-) as a repeating unit. (Where R is alkyl or aryl group).

Manufacture:

When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K, dimethyl dichlorosilane [$(CH_3)_2SiCl_2$] and other methyl substituted chlorosilanes are formed. Hydrolysis of dichlorosilane followed by condensation gives straight chain polymers.

$$2CH_3Cl + Si \xrightarrow{Cu;\ 573K} (CH_3)_2SiCl_2 \xrightarrow{2H_2O} (CH_3)_2Si(OH)_2$$

$$n(CH_3)_2Si(OH)_2 \xrightarrow{\text{polymerisation}}$$



$$-O\left(\begin{array}{c} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{array}\right)_n$$

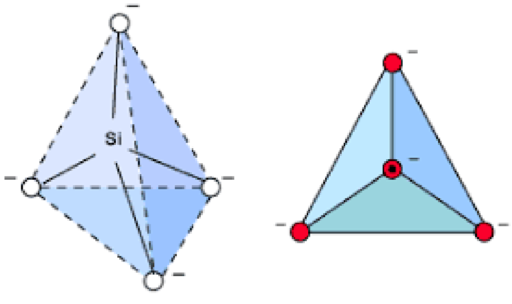
The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ (Trimethyl chlorosilane).

Properties:

They are water repelling in nature. They have high thermal stability, high dielectric strength and resistance to oxidation and chemicals. So they are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

5. Silicates:

These are compounds of Si in which each silicon atom is bonded to four oxygen atoms in tetrahedral manner. In silicates, either the discrete SiO_4^{4-} units are present or a number of such units are joined together by sharing oxygen atoms. When silicate units are linked together, they form chain, ring, sheet or three-dimensional structures. Zeolites, mica, feldspar, asbestos etc. are some examples of silicates.



(a) (b)

6. Zeolites:

Zeolites are aluminosilicates of metals. These are widely used as a catalyst in petrochemical industries for cracking of hydrocarbons and isomerisation. E.g. the zeolite ZSM-5 is used to convert alcohols directly into gasoline. Hydrated zeolites are used as ion exchangers in softening of hard water.

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