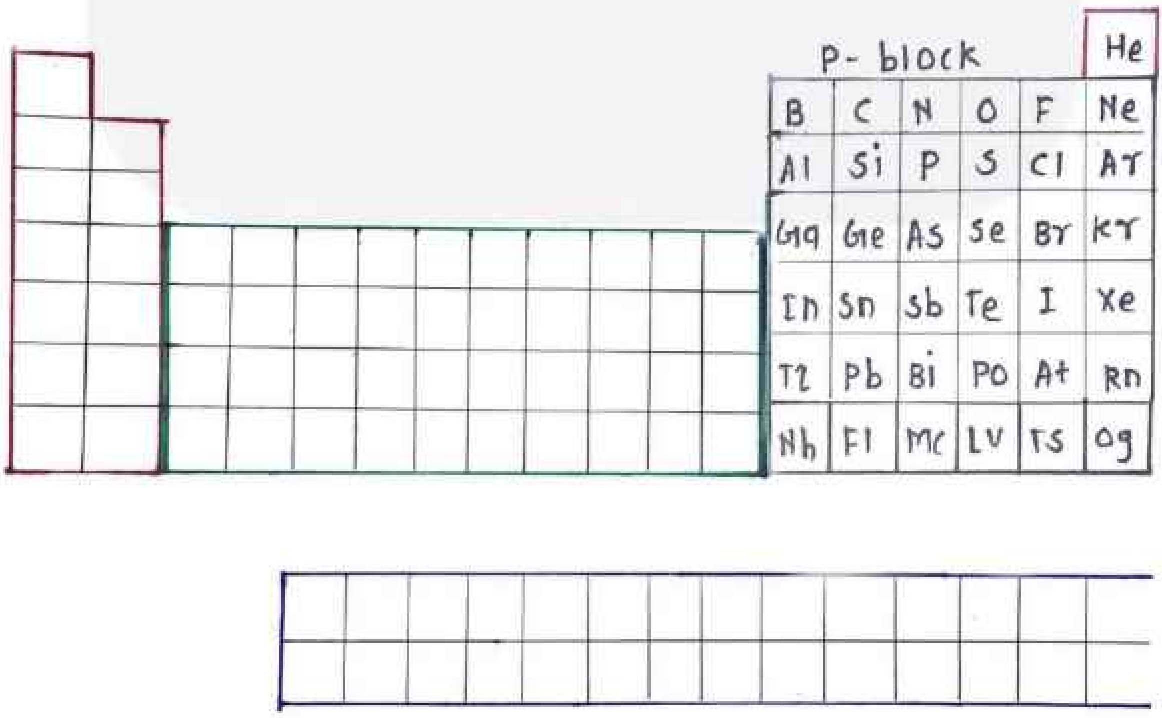
Unit - 11

THE P-BLOCK ELEMENTS

Elements belonging to groups 13 to 18 of the periodic table are called P-Block elements.

The P-Block elements in the periodic table are shown below :



- The general electronic configuration is ns^2np^{1-6} (except He). These elements are usually good conductors of electricity. They have a shiny lustre. They are good conductors, owing to the fact that they have a tendency to lose their electrons.
- A prominent characteristic of these p-Block elements is that the last electron of all these elements enters the outermost p-subshell.

- P-Block elements comprise of the various families that include :

    - Group 13 : The Boron family
    - Group 14 : The carbon family
    - Group 15 : The Nitrogen family
    - Group 16 : The oxygen family
    - Group 17 : The Fluorine family
    - Group 18 : The family of Inert gases.

GROUP 13 : THE BORON FAMILY

- The group 13 elements consist of six elements. They are; boron (B), Aluminium (Al), gallium (Ga), Indium (In), thallium (Tl) and element 113, whis gets the name of ununtrium [Uut].

- Boron is the lightest of the elements in this group. It is a non-metal.

- outer Electronic configuration is ns^2np^1

- Boron compounds are electron deficient, they are lack of an octet of electrons about the B atom.

- Diborane, B_2H_6 is the simplest boron hydride.

- **Electronic configuration** - The outer electronic configuration of these elements is $ns^2 np^1$.

- **Atomic Radii** - The atomic and ionic radii of group 13 elements are smaller than the corresponding elements of alkali and alkaline earth metals.

- on moving down the group both atomic and ionic radii are expected to increase due to addition of new shell. However; the observed atomic radius of Al (143 pm) is slightly more than that of Ga (135 pm)

- **Ionization Enthalpy -** First ionisation enthalpies of the elements of group-13 are less than those of the elements present in group-2 in the same period.

- The removal of p-electron of group elements is much easier than the s-electron, and there fore, the first ionisation enthalpies ($\Delta_i H_1$) of the elements of group 13 are lower as compared to the corresponding elements of group 2.

- On moving down the group 13 from B to Al the first ionisation enthalpies decrease due to an increase in atomic size and screening effect which outweigh the effect of increased nuclear charge.

- There is a discontinuity expected in the ionisation enthalpy values between Al and Ga and between In and Tl, due to enability of d and f-electrons which have low screening effect to compensate the increase in nuclear charge.

- **Electronegativity** - Down the group, electronegativity first decreases from B to Al and then increases. This is due to the discrepancies in the atomic size of the elements.

- **Physical properties** -

i) Due to strong crystalline lattice boron has high melting point. Rest of the elements of this family have low melting points.

ii) Boron is extremely hard and black coloured solid and non-metallic in nature.

iii) other members of this family are soft metals with low melting points and high electrical conductivity.

- **Chemical properties** –

oxidation state and trends in chemical reactivity.

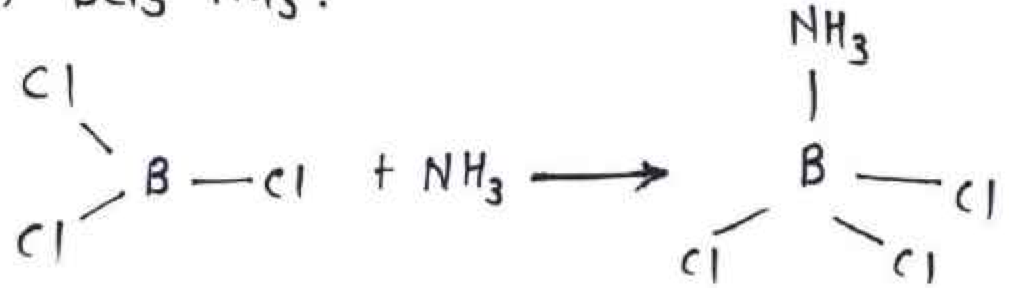
The first two elements boron and aluminium show only +3 oxidation state in the compo-unds but the other elements of this group gallium, indium, and thalium also exhibit +1 oxidation state in addition to +3 oxidation state i.e., They show variable oxidation states.

- As we move down the group, the stability of +3 oxidation state decreases while of +1 oxidation state progressively increases.

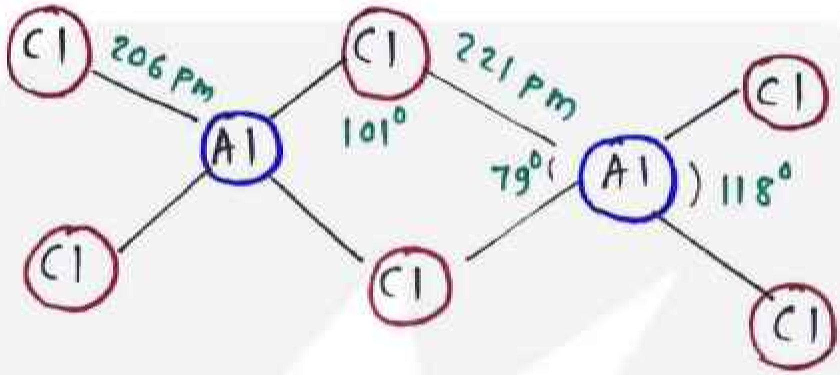
- In thallium +1 oxidation state is predominant where as the +3 oxidation state is highly oxidising in character.

- The compounds in +1 oxidising state, as expected from energy consideration, are more ionic than those in +3 oxidation state.

- The tendency to behave as lewis acid decreases with the increase in the size. down the group. BCl_3 easily accept a lone pair of electrons from ammonia to form $BCl_3 \cdot NH_3$.



- $AlCl_3$ achieves stability by forming a dimer



Tetrahedral

- In trivalent state most of the compounds being covalent are hydrolysed in water.

ex :- the trichlorides on hydrolysis in water form tetrahedral $[M(OH)_4]^-$ species. The hybridisation state of element M is sp^3.

- Aluminium chloride in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3+}$ ion.

i) **Reactivity towards air** - Boron is unreactive in crystalline form. Amorphous Boron and aluminium metal on heating in air form B_2O_3 and Al_2O_3 respectively. With dinitrogen at high temperature they form nitrides.

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

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

ii) **Reactivity towards acids and alkalis** -

Boron does not react with acids and alkalies even at moderate temperature; but aluminium dissolves in mineral acids and aqueous alkalies and thus shows amphoteric character.

- Aluminium dissolves in dilute HCl and liberates dihydrogen.

$$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 6Cl^{-}_{(aq)} + 3H_{2\,(g)}$$

- Aluminium also reacts with aqueous alkali and liberates dihydrogen.

iii) Reactivity towards halogens -

These elements react with halogens to form trihalides

$$2E_{(s)} + 3X_{2(g)} \longrightarrow 2EX_{3\,(s)}$$

(X = F, Cl, Br, I)

Important Trends and Anomalous Properties of Boron

- The tri-chlorides, bromides and iodides of all these elements being covalent in nature are hydrolysed in water.

- species like tetrahedral $[M(OH)_4]^-$ and octahedral $[M(H_2O)_6]^{3+}$, except in boron, exist in aqueous medium.

- The monomeric trihalides, being electron deficient, are strong Lewis acids. Boron trifluoride easily reacts with Lewis bases such as NH_3 to complete octet around boron.

$$F_3B + :NH_3 \longrightarrow F_3B \longleftarrow NH_3$$

- It is due to the absence of d orbitals that the maximum covalence of B is 4. since the d orbitals are available with Al and other elements, the maximum covalence can be expected beyond 4.

Some Important compounds of Boron.

1) **Borax** - It is the most important compound of boron. It is a white crystalline solid of formula $Na_2B_4O_7 \cdot 10H_2O$.

- While containing the tetranuclear units $[B_4O_5(OH)_4]^{2-}$, It correct formula becomes $Na_2[B_4O_5(OH_4)] \cdot 8H_2O$.

- Borax dissolves in water to give an alkaline solution. on heating, borax first loses water molecules and swells up and on further heating it turns into a transparent liquid.

- The transparent liquid which gets solified into a glass like material known as 'Borax Bead'

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

2) orthoboric acid -

orthoboric acid, H_3BO_3 is a white crystalline solid, with soapy touch. It is sparingly soluble in water but highly soluble in hot water. It can be prepared by acidifying an aqueous solution of borax.

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

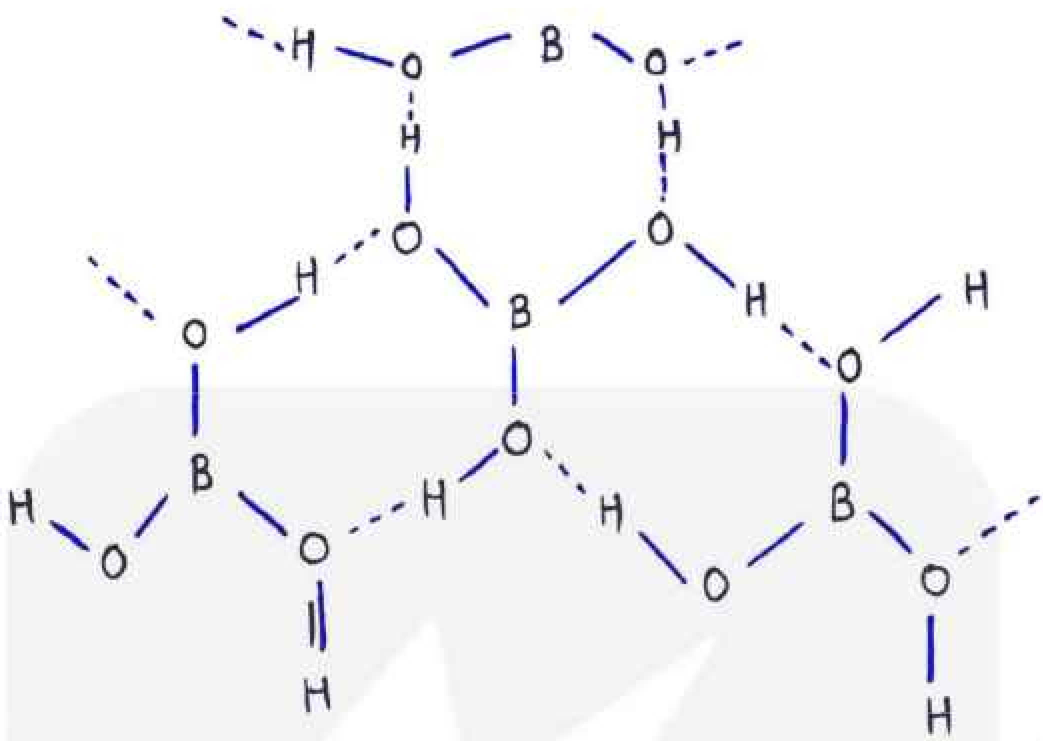


Fig: structure of boric acid; the dotted lines represent hydrogen bonds.

- It has a layer structure in which planer BO_3 units are joined by hydrogen bonds.

- Boric acid is a weak monobasic acid. It is used as a preservative for milk and food stuffs.

- It is also use in the manufacture of enamels and glaze in pottery.

3) Diborane , B_2H_6

- The simplest boron hydride known, is diborane. It is prepared by treating boron trifluoride with $LiAlH_4$ in diethyl ether.

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

- 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.

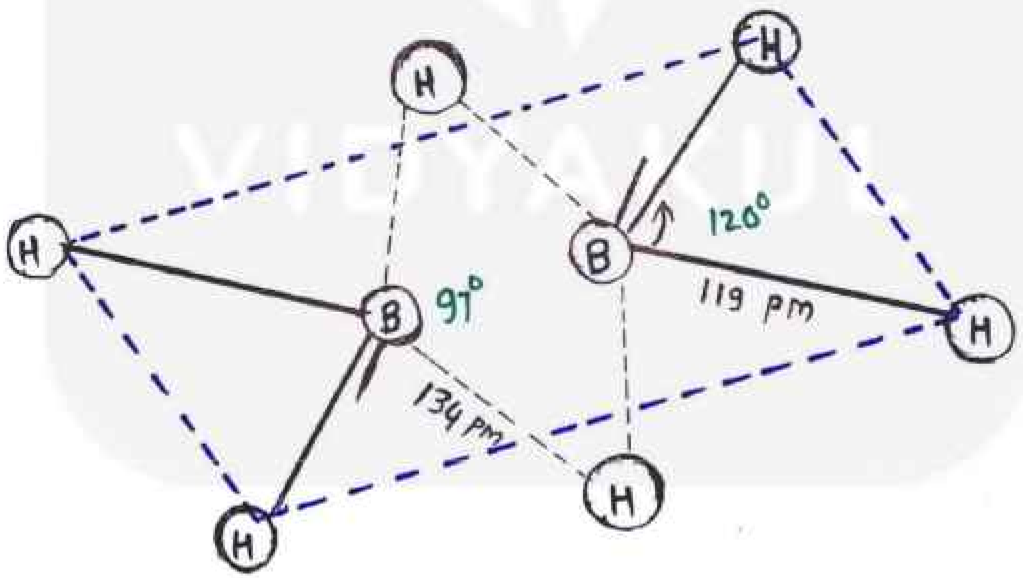
$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O;$$

$$\Delta_c H^{\ominus} = -1976 \text{ kJ mol}^{-1}$$

- Diborane is produced on an industrial scale by the reaction of BF_3 with sodium hydride.

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

- <u>structure of diborane, B_2H_6</u>



The four terminal hydrogen atoms and the two boron atoms lie in one plane, above and below plane, there are two bridging hydrogen atoms.

- The four terminals B - H bonds are regular two centre - two electron bonds while the two bridge (B-H-B) bonds are different and can be described in term of three-centre two electron bonds.

Group 14 Elements : The carbon Family

- The carbon family group 14 includes carbon (C), silicon (Si), Germanium (Ge), tin (Sn) and lead (Pb)

- General electronic configuration of carbon family is ns^2np^2

carbon - carbon is the seventeenth most abundant element by weight in the earth's crust.

- It is available as coal, graphite and diamond. In combined state it is present in metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air

- Naturally occuring carbon contains two stable isotopes ^{12}C and ^{13}C and third isotope ^{14}C. ^{14}C is a radioactive isotope with half life and is used for radiocarbon dating.

- silicon is the second most abundant element on the earth's crust. silicon is a very important component of ceramics, glass and cement.

- Germanium exists only in traces. Tin occurs mainly as cassiternite, SnO_2 and lead as galena, PbS.

Covalent radius - covalent radius expected to increase from C to Si. from Si to Pb small increase is found.

- Due to the addition of a new energy shell in each succeeding element. The increase in covalent radii from Si to Pb is small due to ineffective shielding of the valence electron by the intervening d and f orbitals.

Ionization Enthalpy - The first ionization enthalpies of group 14 elements are higher than those of the corresponding group 13 elements. Because effective nuclear charge increases and the size of the atom becomes smaller.

- first ionization enthalpy decreases on moving down the group from carbon to Tin. The decrease is very sharp from carbon to silicon while there is slight increase in the first ionization enthalpy of lead as compared to that of tin.

Electronegativity -

- Due to small size, the elements of this group are slightly more electronegative than the group 13 elements.
- The electronegativity values for elements from Si to Pb are almost same.

Physical properties -

i) All the elements of group 14 are solids.

ii) They are less metallic than group 13 elements.

iii) melting points and Boiling points of group 14 elements are generally high.

chemical properties -

i) carbon and silicon shows +4 oxidation state.

ii) Germanium form stable compounds in +4 state and only few compounds in +2 state.

iii) Tin forms compounds in both oxidation state. lead forms compounds in +2 state are stable and in +4 state are strong oxidising agents.

i) Reactivity towards oxygen -

All members when heated in oxygen form oxides. There are mainly two types of oxides i.e., monoxide and dioxide, of formula MO and MO_2 respectively.

ii) Reactivity towards water -

carbon, silicon and germanium are not affected by water. Tin decomposes steam to form dioxide and hydrogen gas.

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

Lead is unaffected by water, probably because of a protective oxide film formation.

iii) Reactivity towards halogen -

These elements can form halides of formula MX_2 and MX_4, (X = F, Cl, Br, I)

- Except carbon, all other members react directly with halogen under suitable condition to make halides.
- most of the MX_4 are covalent in nature.
- The central metal atom in these halides undergoes sp^3 hybridisation and the molecule is tetrahedral in shape. Exceptions are SnF_4 and PbF_4, which are ionic in nature.

Important Trends And Anomalous Behaviour of Carbon

carbon, differs from the rest of the member of its family. The main reasons for the anomalous behaviour are as follows:

i) Exceptionally small atomic and ionic size.

ii) Higher ionization enthalpy

iii) Absence of d-orbitals in the valence shell

iv) Higher electronegativity.

- since carbon has only s and p-orbitals, it can accommodate only four pairs of electrons; other member can expand their covalence due to the presence of d-orbitals.

- carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation. Down the group property to show catenation decreases.

C > Si > Ge > Sn > Pb.

- carbon can form $p\pi - p\pi$ mutiple bonds with itself and other atoms having small size and high electronegativity.

Heavier elements do not form $p\pi - p\pi$ bonds because their atomic orbitals are too large and diffuse to have effective overlapping.

Allotropes of Carbon.

carbon exhibits many allotropic forms; both crystalline as well as amorphous. Diamond and graphite are two well known crystalline forms of carbon. Third form of carbon known as the Fullerenes.

Diamond - In diamond each carbon atom undergoes sp^3 hybridisation.

- Each carbon atom is tetrahedrally linked to four other carbon atoms. The C-C bond length is 154 pm.

- The structure extend in space and produces a rigid three-dimensional network of carbon atoms.

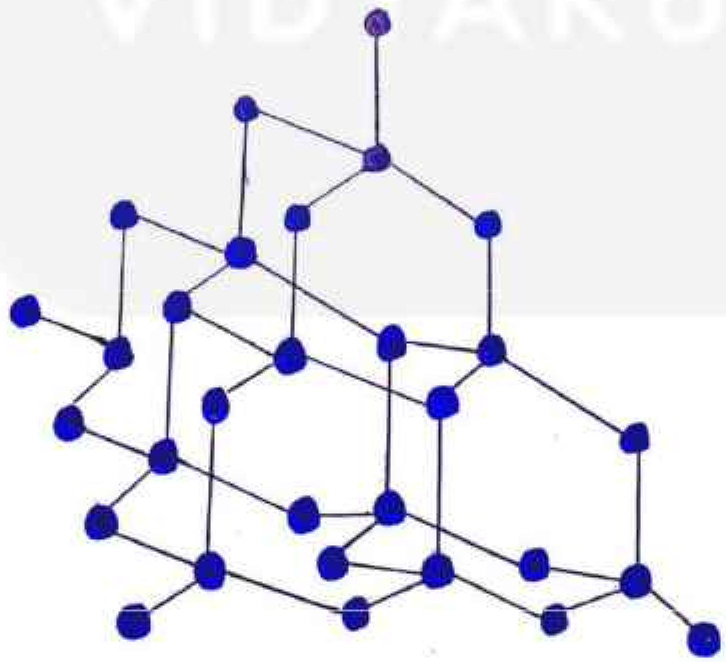


Fig : structure of Diamond.

- Diamond is the hardest substance on earth.
- It is use an abrasive for sharpening hard tools in making dyes and manufacture of tungsten filaments.

Graphite – In graphite, carbon is sp^2 hybridized. Graphite has a two-dimensional sheet like structure; consisting of a number of hexagonal rings fused together.

Layers are held by van der waals forces and distance between two layers is 340 pm.

- Graphite conducts electricity along the sheet. It is very soft and slippery.
- Used as a dry lubricant in machines running at high temperature, where oil cannot be use as a lubricant.

Fullerenes -

- Fullerenes are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon.

- Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds.

- Fullerenes are cage like molecules. C_{60} molecules has a shape like soccer ball and called Buckminsterfullerenes. It is the most stable.

- It contains 20 six-membraned rings and 12 five-membraned rings.

- six - membrane rings are fused to both the other six - membraned rings and five - mem -brandd rings but the five - membraned rings are connected to only six - membraned rings.

- All the carbon atoms are equal and they undergoes sp^2 - hybridization.

- Fullerenes being covalent are soluble in organic solvents. It also forms platinum complexes.

Amorphous allotropic forms of carbon coke :

It is a greyish black hard solid and is obtained by destructive distillation.

Wood charcoal : It is obtained by strong heating of wood in a limited supply of air.

Animal charcoal : It is obtained by the destructive distillation of bones.

Uses of carbon -

- Graphite fibre are used for making superior sports goods such as tennis and badminton rackets, fishing rods.
- Being good conductors graphite is used for making electrodes for batteries and industrial electrolysis.
- carbon black is used as black pigment in black ink and as filler in automobile tyres
- coke is extensively used as reducing agent in metallurgy.
- Diamond is a precious stone and used in Jewellery.
- Being highly porous, activated charcoal is used for absorbing poisonous gases in gas masks. It is used to decolourize sugar.

Some Important Compounds of Carbon and Silicon.

Carbon monoxide - It is prepared by direct oxidation of C in limited supply of oxygen.

$$2C + O_2 \longrightarrow 2CO$$

- Carbon monoxide is a colourless and odourless gas. and it is almost insoluble in water.

- It is powerful reducing agent and reduces almost all metal oxides except alkali and alkaline earth metals. oxides.

- In CO molecule, there are one(σ) sigma and two π bonds between C and oxygen.

  $:C \equiv O:$

- It is highly porous in nature. It forms a complex with haemoglobin which is about 300 times more stable than the oxygen-haemoglobin complex.

Carbon dioxide - It is prepared by complete combustion of carbon and carbon containing fuels in.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

$$CaCO_3 \longrightarrow CaO + CO_2$$

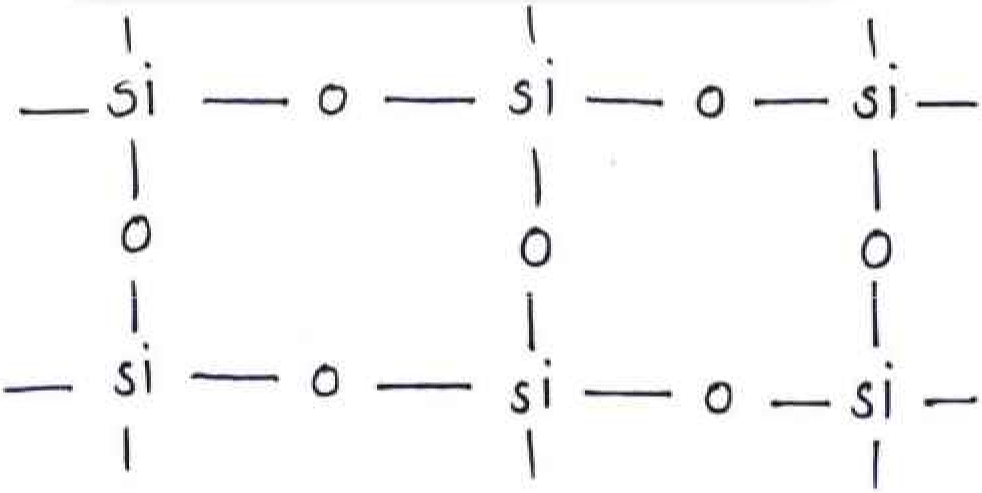
- It is a colourless and odourless gas. It is slightly soluble in water, when CO_2 dissolve in water only some molecules react with water to form carbonic acid.
- It is not poisonous like CO.

silicon dioxide - (SiO_2)

- silicon dioxide, commonly known as silica, occurs in various crystallographic forms.

ex :- Quartz, cristobalite and thermite.

- silicon dioxide is a covalent three-dimensional network solid. Each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms. Each oxygen atom in turn covalently bonded to another silicon atoms.



- In normal form silica is very less reactive.
- At elevated temperature it does not reacts with halogens, dihydrogen and most of the acids and metals. But it reacts with HF and NaOH

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

- Quartz is extensively used as a piezoelectric material.
- silica gel is used as adsorben in the chromatography.
- An Amorphous form of silica, kieselghur is used in filtration plants.