# Compounds of Carbon

Following are the important compounds of carbon which are worth studying.

1. Percarbonic Acids and Percarbonates.
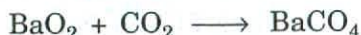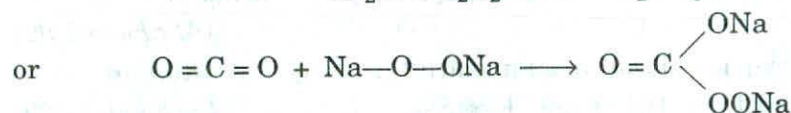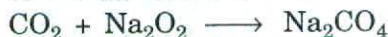
Carbon forms two percarbonic acids which are : (*i*) *Permonocarbonic acid*, H_2CO_4, and (*ii*) *Perdicarbonic acid*, $H_2C_2O_6$. These acids can be regarded as being derived from H_2O_2 by replacing its H-atom by COOH group. Thus :

O—H	O—H	O—COOH
O—H	O—COOH	O—COOH
Hydrogen per-oxide (H_2O_2)	Permonocarbonic acid (H_2CO_4)	Perdicarbonic acid ($H_2C_2O_6$)
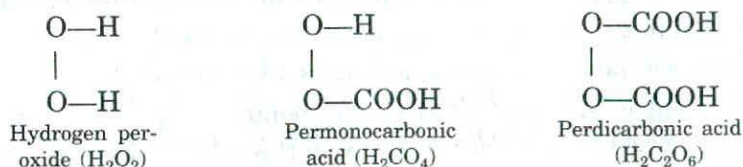
Permonocarbonic acid, H_2CO_4 is not known in the free state but perdicarbonic acid, $H_2C_2O_6$, is formed as an unstable solution by the action of phosphoric acid on an etheral solution of potassium salts of $H_2C_2O_6$ ($K_2C_2O_6$). Salts derived from these acids are called permonocarbonates and perdicorbonates and in general these are called percarbonates. These salts are of three different types given below :

(A) Permonocarbonates. These are the salts of H_2CO_4. Na_2CO_4, K_2CO_4 and $BaCO_4$ are the important examples of such type of salts.

Preparation. Na_2CO_4 and $BaCO_4$ are formed when CO_2 is absorbed by Na_2O_2 or BaO_2 (*Wolffenstein and Peltner, 1908*).

$$CO_2 + Na_2O_2 \longrightarrow Na_2CO_4$$

or $$O = C = O + Na—O—ONa \longrightarrow O = C \big\langle \begin{smallmatrix} ONa \\ OONa \end{smallmatrix}$$

$$BaO_2 + CO_2 \longrightarrow BaCO_4$$

Na_2CO_4 is also obtained by the reaction of Na_2O_2 with phosgene, $COCl_2$.

$$2Na_2O_2 + COCl_2 \longrightarrow Na_2CO_4 + 2NaCl + \tfrac{1}{2}O_2$$

A disodium per monocarbonate having the formula, $Na_2CO_4 . \tfrac{1}{2}H_2O$ has been obtained by passing CO_2 into Na_2O_2 mixed with ice. Sodium permonocarbonate of the formula, $NaHCO_4 . H_2O$ and having the structure shown

$$Na—O—C \big\langle \begin{smallmatrix} O—O—H \\ O \end{smallmatrix}$$
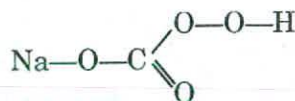
Structure of $NaHCO_4$

in the margin has been obtained by the action of CO_2 on sodium hydroperoxide perhydrate, $NaOOH.\frac{1}{2}H_2O_2$.
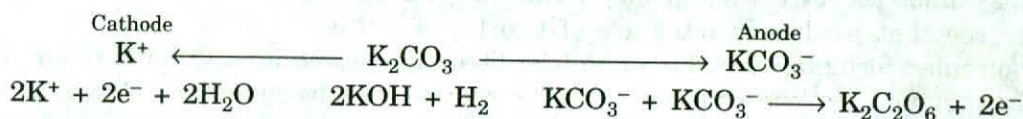
Properties. Freshly prepared permonocarbonates contain water of crystallisation. These are soluble in H_2O and on hydrolysis they give H_2O_2. They liberate I_2 from a solution of KI.

$$O = C \begin{cases} O.ONa \\ O.Na \end{cases}$$

Structure of Na_2CO_4
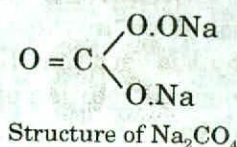
Structure. Na_2CO_4 has the structure shown in the margin.

(B) Perdicarbonates. These are derived from $H_2C_2O_6$. These are best represented by potassium and sodium salts whose formulae are $K_2C_2O_6$ and $Na_2C_2O_6$ respectively.

Preparation. (i) *By anodic oxidation.* $K_2C_2O_6$ is obtained by the electrolysis of a cold saturated solution of K_2CO_3 or $KHCO_3$ at $-12°C$ using a platinum anode enclosed in a porous cell, when a bluish-white amorphous ppt. of $K_2C_2O_6$ is deposited on the anode.
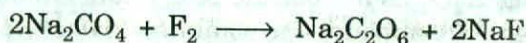
$$\overset{\text{Cathode}}{K^+} \longleftarrow \quad K_2CO_3 \quad \longrightarrow \overset{\text{Anode}}{KCO_3^-}$$

$$2K^+ + 2e^- + 2H_2O \quad 2KOH + H_2 \quad KCO_3^- + KCO_3^- \longrightarrow K_2C_2O_6 + 2e^-$$

$Na_2C_2O_6$ is also obtained in a similar way.

(ii) Wolffenstein and Peltner in 1908 obtained $Na_2C_2O_6$ by the action of CO_2 on Na_2O_2 and ice at $0°C$.

$$Na_2O_2 + 2CO_2 \longrightarrow Na_2C_2O_6$$
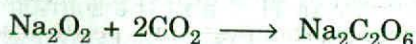
(iii) It is also obtained by passing F_2 in a conc. solution of Na_2CO_3 at $-13°C$ to $-16°C$.
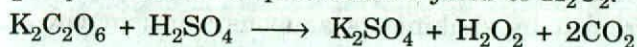
$$2Na_2CO_4 + F_2 \longrightarrow Na_2C_2O_6 + 2NaF$$

Properties. (i) $K_2C_2O_6$ is a hygroscopic, skyblue powder which, on drying, loses its colour and becomes white.

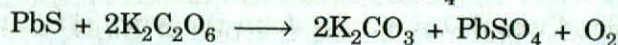(ii) $K_2C_2O_6$ is unstable and decomposes slowly at room temperature and radily on heating.

$$2K_2C_2O_6 \longrightarrow 2K_2CO_3 + 2CO_2 + O_2$$

(iii) With dil. H_2SO_4 we obtain a quantitative yield of H_2O_2.

$$K_2C_2O_6 + H_2SO_4 \longrightarrow K_2SO_4 + H_2O_2 + 2CO_2$$

(iv) It bleaches indigo and oxidises PbS to $PbSO_4$

$$PbS + 2K_2C_2O_6 \longrightarrow 2K_2CO_3 + PbSO_4 + O_2$$

(v) It reduces $KMnO_4$, PbO_2 and MnO_2

$$2K_2C_2O_6 + 8H_2SO_4 + 2KMnO_4 \longrightarrow 2MnSO_4 + 6K_2SO_4 + 8H_2O$$
$$+ 10CO_2 + 5O_2$$

$$PbO_2 + K_2C_2O_6 \longrightarrow K_2CO_3 + PbCO_3 + O_2$$
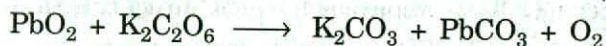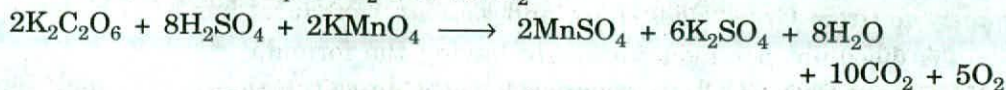
(vi) It liberates I_2 quantitatively in cold from a solution of KI.

$$K_2C_2O_6 + 2KI \longrightarrow 2K_2CO_3 + I_2$$

(vii) Its solution in ice-cold H_2O is also fairly stable, but on long standing or on raising the temperature, it is hydrolysed to $KHCO_3$ and H_2O_2

$$K_2C_2O_6 + 2H_2O \longrightarrow 2KHCO_3 + H_2O_2$$

Structure. The structure of $K_2C_2O_6$ or $Na_2O_2O_6$ is as given in the margin. This structure is confirmed by the fact that $K_2C_2O_6$ or $Na_2O_2O_6$ liberates I_2 from neutral solution of KI which is equivalent to its active oxygen.
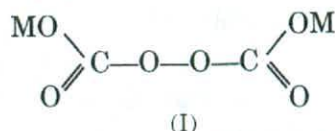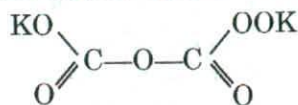
(I)

Symmetrical structure of $M_2C_2O_6$ (M = Na or K)

In 1908 Wolffenstein and Peltner passed CO_2 into an ice cold solution of K_2O_2 in absolute alcohol and obtained a salt. Partington and Fathallah (1934) have shown that the salt formed in the above reaction is isomeric with the bluish potassium perdicarbonate discussed above and represented by structure (I). The new compound liberates only 50% of the theoretical amount of iodine from the neutral solution of KI and loses only one-half of its active oxygen as oxygen gas. Thus it has an unsymmetrical structure given in the margin. Thus we see that perdicarbonates are of two types whose molecular formulae are the same (*i.e.* these are isomeric with each other) but their structures are different. One is represented by structure (I) while the other, by structure (II).

(II)

Unsymmetrical structure of $K_2C_2O_6$

(C) **Perhydrates of simple carbonates.** These compounds contain H_2O_2 of crystallization. Some permonocarbonates when freshly prepared contain water of crystallisation. They are soluble in H_2O and the solution obtained behaves as if it is a mixture of simple carbonate (*i.e.* CO_3^{2-}) containing water of crystallisation and H_2O_2. Thus these salts may be regarded as simple perhydrates of simple carbonates containing H_2O_2 as a molecule of crystallisation. The most important compound of this class of compounds is sodium carbonate perhydrate having the composition, $Na_2CO_3.H_2O_2.\frac{1}{2}H_2O$. This compound is obtained as a ppt. by the action of H_2O_2 on Na_2CO_3 and subsequent addition of alcohol. It is stabilised by the addition of sodium silicate (water glass) or magnesium silicate. This compound is used in washing powders, etc.

The formula of this compound, $Na_2CO_3.H_2O_2.\frac{1}{2}H_2O$, is supported by the fact that it slowly liberates iodine from an aqueous solution of KI and that CO_2 can be extracted from it by shaking its aqueous solution with ether.

2. Carbonyl Chloride or Phosgene, $COCl_2$.

This compound was discovered by John Davy in 1811. Since it is produced by the direct combination of CO with Cl_2 in presence of bright sunlight, the name *phosgene* (from Greek *phos*, light and *gennao*, I produce) has been given to this compound.

Preparation. $COCl_2$ is prepared (*i*) by the direct combination of equal volumes of CO and Cl_2 in the presence of bright sunlight

$$CO + Cl_2 \longrightarrow COCl_2$$

(*ii*) *in the laboratory* by dropping 80% fuming H_2SO_4 into boiling CCl_4 contained in a flask provided with a reflex condenser and dropping funnel. The

resulting gas is passed through cone H_2SO_4 and condensed in a U-tube kept in freezing mixture.

$$CCl_4 + 2SO_3 \longrightarrow COCl_2 + S_2Cl_2O_5$$

Disulphuryl
chloride
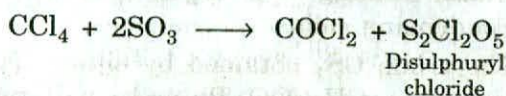
(*iii*) by the oxidation of chloroform ($CHCl_3$) with $K_2Cr_2O_7$ and conc. H_2SO_4.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

$$3CHCl_3 + 3O \longrightarrow 2COCl_2 + H_2O + Cl_2$$

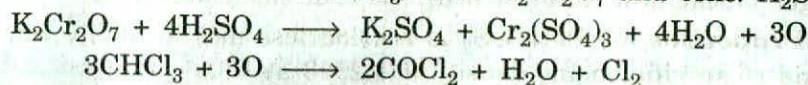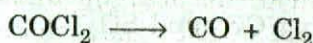**Properties.** (*i*) It is a colourless gas with a penetrating and suffocating odour and is highly poisonous.

(*ii*) It is very soluble in benzene and toluene.

(*iii*) It can be condensed to a liquid which boils at 8.2°C.

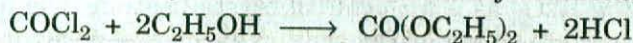(*iv*) *Action of heat.* It is decomposed by heat and the decomposition is complete at 800°C.

$$COCl_2 \longrightarrow CO + Cl_2$$

(*v*) *Hydrolysis.* It does not fume in moist air but is readily hydrolysed by water, giving CO_2 and HCl.

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl$$

(*vi*) *Action of NH_3 and C_2H_5OH.* When it is passed into a solution of NH_3 in toluene, urea, $NH_2.CO.NH_2$ is formed.

$$COCl_2 + 4NH_3 \longrightarrow NH_2.CO.NH_2 + 2NH_4Cl$$

urea

With alcohol it forms ethylchloroformate or diethyl carbonate.

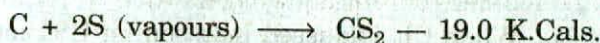$$COCl_2 + 2C_2H_5OH \longrightarrow CO(OC_2H_5)_2 + 2HCl$$

Uses. It is used : (*i*) in dyestuff industry (*ii*) for synthetic work in laboratories. (*iii*) in warfare.

3. Carbon Disulphide, CS_2.

This compound was discovered by W. A. Lampadins in 1796.

Manufacture. CS_2 is manufactured by passing sulphur vapours over red hot charcoal or coke.

$$C + 2S \text{ (vapours)} \longrightarrow CS_2 - 19.0 \text{ K.Cals.}$$

Following two processes are used for the manufacture of CS_2.

(*i*) *Zahn's process.* In this process a vertical cast iron retort set in a furnace is filled with charcoal and sulphur kept in the fused state by the waste heat of furnace is slowly fed in through a tube. The temperature is kept between 800–900°C. The sulphur volatalises and the vapour passes over red hot charcoal forming CS_2. CS_2 so formed escapes at the top of the furnace and is condensed in long condensing coils.

(*ii*) *Taylor's electrical process.* In this process a cylindrical furnace 40 feet high and 16 feet in diameter is packed with coke or charcoal from the top. Separate hoppers are provided for adding fresh coke and sulphur. Heating is done with the help of an electric are struck between two carbon electrodes.

Sulphur is vapourised on the floor of the furnace; the vapour of sulphur passes through red hot charcoal forming CS_2. CS_2 so formed escapes at the top and is condensed in long condensing coils.

Purification. The crude CS_2 obtained by either of the above processes is purified by distillation over $(CH_3COO)_2Pb$ or by agitation with Hg until it no longer blackens it, after which it is redistilled over P_2O_5.

Properties. (*i*) Pure CS_2 is a colourless mobile highly refractory poisonous liquid of specific odour, density = 1.2923 at 0°C.

(*ii*) Boiling and freezing points are 46.25°C and –116°C respectively.

(*iii*) The commercial product possesses yellow colour and usually disagreeable and rancid odour due to the presence of sulphur and H_2S.

(*iv*) It is almost insoluble in H_2O but is completely miscible with absolute alcohol, ether, beuzene and essential oils.

(*v*) *Action of air.* The vapour of CS_2 is highly inflammable and catches fire when healed in air producing CO_2 and SO_2.

$$CS_2 + 3O_2 \longrightarrow CO_2 + 2SO_2$$

(*vi*) *Action of NO.* With NO, CS_2 forms an explosive mixture

$$2CS_2 + 10NO \longrightarrow 2CO + 4SO_2 + 5N_2$$
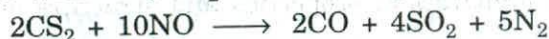
(*vii*) *Action of K.* When heated with K, CS_2 vapour gets decomposed

$$CS_2 + 4K \longrightarrow 2K_2S + C$$

(*viii*) *Action of slaked lime, Ca(OH)$_2$ and NaOH.* When CS_2 vapour is passed over slaked lime, a mixture of $CaCO_3$ and calcium thiocarbonate ($CaCS_3$) is produced.

$$3Ca(OH)_2 + 3CS_2 \longrightarrow CaCO_3 + 2CaCS_3 + 3H_2O$$

Similarly, with NaOH solution. CS_2 vapour gives a mixture of Na_2CO_3 and $NaCS_3$.

$$6NaOH + 3CS_2 \longrightarrow Na_2CO_3 + 2Na_2CS_3 + 3H_2O$$

(*ix*) *Action of basic sulphides.* CS_2 combines with basic sulphides to form thiocarbonates. For example :

$$Na_2S + CS_2 \longrightarrow Na_2CS_3$$
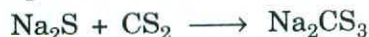
(*x*) *Action of Cl$_2$.* When Cl_2 is passed into boiling CS_2 containing a little of I_2, CCl_4 and S_2Cl_2 are formed.

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$
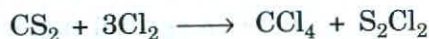
(*xi*) *Action of PCl$_5$.* When CS_2 is heated with PCl_5, thiocarbonyl chloride, $CSCl_2$ (analogous to $COCl_2$) is formed.

$$CS_2 + PCl_5 \longrightarrow CSCl_2 + PSCl_3$$

(*xii*) *Action of SO$_3$.* CS_2 reacts with SO_3 to form carbonyl sulphide, COS.

$$CS_2 + 3SO_3 \longrightarrow COS + 4SO_2$$

(*xiii*) *Action of H$_2$.* When a mixture of CS_2 and H_2 is passed over heated Ni at 450°C, H_2S is evolved.

$$CS_2 + 2H_2 \xrightarrow{\text{Ni (450°C)}} C + 2H_2S$$
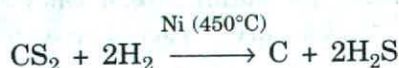
(*xiv*) *Action of Cu.* When CS_2 vapour is passed over red hot copper, CuS is formed.

$$CS_2 + 4Cu \ (red \ hot) \longrightarrow 2Cu_2S + C$$
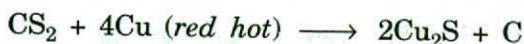
(*xv*) *Action of steam and* H_2S. When a mixture of CS_2 and steam (H_2O) or H_2S is passed over red hot copper, CH_4 is formed.

$$CS_2 + 2H_2O \ (steam) + 6Cu \ (red \ hot) \longrightarrow 2Cu_2S + 2CuO + CH_4$$
$$CS_2 + 2H_2S + 8Cu \ (red \ hot) \longrightarrow 4Cu_2S + CH_4$$
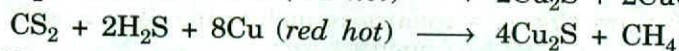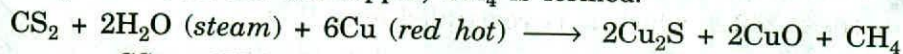
Uses. CS_2 is used (*i*) as a solvent for sulphur, white phosphorus, iodine, bromine, camphor, gums, resins, waxes, fats, oils etc. and also for S_2Cl_2 in cold vulcanization of rubbur. (*ii*) in the manufacture of artificial silk and CCl_2. (*iii*) to kill moths in furs and rats and mice in grain elevators. (*iv*) as an insecticide for curing the insect infected seeds and for killing ants.

University Questions

1. Give the preparation, properties and uses of carbon disulphide.

(Agra 86; Madras 86)

2. Discuss the preparation, properties and structure of peroxy compounds of carbon.   *(Meerut M.Sc. 82)*

3. Give methods of preparation, properties and uses of carbonyl chloride.

Carbides

What are Carbides ?

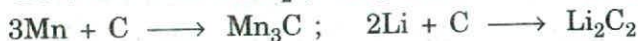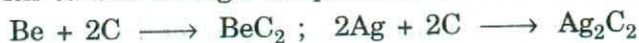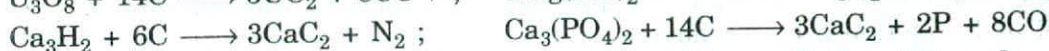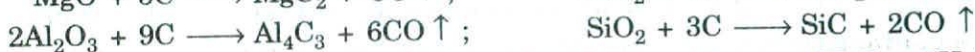The binary compounds of carbon with the elements which are more electropositive than carbon are called carbides. Thus this definition excludes the binary compounds of carbon with N, P, O, S and halogens.
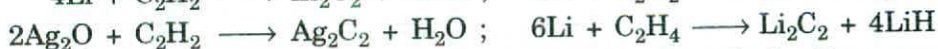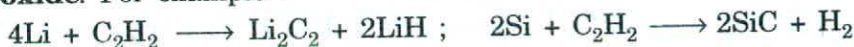
General Methods of Preparation.

1. By heating metal with carbon. Many metals like Be, Ag, Mn, Li, Ta, V etc. combine with carbon at high temperature to form carbides. For example :

$$Be + 2C \longrightarrow BeC_2 ; \quad 2Ag + 2C \longrightarrow Ag_2C_2$$
$$3Mn + C \longrightarrow Mn_3C ; \quad 2Li + C \longrightarrow Li_2C_2$$
$$3Fe + C \longrightarrow Fe_3C ; \quad 2Mn + C \longrightarrow Mn_3C$$

2. By heating oxides, hydroxides, nitrides, phosphates, sulphates etc. with carbon. For example :

$$MgO + 3C \longrightarrow MgC_2 + CO \uparrow ; \quad CeO_2 + 4C \longrightarrow CeC_2 + 2CO \uparrow$$
$$2Al_2O_3 + 9C \longrightarrow Al_4C_3 + 6CO \uparrow ; \quad SiO_2 + 3C \longrightarrow SiC + 2CO \uparrow$$
$$U_3O_8 + 14C \longrightarrow 3UC_2 + 8CO \uparrow ; \quad 2Mg(OH)_2 + 4C \longrightarrow 2MgC_2 + 2H_2O + O_2$$
$$Ca_3H_2 + 6C \longrightarrow 3CaC_2 + N_2 ; \quad Ca_3(PO_4)_2 + 14C \longrightarrow 3CaC_2 + 2P + 8CO$$
$$4AlPO_4 + 19C \longrightarrow Al_4C_3 + 4P + 16CO ; \quad BaSO_4 + 2C \longrightarrow BaC_2 + SO_2 + O_2$$

3. By passing acetylene (C_2H_2) or ethylene (C_2H_4) on heated element or its oxide. For example :

$$4Li + C_2H_2 \longrightarrow Li_2C_2 + 2LiH ; \quad 2Si + C_2H_2 \longrightarrow 2SiC + H_2$$
$$2Ag_2O + C_2H_2 \longrightarrow Ag_2C_2 + H_2O ; \quad 6Li + C_2H_4 \longrightarrow Li_2C_2 + 4LiH$$

4. By heating the metallic oxide or halide with CaC_2. For example :

$$MgO + CaC_2 \longrightarrow MgC_2 + CaO ; CuCl_2 + CaC_2 \longrightarrow CuC_2 + CaCl_2$$
$$MgF_2 + CaC_2 \longrightarrow MgC_2 + CaF_2$$

5. By passing CO over metal at high temperature.

$$2Li + 2CO \longrightarrow Li_2C_2 + O_2 ; \quad 6Al + 3CO \longrightarrow Al_4C_3 + Al_2O_3$$

6. By passing acetylene (C_2H_2) through ammoniacal solution of the metal salt.

$$2CuCl + 2NH_4OH + C_2H_2 \longrightarrow Cu_2C_2 + 2NH_4Cl + 2H_2O$$
$$2AgNO_3 + 2NH_4OH + C_2H_2 \longrightarrow Ag_2C_2 + 2NH_4NO_3 + 2H_2O$$

7. By heating metallic carbonate with carbon in presence of an oxidisable metal.

$$BaCO_3 + C + 3Mg \longrightarrow 3MgO + BaC_2$$
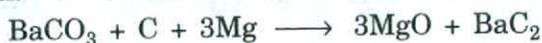
General Properties.

1. Physical state. Generally carbides are transparent crystalline solids. In the solid state they are non-conductors of electricity.

2. Colour. Carbides of alkali metals and of Ca, Sr and Ba are only colourless while most of the remaining carbides are coloured.

3. Softness and hardness. Alkali metal carbides are soft while others are usually hard. For example Be_2C and UC_2 are so hard that they can scratch glass and quartz.

4. Explosive nature. Carbides of U, Cu, A, An, Hg (*ic*) etc. are explosive substances, *e.g.* Hg (*ic*) carbide explodes on rapid heating. Uranium carbide emits sparks when struck and takes fire even when powdered quickly.

5. Reducing property. The carbides of alkali metals and of Ca, Sr and Ba are strong reducing agents, *e.g.* MgO and $MgCl_2$ are reduced to the metals on heating with CaC_2.

$$3MgO + CaC_2 \xrightarrow{\Delta} 3Mg + CaO + 2CO \uparrow$$

$$MgCl_2 + CaC_2 \xrightarrow{\Delta} Mg + CaCl_2 + 2C$$
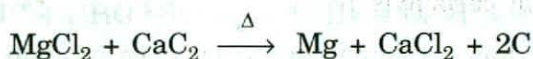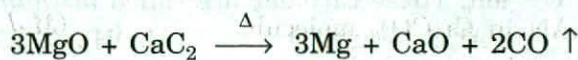
6. Hydrolysis. Ionic carbides can easily be hydrolysed by water or dil. acids with the formation of different types of hydrocarbons.
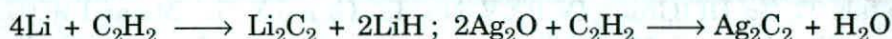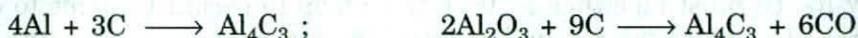
Classification of Carbides.

Carbides are classified into four types depending on the nature of bonding between carbon atoms and other elements. These four types are : (1) *Ionic or salt-like carbides* (2) *Interstitial or metallic carbides* (3) *Iron type or borderline carbides* (4) *Covalent carbides.*

Ionic Carbides

These carbides are given by the metals of groups IA, IIA and III A (except boron), coinage metals, Zn, Cd and some lanthanides.

Preparation.

These are obtained by heating the metal or its oxide with carbon, CO or a hydrocarbon like acetylene

$$2Be + C \longrightarrow Be_2C \; ; \qquad CaO + 3C \longrightarrow CaC_2 + CO$$

$$4Al + 3C \longrightarrow Al_4C_3 \; ; \qquad 2Al_2O_3 + 9C \longrightarrow Al_4C_3 + 6CO$$

$$2Li + 2CO \longrightarrow Li_2C_2 + O_2 \; ; \qquad 6Al + 3CO \longrightarrow Al_4C_3 + Al_2O_3$$

$$4Li + C_2H_2 \longrightarrow Li_2C_2 + 2LiH \; ; \; 2Ag_2O + C_2H_2 \longrightarrow Ag_2C_2 + H_2O$$

Properties.

(*i*) *Physical state.* These carbides form transparent colourless crystals with ionic lattices containing metal cations in the interstices between carbon anions.

(*ii*) *Conductance of electricity.* These are non-conductors of electricity.

(*iii*) *Hydrolysis.* These are easily hydrolysed by water or dil acids to give different hydrocarbons. Depending on the nature of the hydrocarbon formed during the hydrolysis of ionic carbides by water, these carbides can be classified into the following types :
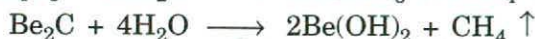
(*a*) *Acetylides.* These are the ionic carbides which give acetylene ($CH \equiv CH$) on hydrolysis. These carbides are, therefore, regarded as derivatives of acetylene and are called *acetylides*. These carbides are said to contain *carbide ion*, $(C \equiv C)^{2-}$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH \equiv CH$$

Some of the carbides like Cu_2C_2, Ag_2C_2 do not hydrolyse to form acetylene and are, therefore, not regarded as true acetylides.

Acetylides have a NaCl type crystal structure. However, in CaC_2 the shape of $(C \equiv C)^{2-}$ ion elongates the unit cell in one direction.

(*b*) *Methanides.* These are the ionic carbides which give methane (CH_4) on hydrolysis. These carbides are regarded as derivatives of methane and hence are said to contain C^{4-} ion. These carbides are called *methanides*.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4 \uparrow$$
$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4 \uparrow$$

Mn_3C probably has a related character, since its hydrolysis also gives CH_4.

$$Mn_3C + 6H_2O \longrightarrow 3Mn(OH)_2 + CH_4 + H_2$$

(*c*) *Allylides.* These are the ionic carbide, which give allylene ($H_2C = C = CH_2$) on hydrolysis. These carbides are regarded as derivatives of allylene and hence are said to contain C_3^{4-} group.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + C_3H_4$$

(*d*) *Mixed carbides.* A few carbides like those of Th and U of the formula MC_2 give, on hydrolysis, a mixture of several hydrocarbons including acetylene, olefins and H_2. These carbides are related in structure to intermetallic compounds.

Structure. The ionic carbides posses ionic lattice. in which the metallic cations are packed into the cavities between carbon anions *viz.* C^{-4}, C_2^{2-} and C_3^{4-}

Interstitial Carbides

These carbides are also called *refractory carbides*. These carbides are formed by those transition metals whose atomic radii (metallic radii for coordination number 12) are generally greater than 1.3A° ($R_M > 1.3A°$), since the radius ratio namely R_C/R_M must be either 1 : 0.41 or 1 : 0.59 to permit C-atoms to enter into the octahedral holes (also called cavities, interstices or interstitial positions) of the cubic close packing of the metallic lattice without distorting it. The radius of the metals Ti, Zr, Hf (Group IV B); V, Nb. Ta (Group V B) : Mo and W (Group VI B) is greater than 1.3 A° and hence these metals give the interstitial carbides which are of two types *viz.* MC type (M = Ti, Zr, Hf, V, Nb, Ta, Mo, W) and MC_2 type (M = V, Mo, W).

Preparation.

Interstitial carbides are prepared :

(i) by direct combination of the metal with carbon. In this method powdered metal is heated with powdered carbon at high temperature. Carbides obtained by this method are purified and made compact by sintering them in vacuum or in an atmosphere of inert gases.

(ii) by reducing the metallic oxide with carbon in an electric furnace at about 2000°C. This method has been used for the preparation of TiC, ZrC, HfC, VC, NbC, TaC, WC.

$$TiO_2 + 3C \longrightarrow TiC + 2CO$$
$$WO_3 + 4C \longrightarrow WC + 3CO$$
$$MoO_3 + 4C \longrightarrow MoC + 3CO$$

(iii) by heating the metal in an atmosphere of CH_4 at different temperatures. HfC, MoC, TaC. WC etc. carbides have been prepared by this method, *e.g.*

$$Hf + CH_4 \longrightarrow HfC + 2H_2$$
$$Mo + CH_4 \longrightarrow MoC + 2H_2$$

Properties.

(i) The melting points of these carbides are very high. For example the melting points of TaC and ZrC are 3900° and 3800°C respectively.

(ii) These are chemically inert, and extremely hard like diamond. For example WC is used for cutting tools on account of its hardness. The hardness on Moh's scale is between 9 and 10.

(iii) The crystal lattice of these carbides is a close-packed type with C-atoms occupying the octahedral holes in the metal lattice. Presence of C-atoms, therefore, does not affect the electrical conductivity of the metal. Thus these carbides possess metallic lustre and high electrical conductivity which increases at lower temperature and may become infinite at absolute zero.

(iv) These are weakly paramagnetic which is characteristic of the presence of metal lattice in their crystal structure.

(v) They are attacked by strong oxidising agents at red heat.

(vi) Carbides of Mo and W are somewhat more reactive than the metals from which they are derived but other carbides are less reactive than the parent metals.

Borderline Carbides

Fe, Mn, Co, Ni and Cr have atomic radii less than 1.3 A° (Mn is an exception) and hence octahedral holes in the metallic lattices of these metals are too small to accommodate C-atoms in them without producing a great deal of distortion in the metallic lattice (or metal structure). Here the metallic lattice is distorted and these carbides are intermediate in properties between the ionic and interstitial carbides but their radius ratio namely R_C/R_M has been found to be equal to 0.60–0.61 which places these carbides closer to the interstitial carbides.

These carbides are relatively less stable and liberate a mixture of hydrocarbons and H_2 on hydrolysis with H_2O or acids.

In these carbides C-atoms are located inside the trigonal prisms formed by metal atoms. The metal lattice is distorted and long chains of C-atoms are running through distorted metal structures. C–C distance is almost equal to 1.65A°

Covalent Carbides

The only covalent carbides are those of silicon and boron (SiC and B_4C).

Preparation.

SiC and B_4C are prepared .by reducing their oxides with carbon in an electric furnace.

$$SiO_2 + 3C \longrightarrow SiC + 2CO \uparrow$$
$$2B_2O_3 + 7C \longrightarrow B_4C + 6CO \uparrow$$
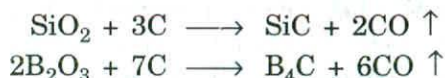
Properties.

These are not attacked by H_2O, dil. and conc. acids. These are extremely hard and decompose at high temperatures. Because of their hardness they are used for cutting and as abrasives.

Silicon carbide or Carborundum , SiC

Preparation.

It is prepared by heating a mixture of coke and SiO_2 in an electric furnace at 2000°C by passing acetylene on heated silicon.

$$SiO_2 + 3C \longrightarrow SiC + 2CO \uparrow$$
$$2Si + C_2H_2 \longrightarrow 2SiC + H_2 \uparrow$$
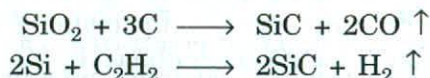
Manufacture.

SiC is manufactured by Acheson's process. In this process a mixture of sand (54%), coke (34%), sawdust (10%) and salt (2%) is heated in an electric furnace made of fire bricks to 1550–2200°C. The bed of the furnace and the end walls of it are permanent while the side walls are built up with the charge and are pulled down after the completion of the process to take out the product. It is provided at each end with carbon electrodes consisting of sixty rods of carbon. A heavy current is passed for 36 hours, whereby a high temperature is rapidly reached. At this high temperature, the following reaction occurs resulting in the formation of SiC.

$$SiO_2 + 3C \longrightarrow SiC + 2CO \uparrow$$

For about two hours in the beginning, the emf gradually decreases from 165 volts to 125 volts and the current increases from 1700 amperes to 6000 amperes due to the gradual decrease in resistance. These conditions persist for the remaining period of time. At the end of the operation, the side walls are pulled down and the dark coloured mass of black crystals of SiC is crushed and washed successively with H_2SO_4 and NaOH solution to remove the impurities. It is finally dried in kilns and graded into various portions according to the size of the particles.

The salt acts as a flux while saw dust increases the porosity of the charge which enables a continuous escape of CO that burns at the top of the charge.

Properties.

It is colourless when pure. The commercial sample is yellow, green or blue. It is nearly as hard as diamond and does not decompose below 2200°C. Chemically it is extremely inert and even at high temperatures it is not attacked even by HF, HCl, O_2 or S. Even a mixture of fuming HNO_3 and HF has no action on it. It is decomposed by fused NaOH in presence of O_2.

$$SiC + 4NaOH + 2O_2 \longrightarrow Na_2CO_3 + Na_2SiO_3 + 2H_2O$$
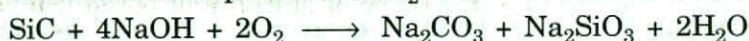
Uses.

(i) It is used as an abrasive for cutting and grinding glasses. (ii) It has a very high m.pt. and is, therefore, used in furnace-lining. (iii) On account of its refractory nature and high heat conductivity, it is used for making crucibles used for melting metals. (iv) It is also used as carbon rods in resistant heaters. (v) It is also used for making wheels, hones, wheatstones by mixing SiC with moistened china clay and felspar, moulding under pressure and firing the article in a kiln. (vi) It is also used as a de-oxidant in metallurgy and as resistor for electrical furnaces.

Structure.

SiC exists in three forms which are related to another as diamond, zinc blende and wurtzite. These forms are different combinations of "layers" corresponding to zinc blende and wurtzite structures. These three forms are : (i) *Carborundum I* represented as *aaa bb* (ii) *Carborundum II* represented as *a a a b b b* (iii) *Carborundum III* represented as *aa bb*. Here *a* a zinc blende layer and *b* is a wurtzite layer.

The lattice of SiC consists of C-atoms at points corresponding to those occupied by atoms in a close-packed face-centred cubic or hexagonal structure, with Si-atoms at half the points corresponding to the positions of the tetrahedral holes. This type of structure of SiC has been confirmed by X-ray studies.

Uses of Carbides

(i) Many metal carbides have been used as reducing agents in metallurgical and electro-thermal process.

(ii) In general, carbides are very hard and used as efficient abrasives, drilling tools and cutting tools.

(iii) Carbides can withstand high temperature and hence are used widely in furnace lining.

(iv) Calcium carbide, CaC_2 is used : (a) in the manufacture of calcium cyanamide, $CaCN_2$ which is employed as a nitrogenous fertiliser and as a source of NH_3. (b) in the preparation of acetylene which is employed in oxy-acetylene blow pipes for welding and illuminating purposes and for the manufacture of a large number of organic compounds like acetaldehyde, acetic acid etc. (c) as a reducing agent.

(v) Boron carbide, B_4O is used (a) for cutting diamonds, since it is the hardest abrasive ever made artificially. It is a better abrasive than carborundum, SiC, (b) for drilling holes in rockets, (c) for making electrodes for electric furnaces, (d) for making lamp filaments, (e) as a shield against radiation.

(vi) Aluminium carbide, Al_4C_2 is used for the preparation of methane.

(vii) Tungsten carbide, WC is used for the manufacture of high speed tools.

(viii) ZrC is used (a) as a component of cemented hard metal cutting tools, (b) as an electrode material, for refractory crucibles and as incandascent filament, (c) as a coating (1–2 mm thick) to delay the release of fission products from uranium carbide fuel elements.
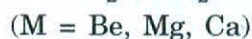
Questions with Answers

Q.1 Classify the following ionic carbides as methanides, acetylides and allylides : Be_2C, Al_4C_3, BeC_2, MgC_2, CaC_2, $Al_2(C_2)_3$ and Mg_2C_3.

Ans : Methanides : Be_2C and Al_4C_3 are called methanides, since they contain C^{4-} ion and give mathane (CH_4) on hydrolysis.

$$Be_2C + 4H_2O \longrightarrow 2Be\,(OH)_2 + CH_4$$
$$Al_4C_3 + 12H_2O \longrightarrow 4Al\,(OH)_3 + 3CH_4$$
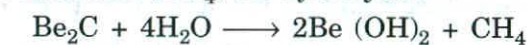
Acetylides : BeC_2, MgC_2, CaC_2 and $Al_2\,(C_2)_3$ are called acetylides, since these contain acetylide ion (C_2^{2-}) and give acetylence ($H - C \equiv C - H$ or C_2H_2) on hydrolysis.

$$MC_2 + 2H_2O \longrightarrow M(OH)_2 + C_2H_2$$
(M = Be, Mg, Ca)
$$Al_2(C_2)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3C_2H_2$$

Allylides : Mg_2C_3 is called magnesium allylide, since it contains allylide ion (C_3^{4-}) and gives alllyene ($CH_3 - C \equiv CH$ or C_3H_4) on hydrolysis.
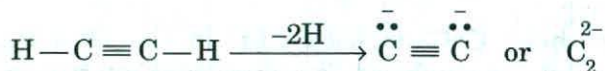
$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg\,(OH)_2 + C_3H_4$$

Q.2 Give the name of the anion present in Be_2C, Al_4C_3, MC_2 (M = Be, Mg, Ca), $Al_2(C_3)_3$ and Mg_2C_3 and give their structure.
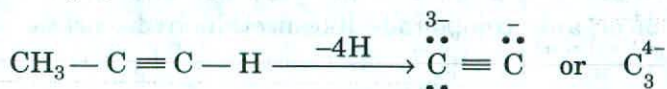
Ans : Be_2C and Al_4C_3 contain C^{4-} ion which is derived from methane molecule (CH_4)

$$CH_4 \xrightarrow{\;-4H\;} \overset{\bullet\bullet}{\underset{\bullet\bullet}{:C:}}{}^{4-} \text{ or } C^{4-}$$
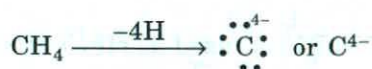
MC_2 (M = Be, Mg, Ca) and $Al_2(C_2)_3$ contain **acetylide ion (C_2^{2-})** which is derived from acetylene molecule ($H - C \equiv C - H$ or C_2H_2).
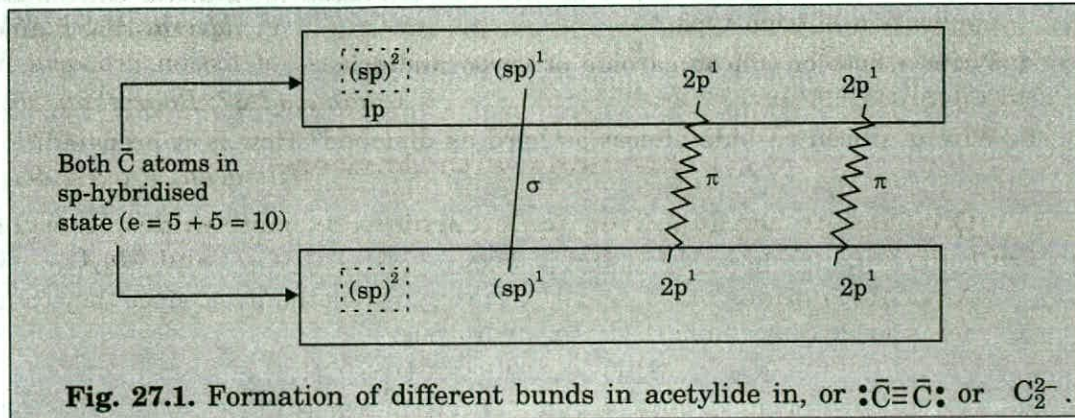
$$H - C \equiv C - H \xrightarrow{\;-2H\;} \overset{-}{\overset{\bullet\bullet}{C}} \equiv \overset{-}{\overset{\bullet\bullet}{C}} \text{ or } C_2^{2-}$$

Mg_2C_3 contains **allylide ion (C_3^{4-})** which is derived from allylene molecule ($CH_3 - C \equiv CH$ or C_3H_4)

$$CH_3 - C \equiv C - H \xrightarrow{\;-4H\;} \overset{3-}{\overset{\bullet\bullet}{\underset{\bullet\bullet}{C}}} \equiv \overset{-}{\overset{\bullet\bullet}{C}} \text{ or } C_3^{4-}$$
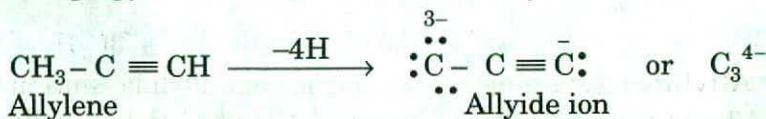
Q.3 Discuss how different bonds are formed in acetylide ion, C_2^{2-}.

Ans : The structure of acetylide ion (C_2^{2-}) is $\overset{\cdot\cdot}{C} \equiv \overset{\cdot\cdot}{C}$. This structure shows that each C-atom is surrounded by one σ-bp and one lp. Hence each $\overline{C}$-atom is sp hybridised $[\overline{C} = (sp)^2 (sp)^1 2p^1 2p^1]$. (C – C) σ bond is obtained by the overlap between two singly filled sp hybrid orbitals on two $\overline{C}$ atoms and two (C – C) π bonds are obtained by the parallel overlap of two unhybridised 2p orbitals on two $\overline{C}$ atoms. Thus both π bonds are $(p\pi - p\pi)\pi$ bonds. (See Fig. 27.1).

Fig. 27.1. Formation of different bonds in acetylide in, or $:\overline{C}\equiv\overline{C}:$ or C_2^{2-}.
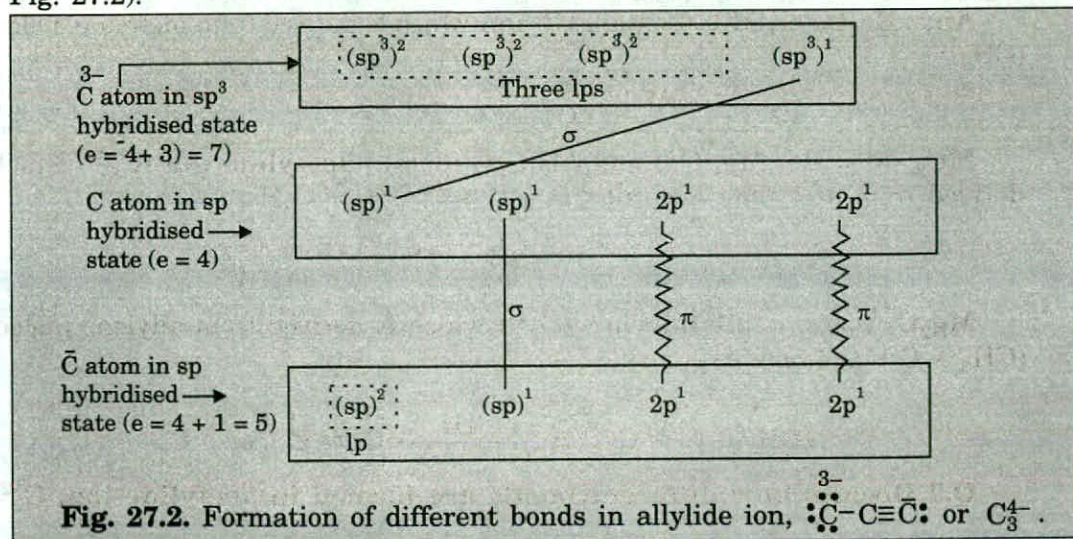
Q.4 Find out the number and type of bonds and type of hydridisation of C-atom in allylide ion.

Ans : Allylide ion is derived by removing all the four H-atoms from allylene molecule (also called propyne or methyl acetylene), $CH_3 - C \equiv CH$.

$$CH_3 - C \equiv CH \xrightarrow{\quad -4H \quad} \overset{3-}{:\overset{\cdot\cdot}{C}} - C \equiv \overline{C}: \quad \text{or} \quad C_3{}^{4-}$$
$$\text{Allylene} \qquad\qquad\qquad \text{Allyide ion}$$

The structure of $C_3{}^{4-}$ given above shows that it has **two σ-bonds and two** π **bonds.** $\overset{3-}{C}$, C and $\overline{C}$ atoms are **sp³, sp** and **sp hybridised** respectively. (See Fig. 27.2).

Fig. 27.2. Formation of different bonds in allylide ion, $:\overset{3-}{\underset{\cdot\cdot}{C}}-C\equiv\overline{C}:$ or C_3^{4-}.

University Questions

1. What are carbides ? Give their general methods of preparation. Discuss about three different types of carbides.   *(Raj. 86 S)*

2. Discuss the classification of carbides. Give suitable examples.
   (Andhra 82; Madurai 86)

3. Describe the important types of carbides. Discuss the characteristics and application of each type.   *(Meerut M.Sc. 85)*

4. Write a note on silicon carbide or carborundum.
   (Allahabad 87; Bharathiar 86)

5. Why is silicon carbide almost as hard as diamond? How is it prepared?
   (Himachal Pradesh 99)

Metallic Carbonyls

What are Metallic Carbonyls ?

The electronic configuration of CO molecule shows that it has a lone pair of electrons on carbon and. oxygen atom each. Carbon atom can donate its electron pair to a transition metal atom (M), forming OC → M coordinate bond. The compounds formed by the combination of CO molecules with transition metals are known as metallic carbonyls. Since the electrons forming OC → M bond are supplied solely by CO molecules, metal atom in carbonyls is said to be in zero oxidation state. In metal carbonyls CO molecules act as neutral ligands.
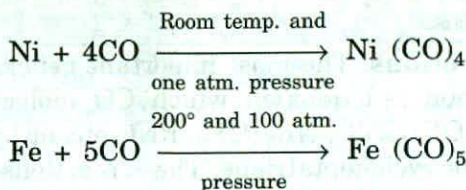
Types of Carbonyls

Depending on the number of metal atoms in a given carbonyl, carbonyls have been classified into the following two types :

1. Mononuclear (or monomeric) carbonyls. *These contain only one metallic atom per molecule and are of the type* $M(CO)_y$. Examples are : $V(CO)_6$. $Cr(CO)_6$ etc.
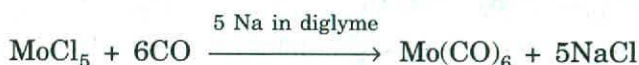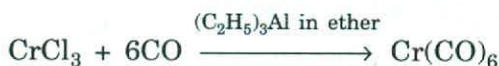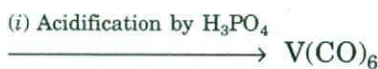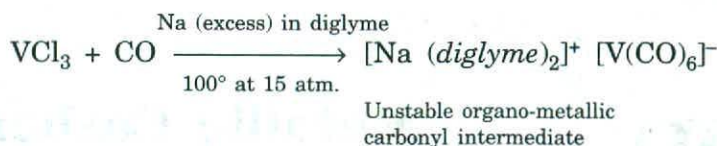
2. Polynuclear carbonyls. *These contain two or more metallic atoms per molecule and are of the type* $M_x(CO)_y$. However some authors call the carbonyls containing two metal atoms as *bridged carbonyls* and those containing more than two metal atoms as *polynuclear carbonyls*. Polynuclear carbonyls may be *homonuclear* [*e.g.* $Fe_3(CO)_{12}$] or *heteronuclear* [*e.g.* $MnCo(CO)_9$, $MnRe(CO)_{10}$].

General Methods of Preparation

1. By direct synthesis. Of the simple carbonyls, nickel tetracarbonyl, $Ni(CO)_4$ and iron pentacarbonyl, $Fe(CO)_5$ can be prepared by the direct combination of CO with finely divided metals at suitable temperature and pressure :

$$Ni + 4CO \xrightarrow[\text{one atm. pressure}]{\text{Room temp. and}} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow[\text{pressure}]{200° \text{ and } 100 \text{ atm.}} Fe(CO)_5$$

2. By the reduction of metal compounds in presence of CO. Some carbonyls may be prepared by treating the transition metal compounds (usually metal halides) in suspension in organic solvents like tetrahydrofuran (THF), ether, diethylene glycol dimethyl ether (diglyme) etc with CO it a pressure of 200–300 atm. and temperature upto 300°C in presence of some suitable reducing agent. The substances used as reducing agents are H_2, metals (*e.g.* Na, Al, Mg, Cu etc.) or compounds such as trialkyl aluminium or sodium benzophenone ketyl, $Ph_2 CO^-Na^+$

$$VCl_3 + CO \xrightarrow[\text{100° at 15 atm.}]{\text{Na (excess) in diglyme}} [Na\ (diglyme)_2]^+\ [V(CO)_6]^-$$

Unstable organo-metallic
carbonyl intermediate

$$\xrightarrow[\text{(ii) Sublimation at 50°}]{\text{(i) Acidification by } H_3PO_4} V(CO)_6$$

$$CrCl_3 + 6CO \xrightarrow{(C_2H_5)_3Al\ \text{in ether}} Cr(CO)_6$$

$$MoCl_5 + 6CO \xrightarrow{\text{5 Na in diglyme}} Mo(CO)_6 + 5NaCl$$

3. From Fe(CO)$_5$. Since CO ligands in Fe(CO)$_5$ are labile, Fe(CO)$_5$ may be used to form certain carbonyls, e.g.

$$\underset{(M = W, Mo)}{MCl_6} + 3Fe(CO)_5 \xrightarrow[\text{ether}]{100°} M(CO)_6 + 3FeCl_2 + 9CO$$
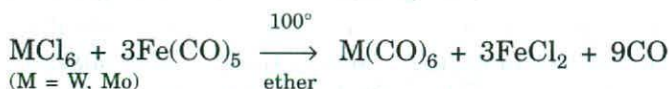
4. By the thermal or photochemical decomposition of simple carbonyls. Polynuclear carbonyls of Fe, Rh, Os, Cu, Rh and Ir are obtained by the thermal or photochemical decomposition of simple carbonyls, e.g.
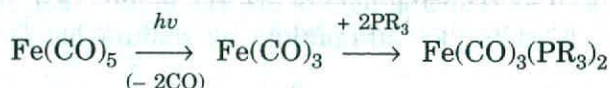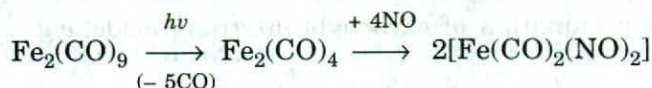
$$\underset{(M = Fe, Os)}{2M(CO)_5} \xrightarrow{\text{ultraviolet light}} M_2(CO)_9 + CO$$
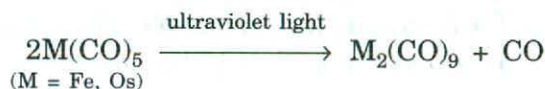
Physical Properties.

With the exception of $Ni(CO)_4$, $Fe(CO)_5$, $Ru(CO)_5$ and $Os(CO)_5$ which are liquids at ordinary temperatures, all other carbonyls are crystalline solids. They melt or decompose at low temperatures. All are typical covalent compounds and for this reason they are soluble in non-polar solvents. With the exception of $Fe_2(CO)_9$, all are more or less soluble in organic solvents. Excepting $V(CO)_6$, all the carbonyls are *diamagnetic*. $V(CO)_6$ is *paramagnetic* and its paramagnetic property corresponds to the presence of unpaired electron. The metals in carbonyls are in zero oxidation state.

Chemical Properties.

1. Substitution reactions. The most important general reactions shown by carbonyls are substitution reactions in which CO molecules are replaced by ligands like PX_3, PR_3, $P(OR)_3$, SR_2, NR_3, OR_2, RNC etc. or by unsaturated organic molecules such as C_6H_6 or cycloheptatriene. These reactions may proceed through photochemical activation according to which the carbonyl group absorbs a photon ($h\upsilon$) to eliminate a CO molecule followed by the entry of the substituent into the co-ordination sphere, e.g.
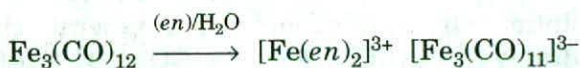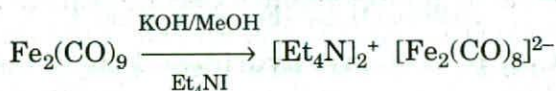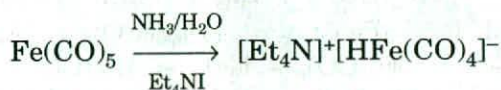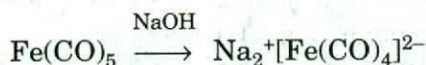
$$Cr(CO)_6 \xrightarrow[(-CO)]{h\upsilon} C(CO)_5 \xrightarrow{+L} Cr(CO)_5L$$

$$Fe(CO)_5 \xrightarrow[(-2CO)]{h\upsilon} Fe(CO)_3 \xrightarrow{+2PR_3} Fe(CO)_3(PR_3)_2$$

$$Fe_2(CO)_9 \xrightarrow[(- 5CO)]{hv} Fe_2(CO)_4 \xrightarrow{+ 4NO} 2[Fe(CO)_2(NO)_2]$$

Bidentate ligands like *diars* replace two CO groups at a time to give the substituted carbonyls like $Mo(CO)_4(diars)$, $Fe(CO)_3$ (*diars*), $Ni(CO)_2$ (*diars*) etc. Substitution reaction in case of $Cr(CO)_6$ gives $Cr(CO)_2$ (*diars*)$_2$.

2. Formation of anionic carbonyl complexes (also called carbonylate anions). Many of the carbonyls form carbonylate anions, *e.g.* $[Fe(CO)_4]^{2-}$, $[Mo(CO)_5Cl]^-$, $[HFe(CO)_4]^-$, $[Fe_2(CO)_8]^{2-}$, $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$ etc. These complex anions can be prepared by any of the following methods :

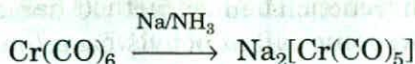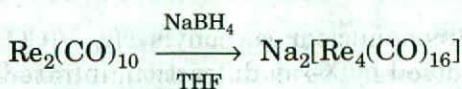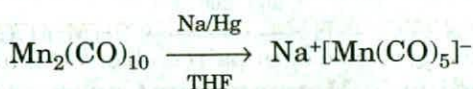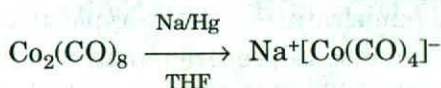(a) *By the action of NaOH or nitrogenous bases (e.g.* NH_3, *amines, pyridine) on metal carbonyls, e.g.*

$$Fe(CO)_5 \xrightarrow{NaOH} Na_2{}^+[Fe(CO)_4]^{2-}$$

$$Fe(CO)_5 \xrightarrow[Et_4NI]{NH_3/H_2O} [Et_4N]^+[HFe(CO)_4]^-$$

$$Fe_2(CO)_9 \xrightarrow[Et_4NI]{KOH/MeOH} [Et_4N]_2{}^+ [Fe_2(CO)_8]^{2-}$$

$$Fe_3(CO)_{12} \xrightarrow{(en)/H_2O} [Fe(en)_2]^{3+} [Fe_3(CO)_{11}]^{3-}$$

$$3Co_2(CO)_8 + 12py \longrightarrow 2[Co(py)_6]^{2+} [Co(CO)_4]_2{}^{2-} + 8CO$$

(b) *By the reduction of carbonyls with alkali metals, alkali metal amalgams or borohydrides, e.g.*

$$Co_2(CO)_8 \xrightarrow[THF]{Na/Hg} Na^+[Co(CO)_4]^-$$

$$Mn_2(CO)_{10} \xrightarrow[THF]{Na/Hg} Na^+[Mn(CO)_5]^-$$

$$Re_2(CO)_{10} \xrightarrow[THF]{NaBH_4} Na_2[Re_4(CO)_{16}]$$

$$Cr(CO)_6 \xrightarrow{Na/NH_3} Na_2[Cr(CO)_5]$$

$$Cr(CO)_6 \xrightarrow[THF]{NaBH_4} Na[HCr_2(CO)_{10}]$$

$$Cr(CO)_6 \xrightarrow[NH_3]{NaBH_4} Na_2[Cr_2(CO)_{10}]$$
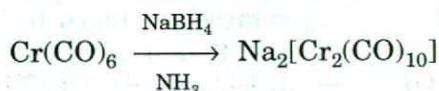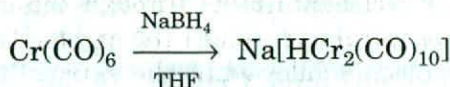
3. Formation of cationic carbonyl complexes (also called carbonylate cations). Carbonylate cations may be prepared from the carbonyls by the following methods :

(a) By the protonation of carbonyls in strong acids, e.g.

$$Fe(CO)_5 \xrightarrow{\text{HCl/BCl}_3} [FeH(CO)_5]^+ [BCl_4]^-$$

n.m.r. spectroscopy has shown that the proton becomes bounded to the metal atom in $[FeH(CO)_5]^+$.

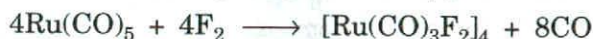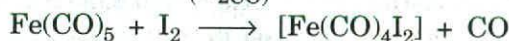(b) By the action of CO and a Lewis acid like $AlCl_3$ or BF_3 on carbonyl halide, e.g.

$$Mn(CO)_5Cl + CO + AlCl_3 \longrightarrow [Mn(CO)_6]^+[AlCl_4]^-$$
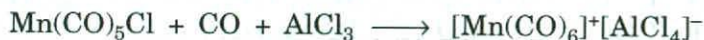
4. Formation of carbonyl halides. The action of Cl_2, Br_2, I_2 or F_2 on some carbonyls gives carbonyl halides, e.g.,

$$2Mo(CO)_6 + 2Cl_2 \longrightarrow [Mo(CO)_4Cl_2] + 4CO$$

$$Mn_2(CO)_{10} + Br_2 \underset{\text{Pet. ether, 120°}}{\rightleftarrows} [Mn(CO)_4Br]_2 + 2CO$$

$$Fe(CO)_5 + I_2 \xrightarrow{(-\ 2CO)} [Fe(CO)_4I_2] + CO$$
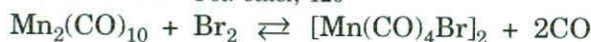
$$4Ru(CO)_5 + 4F_2 \longrightarrow [Ru(CO)_3F_2]_4 + 8CO$$

5. Formation of carbonyl hydrides. Some of the metallic carbonyls [e.g. $Fe(CO)_5$, $Mn_2(CO)_{10}$, $Os_3(CO_{12}$ etc] dissolve in an alkali and give an unidentified colourless solution. On acidification with a mineral acid, this solution gives the carbonyl hydrides. $H_2Fe(CO)_4$ [from $Fe(CO)_5$], $H_3Mn_3(CO)_{12}$ [from $Mn_2(CO)_{10}$]. $H_4Os_4(CO)_{12}$, $H_2Os_4(CO)_{13}$ [from $Os_3(CO)_{12}$] and $Ni(CO)_3H_2$ [from $Ni(CO)_4$] have been obtained by this method.

$$Fe(CO)_5 + 2OH^- \longrightarrow Fe(CO)_4H_2 + CO_3^{2-}$$

$$Ni(CO)_4 + 2OH^- \longrightarrow Ni(CO)_3H_2 + CO_3^{2-}$$

Carbonyl hydrides can also be prepared by treating the carbonyls with H_2, e.g.
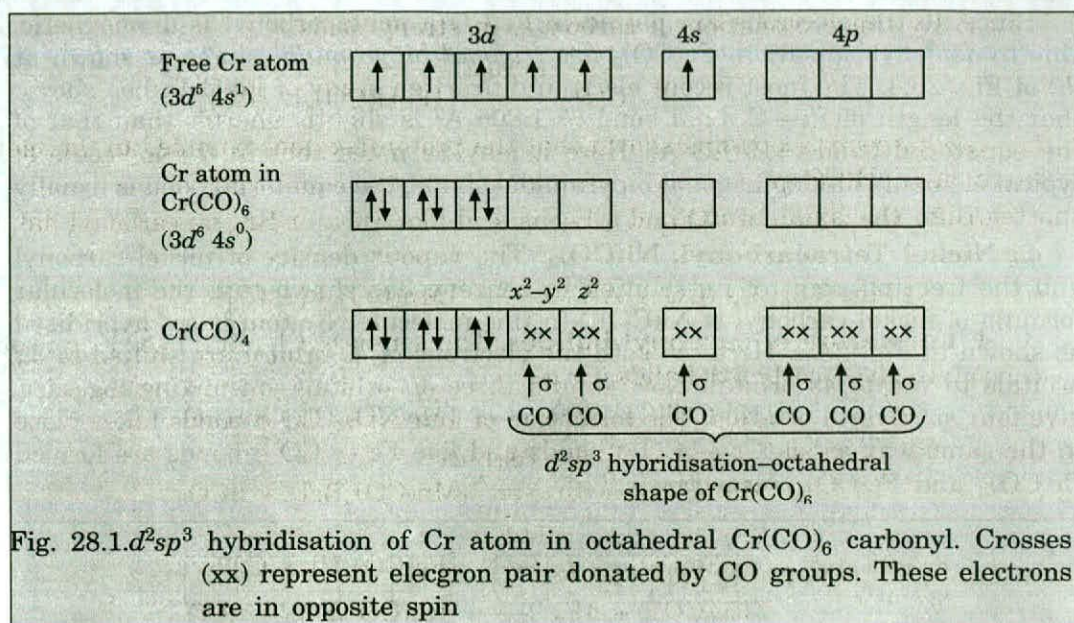
$$Mn_2(CO)_{10} + H_2 \xrightarrow{\text{200°/200 atm.}} 2HMn(CO)_5$$
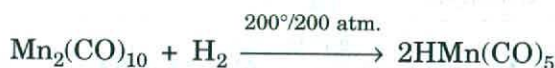
Structure and Bonding in Mononuclear Carbonyls

The structure of mononuclear carbonyls viz. $V(CO)_6$, $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$ have been studied by X-ray diffraction, infrared spectroscopy and [except for $V(CO)_6$] electron-diffraction. The last method has also been used for $Mo(CO)_6$ and $W(CO)_6$. All the mono-nuclear carbonyls have *linear* M—CO bonds in which CO group is linked to the metal atom through the carbon atom.

Now let us discuss the structure of $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$ carbonyls.

1. Chromium Hexacarbonyl, $Cr(CO)_6$. In this carbonyl Cr-atom which is in zero oxidation state is d^2sp^3 hybridised as shown in Fig. 28.1. Since the energy of 3d and 4s orbitals is not very different from each other, both the electrons from 4s orbital go to 3d orbital to make $3d_{x^2-y^2}$, $3d_s^2$ and 4s orbitals empty. Now $3d_{x^2-y^2}$, $3d_z^2$, 4s and all the three 4p orbitals hybridise together to form six d^2sp^3 hybrid orbitals. These vacant six hybrid orbitals overlap with lone-pair containing σ-orbitals on CO ligands to form six Cr ← CO σ bonds as shown in Fig. 28.1.

Fig. 28.1. d^2sp^3 hybridisation of Cr atom in octahedral $Cr(CO)_6$ carbonyl. Crosses (xx) represent elecgron pair donated by CO groups. These electrons are in opposite spin

Due to the presence of all paired electrons, $Cr(CO)_6$ shows diamagnetic character. Due to d^2sp^3 hybridisation. $Cr(CO)_6$ has the expected *octahedral* shape as shown at (*c*) of Fig. 28.4. Cr—C and C—O bond lengths have been found to be 1.92A° and 1.16A°.

2. Iron Pentacarbonyl, Fe(CO)₅. In this carbonyl Fe atom which is in zero oxidation state is dsp^3 hybridised as shown in Fig. 28.2. Here too, both the electrons from 4s orbital go to 3d orbitals. Thus one 3d, 4s and all the three 4p orbitals, on mixing together, give five dsp^3 hybrid orbitals. The formation of five Fe ← CO σ bonds takes place in the same manner as six Cr ← Co σ bonds are formed in $Cr(CO)_6$ carbonyl.

Fig. 28.2. dsp^3 hybridisation of Fe atom in trigonal bipyramidal $Fe(CO)_5$ carbonyl. Crosses (xx) represent electron pair donated by CO group
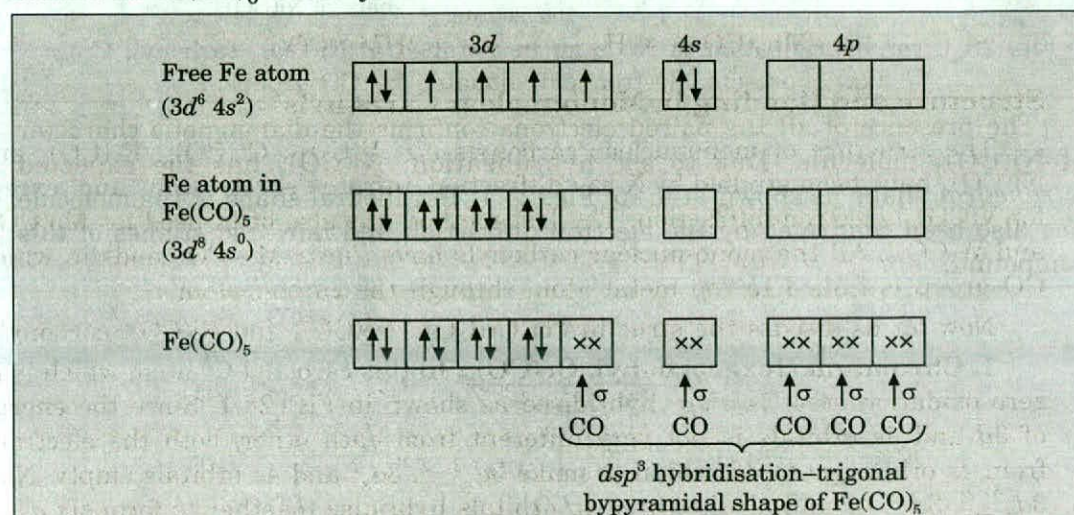
Since all the electrons are paired in $Fe(CO)_5$, pentacarbonyl is diamagnetic. Due to dsp^3 hybridisation, $Fe(CO)_5$ has *trigonal bipyramidal* shape as shown at (b) of Fig. 28.4. The most recent electron diffraction study of $Fe(CO)_5$ has shown that the length of Fe—C axial bond (= 1.806 Å) is slightly shorter than that of the equatorial bond (= 1.833 Å). Here it may be noted that in the molecule of typical elements having trigonal bipyramidal shape, the equatorial bond is usually shorter than the axial bond.

3. Nickel Tetracarbonyl, $Ni(CO)_4$. The vapour density of nickel carbonyl and the freezing point of its solution in benzene has shown that the molecular formula of nickel carbonyl is $Ni(CO)_4$. In this molecule Ni atom is sp^3 hybridised as shown in Fig. 28.3. Here too both the electrons of 4s orbital are shifted to 3d orbitals to vacate 4s orbital. Now 4s and three 4p orbitals, on mixing together, give four sp^3 hybrid orbitals. The formation of four Ni ← CO σ-bonds takes place in the same way as six Cr ← CO σ bonds and five Fe ← CO σ bonds are formed $Cr(CO)_6$ and $Fe(CO)_5$ respectively.
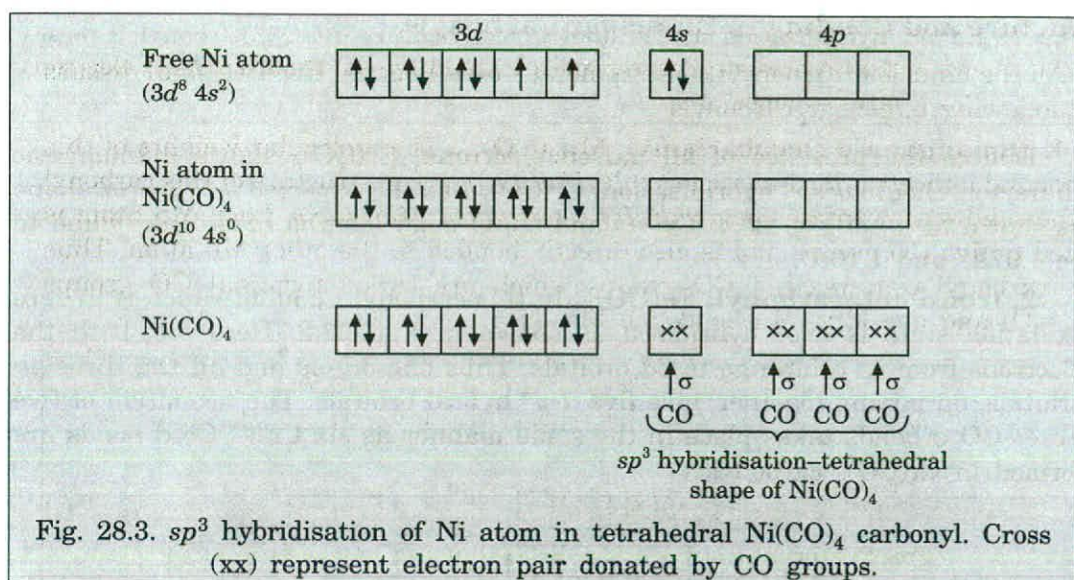
Fig. 28.3. sp^3 hybridisation of Ni atom in tetrahedral $Ni(CO)_4$ carbonyl. Cross (xx) represent electron pair donated by CO groups.

The presence of all the paired electrons confirms the diamagnetic character of $Ni(CO)_4$ molecule. Due to sp^3 hybridisation, $Ni(CO)_4$ has the expected *tetrahedral* shape as shown at (a) of Fig. 28.4. Tetrahedral shape of the molecule has also been confirmed by the electron diffraction and infra-red studies of this compound.
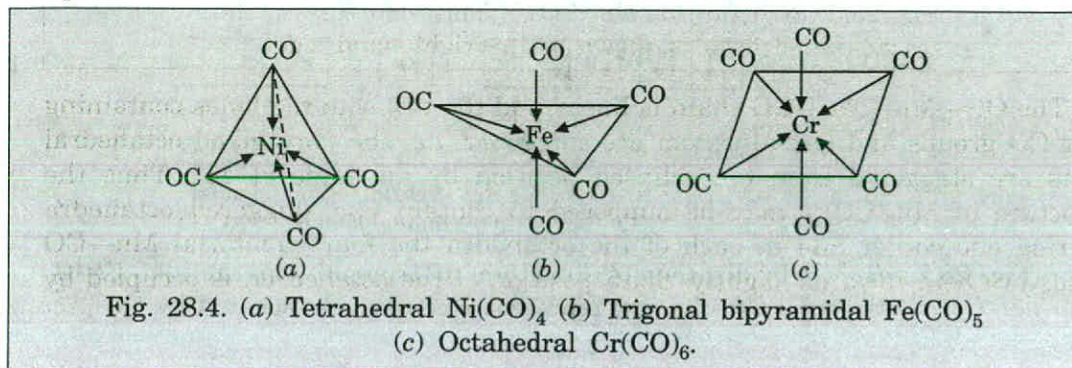
Fig. 28.4. (a) Tetrahedral $Ni(CO)_4$ (b) Trigonal bipyramidal $Fe(CO)_5$
(c) Octahedral $Cr(CO)_6$.

The Ni—C bond length in this molecule has been found to be equal to 1.50 A° which is shorter by 0.32 A° in comparison to Ni—C single bond length (= 1.82 A°) found in carbonyls. The C — O bond length in this carbonyl has been found to be equal to 1.15 A° which is larger than the C — O bond length in CO molecule (= 1.128 A°).

It is to be pointed out here that, due to the formation of four OC → M bonds, a large negative charge is accumulated on the central Ni atom. This is most unlikely. In such a situation, Pauling suggested that the double bonding takes place with the back sonation of d-electron from Ni atom to CO ligands to such an extent that electroneutrality principle is obeyed. According to 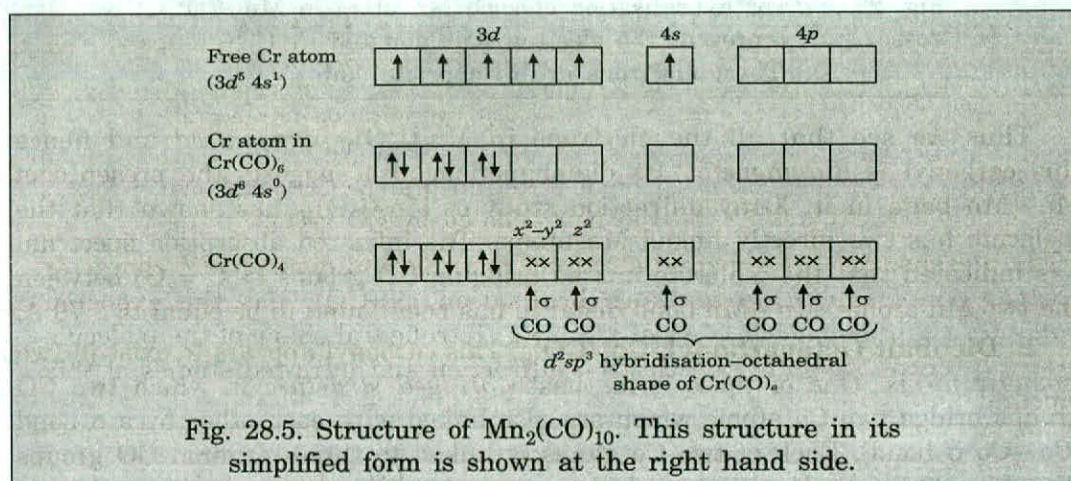this principle the electron pair is not shared equally between Ni and C-atoms of CO ligands but is attracted more strongly by C-atom which prevents the accumulation of negative charge on Ni-atom and is in keeping with the greater electronegativity of C-atom compared to Ni atom (C = 2.5, Ni = 1.8).

Structure and Bonding in Binuclear Carbonyls

All the binuclear carbonyls contain metal—metal bonds. Here we shall discuss the following binuclear carbonyls :

1. Dimanganese Decacarbonyl, $Mn_2(CO)_{10}$. The molecular weights of this compound indicates the dimeric formula, $Mn_2(CO)_{10}$. The structure of this carbonyl in the solid state contains *octahedrally coordinated Mn atoms*. Each Mn atom is linked to five CO groups and is also directly bonded to the other Mn atom. Thus this carbonyl contains ten CO groups which are called terminal CO groups (– C ≡ O) and one Mn—Mn bond See Fig. 28.5.

Fig. 28.5. Structure of $Mn_2(CO)_{10}$. This structure in its simplified form is shown at the right hand side.

The OC—Mn—Mn—CO chain is linear and the two square planes containing four CO groups and one Mn atom are *staggered, i.e.* the two linked octahedral units are staggered from the eclipsed position by an angle of 45°. Thus the structure of $Mn_2(CO)_{10}$ may be supposed to contain two staggered octahedra sharing one corner and in each of the octahedra the four equatorial Mn—CO bonds are bent inwards slightly. Sixth position of the octahedron is occupied by

Mn—Mn bond so that the steric repulsion between the CO groups is reduced. Structure of $Mn_2(CO)_{10}$ in its simplified form can be depicted as shown at the right hand side of Fig. 28.5.

In $Mn_2(CO)_{10}$ both Mn atoms are d^2sp^3 hybridised. Five (which are empty) out of six d^2sp^3 hybrid orbitals on each Mn-atom accommodate a lone pair of electrons donated by each of the five CO groups and the sixth hybrid orbital on one Mn atom which contains one unpaired electron overlaps with a similar d^2sp^3 hybrid orbital of the other Mn atom to form Mn —Mn σ bond (See Fig. 28.6).

Fig. 28.6. d^2sp^3 hybridisation of each Mn atom in $Mn_2(CO)_{10}$.
Crosses (××) represent the electron pair donated by CO groups.
These electrons are in opposite spin.
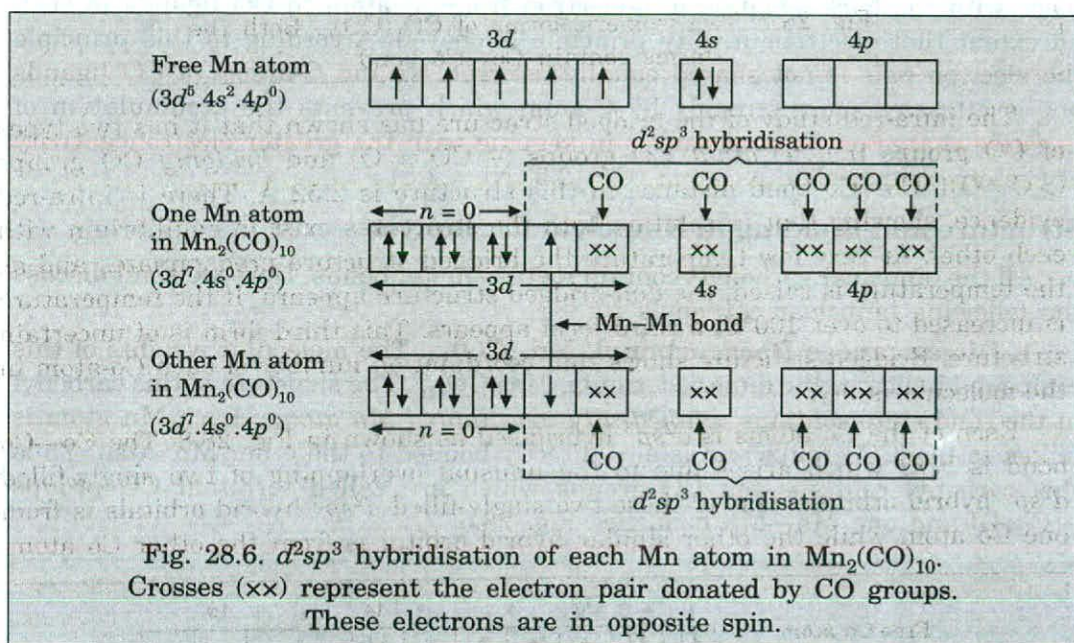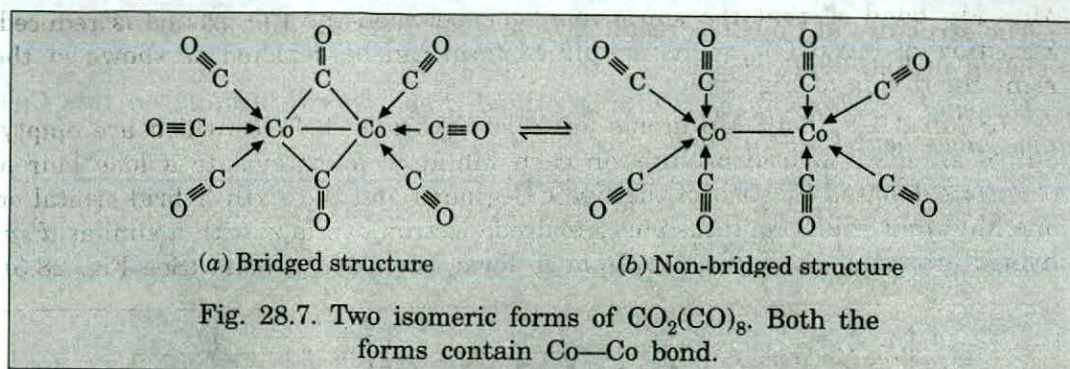
Thus we see that all the electrons in $Mn_2(CO)_{10}$ are *paired* and hence this carbonyl is *diamagnetic*. Its diamagnetism also suggests the presence of Mn—Mn bond in it. X-ray diffraction study of $Mn_2(CO)_{10}$ has shown that the molecule has two directly linked Mn atoms. The infra-red absorption spectrum has indicated that the molecule has no bridging CO groups (> C = O) between the two Mn atoms. Mn—Mn bond distance has been found to be equal to 2.79 Å.

2. Dicobalt Octacarbonyl, $Co_2(CO)_8$. This carbonyl appears to exist in two *isomeric forms*. One of these forms has a *bridged structure* in which two CO groups bridge two Co atoms which are also linked with each other by a σ bond (Co—Co σ bond). Each of two Co atoms is linked to three terminal CO groups (See Fig. 28.7 (*a*)]. The other form has a *non-bridged structure* with a Co—Co σ bond linking two $Co(CO)_4$ groups (See Fig. 28.7 (*b*)]. Thus both the structures have Co—Co σ bonding and the diamagnetic nature of $Co_2(CO)_8$ also confirms the spin-pairing between two Co atoms, *i.e.* diamagnetic character of $Co_2(CO)_8$ is confirmed by the presence of Co—Co σ bond in it. There is very little difference in energy between the two structures.

(a) Bridged structure   (b) Non-bridged structure

Fig. 28.7. Two isomeric forms of $CO_2(CO)_8$. Both the
forms contain Co—Co bond.

The infra-red study of the bridged structure has shown that it has two types of CO groups [i.e. terminal CO groups (– CO ≡ O) and bridging CO groups (> C = O)]. Co—Co bond distance in this structure is 2.52 Å. There is infra-red evidence, showing that in solution both the structures exist in equilibrium with each other. At very low temperature the bridged structure predominates and as the temperature is raised, the non-bridged structure appears. If the temperature is increased to over 100°C, a third form appears. This third form is of uncertain structure. Bridged structure shows that coordination number of each Co-atom in the-molecule is *six*.

Each of the Co atoms is d^2sp^3 hybridised as shown in Fig. 28.8. The Co—Co bond is *bent* which arises due to the unusual overlapping of two singly-filled d^2sp^3 hybrid orbitals. One of these two singly-filled d^2sp^3 hybrid orbitals is from one Co atom while the other similar hybrid orbital is from the other Co atom.

Fig. 28.8. d^2sp^3 hybridisation of Co alum in $Co_2(CO)_8$ carbonyl
Crosses (××) represent the electron pair denoted by terminal
CO groups, while the dot (•) represents an electron on
bridging CO groups. ↑↓ represent electrons on Co atom.
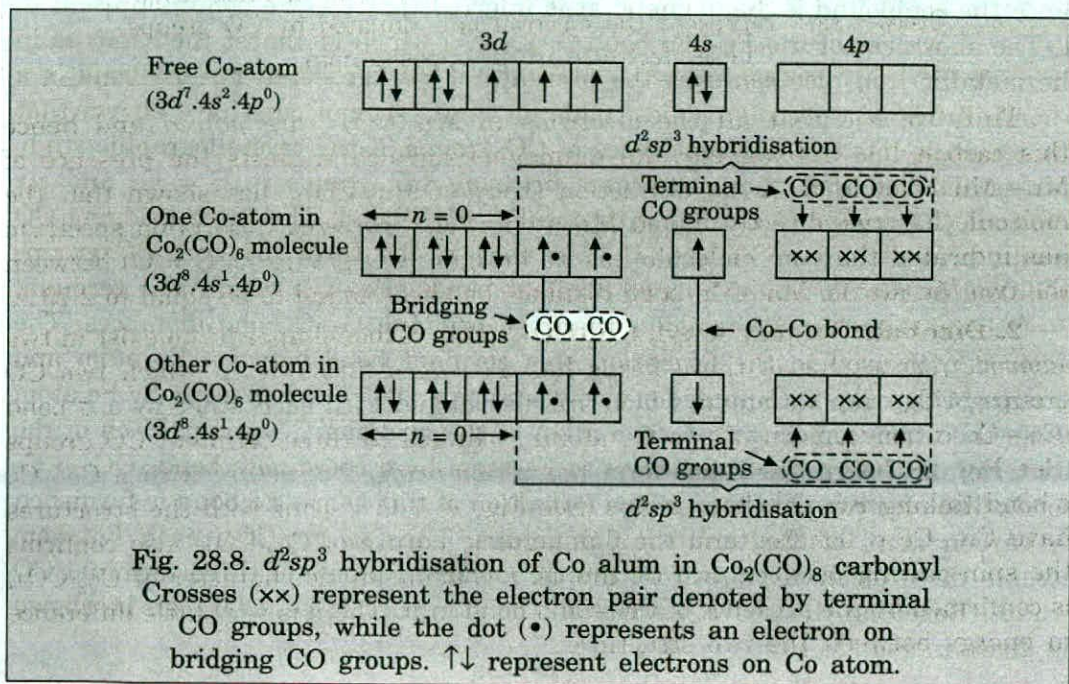
The structure of $Co_2(CO)_8$ resulted from d^2sp^3 hybridisation of each Co atom is shown in Fig. 28.9.

Unusual overlapping of two singly-filled d^2sp^3 hybrid orbitals on two Co atoms gives bent Co—Co bond.
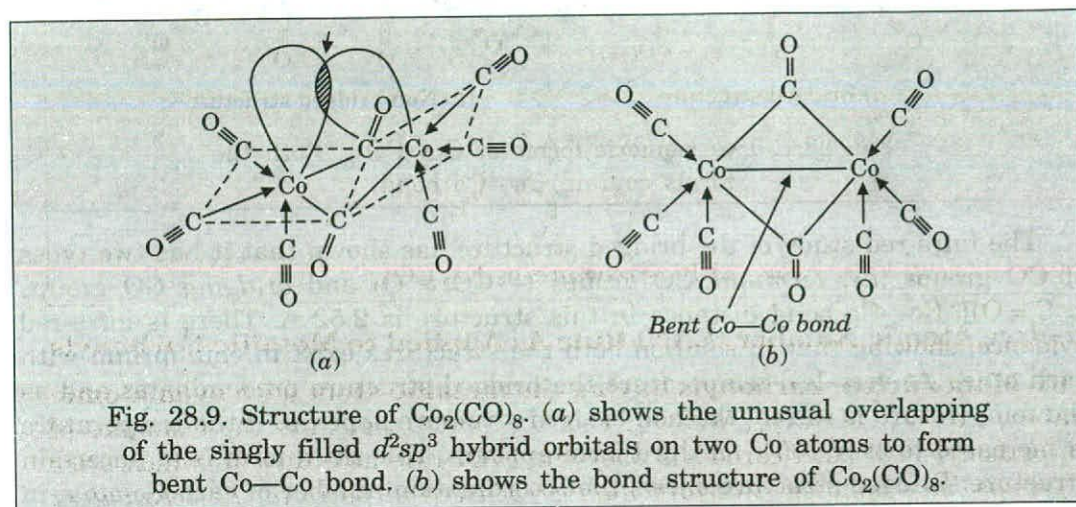

Fig. 28.9. Structure of $Co_2(CO)_8$. (a) shows the unusual overlapping of the singly filled d^2sp^3 hybrid orbitals on two Co atoms to form bent Co—Co bond. (b) shows the bond structure of $Co_2(CO)_8$.

3. Diiron Enneacarbonyl, $Fe_2(CO)_9$. This carbonyl base structure which is related to the of $Co_2(CO)_8$ with ninth CO group occupying a bridging position so that there is three-fold symmetry around the Fe—Fe axis. Its structure consists of two octahedra around each Fe atom and share their faces with each other. Since the compound is diamagnetic, it is inferred that Fe—Fe bond is present in it. The shortness of the Fe—Fe bond (= 2.46 Å) which is almost the same as in the metallic iron also confirms the presence of Fe—Fe bond. Fe—Fe bond is a δ bond. Infra-red spectral studies made on $Fe_2(CO)_9$ molecule have shown that the molecule has two different types of CO groups. X-ray crystallographic study has established that there are *three bridging CO groups* (– C = O) and *six terminal CO groups* (– C ≡ O) with one Fe—Fe δ-bond. The three bridging CO groups bridge the two Fe atoms. Thus each of the three bridging CO groups is linked to two Fe atoms by two covalent bonds (Fe—CO bond). The terminal C—O bond distances are smaller than the bridging C—O bond distances. The electron pair used in the formation of a covalent bond between Fe atom and bridging CO group is composed of two electrons one of which is given by Fe atom while the other comes from carbon atom of the bridging CO group. Each of the six terminal CO groups is attached to Fe atom by a coordinate bond (OC → Fe bond). The electron pair used in the formation of this OC → Fe bond is furnished by carbon atom of the terminal CO groups. Thus in $Fe_2(CO)_9$ each Fe atom accepts three electron pairs from the three carbon atoms of three terminal CO groups. Based on the above description the structure of $Fe_2(CO)_9$ can be shown as given in Fig. 28.10.
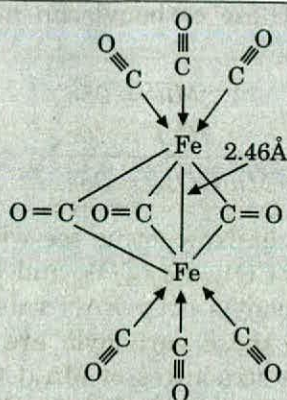
Fig. 28.10. Structure of $Fe_2(CO)_9$.

Effective Atomic Number (EAN) Rule As Applied to Metallic Carbonyls

(A) Mononuclear carbonyls having the metallic atom with even atomic number. $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$ etc. are the examples of such carbonyls. All such carbonyls obey the EAN rule according to which *after CO groups have donated a certain number of electron pairs to the zero valent metal atom through $OC \rightarrow M$ σ-bonding, the total number of electrons on the metal atom including those gained from CO molecules becomes equal to the atomic number of the next inert gas.* This is shown in Table 28.1.

Table 28.1. EAN rule as applied to mononuclear carbonyls having metallic atoms with even atomic number. Note that in all the carbonyls metal atom is in zero oxidation state.

Metal carbonyl	No. of electrons on the central metal atom = At. No. of the metal atom = Z	No. of electrons donated by CO molecules = x	EAN of the metal atom in carbonyl = Z + x (symbol of the next inert gas is given in parentheses)
$Cr(CO)_6$	24	$6 \times 2 = 12$	$24 + 12 = 36$ (Kr)
$Mo(CO)_6$	42	$6 \times 2 = 12$	$42 + 12 = 54$ (Xe)
$W(CO)_6$	74	$6 \times 2 = 12$	$74 + 12 = 86$ (Rn)
$Fe(CO)_5$	26	$5 \times 2 = 10$	$26 + 10 = 36$ (Kr)
$Ru(CO)_5$	44	$5 \times 2 = 10$	$44 + 10 = 54$ (Xe)
$Os(CO)_5$	70	$5 \times 2 = 10$	$76 + 10 = 86$ (Rn)
$Ni(CO)_4$	28	$4 \times 2 = 8$	$28 + 8 = 36$ (Kr)

On the basis of EAN rule it can be explained why Ni atom does not form a hexacarbonyl, $Ni(CO)_6$. Non-formation of $Ni(CO)_6$ is because of the fact that EAN of Ni atom in $Ni(CO)_6$ would be equal to $28 + 2 \times 6 = 40$ which is not the atomic number of any of the noble gases.

(B) Mononuclear carbonyls having the metallic atom with odd atomic number. $V(CO)_6$ and hypothetical carbonyls *viz.* $Mn(CO)_5$ and $Co(CO)_4$ are the

examples of such carbonyls. These carbonyls *do not obey* EAN rule as shown below :

$$V = 23e^- \qquad\qquad Mn = 25e^- \qquad\qquad Co = 27e^-$$
$$\underline{6CO = 12e^-} \qquad\qquad \underline{5CO = 10e^-} \qquad\qquad \underline{4CO = 8e^-}$$
$$V(CO)_6 = 35e^- \qquad Mn(CO)_5 = 35e^- \qquad Co(CO)_4 = 35e^-$$
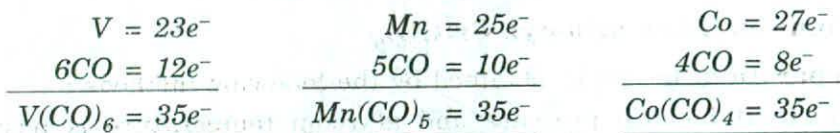
(C) Polynuclear carbonyls. Now let us see whether or not the polynuclear carbonyls like $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Fe_2(CO)_9$ and $Fe_5(CO)_{12}$ obey EAN rule. It has been seen that these carbonyls obey EAN rule, if two electrons from each metal–metal bond present in these carbonyls are included in calculating the electrons per metal atom. The structures of $Mn_2(CO)_{10}$, $Co_2(CO)_8$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ as discussed above show that these molecules contain *one* Mn—Mn, *one* Co—Co, *one* Fe—Fe, *three* Fe—Fe bonds respectively and hence the EAN per metal atom in these molecules is calculated as follows :

(i) $Mn_2(CO)_{10}$: Electrons from 2Mn atoms = 25 × 2 = 50

                 Electrons from 1000 molecules = 10 × 2 = 20

              Electrons from one Mn—Mn bond = $\underline{1 \times 2 = 2}$

$$Mn_2(CO)_{10} = 72$$
$$\therefore \text{ EAN per Mn atom} = 72/2$$
$$= 36(Kr)$$

(ii) $Co_2(CO)_8$: Electrons from 2Co atom   = 2 × 27 = 54

              Electrons from 8CO molecules = 8 × 2 = 16

       Electrons from one Co—Co bond = $\underline{1 \times 2 = 2}$

$$Co_2(CO)_8 = 72$$
$$\therefore \text{ EAN per Co atom} = 72/2$$
$$= 36(Kr)$$

(iii) $Fe_2(CO)_9$: Electrons from 2Fe atoms   = 2 × 26 = 52

            Electrons from 9CO molecules = 9 × 2 = 18

       Electrons from one Fe—Fe bond = $\underline{1 \times 2 = 2}$

$$Fe_2(CO)_9 = 72$$
$$\therefore \text{ EAN per Fe atom} = 72/2$$
$$= 36(Kr)$$

(iv) $Fe_3(CO)_{12}$: Electrons from 3Fe atoms   = 3 × 26 = 78

            Electrons from 12CO molecules = 12 × 2 = 24

      Electrons from three Fe—Fe bonds = $\underline{3 \times 2 = 6}$

$$Fe_3(CO)_{12} = 108$$
$$\therefore \text{ EAN per Fe atom} = 108/3$$
$$= 36(Kr)$$

Some Metallic Carbonyls

1. Chromium Hexacarbonyl, $Cr(CO)_6$

Preparation. In can be obtained by the following methods :

(i) CO at 50 atm pressure and at room temperature is passed into a suspension of $CrCl_3$ in ether, which has been treated with C_6H_5Mg Br at $-70°$ (*Job's reaction*).

(ii) A solution of Cr(+3) salt dissolved in ether is treated with CO at a high temperature and pressure in the presence of a reducing agent such as $Al(C_5H_5)_3$, $LiAlH_4$ etc.

(iii) $CrCl_3$ in presence of $AlCl_3$, powdered Al and benzene is treated with CO. The yield is 88%.

Properties. (i) Chromium hexacarbonyl is a white solid.

(ii) Crystals of $Cr(CO)_6$ are soluble in ether, chloroform, CCl_4 and C_6H_6.

(iii) It is resistant to chemical attack. For example it does not react with air, cold aqueous alkalies and acids (except conc. HNO_3).

(iv) *Decomposition.* It is decomposed by F_2 at $-75°C$ to form CrF_6 by Cl_2 or by conc. HNO_3.

(v) *Reduction.* It is reduced with alkali metals in liq. NH_3 and alkali metals borohydrides. For example.

$$Cr(CO)_6 \xrightarrow{\text{Na/NH}_3} Na_2[Cr(CO)_5]$$

$$Cr(CO)_6 \xrightarrow[\text{(THF)}]{\text{NaBH}_4} Na[HCr_2(CO)_{10}]$$

$$Cr(CO)_6 \xrightarrow[\text{(NH}_3)]{\text{NaBH}_4} Na_2[Cr_2(CO)_{10}]$$
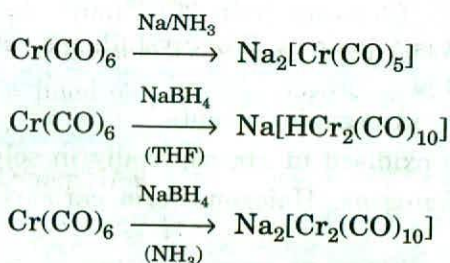
(vi) *Reaction with amines.* $Cr(CO)_6$ reacts with amines like *py, phen, en* to form the products in which CO groups in $Cr(CO)_6$ are replaced by molecules of the amine. For example above $140°$, *py* reacts with $Cr(CO)_6$ to give the following products in succession :

$$Cr(CO)_6 \longrightarrow \underset{\substack{\text{yellow brown} \\ \text{solid}}}{Cr(CO)_4 \ (py)_2} \longrightarrow \underset{\substack{\text{yellow red} \\ \text{solid}}}{Cr_2(CO)_7 \ (py)_5} \longrightarrow \underset{\substack{\text{bright red} \\ \text{solid}}}{Cr(CO)_3 \ (py)_3}$$
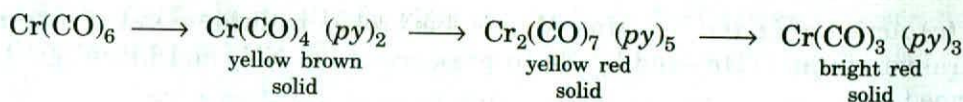
2. Dimanganese Decacarbonyl, $Mn_2 (CO)_{10}$

Preparation. (i) $Mn_2 (CO)$ is obtained when MnI_2 (prepared by special method) is reduced at a high pressure of CO by Mg in diethyl ether. The yield of $Mn_2(CO)_{10}$ is only 1%.

$$Mn + 2CuI \xrightarrow{500°C} MnI_2 + 2Cu$$

$$(MnI_2 + 2Cu) + Mg \xrightarrow[25°C/16 \ hrs]{CO, \ 210 \ atm} Mn_2(CO)_{10} + MgI_2 + CuI_2$$
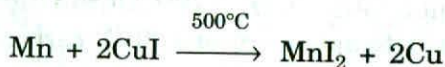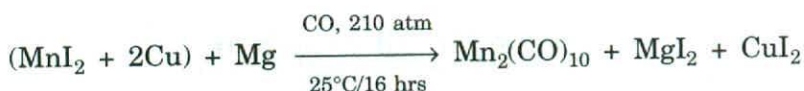
(*ii*) $Mn_2 (CO)_{10}$ has also been prepared in better yield by the reaction of Mn $(CH_3COO)_2$ with triethyl aluminium, $(C_2H_5)_3Al$ under CO at a pressure of 20 atmospheres at 100°C for 5 hours.

$$Mn(CH_3COO)_2 + (C_2H_5)_3 \ Al \xrightarrow[100°C/5 \ hrs]{CO, \ 20 \ atm} Mn_2(CO)_{10}$$
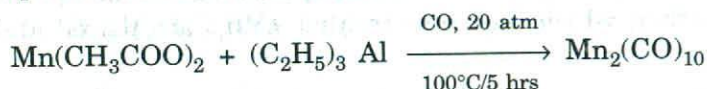
The yield of carbonyl by this method is 53–60%.

(*iii*) Cabonylation of $MnCl_2$ in presence of benzophenone ketyl like $(C_6H_5)_2CONa$ at 165°C gives 32% yield of $Mn_2(CO)_{10}$.

$$MnCl_2 + 2(C_6H_5)_2CONa \longrightarrow NaCl + Mn[CO(C_6H_5)_2]_2$$

$$Mn[OC(C_6H_5)_2] \xrightarrow[165°C]{CO, \ 140 \ atm} Mn_2(CO)_{10} + (C_6H_5)_2CO$$

(*iv*) More recently 48% yield of $Mn_2 (CO)_{10}$ has been obtained by the carbonylation of methyl cyclopentadienyl manganese dicarbonyl, $(CH_3.C_5H_4)$ Mn $(CO)_3$ in presence of Na at 50 atmosphere pressure of CO and 125°C for 8 hours.

$$(CH_3.C_5H_4)Mn(CO)_3 + Na \xrightarrow[125°C/8 \ hrs]{CO, \ 50 \ atm} Mn_2(CO)_{10}$$

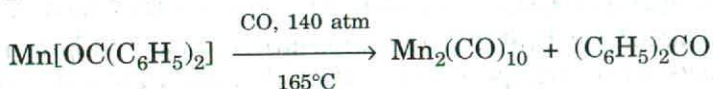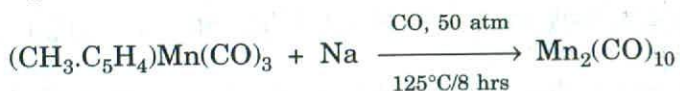**Properties.** (*i*) It is a golden yellow crystalline substance. It has m.pt. = 155°C and sublimes in vacuo.

(*ii*) It is soluble in organic solvents.

(*iii*) It is slowly oxidised in air, especially in solution.

(*iv*) *Action of halogens.* Halogens form carbonyl halides, Mn $(CO)_5$ X as shown below :

$$Mn_2 (CO)_{10} + Br_2 \ (l) \xrightarrow{40°C} 2Mn(CO)_5 \ Br$$
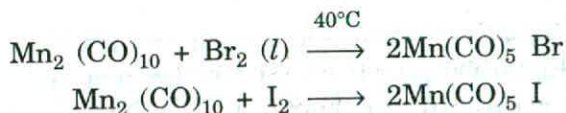
$$Mn_2 (CO)_{10} + I_2 \longrightarrow 2Mn(CO)_5 \ I$$

The order of activity of halogens is as : I > Br > Cl.

(*v*) *Action of Li and Na.* Mn—Mn bond is broken by lithium in the presence of tetrahydrofuran (THF) and by Na in presence of liq. NH_3 and $Li^+ [Mn(CO)_5]^-$ is formed.

$$Mn_2(CO)_{10} + 2Li \xrightarrow{THF} 2Li^+ [Mn(CO)_5]^-$$

$$Mn_2(CO)_{10} + 2Na \xrightarrow{liq. \ NH_3} 2Na^+ [Mn(CO)_5]^-$$
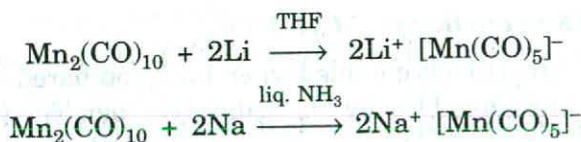
(*vi*) *Reduction.* When $Mn_2 (CO)_{10}$ is reduced by hydrogen under 200 atmospheric pressure at a temperature of 200°C, carbonyl hydride in formed.

$$Mn_2(CO)_{10} + H_2 \xrightarrow[\text{200°C}]{\text{200 atm.}} 2H\ Mn\ (CO)_5$$
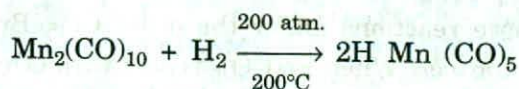
(*vii*) *Action of phosphines, arsines and stibines.* With these materials Mn_2 $(CO)_{10}$ gives monomeric paramagnetic compounds of the type, $Mn\ (CO)_4\ (PR_3)$.

(*viii*) *Diamagnetic nature.* $Mn_2(CO)_{10}$ is a diamagnetic substance. Diamagnetic character confirms the facts that all the electrons in $Mn_2\ (CO)_{10}$ are paired and Mn—Mn bond is also present in it.

3. Carbonyls of Iron

Iron forms these carbonyls which are : (*A*) *Iron pentacarbonyl,* Fe $(CO)_5$. (*B*) *Diiron enneacarbonyl,* $Fe_2\ (CO)_9$ and (*C*) *Tri-iron dodecacarbonyl,* $Fe_3\ (CO)_{12}$.

A. Iron pentacarbonyl, Fe(CO)₅. Preparation. It is prepared :

(*i*) by the action of CO at 200 atm. pressure on iron heated to 200°.

(*ii*) by the action of CO at 200 atm. pressure and 200° on FeI_2 in the presence of Cu which acts as an acceptor for I_2. It is thought that iron carbonyl iodide, $Fe(CO)_4I_2$ is first. formed which reacts a with Cu in presence of CO to form $Fe(CO)_5$.

$$FeI_2 + 4CO \longrightarrow Fe(CO)_4I_2$$
$$CO + Fe(CO)_4I_2 + 2Cu \longrightarrow Fe(CO)_5 + Cu_2I_2$$

In place of FeI_2, FeS can also be used.

Properties. (*i*) Fe $(CO)_5$ is a yellow liquid which is soluble in methyl alcohol, ether, acetone and C_6H_6. It is insoluble in H_2O.

(*ii*) *Decomposition.* On thermal decomposition at 250°C, it gives pure Fe.

$$2Fe(CO)_5 \longrightarrow Fe + 5CO$$

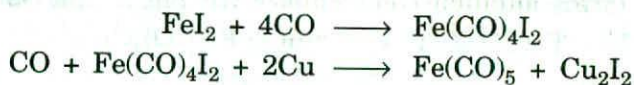(*iii*) *Action of ultra-violet light.* When it is irradiated with near ultra violet light, $Fe_2(CO)_9$ is formed.

$$2Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO$$
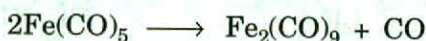
The above reaction is reversed in darkness.

(*iv*) *Hydrolysis.* $Fe(CO)_5$ is hydrolysed by H_2O and acids.

$$Fe(CO)_5 + H_2SO_4 \longrightarrow FeSO_4 + 5CO + H_2$$
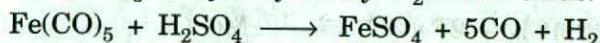
(*v*) *Action of alkalies.* When heated with aqueous NaOH and the solution is acidified, carbonylate anion, $[Fe^{2-}\ (CO)_4H^+]^-$ is formed. The hydrogen atom in this anion is acidic which means that Fe is in –2 oxidation state.

$$\underset{\text{(Fe = 0)}}{Fe(CO)_5} + 3NaOH \longrightarrow \underset{\text{(Fe = –2)}}{Na^+[Fe^{2-}(CO)_4H^+]^-} + Na_2CO_3 + H_2O$$
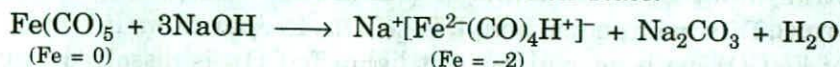
(*vi*) *Action of* NH_3. With NH_3 it gives $Fe(CO)_4H_2$ and carbonic acid, NH_2COOH

$$Fe(CO)_5 + H_2O + NH_3 \longrightarrow Fe(CO)_4H_2 + NH_2COOH$$

(*vii*) *Reaction with halogens.* It reacts with halogens in non- aqueous solvents to form the stable tetra-carbonyl halides, $Fe(CO)_4X_2$.

$$Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$$

The velocities of these reactions follow the order Cl < Br < I.

(*viii*) *Reaction with amines.* When $Fe(CO)_5$ reacts with ethylene diamine (*en*), an addition product, $Fe(CO)_5$ (*en*) is formed. Pyridine (*py*) reacts with it to give $[Fe(py)_6]$ $[Fe_4(CO)_{13}]$.

(*ix*) *Reaction with NO.* With NO, under pressure below 45°, it gives $Fe(NO)_4$ as the final product which is a black crystalline material.

$$Fe(CO)_5 + 2NO \longrightarrow Fe(CO)_2(NO)_2 + 3CO$$
$$Fe(CO)_2(NO)_2 + 2NO \longrightarrow Fe(NO)_4 + 2CO$$
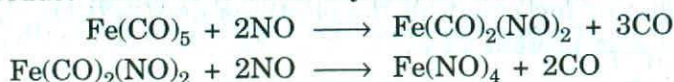
(*x*) *Reactions with metallic and non-metallic halides.* In these reactions, $Fe(CO)_4$ acts as a dehalogenating agent and a carbonylating agent; Fe becomes bi-valent and CO groups are either liberated or transferred to some other atom.

$$Fe(CO)_5 + 2CCl_4 \longrightarrow C_2Cl_6 + FeCl_2 + 5CO$$
$$Fe(CO)_5 + SO_2Cl_2 \longrightarrow SO_2 + FeCl_2 + 5CO$$
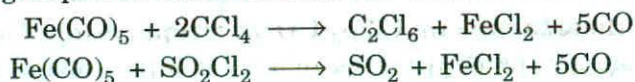
$SnCl_4$ and $SbCl_5$ are reduced to $SnCl_2$ and $SbCl_3$.

$$Fe(CO)_5 + SnCl_4 \longrightarrow SnCl_2 + Fe(CO)_4Cl_2 + CO$$
$$Fe(CO)_5 + SbCl_5 \longrightarrow SbCl_3 + Fe(CO)_4Cl_2 + CO$$
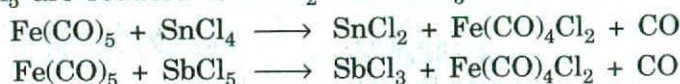
$Fe(CO)_4Cl_2$ then forms addition compounds with $SnCl_2$ and $SbCl_3$.

$$SnCl_2 + Fe(CO)_4Cl_2 \longrightarrow SnCl_2.Fe(CO)_4Cl_2$$
$$(I)$$

$$SbCl_3 + Fe(CO)_4Cl_2 \longrightarrow SbCl_3.Fe(CO)_4Cl_2$$
$$(II)$$
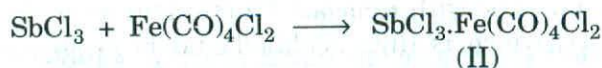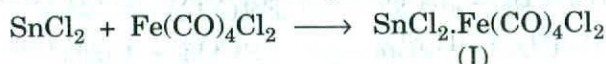
Addition compounds

The addition compounds (I) and (II) are halogen bridged compounds as shown below :

(I)   (II)
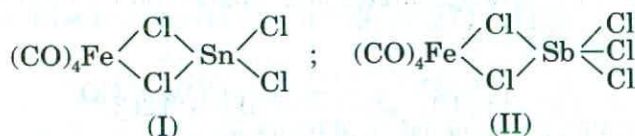
With WCl_6 and $MoCl_6$, $Fe(CO)_5$ gives $W(CO)_6$ and $Mo(CO)_6$ respectively.

$$MCl_6 + 2Fe(CO)_5 \longrightarrow M(CO)_6 + 4CO + 2FeCl_3$$
(M = W, Mo)
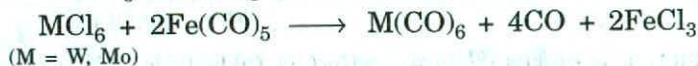
(*xi*) When it is burnt in air, finely divided ferric oxide is obtained which is used as a pigment and a polishing agent.

B. Diiron enneacarbonyl, $Fe_2(CO)_9$. Preparation. It is made by the irradiation of $Fe(CO)_5$ with near ultraviolet light. $Fe(CO)_5$ is dissolved in its own volume of glacial acetic acid and the solution thus obtained is cooled and then irradiated for six hours. Golden crystals of $Fe_2(CO)_9$ are precipitated and are obtained by filtration.

Properties. (*i*) $Fe_2(CO)_9$ forms triclinic crystals which are diamagnetic.

(*ii*) It is slightly soluble in alcohol and acetone and more so in toluene and pyridine and almost insoluble in water, ether, C_6H_6 and many other organic solvents.

(*iii*) It is non-volatile.

(*iv*) *Action of heat.* When warmed to 50°, it gives $Fe_3(CO)_{12}$. At 100° it decomposes to give Fe, CO, and some $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

(*v*) *Action of NO.* With NO it gives $Fe(CO)_2(NO)_2$ together with $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

(*vi*) *Action of phen.* In acetone or benzene solution at 80° $Fe_2(CO)_9$ reacts with *phen* to form $[Fe(phen)_3]$ $[Fe_2(CO)_8]$. In pyridine, with *phen* it gives $[Fe(phen)_3]$ $[Fe_4(CO)_{13}]$.

(*vii*) *Action of alkali metals.* Carbonylate anion is obtained in its reaction with Na in NH_3 solution

$$Fe_2(CO)_9 + 4Na \longrightarrow 2Na_2[Fe(CO)_4] + CO$$
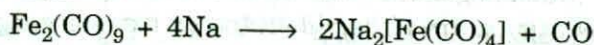
C. Tri-iron dodecacarbonyl, $Fe_3(CO)_{12}$. Preparation. It is prepared : (*i*) by the disproportionation of $Fe_2(CO)_9$. A toluene solution of $Fe_2(CO)_9$ is heated at 70°. On cooling, green crystals of $Fe_2(CO)_{12}$ separate from the solution.

$$3Fe_2(CO)_9 \xrightarrow{\Delta} 3Fe(CO)_5 + Fe_3(CO)_{12}$$
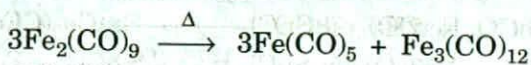
(*ii*) by the oxidation of $Fe(CO)_4H_2$ with H_2O_2 or MnO_2.

$$3Fe(CO)_4H_2 + 3H_2O_2 \longrightarrow Fe_3(CO)_{12} + 6H_2O$$

$$3Fe(CO)_4H_2 + 3MnO_2 + 3H_2SO_4 \longrightarrow Fe_3(CO)_{12} + 3MnSO_4 + 6H_2O$$
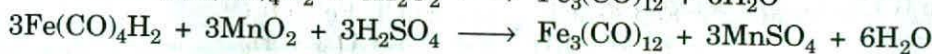
(*iii*) by treating $Fe(CO)_5$ with aqueous tri-ethylamine to form the dark red $[Et_3 NH]$ $[Fe_3(CO)_{11}H]$ which is then acidified and $Fe_3(CO)_{12}$ is extracted with petroleum ether.

Properties. (*i*) $Fe_3(CO)_{12}$ forms deep green crystals which are soluble in organic solvents like toluene, alcohol, ether and pyridine.

(*ii*) *Action of heat.* When heated alone above 100°C, $Fe_3(CO)_{12}$ decomposes to give metallic iron and CO.

$$Fe_3(CO)_{12} \xrightarrow{> 100°C} 3Fe + 12CO$$
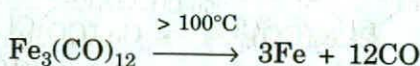
(*iii*) *Disproportionation reaction.* It undergoes disproportionation reactions. For example it reacts with CH_3OH at room temperature and $Fe(CO)_5$ is thereby produced.

$$3Fe(CO)_{12} + nCH_3OH \longrightarrow [Fe(CH_3OH)_n] [Fe_3(CO)_{11}] + 5Fe(CO)_5$$

(*iv*) *Reaction with Na.* Carbonylate anion is obtained when $Fe_3(CO)_{12}$ reacts with Na metal in liq. NH_3.

$$Fe_3(CO)_{12} + 6Na \longrightarrow 3Na_2 [Fe(CO)_4]$$

(*v*) *Substitution reactions.* These reactions occur with pyridine (*py*) and methyl alcohol as shown below :

$$2Fe_3(CO)_{12} + 3py \longrightarrow Fe_3(CO)_9 (py)_3 + 3Fe(CO)_5$$

$$2Fe_3(CO)_{12} + 3CH_3OH \longrightarrow Fe_3(CO)_9 (CH_3OH)_3 + 3Fe(CO)_5$$
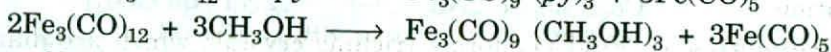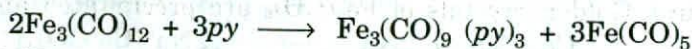
(*vi*) *Action of NO.* At 85° it reacts with NO to form iron dicarbonyl dinitrosyl, $Fe(CO)_2 (NO)_2$.

$$Fe_3(CO)_{12} + 6NO \longrightarrow 3Fe(CO)_2 (NO)_2 + 6CO$$
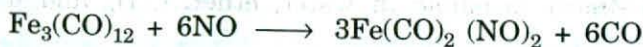
4. Dicobalt Octacarbonyl, $Co_2(CO)_8$.

Preparation. It can be prepared : (i) by the reaction between CO and reduced metallic cobalt at 220° and 250 atm.

$$2Co + 8CO \xrightarrow[220°C]{250 \text{ atm.}} Co_2(CO)_8$$
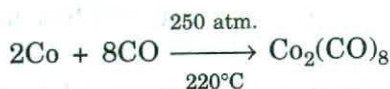
(ii) by the reaction of dry CO at 200° and 200 atm in presence of metallic copper on certain binary compounds of cobalt such as CoS and CoX_2. Here Cu forms Cu_2S or CuX.

$$2CoS + 8CO + 4Cu \longrightarrow Co_2(CO)_8 + 2Cu_2S$$

$$2CoX_2 + 8CO + 4Cu \longrightarrow Co_2(CO)_8 + 4CuX$$

(iii) by the action of CO and H_2 on $CoCO_3$ under high pressure and high temperature.

$$2CoCO_3 + 2H_2 + 8CO \xrightarrow[120-200°C]{250-300 \text{ atm.}} Co_2(CO)_8 + 2CO_2 + 2H_2O$$
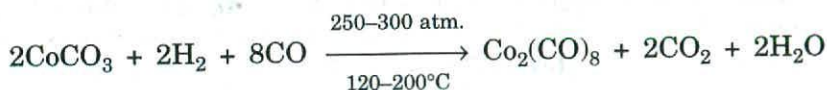
(iv) by the action of an acid on a solution of $Co(CO)_4H$. Hydrogen is evolved and $Co_2(CO)_8$ is left behind.

$$2Co(CO)_4H \longrightarrow Co_2(CO)_8 + H_2$$

(v) by the thermal decomposition of $Co(CO)_4H$.

Properties. (i) $Co_2(CO)_8$ is an orange brown crystalline substance having m.pt. = 51°C. It is soluble in alcohol, ether and CCl_4. The carbonyl is air sensitive both in the solid and solution states.

(ii) *Action of heat.* It is thermally decomposed at 50°C in an inert atmosphere to give tetra cobalt dodecacarbonyl, $Co_4(CO)_{12}$.

$$2Co_2(CO)_8 \xrightarrow{50°C} Co_4(CO)_{12} + 4CO$$
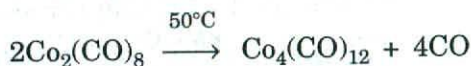
(iii) *Action of air.* On exposure to air, dicobalt octacarbonyl is converted into deep violet basic carbonate of cobalt.

(iv) *Reduction reactions.* It is reduced to cobalt carbonyl hydride, $H^+[Co(CO)_4]$ by H_2 at 165°C and 120 atmospheric pressure.

$$Co_2(CO)_8 + H_2 \xrightarrow[165°C]{120 \text{ atm.}} 2H^+[Co(CO)_4]^-$$
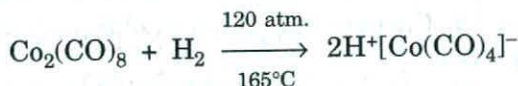
$Co_2(CO)_8$ is also reduced by Na metal in liq. NH_3 below –75°C or tetrahydrofuran (THF).

$$\underset{(Co = 0)}{Co_2(CO)_8} + 2Na \xrightarrow[\text{or liq. } NH_3]{THF} \underset{(Co = -1)}{2Na^+[Co(CO)_4]^-}$$
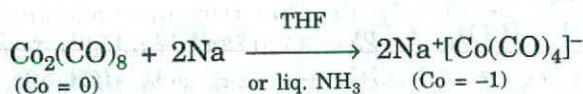
(v) *Disproportionation reactions.* There are two types of such reactions in case of $Co_2(CO)_8$.

(a) Strong bases having nitrogen or oxygen donor atoms cause disproportionation into Co(+2) and Co(−1). For example :

$$2Co_2(CO)_8 + 12NH_3 \longrightarrow 2[Co(NH_3)_6]\,[Co(CO)_4]_2 + 8CO$$
$$(Co = 0) \qquad\qquad\qquad (Co = +2) \qquad (Co = -1)$$
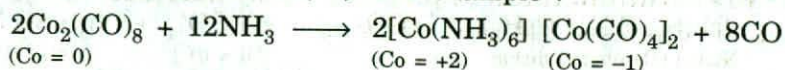
(b) With isocyanides, phosphines, arsines and stibines, however, the disproportionation reaction gives penta-coordinate cobalt (I) cation.

$$Co_2(CO)_8 + 5CNR \longrightarrow [Co(CNR)_5]\,[Co(CO)_4] + 4CO$$
$$(Co = 0) \qquad\qquad (Co = +1) \qquad (Co = -1)$$
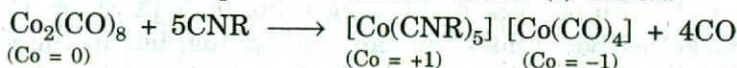
(vi) *Reaction with NO.* $Co_2(CO)_8$ also reacts with NO at 40° and forms $Co(CO)_3(NO)$

$$Co_2(CO)_8 + 2NO \longrightarrow Co(CO)_3(NO) + 2CO$$
$$(Co = 0) \qquad\qquad (Co = -1)$$
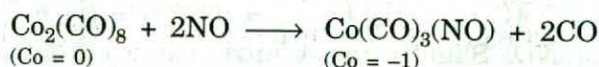
In $Co(CO)_3(NO)$, NO group appears to be more firmly held with Co metal atom than CO groups. This is confirmed by the fact that CO groups can be replaced by the amines very easily, *e.g.* the action of *phen* on $Co(CO)_3(NO)$ gives $[Co(CO)(phen)(NO)]$.

$$Co(CO)_3(NO) + phen \xrightarrow{\;-2CO\;} [Co(CO)(phen)(NO)]$$
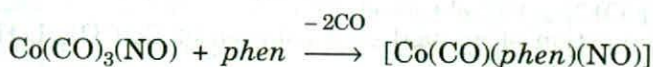
(vii) *Reaction with halogens.* The halogens decompose $Co_2(CO)_8$ according to the following reaction

$$Co_2(CO)_8 + 2X_2 \longrightarrow 2CoX_2 + 8CO$$

5. Nickel Tetracarbonyl, $Ni(CO)_4$

It was the first of the metallic carbonyls to be discovered and has found application in the metallurgy of nickel by *Mond's process.* It has zero valent nickel.

Preparation. (i) It is made by passing carbon monoxide over finely-divided metallic nickel at a temperature below 100°C.

$$Ni + 4CO \longrightarrow Ni(CO)_4$$

(ii) When CO at atmospheric pressure is passed over reduced nickel at 30–50°C, we get $Ni(CO)_4$.

(iii) $Ni(CO)_4$ is also obtained when CO is passed through an alkaline suspension of $Ni(CN)_2$ or NiS.

$$Ni(CN)_2 + 4CO \longrightarrow Ni(CO)_4 + C_2N_2$$
$$NiS + 4CO \longrightarrow Ni(CO)_4 + S$$

(iv) *By the disproportionation of univalent nickel.* (a) On reducing potassium tetracyano nickelate (II), $K_2[Ni(CN)_4]$ with potassium amalgam, a red solution is obtained. From this solution potassium tricyano nickelate (I), $K_2[Ni(CN)_3]$ may be isolated. This compound absorbs CO at 90°C, probably forming $K_2[Ni(CN)_3(CO)]$. On treating the solution of this compound with HCl, $Ni(CO)_4$ is obtained.

$$4K_2[Ni(CN)_3(CO)] + 2HCl \longrightarrow Ni(CO)_4 + 3K_2[Ni(CN)_4] + 2KCl + H_2$$
$$(Ni = +1) \qquad\qquad\qquad (Ni = 0) \qquad\quad (Ni = +2)$$
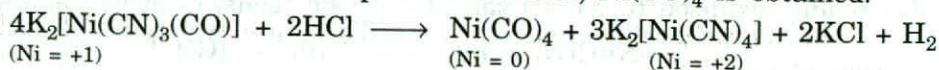
(b) It is most conveniently prepared in the laboratory by the action of CO on nickel(II) phenyl dithiocarbamate, $Ni(S.SC.NH.C_6H_5)_2$.

$$2Ni(S.SC.NH.C_6H_5)_2 + 4CO \longrightarrow Ni(CO)_4 + Ni(S.SC.NH.C_6H_5)_4$$

Nickel (II) phenyl dithio-   (Ni = 0)   Nickel (IV) phenyl
carbamate (Ni = +2)   dithiocarbamate (Ni = +4)
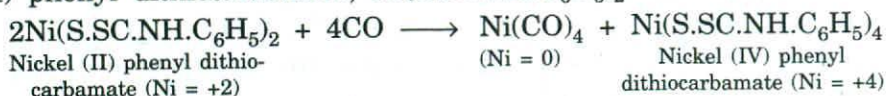
Properties. (i) It is a colourless liquid boiling at 43° and solidifying at –25°C. It is miscible with benzene and is almost insoluble in water. The benzene solution of the nickel carbonyl does the same on boiling, but in the cold, the compound is not acted on by dilute acids or alkalies. Nickel carbonyl is highly poisonous.

(ii) *Action of H_2SO_4.* H_2SO_4 reacts with it as follows :

$$Ni(CO)_4 + H_2SO_4 \longrightarrow NiSO_4 + H_2 + 4CO$$

(iii) *Action of NO.* Slightly moist nitric oxide reacts with $Ni(CO)_4$ in the gaseous state or in solution in chloroform to give a compound of intense blue colour, $Ni(NO)(OH)$.

$$2Ni(CO)_4 + 2NO + 2H_2O \longrightarrow 2Ni(NO)(OH) + 8CO + H_2$$
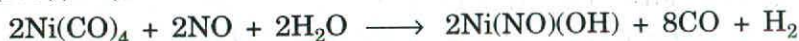
When $Ni(CO)_4$ reacts with NO in the absence of H_2O, the blue solution of the composition, $Ni(NO)(NO_2)$ is obtained.

$$Ni(CO)_4 + 4NO \longrightarrow Ni(NO)(NO_2) + 4CO + N_2O$$
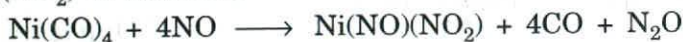
(iv) *Substitution reactions.* CO groups can be replaced by NO_2, PCl_3 and CNR molecules. o-phenanthroline (o.phen) replaces only two CO molecules

$$Ni(CO)_4 + 2NO_2 \longrightarrow Ni(NO_2)_2 + 4CO \uparrow$$

$$Ni(CO)_4 + 4PCl_3 \longrightarrow Ni(PCl_3)_4 + 4CO$$
                                      Yellow non-
                                      volatile

$$Ni(CO)_4 + 4CNR \longrightarrow Ni(CNR)_4 + 4CO \uparrow$$
         Aryl iso-   Yellow crystalline
        cyanide   substance

$$Ni(CO)_4 + o\text{-}phen \longrightarrow Ni(CO_2)\,(o\text{-}phen) + 2CO \uparrow$$
                                Ruby-red needles
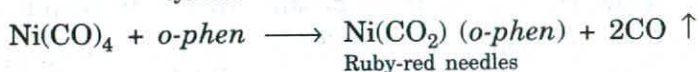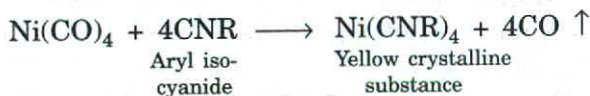
(v) *Action of heat.* $Ni(CO)_4$, when heated to 180°, gives nickel.

$$Ni(CO)_4 \xrightarrow{180°} Ni + 4CO \uparrow$$
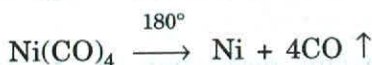
In the pure state nickel carbonyl explodes to form nickel, carbon dioxide and carbon.

$$Ni(CO)_4 \xrightarrow{\Delta} Ni + 2CO_2 + 2C$$
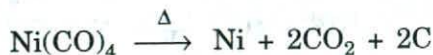
Under high atmospheric pressures (say, 100 atm) it is, however, not decomposed even up to 250°C.

(vi) *Oxidation reactions.* Solution of this carbonyl in organic solvent is readily oxidised by air developing a pale green gelatinous precipitate. Such solutions are also readily oxidised to Ni (II) salts by the halogens, cyanogen and sulphur.

$$Ni(CO)_4 + Br_2 \longrightarrow NiBr_2 + 4CO \uparrow$$
    (Ni = 0)   (Ni = +2)

Gaseous HCl decomposes the solution of $Ni(CO)_4$ evolving H_2 and CO

$$Ni(CO)_4 + 2HCl(g) \longrightarrow NiCl_2 + H_2 + 4CO \uparrow$$
$$\text{(Ni = 0)} \qquad\qquad\qquad \text{(Ni = +2)}$$
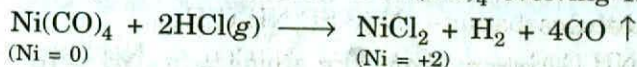
(vii) Reduction reactions. $Ni(CO)_4$ gets reduced by several reducing agents. Examples are :

(a) $N(CO)_4$ can be reduced to $[Ni^-H^+(CO)_3]$ by the reaction of $Ni(CO)_4$ with Na in liq. NH_3.

$$2Ni(CO)_4 + 2Na + 2NH_3 \longrightarrow 2[Ni^-H^+(CO)_3]_2 + 2CO + 2NaNH_3$$
$$\text{(Ni = 0)} \qquad\qquad\qquad\qquad \text{(Ni = -1)}$$
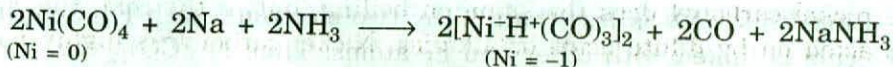
$[Ni^-H^+(CO)_3]$ is isolated as a red tetraammoniate, $[NiH(CO)_3]_2\ 4NH_3$.

(b) When $Ni(CO)_4$ solution in THF is reduced by Na, K or Mg amalgams, the enneacarbonyl tetranickelate is formed.

$$4Ni(CO)_4 + 2Na \longrightarrow Na_2[Ni_4(CO)_9] + 7CO$$
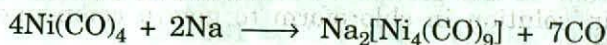
With Li, $Ni(CO)_4$ gives $Li_2\ [Ni_3(CO)_8]$

$$3Ni(CO)_4 + 2Li \longrightarrow Li_2[Ni_3(CO)_8] + 4CO$$
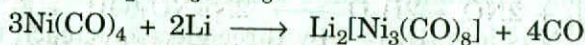
Uses. *(i)* Since $Ni(CO)_4$ is decomposed to metallic nickel, it is used in the production of nickel by Mond's process. *(ii)* It is also used in gas plating and also as a catalyst.

Questions with Answers

Q.1 What are the different types of bonds found in metal carbonyls.

Ans : Following are the important types of bonds found in metal carbonyls.

1. $:O\equiv\!\!\!\equiv C \rightarrow M$ **σ bond.** This bond can also be represented as $OC \rightarrow M\sigma$ or $OC{-}M\sigma$ bond. In this bond CO acts as a terminal carbonyl group. This bond is found in all types of carbonyls.

2. $:\ddot{O}{=}C\diagup^M_{\diagdown M}$ or $:\ddot{O}C\diagup^M_{\diagdown M}$. This system is found in bridged polynuclear carbonyls like $Co_2(CO)_8$ (in the solid state), $M_2(CO)_9$ (M = Fe, Os), $Fe_3(CO)_{10}$ etc. C-atom in the system is sp^2 hybridised.

3. M – M bond. This bond is found in $M_2\ (CO)_9$ (M = Fe, Os), $Co_2\ (CO)_8$ (in solution and solid), $M_3\ (CO)_{12}$ (M = Fe, Os) etc. The length of this bond is larger than that of normal M–M bond. The presence of this bond in metal carbonyls makes all electrons paired and hence carbonyls containing M–M bonds are diamagnetic.

Q.2 Determine the number of M–M bonds present in $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$ and $[(\eta^5 - Cp)\ Mo\ (CO)_3]_2$.

Ans : *(i)* **$Fe_2(CO)_9$.** Electrons from two Fe-atoms = $2 \times 26 = 52$

Electrons from 9 CO groups = $2 \times 9 = 18$

EAN for two Fe atoms in $Fe_2(CO)_9$ = $52 + 18 = 70$

∴ EAN for one Fe atom = $70/2 = 35$

Since this EAN is less than 36 (Kr_{36}) by one electron, there is one Fe–Fe bond in $Fe_2(CO)_9$ molecule.

(ii) $Fe_3(CO)_{12}$. Electrons from 3Fe atoms = 3 × 26 = 78

Electrons from 12 CO groups = 12 × 2 = 24

EAN for three Fe-atoms = 78 + 24 = 102

∴ EAN for one Fe atom = 102/3 = 34

Since this EAN is less than 36 by two electrons, each Fe-atom in $Fe_3(CO)_{12}$ molecule is linked with other two Fe-atoms. Thus $Fe_3(CO)_{12}$ has three Fe – Fe bond.

(iii) $Co_4(CO)_{12}$. Electrons from 4CO atoms = 4 × 27 = 108

Electrons from 12 CO groups = 12 × 2 = 24

EAN of four Co atoms = 108 + 24 = 132

∴ EAN for one Co-atom = 132/4 = 33

Since this EAN is less than 36 by three electrons, each Co-atom in $Co_4(CO)_{12}$ molecule is linked with other three Co-atom. Thus $Co_4(CO)_{12}$ has five Co–Co bonds.

(iv) $[(\eta^5 – Cp) Mo(CO)_3]_2$. Electrons from two Mo-atoms = 2 × 42 = 84

Electrons from two $\eta^5 – Cp$ = 2 × 5 = 10

Electrons from 6CO = 6 × 2 = 12

EAN for two Mo-atoms in $[(\eta^5 – Cp) Mo (CO)_3]_2$ = 84 + 10 + 12 = 106

∴ EAN for one Mo-atom = 106/2 = 53

Since this EAN is less than 54 (Xe_{54}) by one electron, there is one Mo–Mo bond in the given mixed carbonyl.

Q.3 Show that the total number of electrons present in the V.S. of metal atom in the following carbonyls is 18. $Fe_2(CO)_9$, $Co_2(CO)_8$, $Mn_2(CO)_{10}$, $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$.

Ans : (i) $Fe_2(CO)_9$.   2Fe = 2 × 8 = 16 (Fe = $3d^6 4s^2$)

$\qquad\qquad\qquad\qquad$ 9CO = 9 × 2 = 18

$\qquad$ One Fe–Fe bond $\qquad$ = 1 × 2 = 2

∴ Total electrons in two Fe atoms = 16 + 18 + 2 = 36

∴ Electrons in the V.S. of one Fe atom = $\dfrac{36}{2}$ = 18

(ii) $Co_2(CO)_8$.   2Co = 2 × 9 = 18 (Co = $3d^7 4s^2$)

$\qquad\qquad\qquad$ 8CO = 8 × 2 = 16

$\qquad$ One Co–Co bond = 1 × 2 = 2

Total electrons in two Co atoms = 18 + 16 + 2 = 36

Electrons in the V.S. of one Co-atom = $\dfrac{36}{2}$ = 18

(iii) $Mn_2(CO)_{10}$. 2Mn = 2 × 7 = 14 (Mn = $3d^5 4s^7$)

$$10CO = 10 \times 2 = 20$$
$$\text{One Mn–Mn bond} = 1 \times 2 = 2$$

Total electorns on two Mn-atoms = 14 + 20 + 2 = 36

∴ Electrons on one Mn-atom = 36/2 = 18

(iv) **$Fe_3(CO)_{12}$.** $3Fe = 3 \times 8 = 24$ $(Fe = 3d^6 4s^2)$
$$12CO = 12 \times 2 = 24$$

Three Fe–Fe bonds = $3 \times 2 = 6$

Total electrons on three Fe-atoms = 24 + 24 + 6 = 54

$$\text{Electrons on one Fe-atom} = \frac{54}{3} = 18$$

(v) **$Co_4(CO)_{12}$.** $4Co = 4 \times 9 = 36$ $(Co = 3d^7 4s^2)$
$$12CO = 12 \times 2 = 24$$

Six Co–Co bonds = $6 \times 2 = 12$

Total electrons in four Co-atoms = 36 + 24 + 12 = 72

$$\therefore \text{Electrons on one Co-atom} = \frac{72}{4} = 18$$

University Questions

1. Give one method for the preparation of each of the following : $Ni(CO)_4$, $Fe_2(CO)_9$, $Co_2(CO)_8$, $Fe(CO)_5$. *(Himachal Pradesh 99)*

2. What are metal carbonyls ? Give few examples and discuss the nature of M—CO bonding in carbonyls. *(Gorakhpur 99)*

3. Discuss the structure and constitution of $Ni(CO)_4$. *(Allahabad 99)*

4. (a) Why does CO form stable compounds with transition metals though it is a poor donor?

   (b) Define π acidity and give an example.

   (c) Discuss the structure of mononuclear carbonyls.

   (d) Discuss the preparation and structure of $Ni(CO)_4$ and $Fe_2(CO)_9$.

   (e) What is meant by back bonding in metal carbonyls?

   (Himachal Pradesh 2000)

5. Explain the following :

   (i) CO is a Lewis acid.

   (ii) $Fe(CO)_5$ has trigonal bipyramidal structure. *(Lucknow 2000)*

6. Discuss the general methods for the preparation of metal carbonyls. Describe the nature of bonding in binary and polynuclear metal carbonyls with special reference to the structures of $Fe(CO)_5$, $Mn_2(CO)_{10}$ and $Fe_2(CO)_9$.

   (Lucknow 2000)

7. What are metal carbonyls ? Classify them. Give one method of preparation of each class of metal carbonyls. Discuss the structure and bonding in $Fe(CO)_5$, $Cr(CO)_6$ and $Mn_2(CO)_8$.   *(Lucknow 2001)*

8. Describe the preparation, properties and structure of $Ni(CO)_4$.
      (C.S.J.M. Kanpur, 2005)

9. (a) Write a short note on "18-electron rule in metal carbonyls".
    (b) Describe methods of preparation, properties and structure of $Fe(CO)_5$.
      (C.S.J.M. Kanpur 2006)

10. (a) Describe the preparation and constitution of $Cr(CO)_6$.
    (b) What is EAN rule ? How is it applicable in metal carbonyls ?
      (C.S.J.M. Kanpur 2007)

11. Discuss bonding in linear metal carbonyls (M–C–O). How do vibrational spectra help to understand bonding in carbonyls ?
      (M.J.P. Rohilkhand, 2008)

12. Find out EAN in $Cr(CO)_6$ molecule.   *(M.J.P. Rohilkhand 2009)*

13. What are metal carbonyls ?   *(Meerut 2009)*

Compounds of Silicon and Glass Industry

Compounds of Silicon

1. Silicic Acids.

Two silicic acids of silicon are known. These acids are *orthosilicic acid*, H_4SiO_4 or $Si(OH)_4$ and *meta silicic acid*, H_2SiO_3 or H_2SiO_3 or $SiO(OH)_2$. The existence of these acids is not definite but many salts of these acids (called silicates) of definite composition are known. Orthosilicic acid is obtained as a gelatinous ppt. when SiF_4 or $SiCl_4$ is passed into water.

$$3SiF_4 + 4H_2O \longrightarrow \underset{\substack{\text{Gelatinous}\\\text{ppt.}}}{H_4SiO_4} + 2H_2SiF_6$$
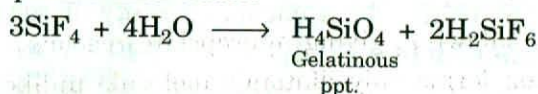
The gelatinous ppt. is filtered, washed, first with water and then with ether and is finally dried between folds of filter paper when a white amorphous powder of H_4SiO_4 is obtained.

Metasilicic acid is obtained as a gelatinous ppt. by adding HCl to a concentrated solution of an alkali silicate like Na_2SiO_3.

$$Na_2SiO_3 + 2HCl \longrightarrow 2NaCl + \underset{\substack{\text{Gelatinous}\\\text{ppt.}}}{H_2SiO_3}$$
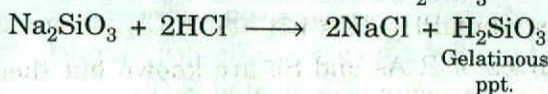
The gelationous ppt. of H_2SiO_3 so formed is filtered, dehydrated with 90% alcohol and finally dried when a white amorphous powder is obtained.

The colloided solution of metasilicic acid is known as *silicic acid sol*. It was discovered by Graham in 1861 and is formed by slowly pouring a cold dilute solution of Na_2SiO_3 (called *water glass*) into an excess of dil HCl.

Na_2SiO_3 (*solution*) + HCl (*dil. and in excess*) $\longrightarrow 2NaCl + H_2SiO_3$
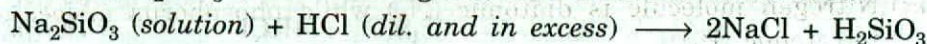
The resulting mixture of liquids is dialysed in a parchment bag placed in distilled water when NaCl and HCl diffuse out of the bag while a pure colloidal solution of silicic acid is left in the dialyser.

2. Sodium Silicate or Water Glass, Na_2SiO_3.

This is a salt of *metasilicic acid*, H_2SiO_3 and is also called *water glass or soluble glass*. It consists of sodium metasilicate containing an excess of silica; the composition may vary from $Na_2SiO_3.SiO_2$ to $Na_2SiO_3.3SiO_2$.

Preparation. (*i*) It is prepared by fusing together sodium carbonate with pure sand in a reverberatory furnace.

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2 \uparrow$$

(*ii*) It is also obtained by fusing together sodium sulphate, charcoal and sand.

$$Na_2SO_4 + 2C \longrightarrow Na_2S + 2CO_2 \uparrow$$
$$Na_2S + 3Na_2SO_4 + 4SiO_2 \longrightarrow 4Na_2SiO_3 + 4SO_2 \uparrow$$
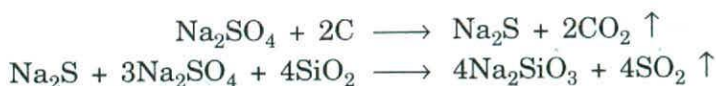
The resulting mass is extracted with water and the solution evaporated to a syrup known as water glass having the Composition $Na_2SiO_3.SiO_2$.

Properties. Water glass is soluble in water and the solution is strongly alkaline due to hydrolysis. Crystals of various soluble coloured salts like $CuSO_4$, $FeSO_4$, $Co(NO_3)_2$, $NiCl_2$, $MnCl_2$ etc. when placed in a solution of water glass having a specific gravity of 1.1 produce beautiful growth which is called *silica garden* or *chemical garden*. The preparation of silica garden is done as follows :

Prepare a concentrated solution of sodium silicate water of density 1.1. Place this liquid in a beaker, sprinkle some crystals of coloured salts like $FeSO_4$, cobalt nitrate, nickel sulphide etc. on the surface of the liquid. Coloured shoots will rise up and grow on long standing like a plant. This is called silica garden or chemical garden.

Uses. Sodium silicate is used : (*i*) in calicoprinting, (*ii*) in fire- proofing wood and textiles, (*iii*) as a. preservative for egg, (*iv*) as a furniture polish, and (*v*) in the soap industry as a filler for a cheaper variety of soap.

3. Silicon Tetrachloride, $SiCl_4$.

Preparation. This compound is prepared:

(*i*) by passing dry Cl_2 over heated amorphous silicon or magnesium silicide (Mg_2Si) or an intimate mixture of SiO_2 and coke.

$$Si + 2Cl_2 \longrightarrow SiCl_4$$
$$Mg_2Si + 4Cl_2 \longrightarrow SiCl_4 + 2MgCl_2$$
$$2SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$
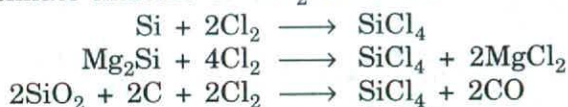
(*ii*) by passing a mixture of dry Cl_2 and S_2Cl_2 vapour over heated SiO_2.

$$2SiO_2 + 3Cl_2 + S_2Cl_2 \longrightarrow 2SiCl_4 + 2SO_2$$
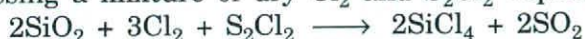
(*iii*) by passing CCl_4 vapour over heated SiO_2

$$SiO_2 + CCl_4 \longrightarrow SiCl_4 + CO_2$$

Properties (*i*) Physical properties. It is a colourless fuming liquid of density 1.50 (at 0°C). Its b.pt. and m.pt. are 56.8°C and 70°C respectively.

(*ii*) *Hydrolysis.* $SiCl_4$ is hydrolysed by H_2O with the formation of orthosilicic acid (H_4SiO_4) and HCl

$$SiCl_4 + 4H_2O \longrightarrow H_4SiO_4 + 4HCl \qquad\qquad ...(A)$$
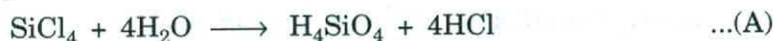
The hydrolysis of SiC_4 takes place through the following steps :

(*a*) $SiCl_4$ coordinates with two H_2O molecules through their O-atoms to form the unstable intermediate compound, $SiCl_4.2H_2O$. In this compound Si atom attains its maximum covalency of 6.

Silicon tetrachloride,	Unstable intermediate
$SiCl_4$	compound, $SiCl_4.2H_2O$
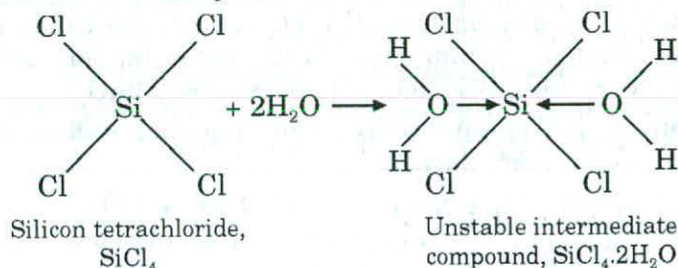
(b) The intermediate compound, $SiCl_4.2H_2O$ then eliminates two HCl molecules to give $SiCl_2(OH)_2$

$SiCl_4.2H_2O$ $SiCl_2(OH)_2$
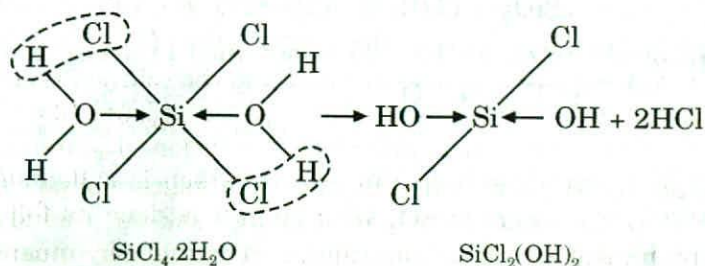
(c) The compound, $SiCl_2(OH)_2$ then combines with two H_2O molecules and forms $SiCl_2(OH)_2.2H_2O$.

$SiCl_2(OH)_2$ $SiCl_2(OH)_2.2H_2O$
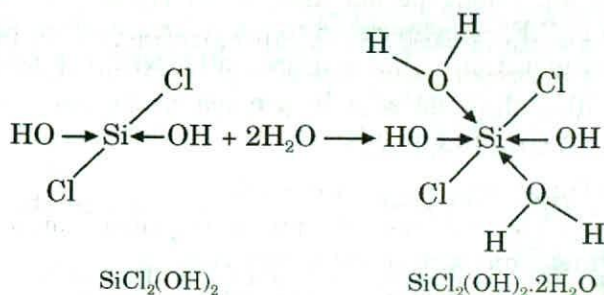
(d) The compound, $SiCl_2(OH)_2.2H_2O$ eliminates two HCl molecules and gives rise to the formation of orthosilicic acid, $Si(OH)_4$ or H_4SiO_4.

$SiCl_2(OH)_2.2H_2O$ Orthosilicic acid
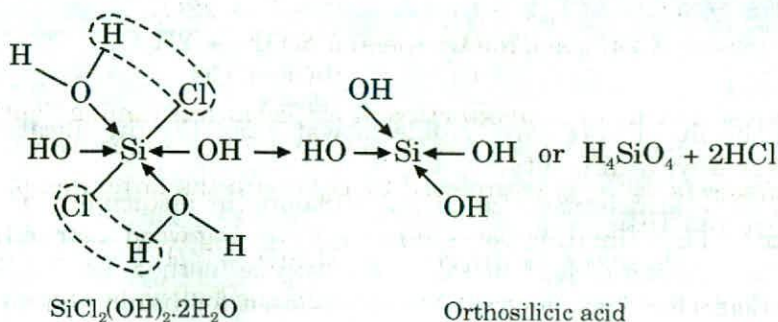
On combining the above equations, we get the equation (A) given above.

Since carbon atom has already attained its maximum covalency of 4 in CCl_4, it cannot coordinate with water molecules to form the compound, $CCl_4.2H_2O$. Hence CCl_4 cannot be hydrolysed and in extremely stable.

Uses. $SiCl_4$ is used in warfare in producing smoke screen. It is more effective when used along with NH_3, as in that case white clouds of NH_4Cl are also formed.

4. Hydrofluosilicic Acid, H_2SiF_6.

Preparation (*i*) The acid is made in solution by dissolving SiO_2 in aqueous HF.

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$$

(*ii*) An aqueous solution of the acid is obtained by passing SiF_4 in water.

$$3SiF_4 + 4H_2O \longrightarrow 2H_2SiF_6 + H_4SiO_4$$
$$\text{(Soluble)} \quad \text{(White gelatinous}$$
$$\text{ppt)}$$
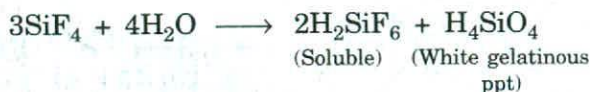
In actual practice SiF_4 is prepared by heating a mixture of powdered fluorspar (CaF_2), sand (SiO_2) and conc. H_2SO_4 in a stout flask on a sand bath. SiF_4 so produced is then passed into H_2O contained in a cylinder by means of a delivery tube, the end of the dry delivery tube dipping under mercury placed at the bottom of the cylinder. This arrangement prevents the chocking of the delivery tube by gelatinous ppt. of H_2SiO_4 formed in this reaction. After passing the gas of SiF_4 for a sufficiently long period into water, H_4SiO_4 is filtered off and the filtrate containing H_2SiF_6 is evaporated to get a concentrated solution. Too much concentration by evaporation is not required otherwise the acid will decompose.

(*iii*) H_2SiF_6 is also obtained as a by-product in the manufacture of calcium superphosphate from the mineral *phosphorite* which contains SiO_2 and fluorides as impurities.

Properties (*i*) Physical state. The concentrated solution of the acid ii a colourless fuming liquid.

(***ii***) ***Decomposition.*** It decomposes on evaporation into HF and SiF_4.

$$H_2SiF_6 \longrightarrow 2HF + SiF_4$$

(***iii***) ***Acidic character.*** It is a strong acid and it is as highly ionised in solution as H_2SO_4. With alkalies it forms salts which are called *fluosilicates* or *silicofluorides*

$$H_2SiF_6 + 2NaOH \longrightarrow Na_2SiF_6 + 2H_2O$$
$$\text{Sod. fluo-}$$
$$\text{silicate}$$
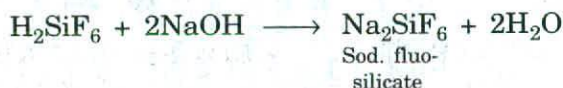
Most of the fluosilicates are soluble in water but the fluosilicates of Na, K, Ba etc. dissolve with difficulty.

Uses. (*i*) The acid is used (*a*) as an antiseptic in medicines, (*b*), for testing barium salts (*c*) for estimating potassium, (*d*) for giving wood a stone-like surface, and (*e*) in the refining of lead metal by electrolytic method. (*ii*) Na_2SiF_4 is used as an insecticide for chickens. (*iii*) $MgSiF_6$ is used for hardening and polishing the surface of concrete floors.

Silicones

What are silicones ?

Silicones are synthetic *polymerised organo-silicon polymers* containing —Si—O—Si—O—Si— linkages along with —C—C—C—C linkages present as the side chains.

Types of silicones on the basis of their structure.

The silicones may be of the following types : (1) *Linear (straight chain) silicones*, (2) *Cyclic silicones*, (3) *Cross-linked (three dimensional) silicones*.

Structures of the three types are given below.

R   R
\ /
Si
/ \
O   O
| |
R   R   R   R   R
| | | \   / \
...O—Si—O—Si—O—Si—O...   Si   Si
| | | / \ / \
R   R   R   R   O   R
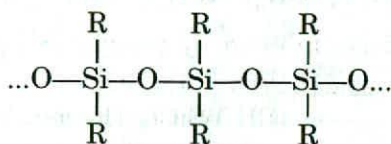
Linear silicone   Cyclic silicone
(Trimer)
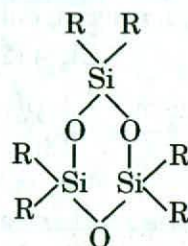
R   R   R
| | |
...O—Si—O—Si—O—Si—O...
| | |
O   O   O
| | |
...O—Si—O—Si—O—Si—O...
| | |
R   R   R
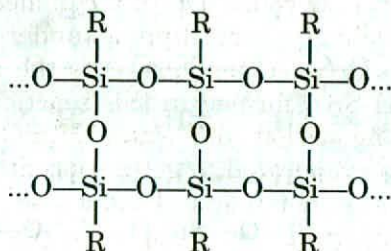
Cross-linked silicone

Here R stands for CH_3, C_2H_5 or C_6H_5 groups.

1. Linear Silicones.

These silicones are obtained by the hydrolysis and subsequent condensation of dialkyl or diaryl substituted silicon chloride, R_2SiCl_2 (B = alkyl or aryl group). For example when $(CH_3)_2 SiCl_2$ is hydrolysed, an *unstable silicol*, $(CH_3)_2Si(OH)_2$ is obtained.

$$
\begin{array}{c}
CH_3 \\
| \\
Cl—Si—Cl + 2H_2O \xrightarrow[(-2HCl)]{\text{Hydrolysis}} HO—Si—OH + 2HCl \\
| \\
CH_3
\end{array}
$$
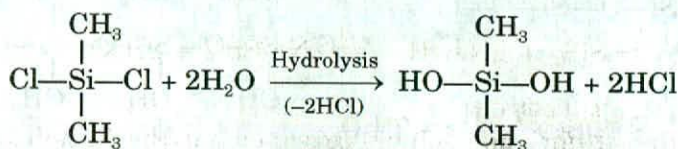
Unstable silicol

Now a number of molecules of this silicol undergo condensation by intermolecular elimination of some H_2O molecules to form linear silicones.

$$
\begin{array}{c}
CH_3 \qquad\qquad CH_3 \qquad\qquad CH_3 \\
| \qquad\qquad\quad | \qquad\qquad\quad | \\
H|O—Si—O|H + OH|—Si—O|H + OH|—Si—O|H + \text{etc.} \xrightarrow[(-xH_2O)]{\text{Condensation}} \\
| \qquad\qquad\quad | \qquad\qquad\quad | \\
CH_3 \qquad\qquad CH_3 \qquad\qquad CH_3
\end{array}
$$

Many molecules of silicol

$$
\begin{array}{c}
CH_3 \quad CH_3 \quad CH_3 \\
| \qquad | \qquad | \\
—O—Si—O—Si—O—Si—O— + xH_2O \\
| \qquad | \qquad | \\
CH_3 \quad CH_3 \quad CH_3
\end{array}
$$
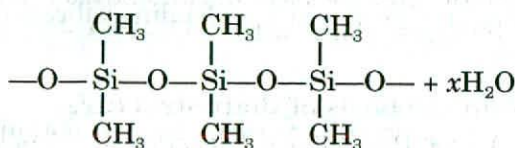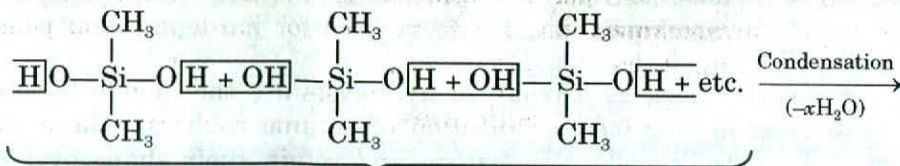
Linear silicone

$(CH_3)_2SiCl_2$ required in the preparation of linear silicones is obtained by the action of Grignard reagent on $SiCl_4$ or by Rochow's method (1945)

$$SiCl_4 + 2CH_3MgCl \longrightarrow (CH_3)_2SiCl_2 + 2MgCl_2$$

Grignard
reagent

$$Si + 2CH_3Cl \xrightarrow{\text{Cu catalyst}} (CH_3)_2SiCl_2 \text{ (Rochow's method)}$$
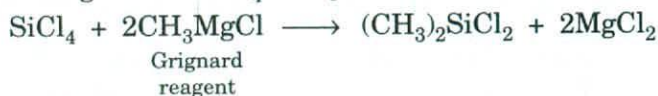
(a) Silicone rubbers are composed of units with very high molecular weights bridged together with ethylene or similar groups as shown below :
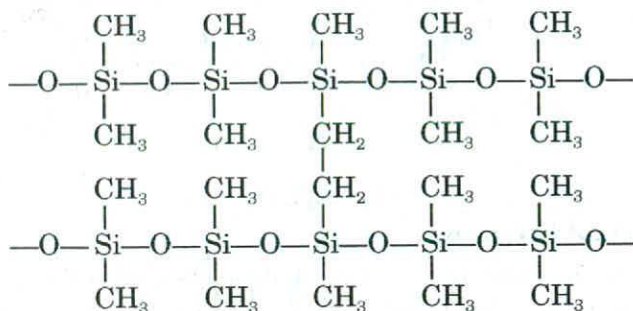
Silicone rubber

(b) Room-temperature-vulcanizing (RTV) silicone rubbers are also available. These contain groups like CH_3COO^- which can easily be hydrolysed and cross link in the presence of atmospheric moisture.
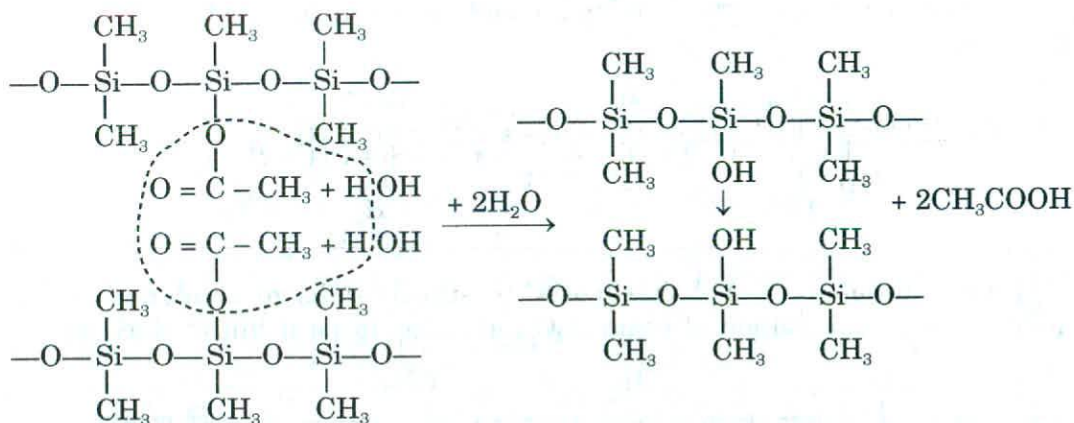
OH^- groups produced as a result of hydrolysis are then made to condense, resulting in cross-linking (*cf* vulcanization of organic rubbers). These silicones are completely water repellent in nature and retain their shape over a wide range of temperatures.

(c) Silicone resins are produced by blending silicones with organic resins such as acrylic esters.

2. Cyclic Silicones.

Like linear silicones, cyclic silicones can also be obtained by the hydrolysis and subsequent condensation of R_2SiCl_2. For example :

$$\underset{\substack{\text{(CH}_3)_2\,\text{SiCl}_2}}{\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{Cl—Si—Cl}}}} + 2\text{H}_2\text{O} \xrightarrow[(-2\text{HCl})]{\text{Hydrolysis}} \underset{\substack{\text{Unstable silicol}}}{\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{HO—Si—OH}}}} + 2\text{HCl}$$

Condensation (–3H$_2$O) → Cyclic silicone + 3H$_2$O
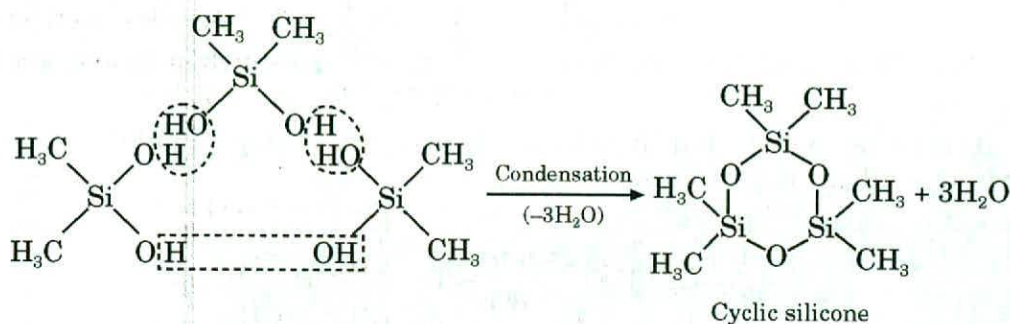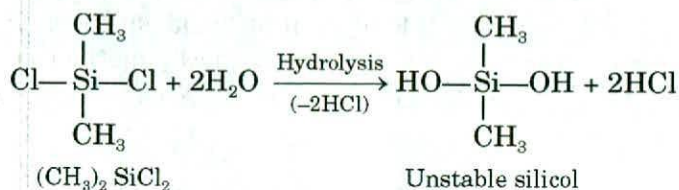
3. Cross-linked Silicones.

Such silicones are obtained by the hydrolysis and subsequent condensation of mono alkyl or aryl substituted silicon chloride, RSiCl$_3$. Its formation takes place through the following steps :

$$(i)\quad \underset{\underset{\text{Cl}}{|}}{\overset{\overset{\text{Cl}}{|}}{\text{R—Si—Cl}}} + 3\text{H}_2\text{O} \xrightarrow[(-3\text{HCl})]{\text{Hydrolysis}} \underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{OH}}{|}}{\text{R—Si—OH}}} + 3\text{HCl}$$

$$(ii)\quad \boxed{\text{H}}\text{O—}\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—}\boxed{\text{OH} + \text{H}}\text{O—}\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—}\boxed{\text{OH} + \text{H}}\text{O—}\underset{\underset{\text{O}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—O}\boxed{\text{H}}$$

$$\xrightarrow[(-x\text{H}_2\text{O})]{\text{Condensation}} \text{—O—}\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—O—}\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—O—}\underset{\underset{\text{OH}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—O—}$$

$$(iii)\quad \text{—O—}\underset{|}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—O—}\underset{|}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—O—}\underset{|}{\overset{\overset{\text{R}}{|}}{\text{Si}}}\text{—O—}$$

$$
\begin{array}{ccccccc}
 & R & & R & & R & \\
 & | & & | & & | & \\
-O- & Si & -O- & Si & -O- & Si & -O- \\
 & | & & | & & | & \\
 & O & & O & & O & \\
 & | & & | & & | & \\
-O- & Si & -O- & Si & -O- & Si & -O- \\
 & | & & | & & | & \\
 & R & & R & & R & \\
\end{array}
$$

Condensation $\xrightarrow{\quad}$ $(-xH_2O)$

Cross-linked silicone
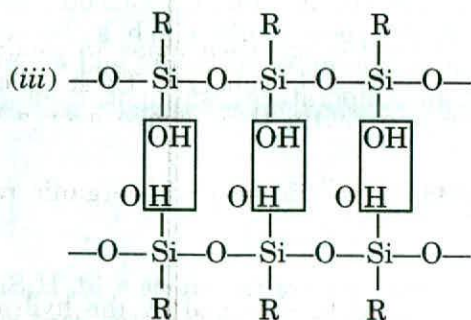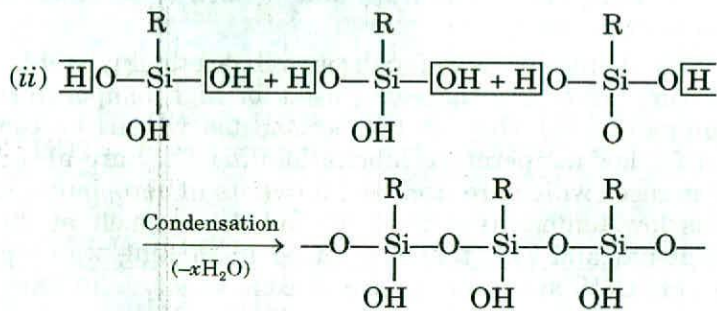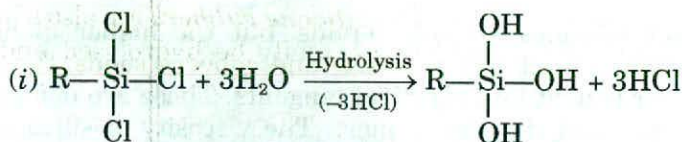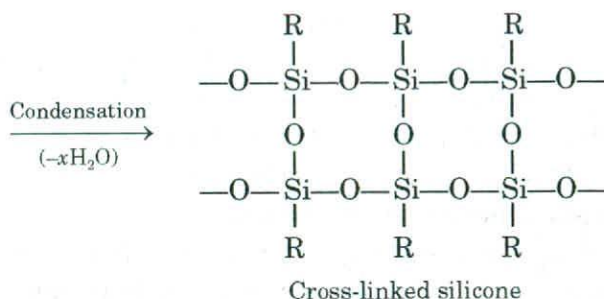
It may be noted that R_2SiCl on hydrolysis produces only a *dimer*, $R_3Si-O-SiR_3$ as shown below :

$$
\begin{array}{c}
R \\
| \\
R-Si-Cl + H_2O \xrightarrow[(-HCl)]{Hydrolysis} R-Si-OH + HCl \\
| \\
R
\end{array}
$$

$$
R-Si-\boxed{OH + H}O-Si-R \xrightarrow[(-H_2O)]{Condensation} R-Si-O-Si-R
$$
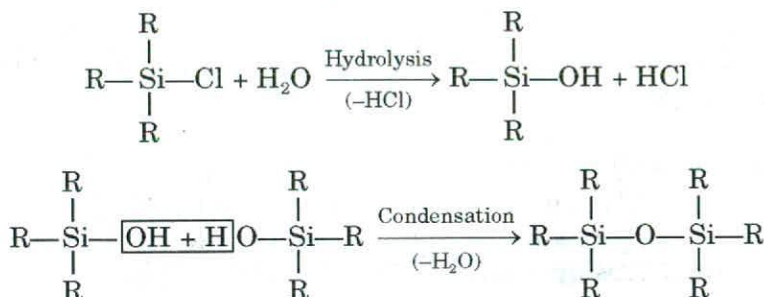
Properties. The lower silicones are oily liquids, but the higher members containing long chains or ring structures are waxy and rubbery solids. Silicones are remarkably stable towards heat and chemical reagents. These are not wetted by water. They are non-toxic and chemically inert. The viscosity of silicone oils remains constant with the change of temperature and as such these silicones do not thicken in cold weather.

Uses. Some of the uses of silicones are (*i*) Silicone-oils are highly stable and non-volatile even on heating. They are, therefore, used for high temperature oil baths, high vacuum pumps etc. (*ii*) They do not become too viscous on cooling and are, therefore, used for low-temperature lubrication (*iii*) They are also used in making vaseline like greases which are used as lubricants in aeroplanes, since they do not freeze at as low temperature as 40°C and do not melt at 200°C. (*iv*) They are water-repellents and are, therefore, used in making water proof cloth and paper by exposing cloth and paper to the silicone vapours. (*v*) They are also used as insulating materials for electric motors and other electric appliances, since they can withstand high temperature without charring. (*vi*) Silicon-rubber, after vulcanization, retains its shape and elasticity permanently and has, therefore, been used in a number of ways. (*vii*) Silicones are mixed in paints and enamels to make them resistant to the effects of high temperatures, sunlight, chemicals and damp.

Silicates

What are Silicates ?

Silicates may be regarded as the metal derivatives of the silicic acid, H_4SiO_4. Silicates can be prepared by fusing metal oxides or metal carbonates with sand (SiO_2). For example :

<div align="center">
Fuse with
sand (SiO_2)
</div>

$$Na_2CO_3 \xrightarrow{\hspace{1.5cm}} Na_2SiO_4, (Na_2SiO_3)_n \text{ etc.}$$
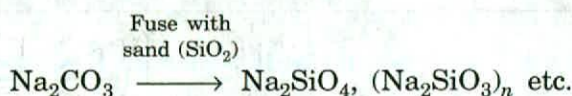
Only some silicates of alkali metals are soluble in water while others are insoluble. The insolubility is due to the great strength of Si—O bond. When silicates are treated with HF, Si—O bond is broken.

Classification and Structure of Silicates.

X-ray diffraction studies of various types of silicates have shown that all the silicates have SiO_4^{4-} anions which are formed by sp^3 hybridisation of Si atom. Si atom in its excited state contains 4 unpaired electrons and hence forms 4 covalent bonds with four negatively-charged O-atoms, resulting in the formation of SiO_4^{4-} anion. Each O-atom becomes negatively charged by picking up an electron from some metal.

Since Si atom undergoes sp^3 hybridisation, SiO_4^{4-} anion has tetrahedral shape as shown in Fig. 29.1.
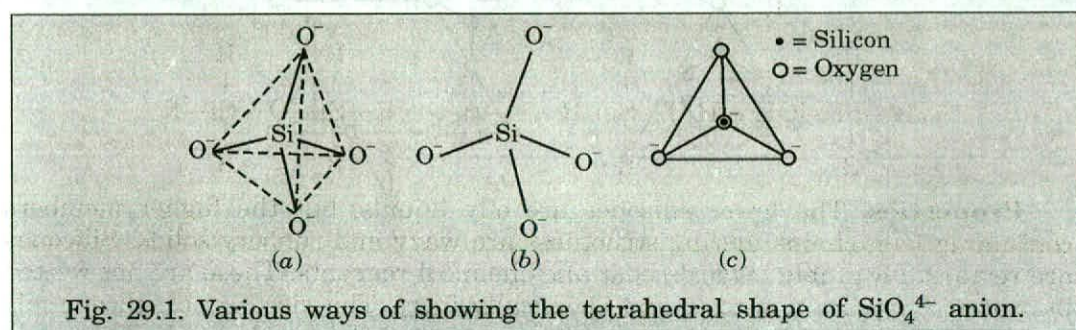
Fig. 29.1. Various ways of showing the tetrahedral shape of SiO_4^{4-} anion.

It is evident from the above discussion that all silicates contain the tetrahedral SiO_4^{4-} anions. These anions differ from one another in the manner in which these anions are linked together.

Silicates are classified according to the nature of linking between the tetrahedral SiO_4^{4-} anions. This basis of classification gives the following types of silicates.

1. Orthosilicates. These silicates contain discrete SiO_4^{4-} tetrahedral anions. The O-atoms of each SiO_4^{4-} anion is also coordinated to the metal ion to impart electrical neutrality to the structure. Examples of such silicates are *phenacite*, Be_2SiO_4; *willemite*, Zn_2SiO_4; *olivine*, Mg_2SiO_4; *zircon*, $ZrSiO_4$; *garnets*, $M_3^{2+} M_2^{3+}$ $(SiO_4)_3$ (where M^{2+} = Mg^{2+}, Ca^{2+}, Fe^{2+} etc. and M^{3+} = Al^{3+}, Cr^{3+}, Fe^{3+} etc.). In garnets SiO_4 tetrahedra are arranged about M^{2+} and M^{3+} so they become 8-and 6-coordinated respectively. Garnets are very hard and find extensive uses as industrial abrasives.

2. Pyrosilicates. These silicates contain the discrete $Si_2O_7^{6-}$ anion which is formed by joining two SiO_4 tetrahedral units through one oxygen atom (See Fig. 29.2).

Examples of silicates containing $Si_2O_7^{6-}$ anion are *thorteveitite*, $Sc_2(Si_2O_7)$ and *hemimorphite*, $Zn_3(Si_2O_7).Zn(OH)_2.H_2O$.
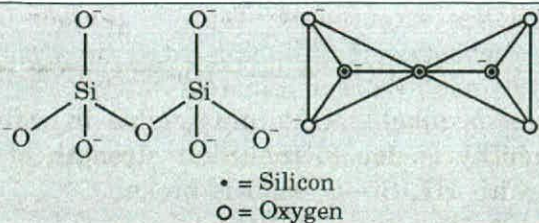
• = Silicon
o = Oxygen

Fig. 29.2. Structure of $Si_2O_7^{-6}$ ion found in pyrosilicates.

3. Cyclic or ring silicates. Such silicates contain the cyclic or ring anions like $Si_3O_9^{6-}$ or $Si_6O_{18}^{12-}$. The structure of these anions is given in Fig. 29.3. These anions are obtained when each SiO_4 tetrahedral unit shares an O-atom with each of the two neighbouring SiO_4 units.

• = Silicon
o = Oxygen

(a)   (b)
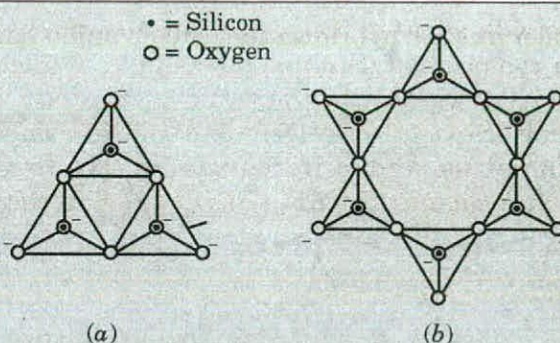
Fig. 29.3. Structure of (a) $Si_3O_9^{6-}$ (b) $Si_6O_{18}^{12-}$ anions found in cyclic silicates.

Examples of cyclic silicates containing $Si_3O_9^{6-}$ anion are *benitoite*, $BaTiSi_3O_9$; *wollastonite*, $Ca_3Si_3O_9$; *catapleite*, $Na_2ZrSi_3O_9.2H_2O$ while the example containing $Si_6O_{18}^{12-}$ anion is beryl, $Be_3Al_2Si_6O_{18}$.

4. Chain silicates. Such silicates contain the anions which are formed by the sharing of two oxygen atom by each tetrahedron The anions may be one of the types (a) $(SiO_3)_n^{2n-}$ (b) $(Si_4O_{11})_n^{6n-}$ whose structures are shown in Fig. 29.4.

• = Silicon
o = Oxygen

(a)   (b)
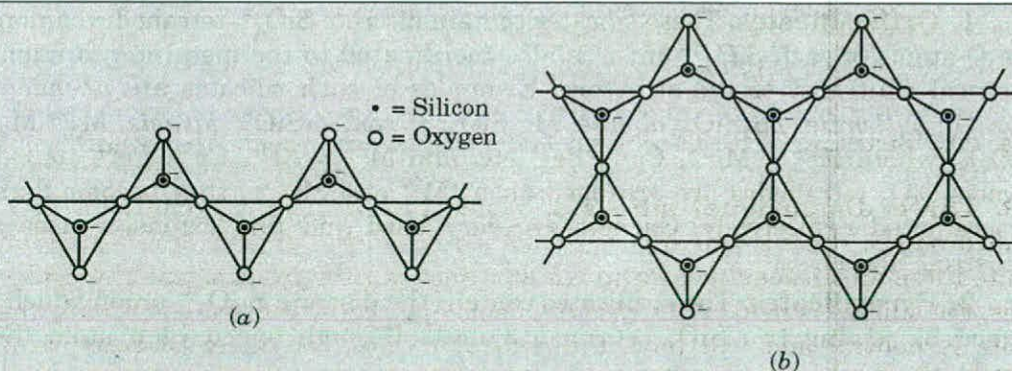
Fig. 29.4. Structure of (a) $(SiO_3)_n^{2n-}$ (b) $(Si_4O_{11})_n^{6n-}$ anions found in chain silicates.

The chains in the silicates containing $(SiO_3)_n{}^{2n-}$ anions lie parallel to each other and the cations lie between the chains and bind them together. Such silicates are presented by the *pyroxene* minerals and several synthetic silicates. Examples are (*a*) *synthetic silicates* e.g. Li_2SiO_3, Na_2SiO_3 (*b*) *pyroxene minerals* e.g. spodimene, $LiAl(SiO_3)_2$; jadeite, $NaAl(SiO_3)_2$; enstatite, $MgSiO_3$; diopside, $CaMg (SiO_3)_2$.

The silicates containing $(Si_4O_{11})^{6n-}$ anions have double chains in which the simple cations are held together by shared oxygens. Such silicates are represented by the *amphibole minerals* which include most asbestos minerals. Structurally amphiboles are similar to pyroxenes though they contain some OH groups which are attached to the cations. *Tremolite*, $Ca_2Mg_5 (Si_4O_{11})_2 (OH)_2$ is an example of amphibole.

5. Two-dimensional sheet silicates. When three 0.atoms of each SiO_4 tetrahedron are shared with adjacent SiO_4 tetrahedra, an infinite two-dimensional sheet structure of the composition $(Si_2O_5)_n{}^{2n-}$ results. (See Fig. 29.5). The metal ions present hold the layers together by the weak electrostatic forces. As a result, the minerals containing $(Si_2O_5)_n{}^{2n-}$ are soft and cleave easily. Such sheet-like anions are found in micas and different types of clay minerals. *Talc*, $Mg_2(Si_2O_5)_2.Mg(OH)_2$ and *kaolin*, $Al_2(OH)_4 (Si_2O_5)$ are the common examples of clay minerals.
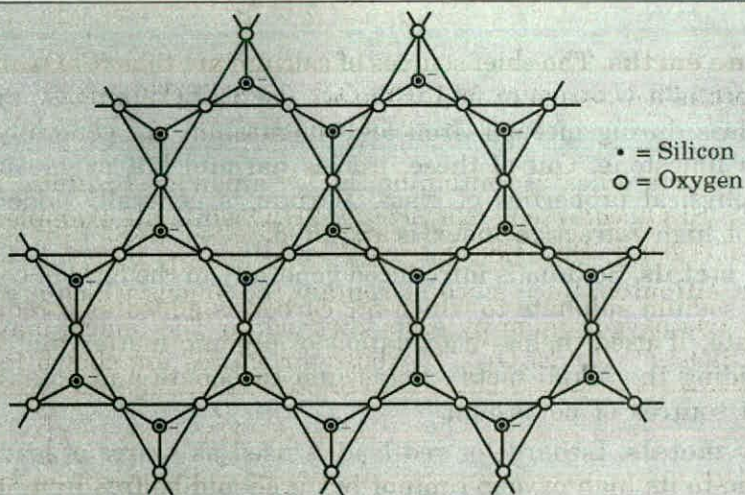
Fig. 29.5 Structure of $(Si_2O_5)_n{}^{2n-}$ ion found in two-dimensional sheet silicates.

6. Three dimensional silicates. When all the four oxygens of a SiO_4 tetrahedron are shared with adjacent tetrahedra and the process is repeated, an infinite three-dimensional structure results. Since all the oxygens are the bridge atoms, the silicate is neutral. In case Si is not replaced by other metal atoms, the silicate is neutral and will have the neutral formula SiO_2. Such structure is found in *quartz, tridymite* and *crystobalite*. This explains the structure of silica, SiO_2.

However, if some Si^{4+} ions are replaced by Al^{3+} ions in the tetrahedral positions in the SiO_2 structure, in order to maintain electrical neutrality, some other monovalent cations (*e.g.* K^+, Na^+ etc.) must be introduced. Such a replacement of Si^{4+} cations by Al^{3+} and monovalent cations gives the minerals like *feldspars, zeolites* and *ultra marines*.

Glass Industry

Any substance which has solidified from the liquid state without crystallization is known as glass. Glass is therefore, classified as a 'super cooled liquid'. Commonly the word glass means the transparent substance obtained by the fusion of certain metal oxides with white sand. Glass does not have a sharp melting point. When such a substance is heated, it begins to soften at a temperature far below the one at which it flows like a liquid.

Raw Materials Used in the Manufacture of Glass.

Following are the main raw materials used in the manufacture of glass :

1. Silica. It is added in the form of sand which must be of uniform size (too coarse variety prevents reaction while too fine one makes it violent). The chief impurities with which natural sand is frequently associated are alumina, iron and organic matter. Small quantities of alumina are not harmful but iron acts as a colouring matter, and, therefore, must be removed along with the organic matter.

2. Alkaline earths. The chief sources of calcium are lime (CaO) and limestone ($CaCO_3$). There is a wastage of fuel when we use $CaCO_3$ but CO_2 evolved helps in stirring glass during melting. Iron and magnesium are generally present as impurities in limestone. Out of these, iron is harmful but magnesium helps to control the physical properties of glass. Barium is generally added as $BaCO_3$ when glass of high refractive index is required.

3. Alkali metals. Sodium is introduced generally in the form of coarse sodium carbonate or sodium sulphate to which 5% carbon is added as a reducing agent. Sodium nitrate, if used, helps in oxidation of organic matter and ferrous iron besides providing the alkali metal. Potassium carbonate and potassium nitrate are the chief sources of potassium.

4. Heavy metals. Litharge or red lead is used as source of lead. The latter preferable due to its high oxygen content but it should be free from metallic lead and oxides of copper or iron.

In the modern heat resisting glass, calcium or lead is replaced by zinc which is added in the form of zinc oxide along with boric acid or borax which decreases the coefficient of expansion.

Phosphates when required are added as $Ca_3(PO_4)_2$ while arsenic and antimony are added as oxides. Addition of these helps to produce glass which is opalescent.

5. Colouring materials. Certain metallic oxides if added to the molten mass produce different shades of colours, and are used in the manufacture of coloured glasses *e.g.*, the following colours are produced by substances noted against each

(i) Red glass contains Cu_2O and selenium metal, (ii) *Green glass* contains CuO and Cr_2O_3, (iii) *Yellow glass* contains CdS, carbon, (iv) *Blue glass* contains CuO, CoO. (v) *Violet glass* contains MnO_2, (vi) *Milky glass* contains SnO, $Ca_3(PO_4)_2$, (vii) *Black glass* contains oxides of cobalt, manganese, nickel etc.

6. Borax. It is used as a flux. Borax also lowers the coefficient of expansion of the glass and increases its durability.

7. Alumina. Alumina makes glass resistant to sudden changes of temperature. Alumina is often used in the form of feldspar. It is a naturally occurring mineral with a formula $Na_2O\ Al_2O_3.6SiO_2$ (soda feldspar) or $K_2O.Al_2O_3.6SiO_2$ (potash feldspar).

8. Cutlets. These are pieces of waste glass. These serve two purposes—these facilitate fusion and secure utilization of waste.

Manufacture of Glass.

The manufacture of glass consists of the following steps :

1. Fusion of raw materials. The raw materials to be used depend upon the variety of glass to be obtained. For ordinary soda-lime glass the raw materials are sand, washing soda and limestone. These are mixed in the proper proportion and ground together. The resulting mass known as "*batch*" is mixed with broken glass called "*cullet*" and introduced either into the pots of a pot furnace or into the tank of a *tank furnace*.

(a) Pot furnace. In this furnace the pots are placed in a circle around a central opening in its bottom. Hot gases and the flames come out of this opening. The roof over the pots is of refractory material which reflects the heat on to the pots. Pots are of two types *viz.* open and closed. Clay rings are placed in pots which facilitate withdrawal of the molten material. (See Fig. 29.6.)

Fig. 29.6 A pot furnace.
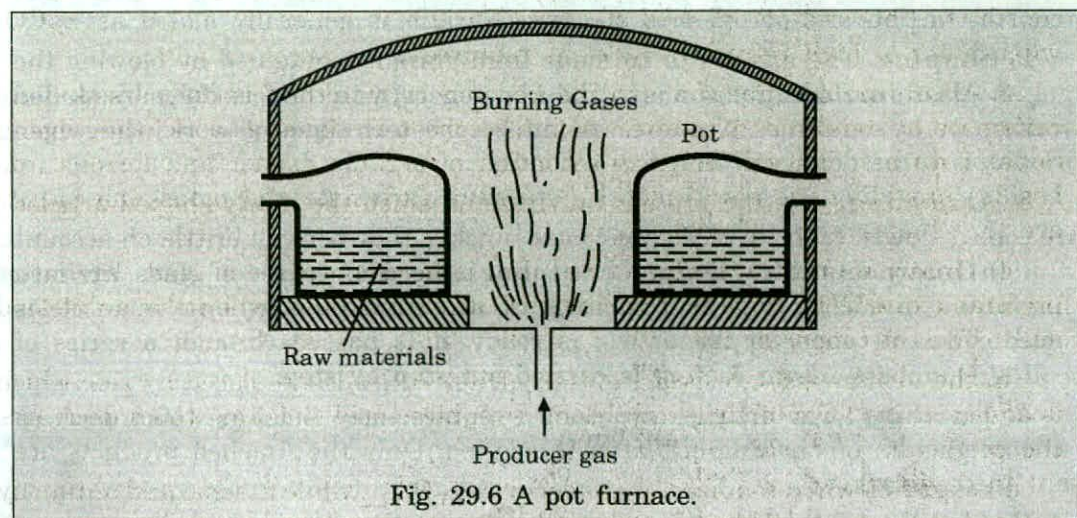
(b) Tank furnace. In this furnace the batch materials are charged at one end and the molten glass taken out at the other. Tank furnace is a type of reverberatory furnace in which the molten mass forms a pool over the hearth. Heating is done by means of producer gas which is burnt inside. (See Fig. 29.7).

Fig. 29.7. A tank furnace
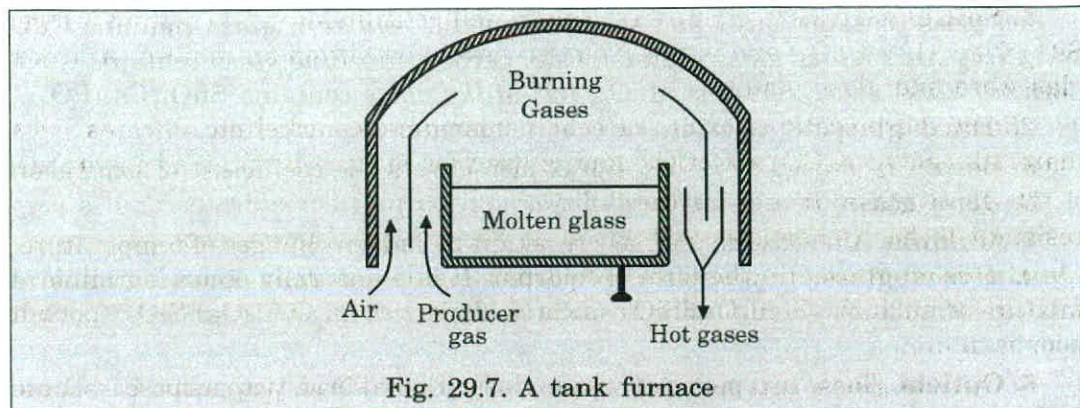
During melting a good deal of frothing is caused owing to the evolution of gases like CO_2, SO_2, O_2 etc. When froth subsides, the temperature is raised and the molten glass is allowed to stand for some time. In this way a homogeneous mass free from gas bubbles is obtained.

In tank furnace the products obtained may not be of a superior quality because the molten glass cannot be stirred and the glass is not of a uniform composition.

The chemical reactions taking place during the process are :

$$Na_2CO_3 + n_1SiO_2 \longrightarrow Na_2O.n_1SiO_2 + CO_2$$
$$Na_2SO_4 + C \longrightarrow Na_2O + CO + SO_2$$
$$Na_2O + n_2SiO_2 \longrightarrow Na_2O.n_2SiO_2$$
$$CaCO_3 + n_3SiO_2 \longrightarrow Na_2O.n_3SiO_2 + CO_2$$
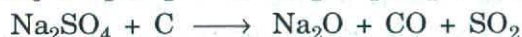
Commercial glass is the mixture of all the silicates *viz.* $Na_2O.n_1SiO_2$. $Na_2O.n_2SiO_2$ and $Na_2O.n_3SiO_2$.

2. Shaping. The articles to be made from glass are obtained by blowing the molten glass into definite shapes. The blowing or moulding is done by skilled workers or by machine. Whatever might be the technique of work, the whole process is to be done within a few seconds.

3. Annealing. It is the process by virtue of which the newly shaped articles are cooled slowly. If the articles are cooled quickly, they become brittle on account of high internal strain. During annealing, the molecules of glass arrange themselves in such a way that there is no strain on them when the article is cooled. Thus as soon as the article is ready, it is passed through a series of cooling chambers where cooling is carried out step by step.

4. Finishing. The articles so obtained require some finishing touch such as cutting, grinding, polishing etc. after annealing. Only the finished products are sent to the market.

Varieties of Glass.

Large varieties of glass are obtained by varying the composition of the batch. Some of these are as follows :

1. Soft glass. It is a mixture of sodium and calcium silicates (raw materials: SiO_2, Na_2CO_3 + CaO_3) and is the common variety employed for making ordinary glassware and glass plates.

2. Hard glass. It is a mixture of potassium and calcium silicates (raw materials : SiO_2, K_2CO_3 + $CaCO_3$) and is used for making hard glass apparatus.

3. Jena glass. It is a mixture of zinc and barium borosilicates and is very resistant to heat, chemicals and shock. It has a high alumina content.

4. Pyrex glass. It possesses properties similar to Jena glass but it is a mixture of sodium aluminium borosilicates. It is rich in silica (about 80%) but poor in alumina.

5. Optical glass. It is generally made by fusing red lead, potassium carbonate and sand. Special varieties contain boron trioxide in place of silica and barium and zinc oxide in place of red lead. *Crookes glass* contains cerium oxide which cuts off ultraviolet light harmful to eyes.

6. Safety glass. It is obtained by placing a layer of butyral plastic with a suitable adhesive between two layers of glass and cementing them by heat and pressure. It does not shatter and is used in making automobile wind shields. Fine layer laminated glass prepared as above is used in building construction.

7. Glass wool. It is glass fibre obtained by forcing molten glass through tiny holes in presence of a jet of high pressure system.

Glass being a thermal insulator is wrapped round various articles in the form of glass wool. Glass fibres are used for making fire proof clothing. These would incidentally be stain resistant as well s bad conductors of electricity. Hollow glass bricks are used in constructing walls where light would come in but cold could be kept out. Glass fibres have also been used as the base of several useful plastic moulded articles.

8. Coloured glass. To produce glass of different colours, various mineral substances are mixed with it during the process of manufacture. Examples have already been given on page 969.

<div align="center">

┌─────────────────────────────┐
│   **Questions with Answers**   │
└─────────────────────────────┘

</div>

Q.1 Give different groups of silicones which are commercially important.

Ans : Silicones which are commercially important can be classified into four groups namely *silicone fluids* or *oils, silicone greases, silicone rubbers and silicon resins.*

1. Silicone Fluids or Oils.

These silicone fluids are mixtures of straight chain polymers differing in viscosities. Most of these are made from dimethyldichlorosilane, hence have methly groups attached to the silicon atoms of the polymers chain. Other organic groups may be introduced to alter the properties of the fluids.

$$2(CH_3)_3Si-Cl + n\ Cl-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-Cl \xrightarrow[\text{condensation}]{\text{hydrolysis}} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}\left[O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O\right]_n\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3$$

<div align="center">silicon oil or fluid</div>
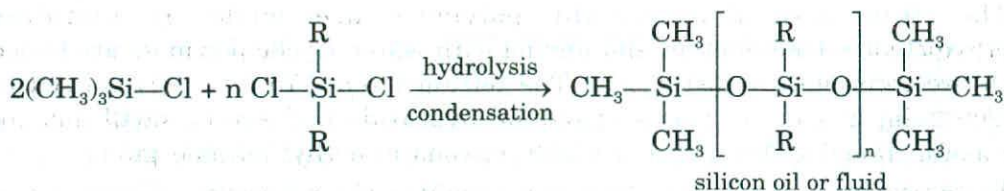
Properties and uses of silicone fluids. (*i*) Silicon fluids are *good lubricants under vacuum* and at high temperature. They are used in vacuum pumps, jet turbines and guided missiles as lubricants.

(*ii*) They are used in heating baths for industrial *heating and as damping fluid* in instruments and electrical switchgears.

(*iii*) They are used as *antifoaming agents* in several industries such as dyes, textiles, brewing, paint, glue, paper, food processing and sewage disposal.

(*iv*) The *water repellent properties* of silicones have become a boon in the manufacture of water proofing textiles, leather, paper, glass and other matericals.

(*v*) They are also used for coating glass and ceramics insulators *to prevent electrical leakage during rain.*

(*vi*) Silicones added to *wax polishes give a high gloss finish.*

(*vii*) Silicones resist adhesion to several surfaces and are used *as release agents*. They are coated in moulds for easy removal of plastic articles and rubber tyers form moulds.

(*viii*) *Greases are made from silicone* fluids by mixing with meatllic soap, graphite or silica.

2. Silicone Greases :

Silicon grease is the modified form of silicon fluid. It can be prepared by adding some fillers like silica, carbon black, etc. to silicone fluids.

Properties and Uses : (*i*) Silicon greases are stable to a wide range of temperature from −100°C to 450°C. So they are used in industries as very effective lubricants.

(*ii*) When treated with silica they are used as electrical greases in car ignition systems.

(*iii*) Greases with lithium soap filler are used for ball-bearings, etc.

(*iv*) Greases with carbon black filler are used in high temperature conveyers and oven doors, etc.

3. Silicone Rubbers :

Silicone elastomers are made form high molecular weight linear polymers containing about 9000 monomers by cross-linking. General purpose silicone elastomers are made from polydimethylsioxanes. Other special ealstomers contain a small proportion of groups other than methyl. The linear polymer silicon oil is mixed with filler such as silica, nodifying additives and organic peroxide catalyst and cured by heating.

The high moleculear weight polymers are made by dissoling dimethydichlorosilane in ether and mixing with water. Cyclic polymers are fomed which are recovered by distillation. The tetramer b.p. 175°C is polymerised at 150-200°C in presence of traces of sodium hydroxide and a very small amount of monofunctional silane to yield highly viscous dimethyl silicone gum.

Properties : *The silicone elastomers combine the properties of rubber and silicones.* They retain flexibility over −90°C to 250°C temperature range. They can withstand exposure to ozone, ultraviolent light and weathering. They have excellent dielectric properties and are not affected by oils. They get more easily torn than rubber and dissolve in aromatic solvents.

Silicone rubbers are masticated and cured with 2, 4-dichloro-benzoyl peroxide at higher temperature. Prolonged curing makes the rubber less elastic but hard and more resistant to oil and chemicals.

Vinyl silicone rubbuers are made by incorporating a small percentage of vinylsubstituted silanes. These are more elastic at higher temperature. Curing is done with ditertiarybutyl and dicumyl peroxides.

Curing of silicone rubbers can be done with high-energy radiation such as gammasays.

Uses : (*i*) Silicone rubbers are extensively used *in aircraft industry* in diaphargms, gaskets, insulation, hot air ducting, tyers etc.

(*ii*) They are used for insulation for electrical wiring in naval ships.

(*iii*) They are used *for coating metal roller used in several industries,* for coating, pipes and ducting carring chemicals.

(*iv*) Silicone rubber is *used in moulds* for making chocolate or jelly, sterilizable baby bottle nipples, insulation for domestic machines etc.

(*v*) It has become important in *medical appliactions e.g.* transfusion tubing, heart valves, plastic surgey, nerves repairs etc.

4. Silicone Resins :

These are compact cross-linked silicones which are hard. They are made by hydrolysis of a mixture of dimethyldichlorosilan and silicon tetrachloride or methylsilicon trichloride. The resins are polymersied only upto gel points, then they are dissolved in a solvent and applied to a surface or shared and polymerished further to a hard infusible solid. Phenyl methyl silicon resins can withsatnd 300°C for long time.

Uses : (*i*) They can be reinforced with glass fibre to provide structural material resistant it heat.

(*ii*) Silicone resin varnishes are used for coating armatures and transformer windings.

(*iii*) Silicone resin based paints are used where resistant to weathering, light, water and oxidation are required *e.g.* factory chimneys, ventillators, exhaust pipes, open plants in chemicals industries.

(*iv*) Silicone resins give a non-stick surface to frying pans, baking vessels etc.

(*v*) Silicone laminate with gass fiber or asbestos is fireproof, damp proof with good electrical insulation properties. It is used for making fire barries in aircrafts etc.

(*vi*) Silicone resin emulsions are sprayed on bricks, concrete mortan or stone to give water repellent finish.

Q.2 Starting from SiCl$_4$, prepare in not more than four steps, a linear silicone containing methyl groups only. *(I.I.T. 2001)*

Ans : Various steps involved in the preparation of linear silicone by SiCl$_4$ consists of the following steps :

(*i*) First of all SiCl$_4$ is treated with CH$_3$MgCl (Grignard reagent) so that it is converted into dimethyl dichloro silane, (CH$_3$)$_2$SiCl$_2$.

$$SiCl_4 + 2CH_3MgCl \longrightarrow (CH_3)_2SiCl_2 + 2MgCl_2$$
$$\text{Dimethyl}$$
$$\text{dichloro silane}$$
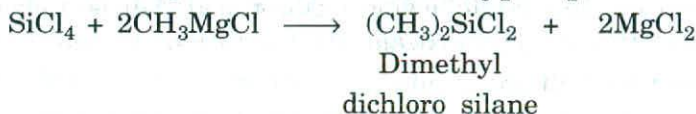
(*ii*) (CH$_3$)$_2$SiCl$_2$ obtained as above is hydrolysed to get dimethyl silandiol, (CH$_3$)$_2$ Si(OH)$_2$.

$$(CH_3)_2\ SiCl_2 + 2H.OH \xrightarrow{\quad Hydrolysis \quad} (CH_3)_2Si(OH)_2 + 2HCl$$
$$\text{Dimethyl}$$
$$\text{silandiol}$$
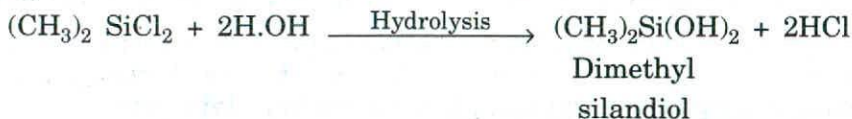
(*iii*) Many molecules of (CH$_3$)$_2$Si(OH)$_2$ obtained as above in step (*ii*) get polymerised to form linear silicone.

$$n\left[HO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH \right] \xrightarrow[(-nH_2O)]{Polymerisation} \left[-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O- \right]_n + nH_2O$$

Linear silicon
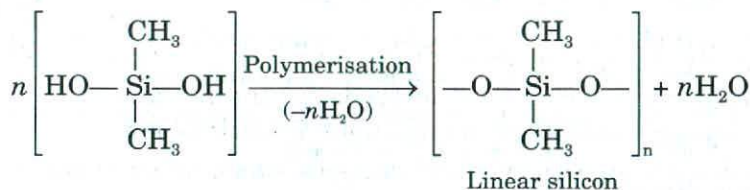
Q.3 Classify the following silicates : Zircon, hemimorphite, wallastonite, beryl, spodumene, asbestos, talc and silica.

Ans : Zircon (ZrSiO$_4$) – *orthosilicate*, hemimorphite [Zn$_3$(Si$_2$O$_7$). Zn(OH)$_2$ or Zn$_4$(Si$_2$O$_7$) (OH)$_2$] – *pyrosilicate*, wallastonite (Ca$_3$Si$_3$O$_9$ or 3CaO. 3SiO$_2$) – *cyclic (ring) silicate*, beryl (Be$_3$ Al$_2$ Si$_6$ O$_{18}$ or 3BeO. Al$_2$O$_3$. 6SiO$_2$) – *cyclic or ring silicate*, spodumene [LiAl (SiO$_3$) or $\frac{1}{2}$ (Li$_2$O. Al$_2$O$_3$. 4SiO$_2$)] – *single chain silicate*, asbestos [CaMg$_3$ O(Si$_4$O$_{11}$) or CaO.3MgO. 4SiO$_2$] – *double chain silicate*, talc [2Mg (Si$_2$O$_5$). Mg(OH)$_2$ or 3MgO. 4SiO$_2$. H$_2$O] – *two dimensional sheet silicate*, silica (SiO$_2$) – *three dimensional silicate*.

Q.4 Beryl and pyroxenes both share two O-atoms with other SiO$_4^{4-}$ tetrahedral ions and have the same anion *viz* [(SiO$_3$)$_n$]$^{2n-}$. How do they differ ?

Ans : Beryl (Be$_3$ Al$_2$ Si$_6$ O$_{18}$) contains Si$_6$O$_{18}^{12-}$ ion which is [(SiO$_3$)$_n$]$^{2n-}$ ion having n = 6. Si$_6$O$_{18}^{12-}$ ion is obtained when two O-atoms of each SiO$_4^{4-}$ ion are

shared with other SiO_4^{4-} ions in such a way that cyclic ring is fromed. Thus $Si_6O_{18}^{12-}$ ion is a cyclic ion.

Pyroxenes contain $[(SiO_3)_2]^{4-}$ ion which is a $[(SiO_3)_n]^{2n-}$ ion having $n = 2$. $[(SiO_3)_2]^{4-}$ ion is obtained when two O-atoms of each SiO_4^{4-} ion are shared with other SiO_4^{4-} ions in such away that single chain is formed. Thus $[(SiO_3)_2]^{4-}$ ion found in pyroxenes is a single chain ion.

Above discussion shows that beryl is a cyclic silicate whereas pyroxenes are chain silicates.

University Questions

1. How will you prepare the following : Silicic acid, Silicon tetrachloride and Hydrofluosilicic acid ?   (*Utkal 86; Bharathidasan 83; Gorakhpur 85*)

2. Write a note on "Sodium silicate".   (*Madras 86*)

3. What is silica gel ?   (*Delhi 87*)

4. Describe the preparation, properties and uses of silicones.
                                                      (*Allahabad 87, 89*)

5. How are silicates classified? Discuss in brief the structure of chain silicates.
                                                (*Himachal Pradesh 99*)

6. Write a short note on "Glass".   (*R.E.E. 82*)

7. Write short notes on "Silicates".   (*Delhi 99*)

8. How are silicates classified? Discuss in brief the structure of chain silicates.
                                                (*Himachal Pradesh 99*)

9. Describe the method of preparation and uses of silicone.   (*Allahabad 99*)

  (*a*) What are silicones ? Give methods for the formation of different types of silicones. Give their applications in technology.

  (*b*) Discuss the physico-chemical changes which occur during the setting of cement.   (*Himachal Pradesh 2000*)

10. Write a note on "Glass".   (*Kanpur 2000*)

11. Write the composition of borosilicate.   (*Banglore 2001*)

12. Describe different varieties of glass.   (*Banglore 2002*)

13. Discuss the preparation, properties and uses of silicones.   (*Meerut 2009*)

General Characteristics of Group 15 (VA) Elements : Nitrogen Group Elements

Group VA of the periodic table consists of five elements *viz. Nitrogen* (N), *Phosphorous* (P), *Arsenic* (As), *Antimony* (Sb) and *Bismuth* (Bi).

Position of Nitrogen Group Elements in the Periodic Table

The inclusion of nitrogen group elements namely N, P, As, Sb and Bi in the same sub-group of the periodic table is justified by the following general characteristics of these elements.

I. Electronic Configurations.

The electronic configurations of these elements are N(Z = 7) → 2, 5 ($2s^2p^3$); (P = 15) → 2, 8, 5($3s^2p^3$); As (Z = 33) → 2,8, 18, 5 ($4s^2p^3$); Sb(Z = 51) → 2, 8,18,18, 5($5s^2p^3$); Bi(Z = 83) → 2, 8, 18, 32, 18, 5 ($6s^2p^3$). It is evident from these configurations that all of these elements have five electrons in the outermost orbit which are distributed as ns^2, np^3 electrons. The three P electrons are equally distributed in accordance with *Hunds rule* amongst the three orbitals np_x^1, np_y^1 and np_z^1 and since the orbitals are exactly half-filled, the elements are fairly stable and not so reactive, *e.g.* nitrogen behaves almost as an inert element. The shell previous to outermost shell contains in nitrogen the group s^2 (*saturated*), in phosphorus s^2p^6 (*saturated*), in arsenic $s^2p^6d^{10}$ (*saturated*) whereas in antimony and bismuth $s^2p^6d^{10}$ (*unsaturated*). This shows why nitrogen differs from phosphorus and these two from the remaining elements of this sub-group.

II. Similarities in Physical Properties and Gradation in Them.

Some of the physical properties of these elements are discussed below :

1. Occurrence. Nitrogen occurs in the free state in nature while all the remaining elements occur in the combined state. Nitrogen occurs as the diatomic gas (N_2) and constitutes approximately four-fifth part of the earth's atmosphere and in chemical combination it occurs mainly as a nitrate. Phosphorus is very reactive and hence does not occur in the native state. Rather it occurs as phosphates in its ores. As, Sb and Bi are less abundant and occur chiefly as sulphide ores such as arsenical pyrites (FeAsS), stibnite (Sb_2S_3) and bismuth glance (Bi_2S_3j)

2. Allotropy. All the elements except bismuth show allotropy. Nitrogen exists in two solid allotropic forms *viz.* α-*nitrogen* and β-*nitrogen* Phosphorus exists in the allotropic forms such as *white, red, scarlet,* α-*black,* β-*black* and *violet.* Arsenic exists in three allotropic forms namely grey, yellow and black whilst antimony exists as *yellow, black,* β and *explosive antimony.*

3. Physical State and Elemental Structure. Nitrogen is a gas, phosphorus is a soft, waxy and lustreless solid, As is a hard lustreless solid and Sb and Bi are hard solids and have characteristic metallic lustre. Nitrogen exists as diatomic molecule, N_2 while phosphorus, arsenic and antimony exist as tetratomic molecules P_4, As_4 and Sb_4. Here a very important question arises : *Why do phosphorus and arsenic atoms not form P_2 and As_2 species while nitrogen atoms form N_2 species?* The answer to this question is that it is not possible for P and As atoms to form $p\pi$–$p\pi$ bonds because these atoms cannot come closer to each other to form $p\pi$–$p\pi$ bonds due to the increased repulsions from the non-bonding electrons of penultimate shell. However, N-atoms do not encounter any repulsion, since they contain $1s^2$ electrons in their penultimate shell. Thus N-atoms can form N_2 species. Moreover all the elements form giant lattices in which the bonding changes form covalent to metallic, *e.g.* violet and red phosphorus have layered covalent structure with a coordination of three; As and Sb have more closely packed layers which have intermediate bonding while Bi has truly metallic bonding.

4. Atomic Volume and Atomic Radius. Both the atomic volume and atomic radius increase as we move down the group. However, As has an exceptionally low value of atomic volume.

5. Ionisation Potentials. With the increase of size from N to Bi, the values of first ionisation energies decrease on descending the group.

6. Metallic and Non-metallic Character. Due to the decrease in the values of ionisation energies from N to Bi, the metallic character of these elements increases in the same direction. For example, the first two elements *viz.* N and P are exclusively non-metals, the next two elements *viz.* As and Sb are metalloids while the last element namely Bi is definitely a metal.

7. Electronegativity and Heat of Atomisation. From N to Bi electronegativity and heat of atomisation decrease. This decrease confirms the gradual increase in the metallic character of the elements from N to Bi.

8. Melting and Boiling Points. The melting points (except for Sb and Bi) and the boiling points both increase as we move down the group. The melting point of Bi is usually low. Low melting point of Bi suggests that there is little possibility of the availability of the pair of electrons in *s*-orbital. The elements of this group are more volatile than their intermediate neighbours. This is because of the fact that these elements have 5 electrons in their valence shell.

9. Hardness and Density. There is a pronounced increase in hardness and density in going from P to Bi.

10. Oxidation States. (*a*) *Formation of M^{3+} and M^{5+} cations.* M^{3+} cations are formed only when all the three electrons of *np* orbital from ns^2p^3 configuration are lost and ns^2 electrons remain inert (*inert pair effect*). Since the inert pair effect increases down the group, the heavier elements namely Sb and Bi lose their three electrons from *np* orbital and form M^{3+} cations. For example $Sb_2(SO_4)_3$ contains Sb^{3+} ion and similarly $Bi F_3$ and $Bi(ClO_4)_3.5H_2O$ both contain Bi^{3+} ions. Here it should be noted that Bi^{3+} and Sb^{3+} ions in $Bi(ClO_4)_3.4H_2O$ and $Sb_2(SO_4)_3$

respectively are not stable in presence of water because of hydrolysis to form bismuthyl (BiO^+) and antimonyl (SbO^+) ions.

In order to get noble gas configuration it is not possible for N and P to lose all its five ns^2p^3 electrons to form M^{5+} cations, since the energy requirements for the formation of M^{5+} cations are prohibited. Thus in case of nitrogen and phosphorus M^{5+} cations do not exist.

(*b*) *Formation of M^{3-} anions.* We have seen that the valence shell configuration of these elements is ns^2p^3. Thus, in order to achieve noble gas configuration, these elements accept three electrons from strongly electropositive elements and form M^{3-} anions. As the size of the atoms increases on moving down the group, the attraction of the nucleus, for the newly added electrons decreases. Thus, on moving down the group, the tendency of the elements to give M^{3-} ions decreases Thus, N-atom which is of the smallest size has the strongest tendency to give M^{3-} ion, P forms P^{3-} ion less readily while other members of the group show little or no tendency to form M^{3-} ions.

(*c*) *Covalency of 3 and 5.* As is evident from the valence-shell configuration, each of these elements has two paired *s*-electrons and three unpaired *p*-electrons. The elements form *three covalent bonds* and thereby attain the noble gas electronic configuration (ns^2p^6) when they use all their *p*-electrons. Except nitrogen all other elements have *d* orbitals as well. As a result, one of the two *ns*-electrons may be promoted to the vacant *nd*-orbitals to have five unpaired electrons in the valence-shell. These five unpaired electrons can be used in forming *five covalent bonds.* Thus P, As, and Sb show 5-covalent state. This is not possible for N-atom, since it has no *d*-orbital. This explains why nitrogen forms only trihalide and not pentahalide.

Due to the presence of lone pair of electrons on N and P atoms in NH_3 and PH_3 molecules, these molecules can act as Lewis bases towards H^+ and BF_3 to form NH_4^+, PH_4^+, $H_3N \rightarrow BF_3$ and $H_3P \rightarrow BF_3$ species in which N and P atoms show a covalency of 4. P, As and Sb show a covalency of 6 in $[PCl_6]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ complexions.

11. Tendency of the Elements for Catenation. Nitrogen and phosphorus have a tendency to form M—M links. For example N-atoms are linked together in hydrazine (H_2N—NH_2) and azide [(N—N—N) skeleton]. In case of phosphorus P—P links are limited only to two atoms (*e.g.* P_2H_4) while As has no tendency for catenation. The decrease in the tendency from N to As to form M—M links is due to the decrease in their M—M bond energies as shown : N—N = 83.7 kJ/mole, P—P = 79.09 kJ/mole, As—As = 63.19 kJ/mole.

12. Electrical and Thermal Conductivity. Both these properties increase as we move down the group because the delocalisation of electrons increases on moving from nitrogen (which is represented as: $N \equiv N$: with a coordination number of one) to bismuth (which has metallic crystal with a coordination number of six). Thus N and P are non-conductors, As is a. poor conductor, Sb is a good conductor and Bi is an excellent conductor.

III. Similarities in Chemical Properties and Gradation in Them.

Some chemical properties are discussed below :

1. Formation of Hydrides. All the elements of this group form the hydrides like MH_3 (M = N, P, As, Sb, Bi), M_2H_4 (M = N, P). It has been seen that all the elements form MH_3 type hydrides. Their methods of preparation, properties etc. are discussed below :

Preparation. MH_3 type hydrides are prepared by the action of water or dil. acids on the binary metallic compounds such as Mg_3N_2, Ca_3P_2, Zn_3As_2, Mg_3Sb_2 and Mg_3Bi_2.

Properties. (*i*) *Physical state.* All the hydrides are colourless and volatile gases.

(*ii*) *Basic character.* The basic character, *i.e.* the ability to act as electron pair donor, decreases on proceeding from NH_3 to BiH_3 Thus NH_3 readily coordinates with H^+ to give the stable cation, NH_4^+ whereas PH_4^+ ion is much less stable and MH_4^+ ion for As, Sb and Bi elements do not exist. The electron donor ability of the hydrides is increased by the replacement of the H-atom by alkyl groups. For example $P(CH_3)_3$ shows stronger basic character than PH_3.

NH_3 is the strongest electron pair donor, because N-atom has the smallest size and hence the electron density of the Lone pair of electrons present in one of the four sp^3 hybrids on N-atom is concentrated over a small region. As we move downwards in the group, due to the increase in the size of the central atom, the electron density of the lone pair gets diffused over a large region and hence the ability to donate electron pair (*i.e.* basic character) decreases.

(*iii*) *Thermal stability.* Thermal stability of the hydrides decreases gradually from NH_3 to BiH_3 as is evident from a decrease in the temperature of their decomposition, *i.e.* $NH_3(1300°C) > PH_3 (440°C) > AsH_3 (280°C) > SbH_3$ (room temperature) $> BiH_3$ (very unstable). The temperatures given in brackets are the decomposition temperatures of the hydrides. The least stable nature of BiH_3 confirms the fact that only trace quantities of this hydride have been identified. The decrease in thermal stability from NH_3 to BiH_3 means that M—H bond goes on weakening.

(*iv*) *Covalent character.* Since the electronegativity difference between nitrogen and hydrogen (in NH_3) is more than that between phosphorus and hydrogen (in PH_3), NH_3 molecule has more ionic character than PH_3 ($NH_3 > PH_3$). Similarly it can be shown that the ionic character of MH_3 molecules decreases on moving from NH_3 to BiH_3, *i.e.* the covalent character of these hydrides increases from NH_3 to BiH_3.

(*v*) *Ruducing property.* We have seen that the thermal stability of MH_3 molecules goes on decreasing as we move from NH_3 to BiH_3. This means that M—H bond goes on weakening or the reducing property of MH_3 hydrides goes on increasing. Thus NH_3 is a mild reducing agent while SbH_3 and BiH_3 are powerful reducing agents.

(*vi*) *Shape of hydrides and HMH bond angles.* The shape of MH_3 type hydrides is *trigonal pyramidal*. This shape may be regarded as tetrahedral shape having one lone pair of electrons occupying one of the four tetrahedral positions. Trigonal pyramidal shape results from sp^3 hybridisation of the central atom (M atom). The HMH bond angle in all the four MH_3 hydride (M = N, P, As, Sb) is

never equal to the ideal tetrahedral angle (= 109.5°) but less than this value. HMH bond angles are as : $NH_3 = 107.5°$, $PH_3 = 93.3°$, $AsH_3 = 91.8°$, $SbH_3 = 91.3°$. The decrease in HMH bond angle from NH_3 to SbH_3 can be explained on the basis of electronegativity values of the central atom (M atom) as discussed on pages 326–327.

2. Formation of Halides. These elements form two types of halides namely trihalides (MX_3) and pentahalides (MX_5). With the exception of BiF_3, all other trihalides have covalent character which decreases as we descend the group. Except NF_3 and BiF_3, all other trihalides are readily hydrolysed by water. NX_2 trihalides (X = Cl, Br, I) are completely hydrolysed by water, giving NH_3 and hypohalous acid (HOX). For PX_3, AsX_3 and SbX_3 trihalides the ease and extent of hydrolysis generally increase with the decreasing electronegativity of halogen atom with a given central atom and decrease with the increasing metallic character of the central atom.

The structure of MX_3 trihalides is similar to that of NH_3. In these molecules the central atom (M) is sp^3 hybridised. Out of four sp^3 hybrid orbitals, one contains a lone pair of electrons. Although the spatial arrangement of four electron pairs ($bps = 3$, $lp = 1$) round the central atom is tetrahedral, the shape of MX_3 molecule gets distorted and becomes trigonal pyramidal. The distortion in shape is due to the presence of a lone pair of electrons in one of the sp^3 hybrid orbitals. Due to the presence of a lone pair of electrons, the trihalides (except NF_3) can act as electron donors (Lewis bases). NF_3 is not able to act as electron donor, since the highly electronegative F-atom draws electron pair away from N-atom and thus makes NF_3 molecule a poor electron donor.

Nitrogen and bismuth cannot form pentahalides. Nitrogen cannot form pentahalides because it cannot expand its octet due to the non-availabilty of d-orbitals. Bismuth cannot form pentahalides because the electron pair present in $6s$ orbital is inert (inert pair effect) and hence does not participate in bond formation. PX_5 halides are rapidly hydrolysed, forming H_3PO_4 and HX. SbX_5 halides are hydrolysed with excess of H_2O to hydrated $Sb_2O_5.2H_2O$.

$$PX_5 + 4H_2O \longrightarrow H_3PO_4 + 5HX$$
$$2SbX_5 + 7H_2O \longrightarrow Sb_2O_5.2H_2O + 10HX$$
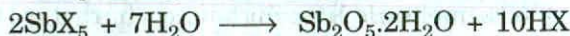
X-ray studies of MX_5 type halides (*e.g.* PCl_5) in the liquid and gaseous state have shown that those molecules have *trigonal bipyramidal* shape. This shape results from sp^3d^2 hybridisation of the central atom (M atom). In the solid state PCl_5 is ionic and exists as $[PCl_4]^+ [PCl_6]^-$ in which $[PCl_4]^+$ is tetrahedral and $[PCl_6]^+$ is octahedral. Similarly PBr_5 is also ionic and exists as $[PBr_4]^+ [Br]^-$.

3. Formation of Oxides. All the elements of this group form oxides. More important oxides are *trioxides* (M_2O_3), *tetraoxides* (M_2O_4) and *pentoxides* (M_2O_5). Besides these three types of oxides nitrogen also gives *nitrous oxide* (N_2O) and *nitric oxide* (NO). Both these oxides are neutral. Bismuth also forms bismuth monoxides (BiO).

Thermal stability and acidic character of M_2O_3 type oxides decreases from N_2O_3 to Bi_2O_3. Thus N_2O_3 and P_2O_3 are completely acidic, since with water they

give nitrous and phosphorus acid respectively. As_2O_3 and Sb_2O_3 are amphoteric and hence form salts with acids as well as with alkalies.

$$As_2O_3 + 6HCl \longrightarrow 2AsCl_3 + 3H_2O; \quad As_2O_3 + 6NaOH \longrightarrow 2Na_3AsO_3 + 3H_2O$$
Sod. arsenite

$$Sb_2O_3 + 6HCl \longrightarrow 2SbCl_3 + 3H_2O; \quad Sb_2O_3 + 6NaOH \longrightarrow 2Na_3SbO_3 + 3H_2O$$
Sod. antimonite
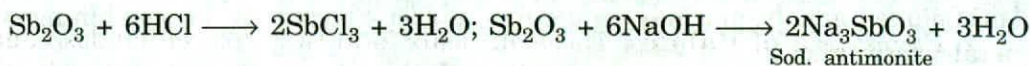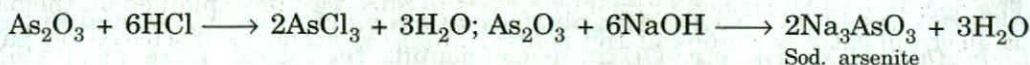
Bi_2O_3 is predominantly basic and forms salts with acids. Bi_2O_3 also shows feeble acidic character, since it slightly dissolves in conc, alkalies due to the formation of bismuthites (BiO_2^-)

$$Bi_2O_3 + 6HCl \longrightarrow 2BiCl_3 + 3H_2O$$

$$Bi_2O_3 + 2NaOH \longrightarrow 2NaBiO_2 + H_2O$$
Sod. bismu-
thite
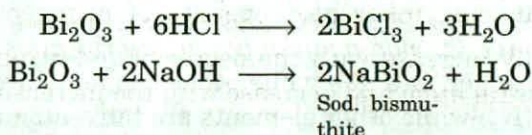
The decrease in acidic character from N_2O_3 to Bi_2O_3 is accounted for by saying that N^{3+} ion, being smaller in size than Bi^{3+} ion, interacts with H_2O more strongly and thus gives an acidic N_2O_3 oxide while Bi^{3+} ion forms basic Bi_2O_3 oxide. This also explains the fact that an oxide in lower oxidation state is less acidic than that in higher oxidation state. For example N_2O (oxidation state of N = + 1) is neutral while N_2O_4 (oxidation state of N = + 4) is acidic. The decrease in acidic character from N_2O_3 to Bi_2O_3 is also consistent with the increasing metallic character of the elements in passing from nitrogen to bismuth.

P_2O_3 is readily oxidised to P_2O_5 while the trioxides of other elements are rather stable towards oxidation to pentaoxides. Bi_2O_3 shows maximum stability towards oxidation. The acidic character of pentaoxides decreases from N_2O_5 to Bi_2O_5. Thus N_2O_5, P_2O_5 and As_2O_5 are exclusively acidic and react with H_2O or alkalies to form oxyacids or their salts. Sb_2O_5 is acidic and forms salts called antimonates. Bi_2O_5 is feebly acidic and forms salts when fused with alkalies. These salts are called bismuthates. The decrease in the acidic character from N_2O_5 to Bi_2O_5 is due to the decrease in the size of M^{5+} ion from N^{5+} to Bi^{5+}. The decrease in acidic character is also in accordance with the increase of metallic character of the elements from N to Bi.

N_2O_5, P_2O_5 and As_2O_5 are readily soluble in water and form acids while Sb_2O_5 and Bi_2O_5 are relatively insoluble. Thus the solubility of these oxides decreases from N_2O_5 to Bi_2O_5.

N_2O_5 is the least stable and hance gets dissociated into nitrogen dioxide (NO_2) and O_2 even at room temperature. P_2O_5 is thermally stable : it sublimes on heating. As_2O_5 decomposes into trioxide (As_2O_3) and O_2 at red heat. Sb_2O_5 is less stable and decomposes into trioxide (Sb_2O_3) and O_2 above 450°C. Excepting P_2O_5, all other pentoxides show oxidizing property. N_2O_5 is the strongest oxidizing agent.

4. Formation of Oxy-acids. Excepting bismuth, all other elements form oxy-acids in various oxidation states. Oxy-acids of nitrogen and phosphorus are quite common and useful. These will be discussed separately in chapters 34 and 37 respectively. The strength and solubility of oxy-acids having the element in the same oxidation state (e.g. HNO_3, H_3PO_4, H_3AsO_4, H_3SbO_4) decreases gradually.

5. Combination with Metals. All these elements form compounds with metals, *e.g.* N forms *nitrides* : Li_3N, Mg_3N_2 etc. ; P gives *phosphides* : Ca_3P_2 etc.; As forms *arsenides* : Na_3As etc. ; Sb gives *antimonides* : Mg_3Sb_2 etc. and Bi forms *bismuthides*, Mg_3Bl_2 etc. Of these compounds the nitrides are most stable. Antimonides and bismuthides are rare. In fact Sb and Bi, on combining with metals, form alloys.

Difference Between Nitrogen and Other Elements of Group VA.

Nitrogen which is the first element of VA group differs considerably, like carbon (first element of IVA group), from the other elements of this group. This is because of the following inherent properties of nitrogen : (*a*) *small size* (*b*) *higher electronegativity* (*c*) *non-availability of d-orbitals*. The main points of difference are : (*i*) Nitrogen is a gas while other elements are solids (*ii*) Nitrogen molecule is diatomic (N_2) while other elements are tetra-atomic and are, therefore, represented as P_4, As_4 and Sb_4. (*iii*) Nitrogen does not show allotropy while other elements (excepting Bi) show allotropy. (*iv*) Nitrogen occurs in the free state while none of the other elements occurs in the free state. (*v*) Nitrogen shows a large number of oxidation states such as + 1 (in N_2O), + 2 (in NO), + 3 (in N_2O_3), + 4 (in N_2O_4), + 5 (in N_2O_5), –1 (in NH_2OH), –2 (in N_2H_4) and –3 (in NH_3). Other elements do not show such a variety of oxidation states. (*vi*) NH_3 which is a hydride of N is highly stable and non-poisonous while the hydrides of the other elements are progressively less stable and poisonous. Moreover, NH_3 forms an associated molecule $(NH_3)_x$ due to the occurrence of hydrogen bonding in this molecule, while other hydrides do not show such behaviour due to the absence of H-bonding. (*vii*) NCl_3 is highly reactive and unstable while the trichlorides of the remaining elements are progressively more stable and less reactive. N does not form pentachloride while P and Sb form such chlorides. (*viii*) The phenomenon of catenation is more common in phosphorus compounds than in nitrogen compounds. This is due to the relative weakness of the N—N single bond as compared to P—P single bond (*ix*) The oxides of N are gaseous and contain multiple bonds between N and O (*e.g.* NO) whereas the oxides of phosphorus are solids containing single P—O bonds. This is due to the relatively high N = O and N ≡ O bond strength and relatively low N—O bond strength but reverse is true for P—O, P = O and P ≡ O bond strengths. (*x*) Due to the absence of *d*-orbitals in nitrogen atom, it can not expand its octet while other elements of this group can do so. Therefore N cannot have coordination number greater than 4 whereas other elements can have coordination number greater than 4. Thus other elements can form the compounds like PF_5, PCl_5 etc. and complexes like PF_6^- while N does not form compounds like NF_5 and complexes like NF_6^-. (*xi*) Nitrogen is chemically inert in spite of its being the third most electronegative element. This is due to the high dissociation energy of N ≡ N bond. However, other elements of the group are quite reactive as they have low M—M bond dissociation energy.

Transition From Non-metallic Character to Metallic Character of Group VA Elements.

We have already said that, on proceeding from N to Bi in group VA, there is a transition from non-metallic to metallic character of the elements. The variation

(*i.e.* increase or decrease) of the properties like (*i*) physical state of the elements (*ii*) electrical and thermal conductivity of the elements (*iii*) hardness and density (*iv*) stability of hydrides of these elements (*v*) acid character and solubility of oxides (*vi*) strength and solubility of oxy-acids (*vii*) hydrolysis of halides as studied on the previous pages confirms the fact that there is a transition from non-metallic to metallic character from N to Bi in group VA.

Questions with Answers

Q.1 Elemental nitrogen exists as a diatomic molecule (N_2) while white phoshorus exists as a tertratomic molecule (P_4). Explain the difference

or Nitrogen exists as a gas but phosphoras exsits as a solid. Explain the difference.

Ans : Since N-atom is small in size, it forms two $(p\pi - p\pi)\pi$ bonds with other N-atom to give $N \equiv N$ or N_2 molecule and thus nitrogen exists as a triply bonded diatomic gaseous molecule at room temperature. On the other hand, since P-atom is larger in size, it does not form $p\pi - p\pi$ bonds with other P-atoms to give $P \equiv P$ or P_2 molecule. Instead, it prefers to form single P–P bonds with other three P-atoms and gives discrete tetratomic tetrahedral P_4 molecule in which each P-atom is linked with other three P-atoms by three P–P single covalent bonds and four P-atoms of P_4 molecule lie on the corners of a regular tetrehedron with PPP bond angle = 60° and P–P bond length = 221 pm as shown in Fig. 32.1 Each P-atom in P_4 molecule completes its octet. Each P-atom has a lone pair of electrons on it.

In white phosphorus individual P_4 tetrahedrons are linked together by weak vender Waals forces. Structure of P_4 molecule given in Fig.30.1 shows that this structure contains six P–P sigma bonds, four lone pairs of electrons and PPP angle equal to 60°.

Fig.30.1 Tetrahedral structure of P_4 molecule (white phosphorus)
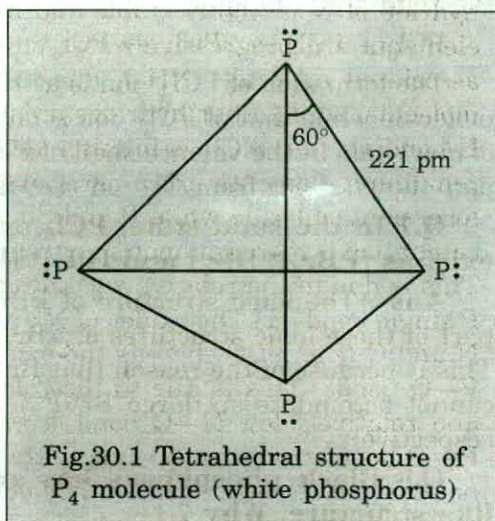
Since P_4 molecule has high molecular mass, phosphorus exists as a solid.

Q.2 White phophorus catches fire in air but red phosphorus does not catch fire easily. Explain the difference.

Ans : White phophorus catches fire in air due to its low ignition temperature which is equal to 303K. On the other hand, since ignition temperature of red phophorus (= 543K) is much higher that that of white phosphorus, this phosphorus does not catch fire easily.

Q.3 NF_3 is an exothermic compound but NCl_3 is an endothermic compound. Explain.

Ans : NF_3 is an exothermic compound, since in the formation of one mole of NF_3 heat is released (negative value of heat of formation). Heat is released, since F_2 is stronger oxidising agent.

$$\frac{1}{2}N_2 + \frac{3}{2}Fe \longrightarrow NH_3 \text{ (one mole); } \Delta H = \text{Heat released} = -\Delta H_f \text{ of } NF_3$$
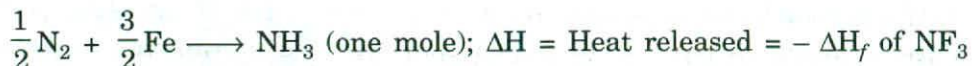
On the other hand, NCl_3 is an endothermic compound, because in the formation of one mole of NCl_3 heat is obsorbed (positive value of heat of formation). Heat is absorbed, since Cl_2 is comparatively weaker oxidising agent.

$$\frac{1}{2}N_2 + \frac{3}{2}Cl_2 \rightarrow NCl_3 \text{ (one mole); } \Delta H = \text{Heat absorbed} = +\Delta H_f \text{ of } NCl_3$$

Q.5 PCl_5 is known but PI_5 is unknown. Why ?

Ans : Since Cl-atoms are smaller in size, these atoms can easily be accomdated round P-atom to form PCl_5. On the other hand, since I-atoms are larger in size, these atoms cannot be accomdated round P-atom and hence PI_5 cannot be formed.

Q.6 Expalin why PCl_5 is ionic in the solid state.

Ans : X-ray study of the structure of PCl_5 molecule in the solid state has shown that two molecules of this compound unite together and then get splitted into $[PCl_4]^+$ and $[PCl_6]^-$ ions. Due to the presence of these ions, PCl_5 molecule, in the solid state, is ionic.

$$PCl_5 + PCl_5 \rightarrow 2PCl_5 \rightarrow PCl_4^+ + PCl_6^- \rightarrow [PCl_4]^+ [PCl_6]^- \text{ (Ionic solid)}$$

The formation of PCl_4^+ ion is attributed to the cleavage of a P–Cl bond in PCl_5 molecule while that of PCl_6^- ion is on accound of the fact that, due to the presence of d-orbitals in the valence shell of P-atom, this atom in PCl_5 accepts one electron pair (Lewis acid) from Cl^- ion (Lewis base) and forms PCl_6^- ion.

Q.7 In the solid state, PCl_5 exists as $[PCl_4]^+ [PCl_6]^-$ but PBr_5 and PI_5 exist as $[PBr_4]^+ [Br^-]$ and $[PI_4]^+ [I^-]$ respectively. Explain this difference.

Ans : The ionic structure of PBr_4 and PI_4 molecules show that the anionic part of these ionic structures are Br^- and I^- ions and not $[PBr_6]^-$ and $[PI_6]^-$ ions. This is because of the reason that Br^- and I^- ions are so large in size that P-atom cannot accomdate six large Br^-/I^- ions round it to form $[PBr_6]^-$ and $[PI_6]^-$ ions respectively.

Q.8 Black phosphorus has graphite-like structure. Why ?

Ans : Black phophorus has a layered structure in which each phosphorus atom is covalently bonded to three neighbouring phophorus atoms as shown in Fig.30.2. The P – P – P angles are of 99° and P – P distance is 218 pm.

The adjacent layers are held 368 pm apart. The atoms within a layer are more strongly bound than the atoms in adjacent layers. This gives black phosphorus graphite-like structure.
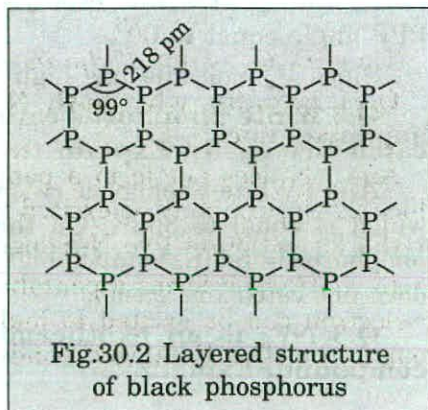

Fig.30.2 Layered structure of black phosphorus

The black phosphorus is a highly polymerised form of phosphorus.

It is due to its graphite-like structure that black phoshorus is a fairly good conductor of electricity. Black phosphorus is the only allotropic form of phosphorus which is a good conductor of electricity.

Q.9 Bond angle in PH_4^+ is larger than that in PH_3. Why ?

Ans : P in PH_3 is sp^3 hybridized. PH_3 has three bond pairs and one lone pair around P. Due to stronger lone pair–bond pair repulsions than bond pair–bond pair replulsions, the tetrahedral angle decreases from 109.5° to 93.3°. As a result, PH_3 is pyramidal. However, when it reacts with a proton, it forms PH_4^+ ion which has four bond pairs and no lone pair. Due to the absence of lone pair–bond pair repulsions and presence of four identical bond pair–bond pair interactions, PH_4^+ assumes tetrahedral geometry with bond angle of 109.5°. This explains why the bond angle in PH_4^+ is higher than in PH_3. (See Fig. 32.3)

Fig 32.3 Bond angle in PH_4^+ is larger than that in PH_3.
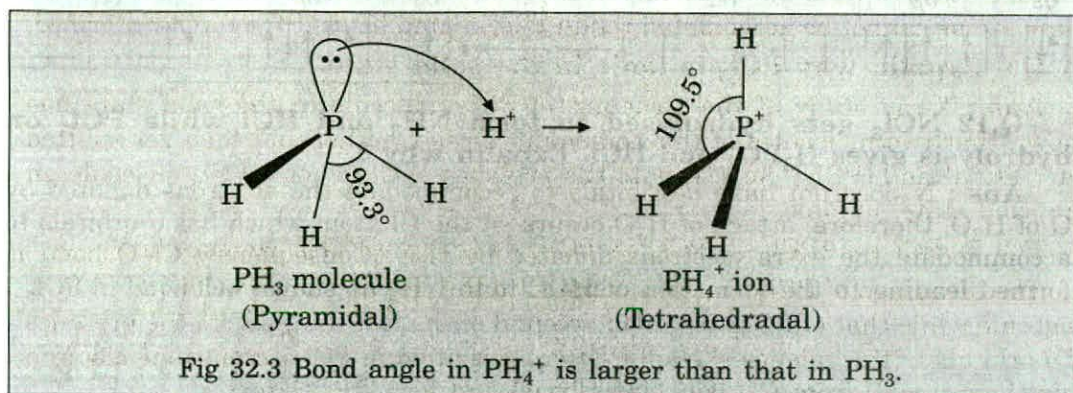
Q.10 Explain why Bi_2O_3 is not acidic in any of its reactions.

Ans : The size of Bi^{3+} is very large and thus has a very weak +ve field around it. Therefore, it does not interact with H_2O to release H^+ ions.

$$Bi^{3+} + 3\ H–O–H \xrightarrow{\quad} Bi(OH)_3 + 3H^+$$

In contrast, the O^{2-} is small and has a strong –ve electric field around it. It, therefore, interacts with water releasing OH^- ions.

$$O^{2-} + H–OH \longrightarrow 2OH^-$$

Thus, *Bi_2O_3 is not acidic in any of its reactions but acts as a base.*

Q.11 Expalin why both N and Bi do not form pentahalides while phophorus does.

Ans : N does not form a pentahalide because it does not have d-orbitals to which 2s electron may be excited to make available five half-filled orbitals needed for the formation of five N-halogen bonds.

In contrast, P forms a pentahalide because it has vacant 3d-orbitals to which 3s electron can be excited to make available five half-filled orbitals needed for fromation of five P-halogen bonds.

P is the ground state   P in the excited state

Five half–filled orbitals
needed for formation of
five P–halogen bonds.
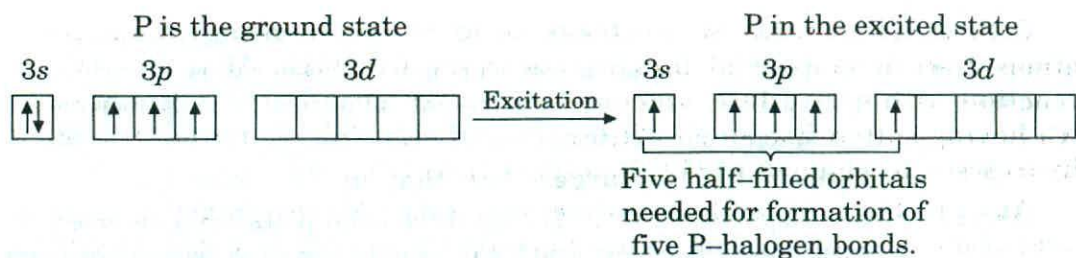
Like P, Bi also has vacant $6d$-orbitals in the valence shell. But due to inert pair effect, the energy needed for excitation of $6s$-electron to $6d$-orbital is much more than the energy released when two additional Bi-hlaogen bonds are formed. Thus, bismuth does not form a pentahalide (except BiF_5) but forms only a trihalide.

Bi in the ground state   Bi in the excited state
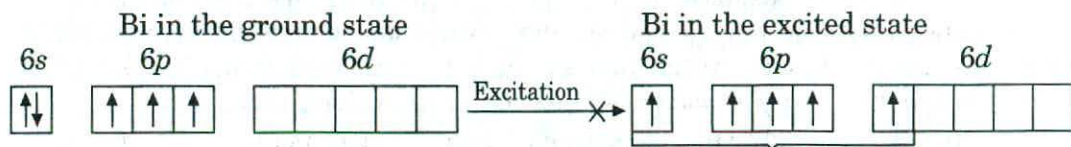
Q.12 NCl_3 gets hydrolysed to form NH_3 and HCl while PCl_3 on hydrolysis gives H_3PO_3 and HCl. Expalin why ?

Ans : N does not have d-oribitals to accommodate the electrons donated by O of H_2O, therefore, attack of H_2O occurs on the Cl atom which has d-orbitals to accommodate the extra electrons donated by H_2O. Consequently Cl–O bond is formed leading to the formation of HOCl and NH_3 as shown below :
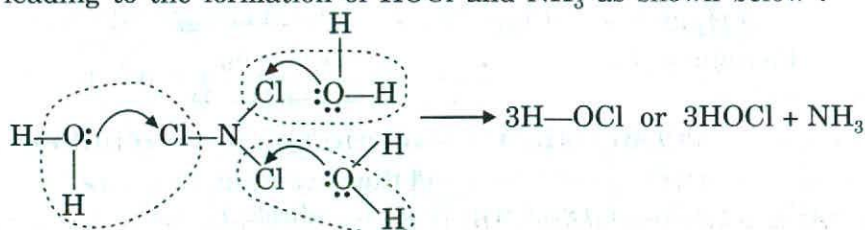
In contrast, both P and Cl have d-orbitals to accommodate electrons donated by H_2O. But P–O bond is much stronger than Cl–O bond. As a result, attack of H_2O molecules occurs preferentially on P of PCl_3 to form H_3PO_3 and HCl.

$$PCl_3 + 3H_2O \rightarrow 3HCl + P(OH)_3 \text{ or } H_3PO_3 \ldots \ldots (A)$$

As a matter of fact the above reaction takes place through the following steps:

$$P(OH)_3 \text{ or } H_3PO_3 + 3HCl$$
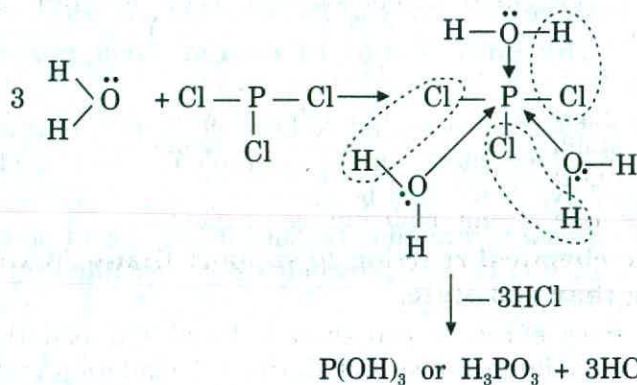
Q.13 A translucent white waxy solid (A) on heating in an inert atmosphere is converted into its allotropic form (B). Allotrope (A) on reaction with very dilute aqueous KOH liberates a hig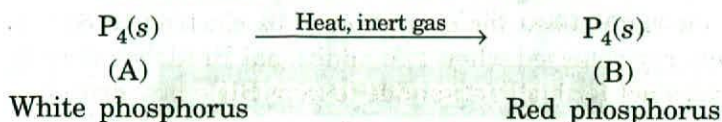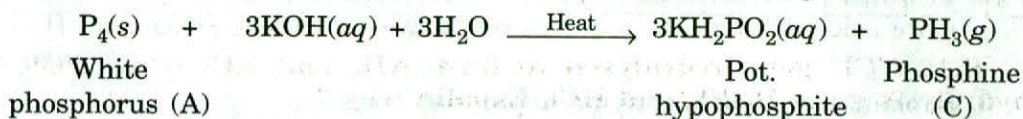hly poisonous gas (C) having rotten fish smell. With excess of chlorine (C) forms (D) which hydrolyses to compound (E). Identity (A) to (E).
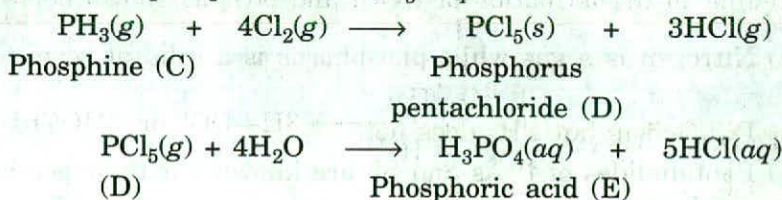
Ans : (*i*) Since a translucent white waxy solid (A), on heating in an inert atmosphere, is converted into its allotrope (B), *(A) is white or yellow phophorus while (B) is red phosphorus.*

$$P_4(s) \xrightarrow{\text{Heat, inert gas}} P_4(s)$$

      (A)   (B)

   White phosphorus   Red phosphorus

(*ii*) Since allotrope (A) on boiling with dilute aqueous KOH gives a highly poisonous gas (C) having rotten fish smell, it is confirmed that *allotrope (A) is white phosphorus and the poisonous gas (C) is phosphine (PH$_3$)*

$$P_4(s) \; + \; 3KOH(aq) + 3H_2O \xrightarrow{\text{Heat}} 3KH_2PO_2(aq) \; + \; PH_3(g)$$

  White   Pot.   Phosphine
phosphorus (A)   hypophosphite   (C)

(*iii*) Since phosphine (C) reacts with excess of chlorine to form a compound (D) which upon hydrolysis gives compound (E), *(D) must be phosphorus pentachloride (PCl$_5$) and (E) must be phosphoric acid (H$_3$PO$_4$).*

$$PH_3(g) \; + \; 4Cl_2(g) \longrightarrow PCl_5(s) \; + \; 3HCl(g)$$

   Phosphine (C)   Phosphorus
                                 pentachloride (D)

$$PCl_5(g) + 4H_2O \longrightarrow H_3PO_4(aq) \; + \; 5HCl(aq)$$

     (D)   Phosphoric acid (E)

Thus, (A) is white phosphorus, (B) is red phophorus, (C) is phosphine (PH$_3$) (D) is phosphorus pentachloride (PCl$_5$) and (E) is phosphoric acid (H$_3$PO$_4$).

Q.14 Bismuth is a strong oxidising agent in the pentavalent state. Expalin.

Ans : Since the inert pair effect is very prominent in Bi, its + 5 oxidation state is much less stable than its + 3 oxidation state. In other words, bismuth in the poentavalent state can easily accept two electrons and thus gets reduced to trivalent bismuth.

$$Bi^{5+} \; + \; 2e^- \xrightarrow{\text{Reduction}} Bi^{3+}$$

     Less   More
   stable   stable
    (OA)
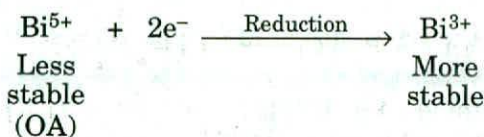
Thus Bi^{5+} acts as a strong oxidising agent (OA).

Q.15 Give the chemical reaction to support that + 5 oxidation state of Bi is less stable than + 3 state.

Ans : Due to inert effect, Bi can show + 3 and + 5 oxidation states. Since inert pair effect is maximum in case of Bi, its + 5 oxidation state is less stable

than its + 3 oxidation state. This is evident from the observation that $BiCl_3$ even on prolonged heating with Cl_2 does not form $BiCl_5$

$BiCl_3 + Cl_2 \rightarrow BiCl_5$ (*This reaction does not take place*).
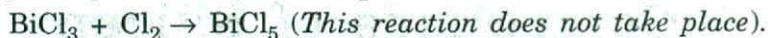
Q.16 Of Bi(V) and Sb(V) which may be a stronger oxidising agent and why ?

Ans : On moving down the group, the stability of + 5 oxidation state decreases while that of + 3 oxidation state increases due to inert pair effect. Thus, + 5 oxidation state of Bi is less stable than + 5 oxidation of Sb. Therfore, Bi(V) is a stronger oxidising agent than Sb(V).

University Questions

1. Justify the inclusion of N, P, As, Sb and Bi in the same group of the periodic table.   (*Raj. 84 S, 86, 87, 87 S; Pune 86; Kashmir 85*)

2. In which oxidation state (+ 3 or + 5) the elements of group VA are generally more acidic ? Illustrate your answer from examples of HNO_4 and HNO_5.
(*Punjab 86*)

3. Explain the following, giving appropriate reasons.

   (*i*) Nitrogen forms only diatomic molecule unlike phosphorus and other members of group VA.   (*Allahabad 87*)

   (*ii*) Nitrogen is quite inert, particularly at temperature near 300 K.
(*Allahabad 89*)

   (*iii*) Nitrogen is a gas while phosphorus is a solid at room temperature.
(*Delhi 89*)

   (*iv*) PCl_5 exists but PH_5 does not.   (*Delhi Hons. 87*)

   (*v*) Pentahalides of P, As and Sb are known but their pentahydrides are not known.   (*Allahabad 88*)

   (*vi*) Black phosphorus and nitrogen have low chemical activity.
(*Delhi Hons. 87*)

   (*vii*) White phosphorus is more reactive than red phosphorus.   (*Delhi 87*)

   (*viii*) White phosphorus is soluble in CS_2.   (*Delhi Hons. 87*)

   (*ix*) Nitrogen molecule is diatomic (N_2) while phosphorus molecule is tetratomic (P_4).

   (*x*) Reactions of P, As, Sb and Bi with oxidising agents reflect metallic character.   (*Delhi Hons. 82*)

   (*xi*) The stability of the trihalides of MX_3 type (M = N, P, As etc.) increases down the group.

   (*xii*) $BiCl_3$ is more stable than $BiCl_5$.

   (*xiii*) NF_3 is extremely stable while NCl_3 is readily hydrolysed.

   (*xiv*) The trihalides of group VA elements give different products on hydrolysis.   (*Delhi Hons. 86*)

   (*xv*) NF_3 has little tendency to act as electron donor but PF_3 is a good donor.   (*Allahabad 88*)

(xvi) NCl_3 is hydrolysed but NH_3 is not.

(xvii) All P—F bonds in PF_5 molecule are not equivalent.   *(Punjab 86)*

(xviii) PI_5 is unknown.

(xix) (a) PCl_5 is stable while NCl_5 cannot be prepared.   *(Delhi 82)*

(b) PCl_5 exists while NCl_5 does not exist.   *(Delhi 80)*

(c) Nitrogen exhibits 3-covalent state while P, As and Sb exhibit 5-covalent state.   *(Himachal 84)*

(d) Nitrogen does not form pentahalides while P and Sb give PCl_5 and $SbCl_5$ respectively.   *(Delhi 86; Raj. 87)*

(e) NF_3 is known but NF_5 is not known.   *(Delhi 84)*

(f) N-atom forms only one chloride *viz.* NCl_3 while P-atom forms both PCl_3 and PCl_5.   *(Gorakhpur 84)*

(g) PCl_5 is more stable than NCl_5.   *(Poona 86)*

(xx) $[NF_6]^-$ ion does not exist but $[PF_5]^-$ ion exists.

(xxi) N-atom shows a maximum coordination number of 4 but phosphorus how a coordination number of 6.   *(Allahabad 88)*

4. Compare the elements of nitrogen group elements with respect to :
(i) Electronic configuration (ii) Electronegative character (iii) Oxidation states (iv) Stability of MH_3 hydrides. (v) Acidic properties of oxides.

    (Gorakhpur 99)

5. Explain why NF_3 is stable while NCl_3 and NI_3 are explosive.

    (Allahabad 99)

6. Explain why white phosphorus is more reactive than red phosphorus.

    (Delhi 99)

7. Compare the properties of Sb and Bi pair.   *(Kanpur 2000)*