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 $\rightarrow$ 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 $\rightarrow$ 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.
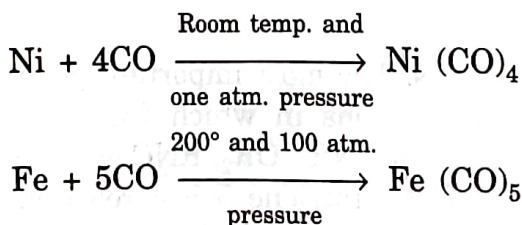
Types of Carbonyls

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.
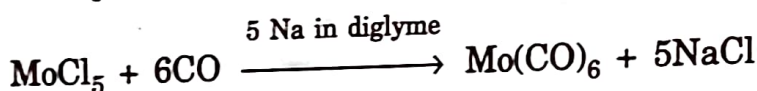
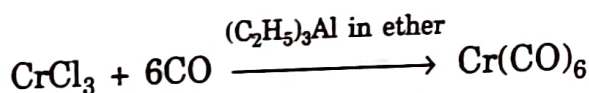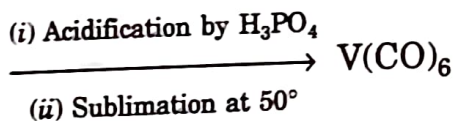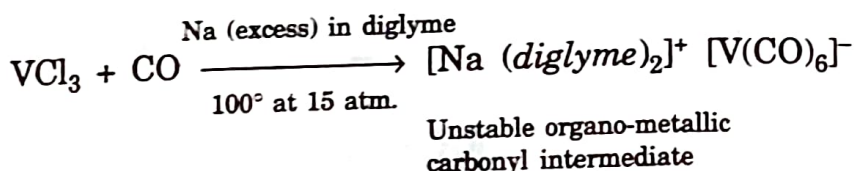**2. Polynuclear carbonyls.** *These contain two or more metallic atoms per molecule* and are of the type $M_x(CO)_y$. However some authors call the carbonyls containing two metal atoms as *bridged carbonyls* and those containing more than two metal atoms as *polynuclear carbonyls*. Polynuclear carbonyls 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 :

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

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

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

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

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

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

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.

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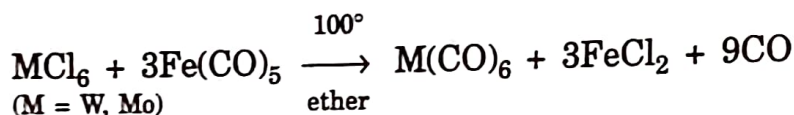
4. By the thermal or photochemical decomposition of simple carbonyls. Polynuclear carbonyls of Fe, Rh, Os, Cu, Rh and Ir are obtained by the thermal or photochemical decomposition of simple carbonyls, e.g.
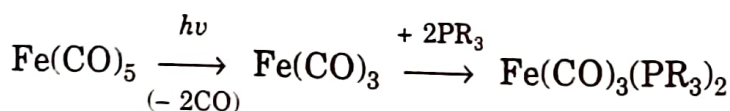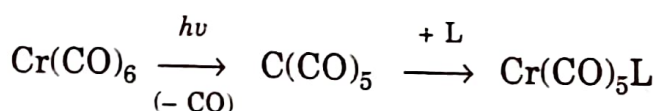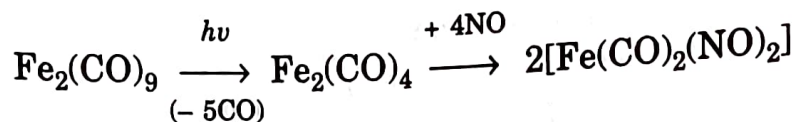
$$\underset{(M\ =\ Fe,\ Os)}{2M(CO)_5} \xrightarrow{\text{ultraviolet light}} M_2(CO)_9 + CO$$
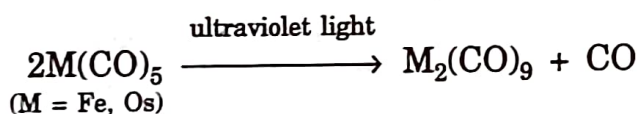
Physical Properties.

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.
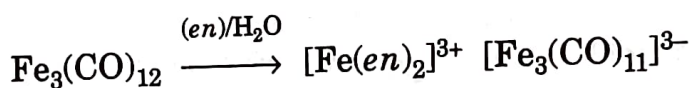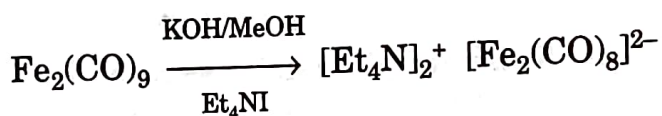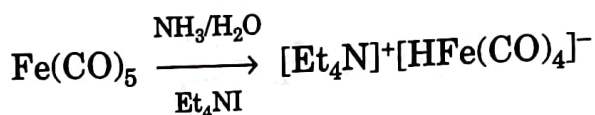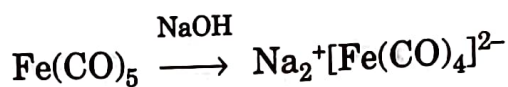
$$Cr(CO)_6 \xrightarrow[(-\ CO)]{h\upsilon} C(CO)_5 \xrightarrow{+\ L} Cr(CO)_5L$$

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

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

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 :
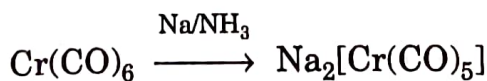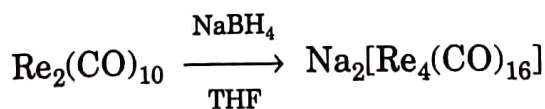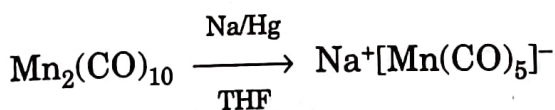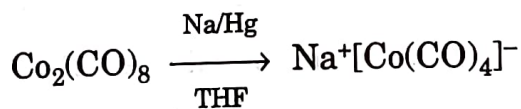
(a) *By the action of NaOH or nitrogenous bases (e.g. NH$_3$, amines, pyridine) on metal carbonyls, e.g.*

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

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

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

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

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

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

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

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

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

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

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

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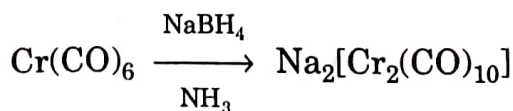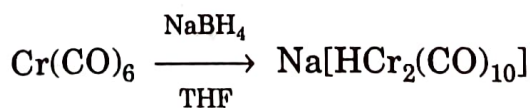
3. Formation of cationic carbonyl complexes (also called carbonylate cations). Carbonylate cations may be prepared from the carbonyls by the following methods :

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

$$Fe(CO)_5 \xrightarrow{HCl/BCl_3} [FeH(CO)_5]^+ [BCl_4]^-$$
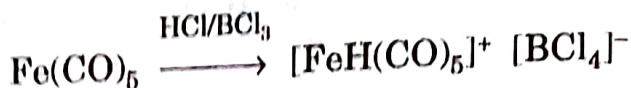
n.m.r. spectroscopy has shown that the proton becomes bounded to the metal atom in $[FeH(CO)_5]^+$.
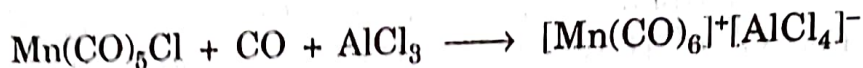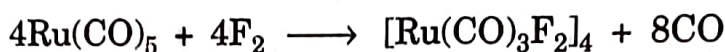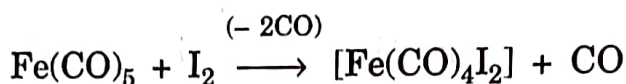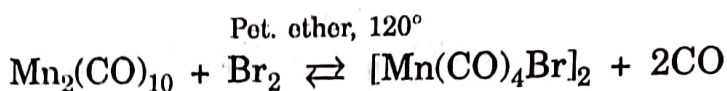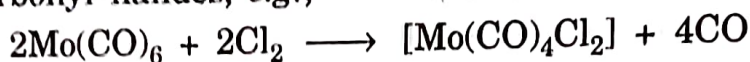
(b) By the action of CO and a Lewis acid like $AlCl_3$ or BF_3 on carbonyl halide, *e.g.*

$$Mn(CO)_5Cl + CO + AlCl_3 \longrightarrow [Mn(CO)_6]^+[AlCl_4]^-$$

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.*,

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

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

$$Fe(CO)_5 + I_2 \xrightarrow{(-2CO)} [Fe(CO)_4I_2] + CO$$

$$4Ru(CO)_5 + 4F_2 \longrightarrow [Ru(CO)_3F_2]_4 + 8CO$$

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.

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

$$Ni(CO)_4 + 2OH^- \longrightarrow Ni(CO)_3H_2 + CO_3^{2-}$$
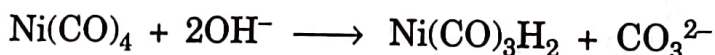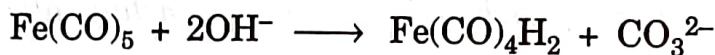
Carbonyl hydrides can also be prepared by treating the carbonyls with H_2, *e.g.*

$$Mn_2(CO)_{10} + H_2 \xrightarrow{200°/200 \text{ atm.}} 2HMn(CO)_5$$
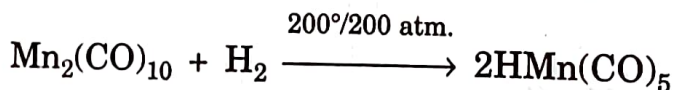
Structure and Bonding in Mononuclear Carbonyls

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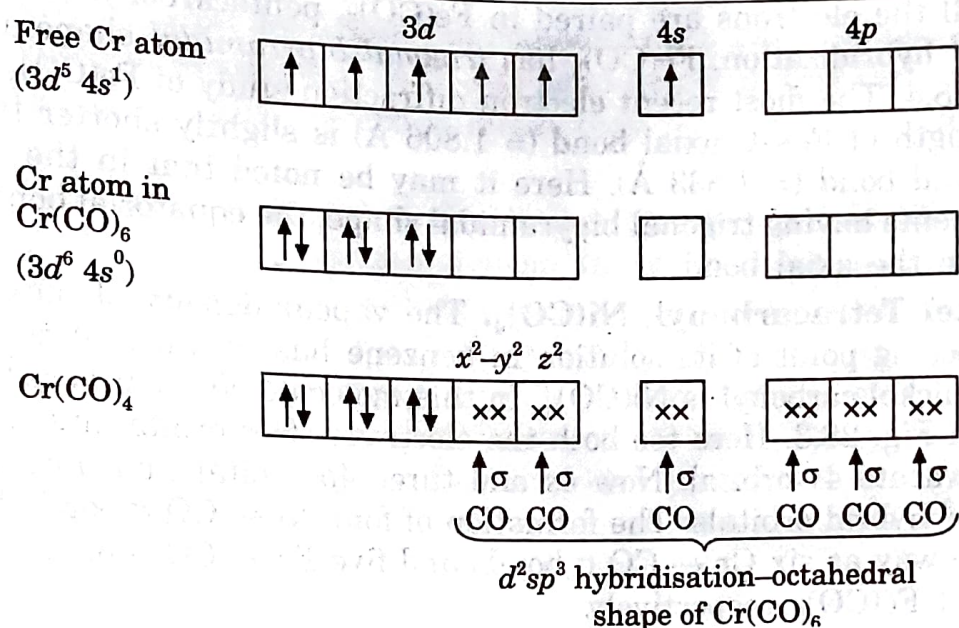
Fig. 28.1. d^2sp^3 hybridisation of Cr atom in octahedral $Cr(CO)_6$ carbonyl. Crosses (xx) represent elecgron pair donated by CO groups. These electrons are in opposite spin

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 $Fe \leftarrow CO$ σ bonds takes place in the same manner as six $Cr \leftarrow Co$ σ bonds are formed in $Cr(CO)_6$ carbonyl.
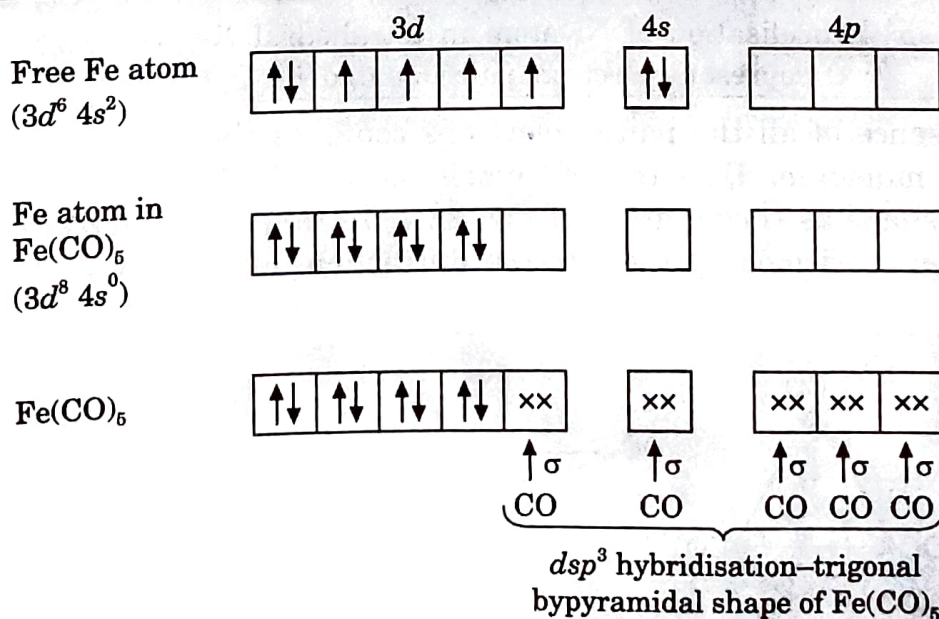

Fig. 28.2. dsp^3 hybridisation of Fe atom in trigonal bipyramidal $Fe(CO)_5$ carbonyl. Crosses (xx) represent electron pair donated by CO group

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.
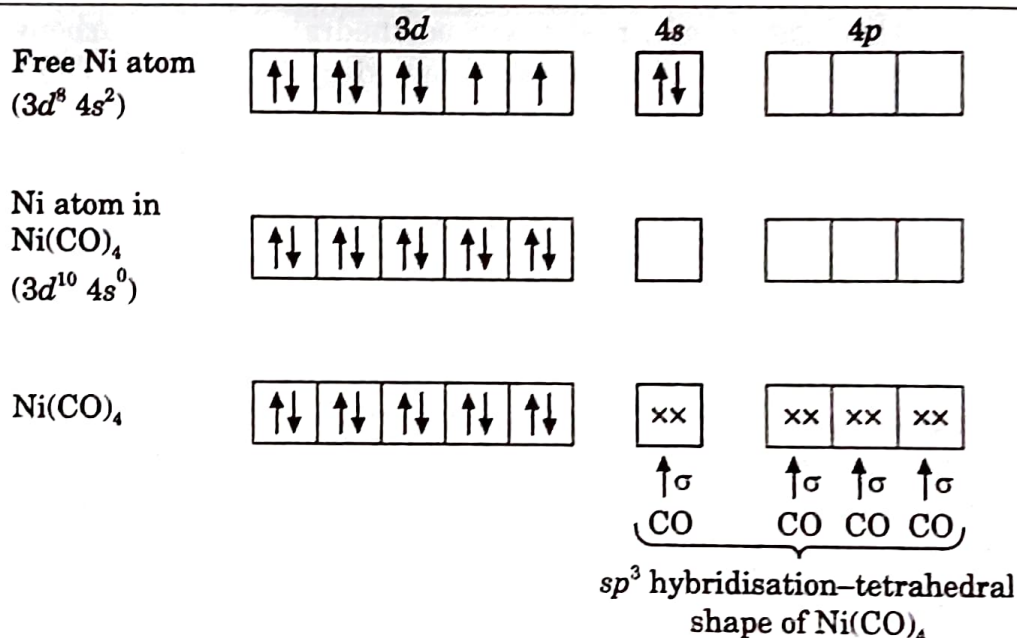
Fig. 28.3. sp^3 hybridisation of Ni atom in tetrahedral $Ni(CO)_4$ carbonyl. Cross (xx) represent electron pair donated by CO groups.

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.
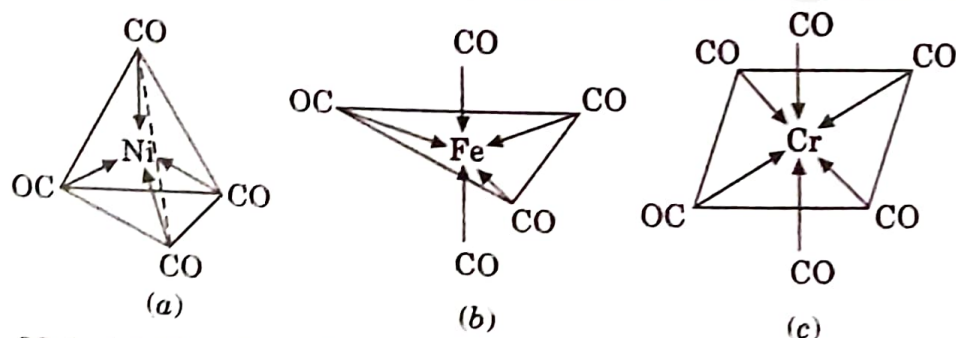
Fig. 28.4. (a) Tetrahedral $Ni(CO)_4$ (b) Trigonal bipyramidal $Fe(CO)_5$
(c) Octahedral $Cr(CO)_6$.

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 p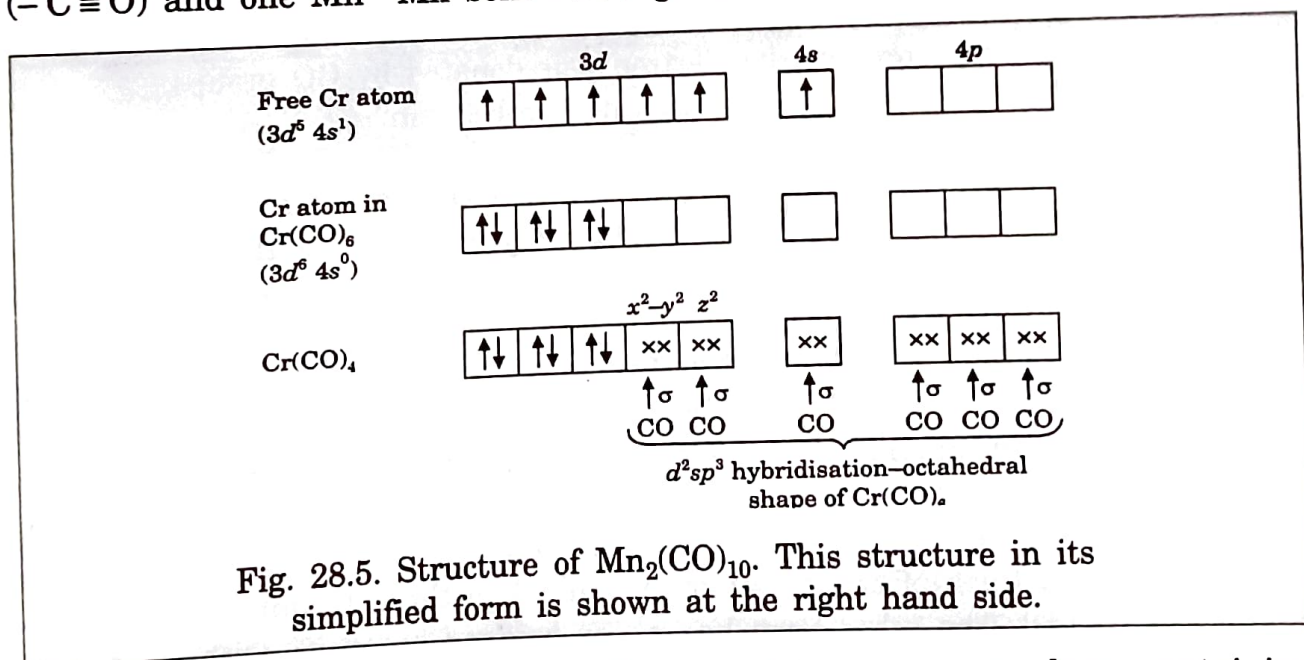lace with the back sonation of d-electron from Ni atom to CO ligands to such an extent that electroneutrality principle is obeyed. According to this principle the electron pair is not shared equally between Ni and C-atoms of CO ligands but is attracted more strongly by C-atom which prevents the accumulation 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 ($-C \equiv O$) 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.
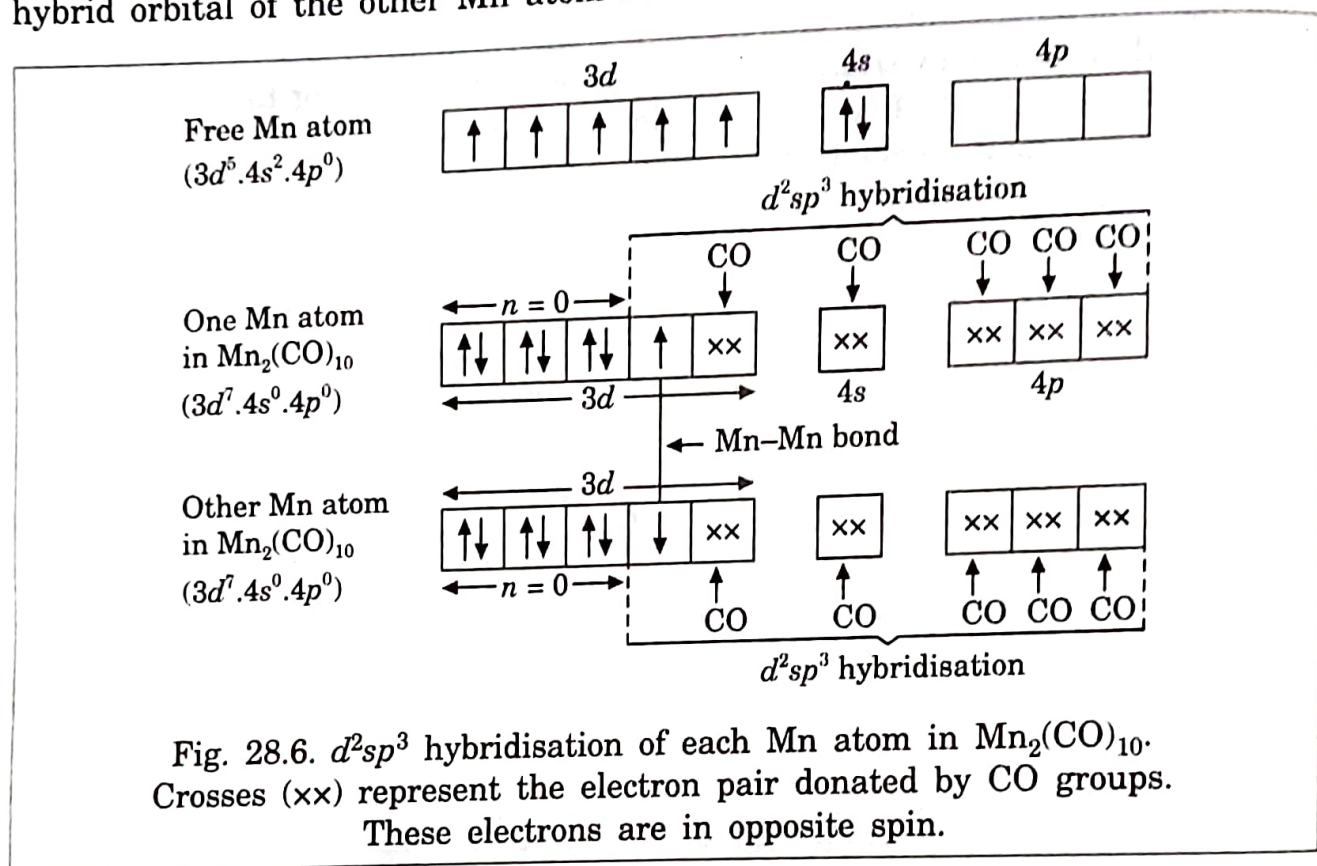
Thus we see that all the electrons in $Mn_2(CO)_{10}$ are *paired* and hence this carbonyl is *diamagnetic*. Its diamagnetism also suggests the presence of Mn—Mn bond in it. X-ray diffraction study of $Mn_2(CO)_{10}$ has shown that the molecule has two directly linked Mn atoms. The infra-red absorption 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
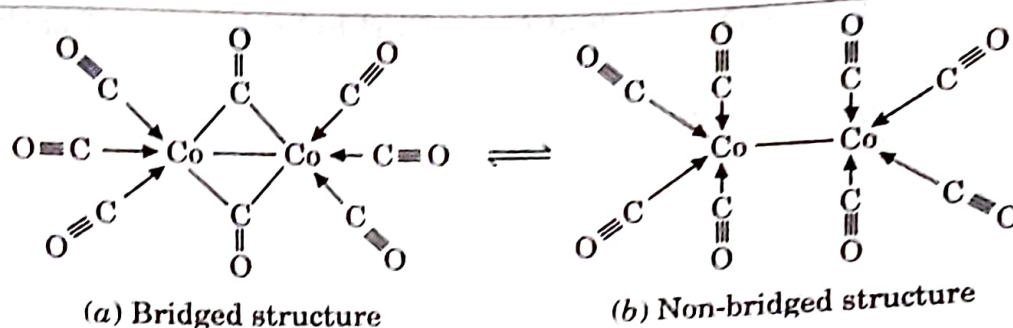
Fig. 28.7. Two isomeric forms of $CO_2(CO)_8$. Both the forms contain Co—Co bond.

The infra-red study of the bridged structure has shown that it has two types of CO groups [i.e. *terminal* CO groups (– CO $\equiv$ 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.
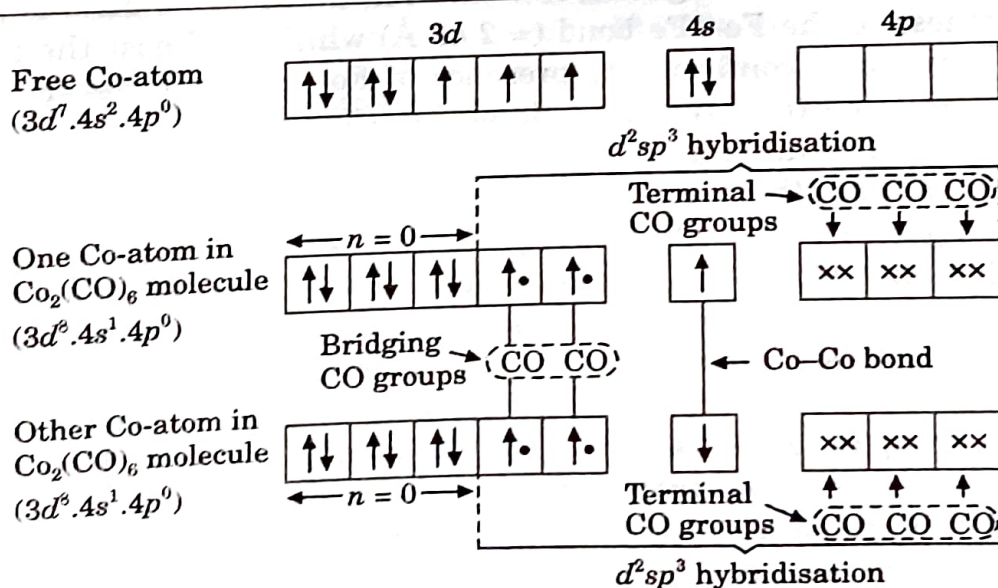

Fig. 28.8. d^2sp^3 hybridisation of Co alum in $Co_2(CO)_8$ carbonyl Crosses (xx) represent the electron pair denoted by terminal CO groups, while the dot (•) represents an electron on bridging CO groups. ↑↓ represent electrons on Co atom.

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.
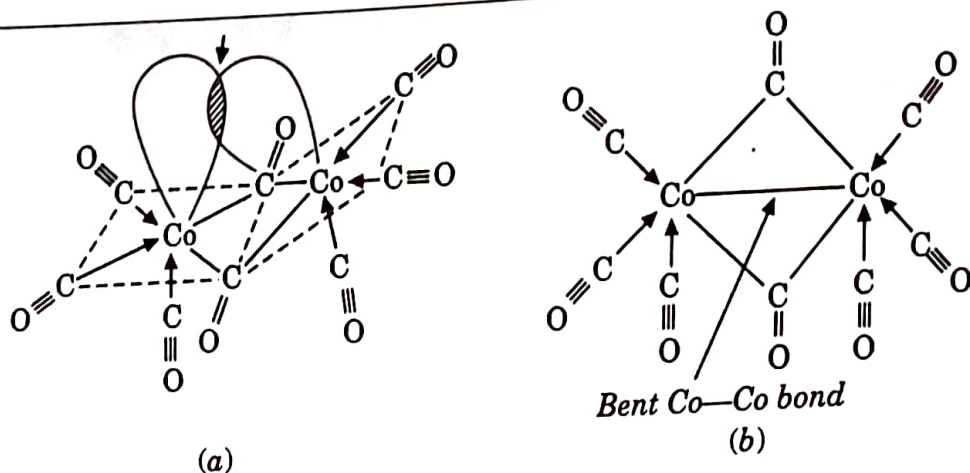

(a)

(b)

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.
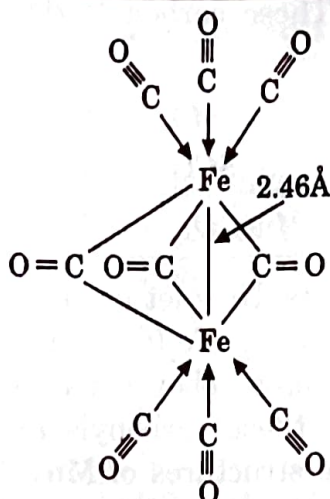
Fig. 28.10. Structure of $Fe_2(CO)_9$.

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 × 2 = 12	24 + 12 = 36 (Kr)
$Mo(CO)_6$	42	6 × 2 = 12	42 + 12 = 54 (Xe)
$W(CO)_6$	74	6 × 2 = 12	74 + 12 = 86 (Rn)
$Fe(CO)_5$	26	5 × 2 = 10	26 + 10 = 36 (Kr)
$Ru(CO)_5$	44	5 × 2 = 10	44 + 10 = 54 (Xe)
$Os(CO)_5$	70	5 × 2 = 10	76 + 10 = 86 (Rn)
$Ni(CO)_4$	28	4 × 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 :

$$\begin{array}{ccc} V = 23e^- & Mn = 25e^- & Co = 27e^- \\ \underline{6CO = 12e^-} & \underline{5CO = 10e^-} & \underline{4CO = 8e^-} \\ V(CO)_6 = 35e^- & Mn(CO)_5 = 35e^- & Co(CO)_4 = 35e^- \end{array}$$

(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 = $\underline{1 × 2 = 2}$

$Mn_2(CO)_{10}$ = 72

∴ 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 = $\underline{1 × 2 = 2}$

$Co_2(CO)_8$ = 72

∴ 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 = $\underline{1 × 2 = 2}$

$Fe_2(CO)_9$ = 72

∴ 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 = $\underline{3 × 2 = 6}$

$Fe_3(CO)_{12}$ = 108

∴ 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%.

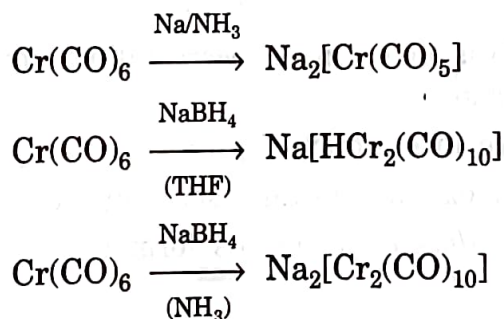**Properties.** (i) Chromium hexacarbonyl is a white solid.

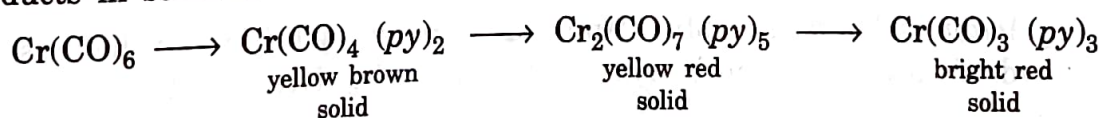(ii) Crystals of $Cr(CO)_6$ are soluble in ether, chloroform, CCl_4 and C_6H_6.

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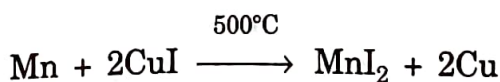
$$Cr(CO)_6 \xrightarrow{Na/NH_3} Na_2[Cr(CO)_5]$$

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

$$Cr(CO)_6 \xrightarrow[\text{(NH}_3)]{NaBH_4} Na_2[Cr_2(CO)_{10}]$$

(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%.

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

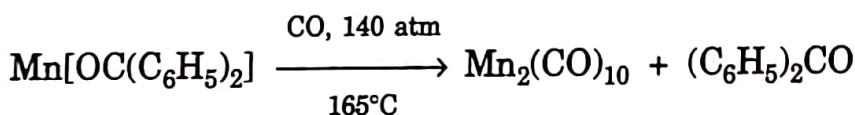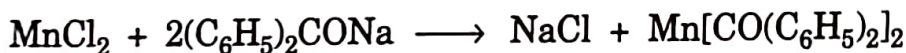$$(MnI_2 + 2Cu) + Mg \xrightarrow[25°C/16 \text{ hrs}]{CO, 210 \text{ atm}} Mn_2(CO)_{10} + MgI_2 + CuI_2$$
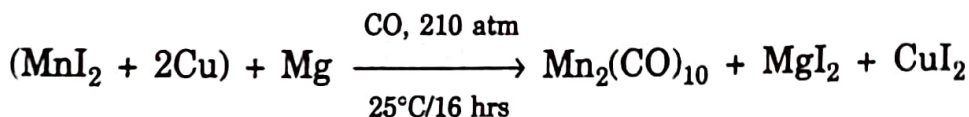
(ii) $Mn_2(CO)_{10}$ has also been prepared in better yield by the reaction of Mn $(CH_3COO)_2$ with triethyl aluminium, $(C_2H_5)_3Al$ under CO at a pressure of 20 atmospheres at 100°C for 5 hours.

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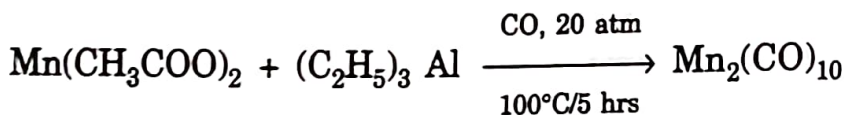
The yield of carbonyl by this method is 53–60%.

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

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

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

(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.

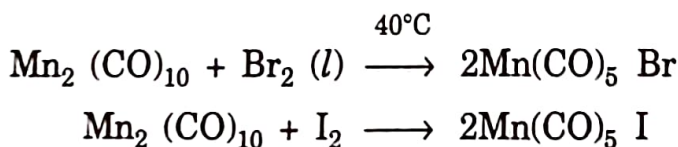$$(CH_3.C_5H_4)Mn(CO)_3 + Na \xrightarrow[125°C/8 \text{ hrs}]{CO, 50 \text{ atm}} Mn_2(CO)_{10}$$
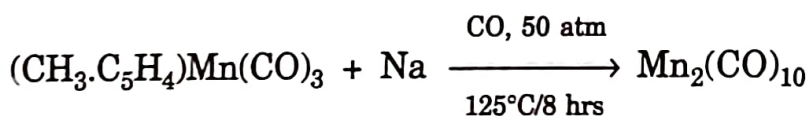
Properties. (i) It is a golden yellow crystalline substance. It has m.pt. = 155°C and sublimes in vacuo.

(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.

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

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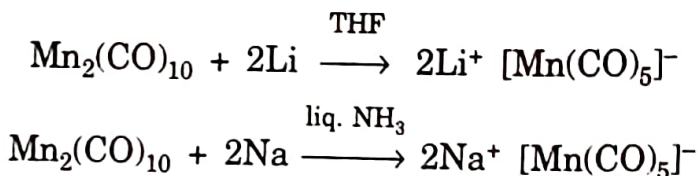
(vi) *Reduction.* When $Mn_2(CO)_{10}$ is reduced by hydrogen under 200 atmospheric pressure at a temperature of 200°C, carbonyl hydride in formed.

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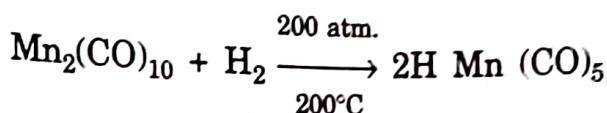
(vii) *Action of phosphines, arsines and stibines.* With these materials $Mn_2(CO)_{10}$ gives monomeric paramagnetic compounds of the type, $Mn\,(CO)_4\,(PR_3)$.

(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 $Fe(CO)_5$.

$$FeI_2 + 4CO \longrightarrow Fe(CO)_4I_2$$
$$CO + Fe(CO)_4I_2 + 2Cu \longrightarrow Fe(CO)_5 + Cu_2I_2$$
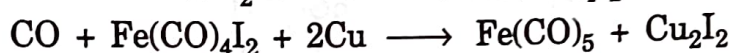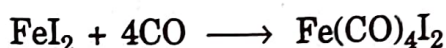
In place of FeI_2, FeS can also be used.

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.

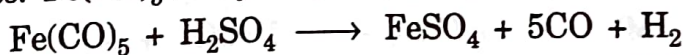(ii) *Decomposition.* On thermal decomposition at 250°C, it gives pure Fe.

$$2Fe(CO)_5 \longrightarrow Fe + 5CO$$
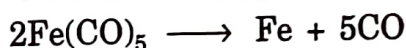
(iii) *Action of ultra-violet light.* When it is irradiated with near ultra violet light, $Fe_2(CO)_9$ is formed.

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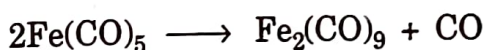
The above reaction is reversed in darkness.

(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.

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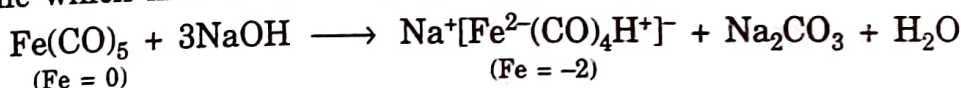
(vi) *Action of NH_3.* With NH_3 it gives $Fe(CO)_4H_2$ and carbonic acid, NH_2COOH

$$Fe(CO)_5 + H_2O + NH_3 \longrightarrow Fe(CO)_4H_2 + NH_2COOH$$
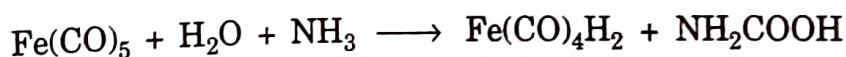
(vii) *Reaction with halogens.* It reacts with halogens in non- aqueous solvents to form the stable tetra-carbonyl halides, $Fe(CO)_4X_2$.

$$Fe(CO)_5 + X_2 \longrightarrow Fe(CO)_4X_2 + CO$$
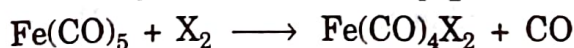
The velocities of these reactions follow the order Cl < Br < I.

(*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.

$$Fe(CO)_5 + 2NO \longrightarrow Fe(CO)_2(NO)_2 + 3CO$$

$$Fe(CO)_2(NO)_2 + 2NO \longrightarrow Fe(NO)_4 + 2CO$$

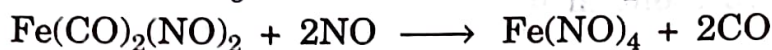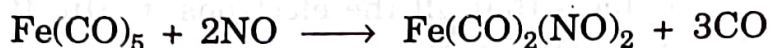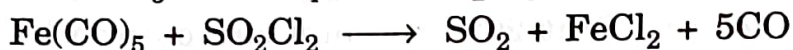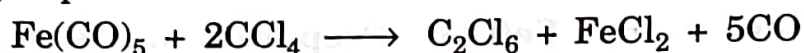(*x*) *Reactions with metallic and non-metallic halides.* In these reactions, $Fe(CO)_4$ acts as a dehalogenating agent and a carbonylating agent; Fe becomes bi-valent and CO groups are either liberated or transferred to some other atom.

$$Fe(CO)_5 + 2CCl_4 \longrightarrow C_2Cl_6 + FeCl_2 + 5CO$$

$$Fe(CO)_5 + SO_2Cl_2 \longrightarrow SO_2 + FeCl_2 + 5CO$$

$SnCl_4$ 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 $SbCl_3$.

$$SnCl_2 + Fe(CO)_4Cl_2 \longrightarrow SnCl_2.Fe(CO)_4Cl_2$$
$$(I)$$
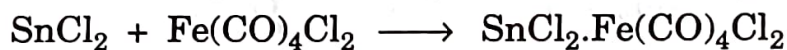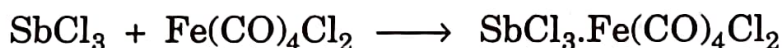
$$SbCl_3 + Fe(CO)_4Cl_2 \longrightarrow SbCl_3.Fe(CO)_4Cl_2$$
$$(II)$$

Addition compounds

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

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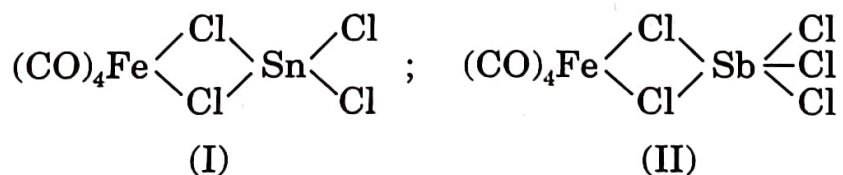
With WCl_6 and $MoCl_6$, $Fe(CO)_5$ gives $W(CO)_6$ and $Mo(CO)_6$ respectively.

$$MCl_6 + 2Fe(CO)_5 \longrightarrow M(CO)_6 + 4CO + 2FeCl_3$$
(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 $Fe_3(CO)_{12}$.

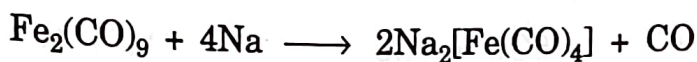(*vi*) *Action of phen.* In acetone or benzene solution at 80° $Fe_2(CO)_9$ reacts with *phen* to form $[Fe(phen)_3]$ $[Fe_2(CO)_8]$. In pyridine, with *phen* it gives $[Fe(phen)_3]$ $[Fe_4(CO)_{13}]$.

(*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 $Fe_3(CO)_{12}$ separate from the solution.

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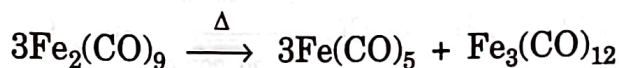
(*ii*) by the oxidation of $Fe(CO)_4H_2$ with H_2O_2 or MnO_2.

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

$$3Fe(CO)_4H_2 + 3MnO_2 + 3H_2SO_4 \longrightarrow Fe_3(CO)_{12} + 3MnSO_4 + 6H_2O$$
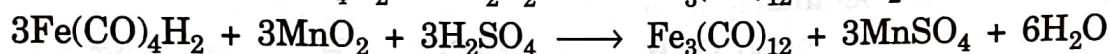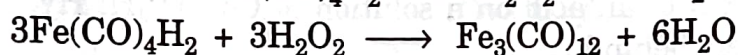
(*iii*) by treating $Fe(CO)_5$ with aqueous tri-ethylamine to form the dark red $[Et_3NH]$ $[Fe_3(CO)_{11}H]$ which is then acidified and $Fe_3(CO)_{12}$ is extracted with petroleum ether.

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.

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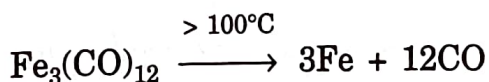
(*iii*) *Disproportionation reaction.* It undergoes disproportionation reactions. For example it reacts with CH_3OH at room temperature and $Fe(CO)_5$ is thereby produced.

$$3Fe_3(CO)_{12} + nCH_3OH \longrightarrow [Fe(CH_3OH)_n] [Fe_3(CO)_{11}] + 5Fe(CO)_5$$
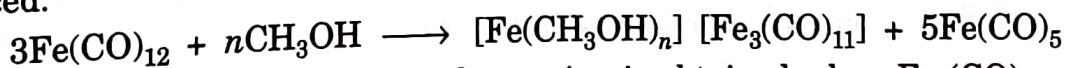
(*iv*) *Reaction with Na.* Carbonylate anion is obtained when $Fe_3(CO)_{12}$ reacts with Na metal in liq. NH_3.

$$Fe_3(CO)_{12} + 6Na \longrightarrow 3Na_2 [Fe(CO)_4]$$
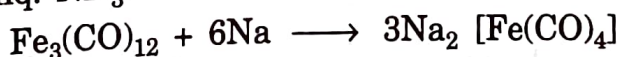
(*v*) *Substitution reactions.* These reactions occur with pyridine (*py*) and methyl alcohol as shown below :

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

$$2Fe_3(CO)_{12} + 3CH_3OH \longrightarrow Fe_3(CO)_9 (CH_3OH)_3 + 3Fe(CO)_5$$

(*vi*) *Action of NO.* At 85° it reacts with NO to form iron dicarbonyl dinitrosyl, $Fe(CO)_2 (NO)_2$.

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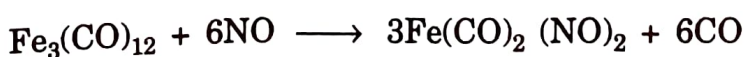
4. Dicobalt Octacarbonyl, $Co_2(CO)_8$.

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

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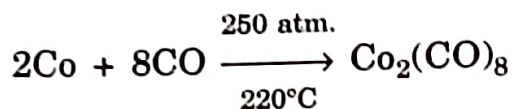
(ii) by the reaction of dry CO at 200° and 200 atm in presence of metallic copper on certain binary compounds of cobalt such as CoS and CoX_2. Here Cu forms Cu_2S or CuX.

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

$$2CoX_2 + 8CO + 4Cu \longrightarrow Co_2(CO)_8 + 4CuX$$
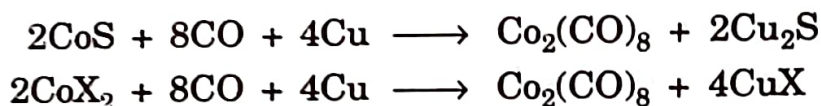
(iii) by the action of CO and H_2 on $CoCO_3$ under high pressure and high temperature.

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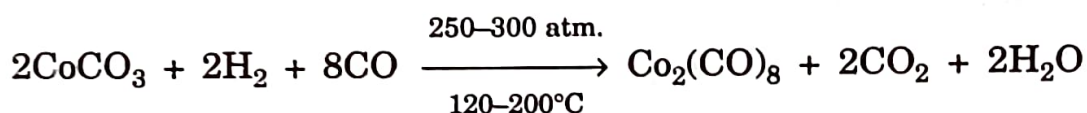
(iv) by the action of an acid on a solution of $Co(CO)_4H$. Hydrogen is evolved and $Co_2(CO)_8$ is left behind.

$$2Co(CO)_4H \longrightarrow Co_2(CO)_8 + H_2$$
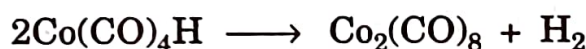
(v) by the thermal decomposition of $Co(CO)_4H$.

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, $Co_4(CO)_{12}$.

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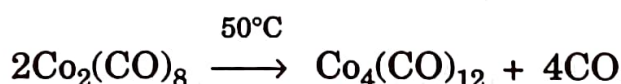
(iii) *Action of air.* On exposure to air, dicobalt octacarbonyl is converted into deep violet basic carbonate of cobalt.

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

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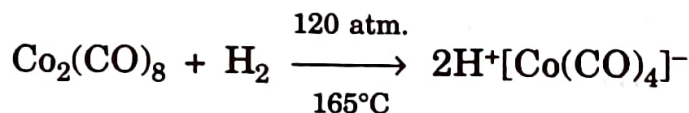
$Co_2(CO)_8$ is also reduced by Na metal in liq. NH_3 below –75°C or tetrahydrofuran (THF).

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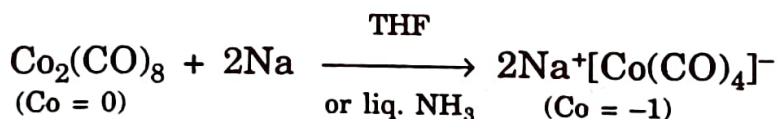
(v) *Disproportionation reactions.* There are two types of such reactions in case of $Co_2(CO)_8$.

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

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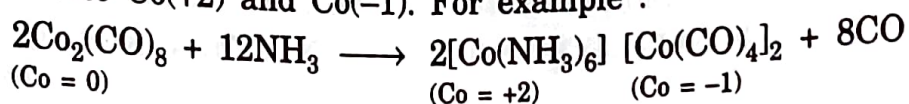
(b) With isocyanides, phosphines, arsines and stibines, however, the disproportionation reaction gives penta-coordinate cobalt (I) cation.

$$Co_2(CO)_8 + 5CNR \longrightarrow [Co(CNR)_5] [Co(CO)_4] + 4CO$$
$$\underset{(Co = 0)}{} \qquad\qquad \underset{(Co = +1)}{} \quad \underset{(Co = -1)}{}$$

(vi) *Reaction with NO.* $Co_2(CO)_8$ also reacts with NO at 40° and forms $Co(CO)_3(NO)$

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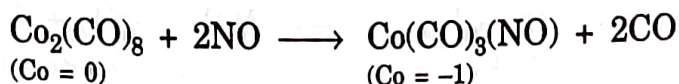
In $Co(CO)_3(NO)$, NO group appears to be more firmly held with Co metal atom than CO groups. This is confirmed by the fact that CO groups can be replaced by the amines very easily, *e.g.* the action of *phen* on $Co(CO)_3(NO)$ gives $[Co(CO)(phen)(NO)]$.

$$Co(CO)_3(NO) + phen \xrightarrow{-2CO} [Co(CO)(phen)(NO)]$$

(vii) *Reaction with halogens.* The halogens decompose $Co_2(CO)_8$ according to the following reaction

$$Co_2(CO)_8 + 2X_2 \longrightarrow 2CoX_2 + 8CO$$
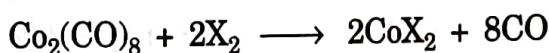
5. Nickel Tetracarbonyl, $Ni(CO)_4$

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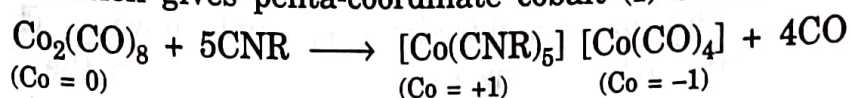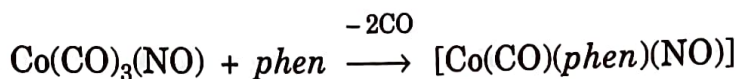
Preparation. (i) It is made by passing carbon monoxide over finely-divided metallic nickel at a temperature below 100°C.

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

(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.

$$Ni(CN)_2 + 4CO \longrightarrow Ni(CO)_4 + C_2N_2$$
$$NiS + 4CO \longrightarrow Ni(CO)_4 + S$$
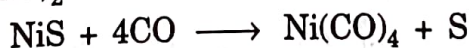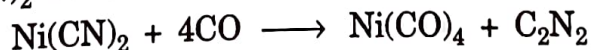
(iv) *By the disproportionation of univalent nickel.* (a) On reducing potassium tetracyano nickelate (II), $K_2[Ni(CN)_4]$ with potassium amalgam, a red solution is obtained. From this solution potassium tricyano nickelate (I), $K_2[Ni(CN)_3]$ may be isolated. This compound absorbs CO at 90°C, probably forming $K_2[Ni(CN)_3(CO)]$. On treating the solution of this compound with HCl, $Ni(CO)_4$ is obtained.

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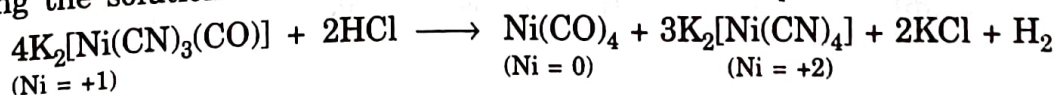
(b) It is most conveniently prepared in the laboratory by the action of CO on nickel(II) phenyl dithiocarbamate, $Ni(S.SC.NH.C_6H_5)_2$.

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

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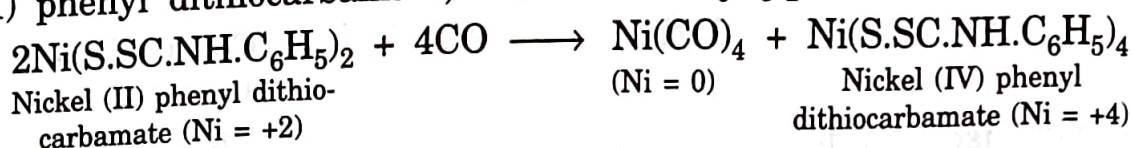
Properties. (i) It is a colourless liquid boiling at 43° and solidifying at −25°C. It is miscible with benzene and is almost insoluble in water. The benzene solution of the nickel carbonyl does the same on boiling, but in the cold, the compound is not acted on by dilute acids or alkalies. Nickel carbonyl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

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

$$Ni(CO)_4 + H_2SO_4 \longrightarrow NiSO_4 + H_2 + 4CO$$
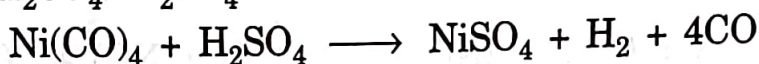
(iii) *Action of NO.* Slightly moist nitric oxide reacts with $Ni(CO)_4$ in the gaseous state or in solution in chloroform to give a compound of intense blue colour, $Ni(NO)(OH)$.

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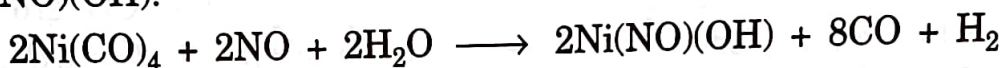
When $Ni(CO)_4$ reacts with NO in the absence of H_2O, the blue solution of the composition, $Ni(NO)(NO_2)$ is obtained.

$$Ni(CO)_4 + 4NO \longrightarrow Ni(NO)(NO_2) + 4CO + N_2O$$

(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
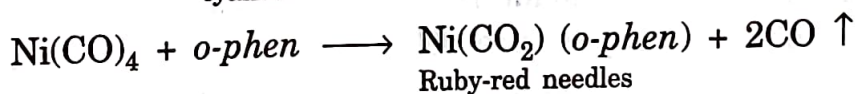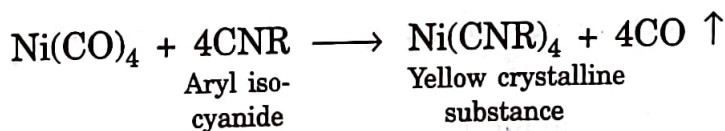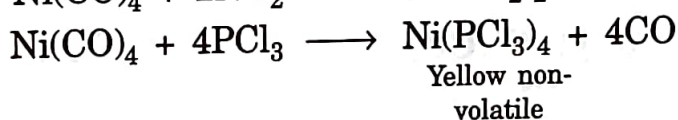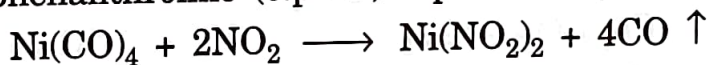
(v) *Action of heat.* $Ni(CO)_4$, when heated to 180°, gives nickel.

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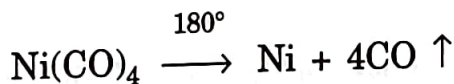
In the pure state nickel carbonyl explodes to form nickel, carbon dioxide and carbon.

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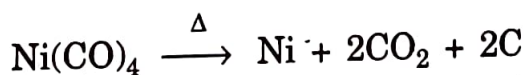
Under high atmospheric pressures (say, 100 atm) it is, however, not decomposed even up to 250°C.

(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)
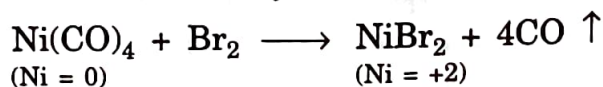
Metallic Carbonyls

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

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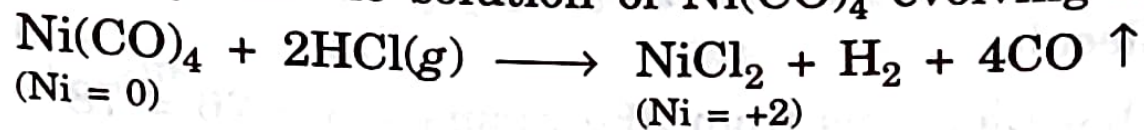
(vii) *Reduction reactions.* $Ni(CO)_4$ gets reduced by several reducing agents. Examples are :

(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.

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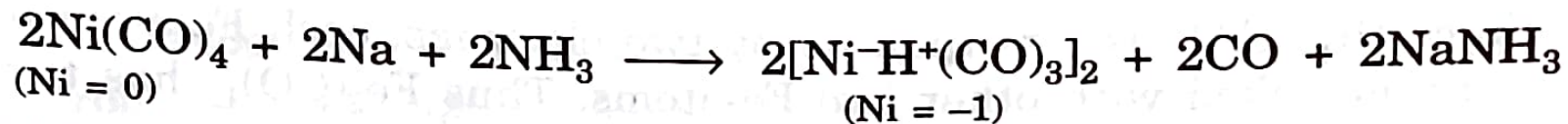
$[Ni^-H^+(CO)_3]$ is isolated as a red tetraammoniate, $[NiH(CO)_3]_2\ 4NH_3$.

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

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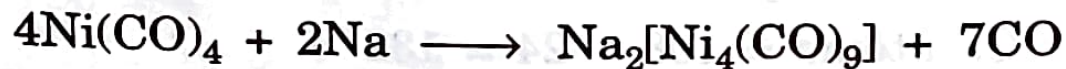
With Li, $Ni(CO)_4$ gives $Li_2\ [Ni_3(CO)_8]$

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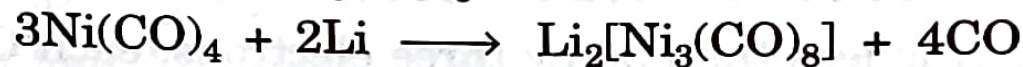
Uses. (i) Since $Ni(CO)_4$ is decomposed to metallic nickel, it is used in the production of nickel by Mond's process. (ii) It is also used in gas plating and also as a catalyst.

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 :

$$2Be + 2C \longrightarrow BeC_2 \; ; \quad 2Ag + 2C \longrightarrow Ag_2C_2$$
$$3Mn + C \longrightarrow Mn_3C \; ; \quad 2Li + C \longrightarrow Li_2C_2$$
$$3Fe + C \longrightarrow Fe_3C \; ; \quad 2Mn + C \longrightarrow Mn_3C$$
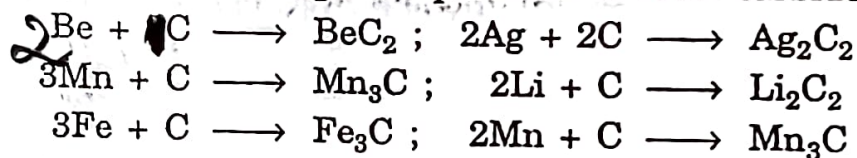
2. **By heating oxides, hydroxides, nitrides, phosphates, sulphates etc. with carbon.** For example :

$$MgO + 3C \longrightarrow MgC_2 + CO \uparrow \; ; \qquad CeO_2 + 4C \longrightarrow CeC_2 + 2CO \uparrow$$
$$2Al_2O_3 + 9C \longrightarrow Al_4C_3 + 6CO \uparrow \; ; \qquad SiO_2 + 3C \longrightarrow SiC + 2CO \uparrow$$
$$U_3O_8 + 14C \longrightarrow 3UC_2 + 8CO \uparrow \; ; \quad 2Mg(OH)_2 + 4C \longrightarrow 2MgC_2 + 2H_2O + O_2$$
$$Ca_3H_2 + 6C \longrightarrow 3CaC_2 + N_2 \; ; \qquad Ca_3(PO_4)_2 + 14C \longrightarrow 3CaC_2 + 2P + 8CO$$
$$4AlPO_4 + 19C \longrightarrow Al_4C_3 + 4P + 16CO \; ; \quad BaSO_4 + 2C \longrightarrow BaC_2 + SO_2 + O_2$$
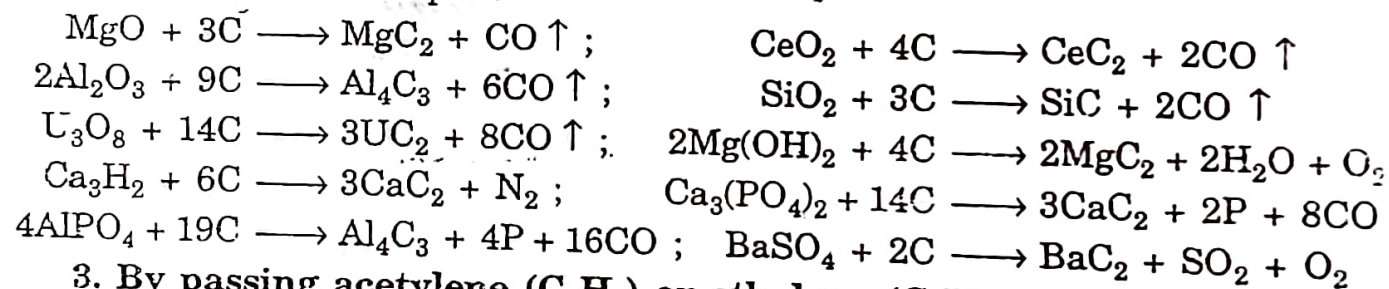
3. **By passing acetylene (C_2H_2) or ethylene (C_2H_4) on heated element or its oxide.** For example :

$$4Li + C_2H_2 \longrightarrow Li_2C_2 + 2LiH \; ; \quad 2Si + C_2H_2 \longrightarrow 2SiC + H_2$$
$$2Ag_2O + C_2H_2 \longrightarrow Ag_2C_2 + H_2O \; ; \quad 6Li + C_2H_4 \longrightarrow Li_2C_2 + 4LiH$$
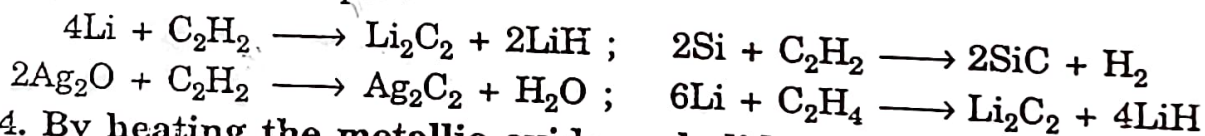
4. **By heating the metallic oxide or halide with CaC_2.** For example :

$$MgO + CaC_2 \longrightarrow MgC_2 + CaO \; ; \; CuCl_2 + CaC_2 \longrightarrow CuC_2 + CaCl_2$$
$$MgF_2 + CaC_2 \longrightarrow MgC_2 + CaF_2$$
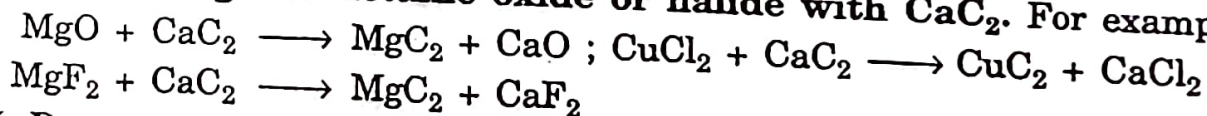
5. **By passing CO over metal at high temperature.**

$$2Li + 2CO \longrightarrow Li_2C_2 + O_2 \; ; \qquad 6Al + 3CO \longrightarrow Al_4C_3 + Al_2O_3$$
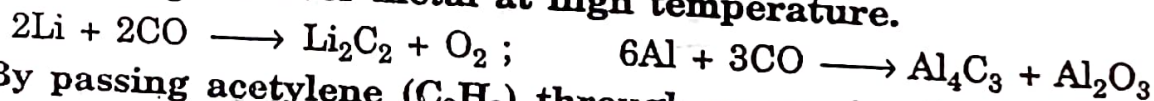
6. **By passing acetylene (C_2H_2) through ammoniacal solution of the metal salt.**

$$2CuCl + 2NH_4OH + C_2H_2 \longrightarrow Cu_2C_2 + 2NH_4Cl + 2H_2O$$
$$2AgNO_3 + 2NH_4OH + C_2H_2 \longrightarrow Ag_2C_2 + 2NH_4NO_3 + 2H_2O$$
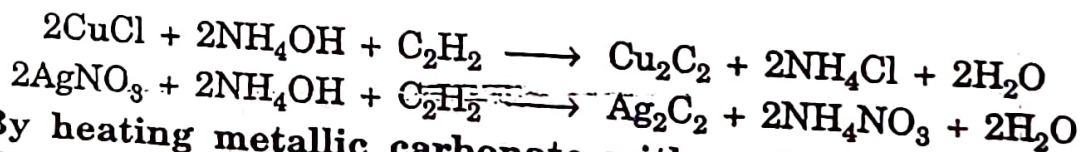
7. **By heating metallic carbonate with carbon in presence of an oxidisable metal.**

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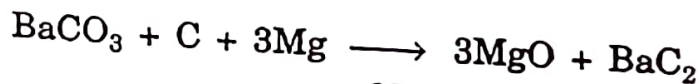
General Properties.

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.
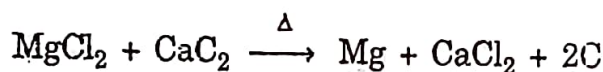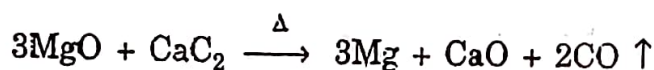
Preparation.

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

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

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

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

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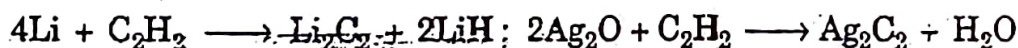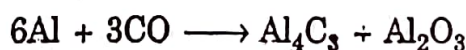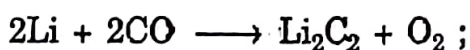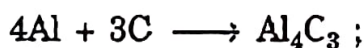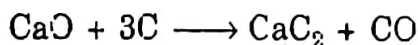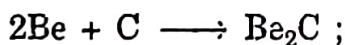
Properties.

(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.

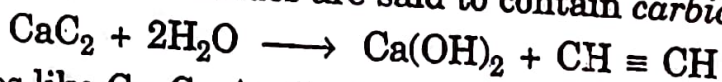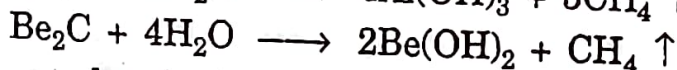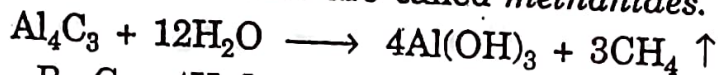$$Mn_3C + 6H_2O \longrightarrow 3Mn(OH)_2 + CH_4 + H_2$$
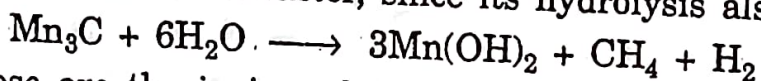
(c) Allylides. These are the ionic carbide, which give allylene ($H_2C = C = CH_2$) on hydrolysis. These carbides are regarded as derivatives of allylene and hence are said to contain C_3^{4-} group.

$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + C_3H_4$$
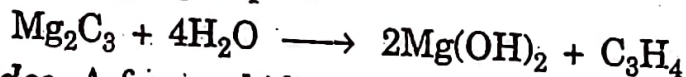
(d) Mixed carbides. A few carbides like those of Th and U of the formula MC_2 give, on hydrolysis, a mixture of several hydrocarbons including acetylene, olefins and H_2. These carbides are related in structure to intermetallic compounds.

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° ($R_M > 1.3$A°), 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.

$$TiO_2 + 3C \longrightarrow TiC + 2CO$$

$$WO_3 + 4C \longrightarrow WC + 3CO$$

$$MoO_3 + 4C \longrightarrow MoC + 3CO$$
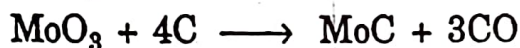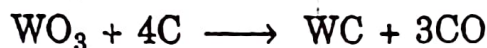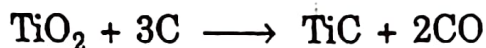
(iii) **by heating the metal in an atmosphere of CH_4 at different temperatures.** HfC, MoC, TaC. WC etc. carbides have been prepared by this method, e.g.

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

$$Mo + CH_4 \longrightarrow MoC + 2H_2$$
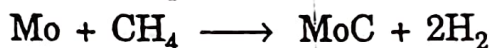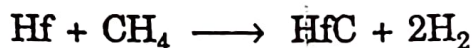
Properties.

(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.

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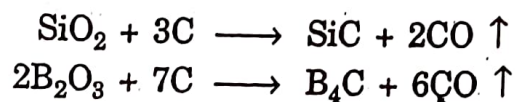
Properties.

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.

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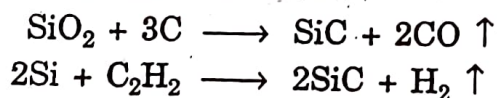
Manufacture.

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.

$$SiO_2 + 3C \longrightarrow SiC + 2CO \uparrow$$
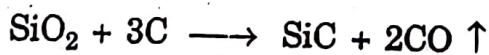
For about two hours in the beginning, the emf gradually decreases from 165 volts to 125 volts and the current increases from 1700 amperes to 6000 amperes due to the gradual decrease in resistance. These conditions persist for the remaining period of time. At the end of the operation, the side walls are 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 porousity 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.

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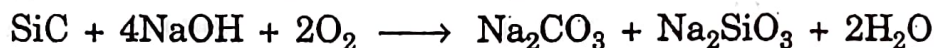
Uses.

(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.

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.

Linear silicone

Cyclic silicone
(Trimer)

Cross-linked silicone
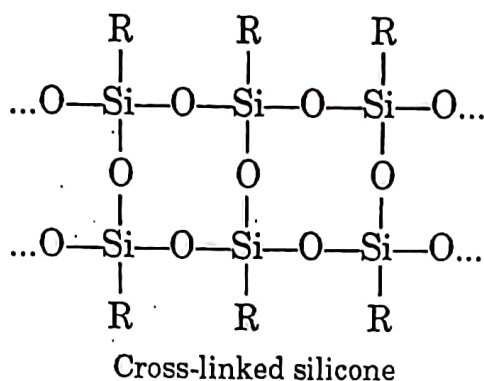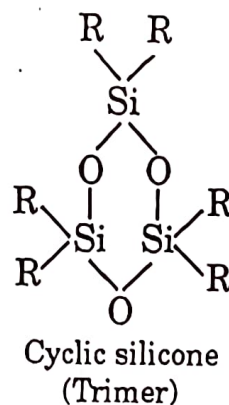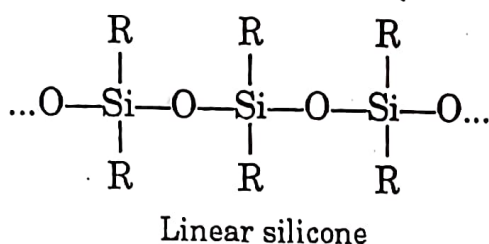
Here R stands for CH_3, C_2H_5 or C_6H_5 groups.

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.

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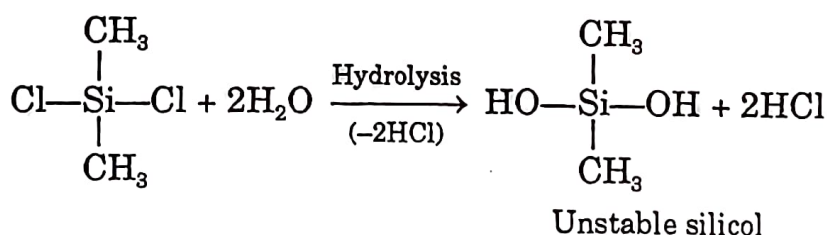
Now a number of molecules of this silicol undergo condensation by intermolecular elimination of some H_2O molecules to form linear silicones.

Many molecules of silicol
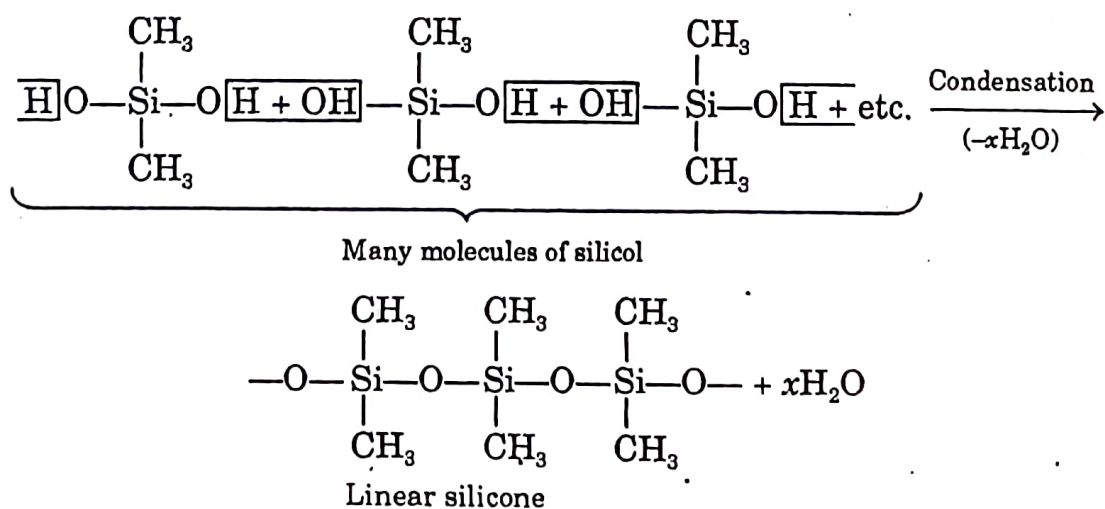
Linear silicone

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

$$SiCl_4 + \underset{\substack{\text{Grignard} \\ \text{reagent}}}{2CH_3MgCl} \longrightarrow (CH_3)_2SiCl_2 + 2MgCl_2$$

$$Si + 2CH_3Cl \xrightarrow{\text{Cu catalyst}} (CH_3)_2SiCl_2 \text{ (Rochow's method)}$$

(a) Silicone rubbers are composed of units with very high molecular weights bridged together with ethylene or similar groups as shown below :
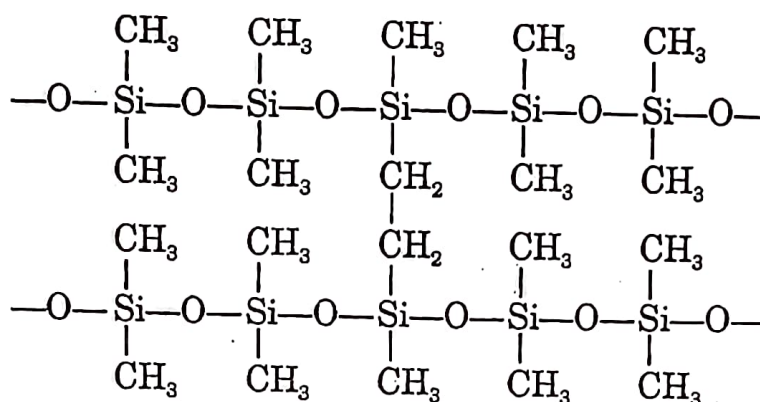
Silicone rubber

(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.
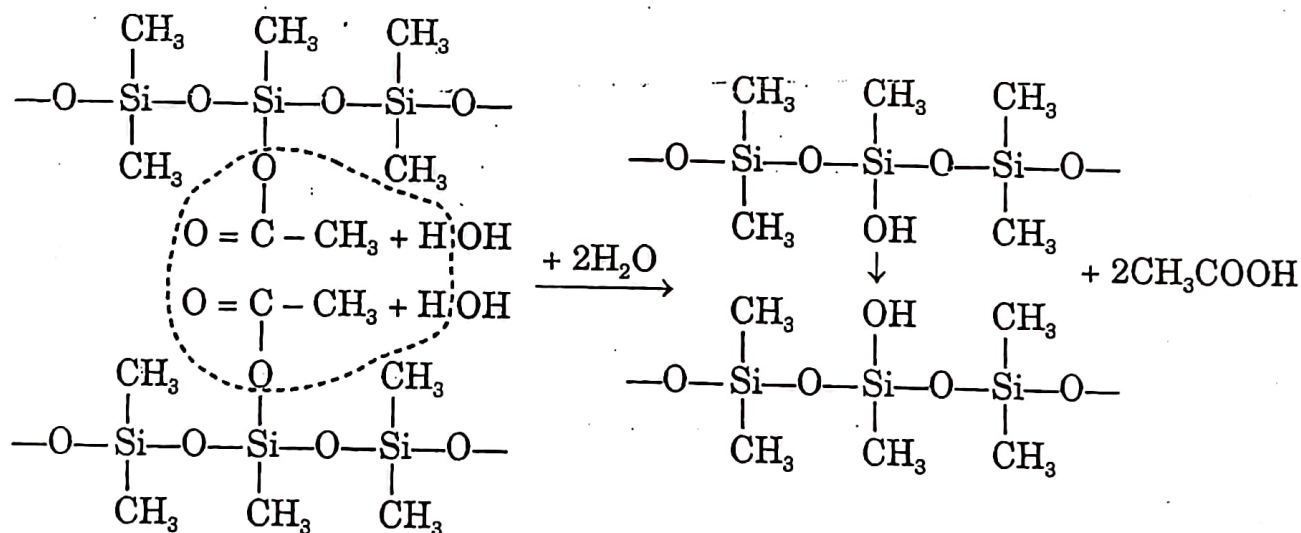
OH$^-$ groups produced as a result of hydrolysis are then made to condense, resulting in cross-linking (*cf* vulcanization of organic rubbers). These silicones are completely water repellent in nature and retain their shape over a wide range of temperatures.

(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 :

$$(CH_3)_2 SiCl_2 \quad\quad\quad \xrightarrow[\text{(-2HCl)}]{\text{Hydrolysis}} \quad\quad \text{Unstable silicol}$$

$$Cl-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl + 2H_2O \xrightarrow[\text{(-2HCl)}]{\text{Hydrolysis}} HO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-OH + 2HCl$$

$$\xrightarrow[\text{(-3H}_2\text{O)}]{\text{Condensation}} \text{Cyclic silicone} + 3H_2O$$
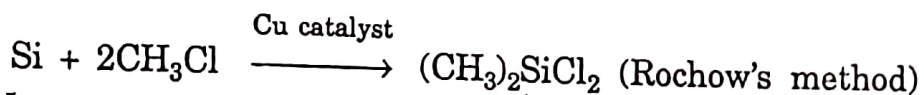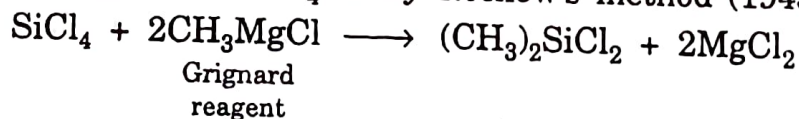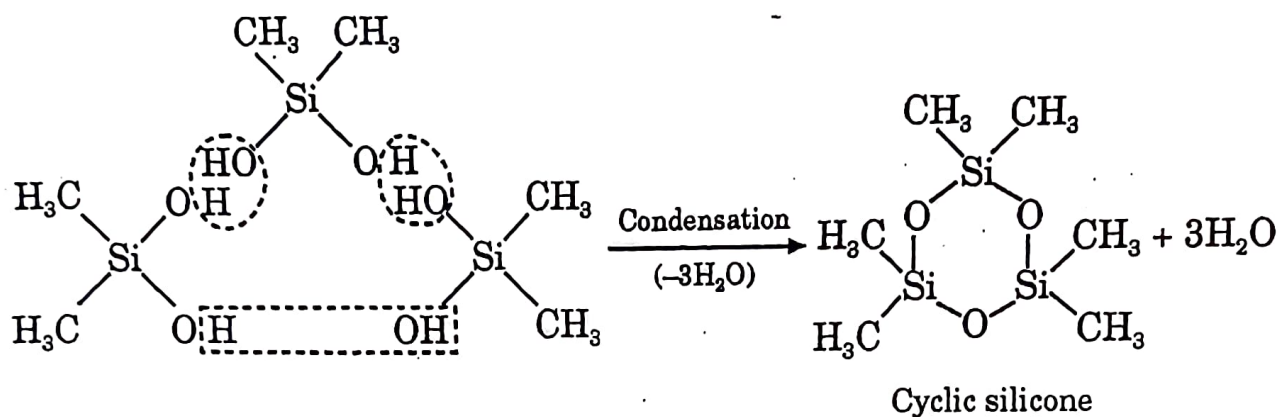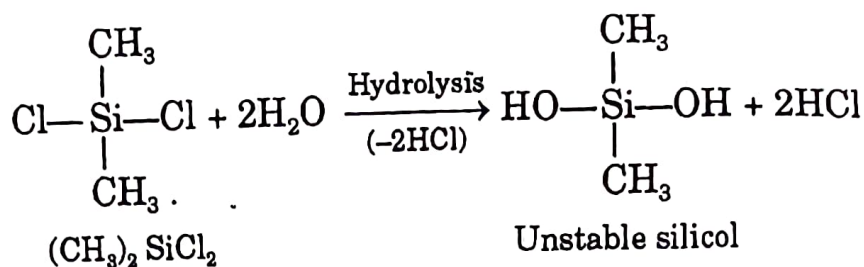
3. Cross-linked Silicones.

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 :

$$(i) \quad R-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Si}}-Cl + 3H_2O \xrightarrow[\text{(-3HCl)}]{\text{Hydrolysis}} R-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-OH + 3HCl$$

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

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

$$(iii) \quad -O-\underset{\underset{\boxed{OH}}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{\boxed{OH}}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{\boxed{OH}}{|}}{\overset{\overset{R}{|}}{Si}}-O-$$

$$-O-\underset{\underset{R}{|}}{\overset{\overset{O\boxed{H}}{|}}{Si}}-O-\underset{\underset{R}{|}}{\overset{\overset{O\boxed{H}}{|}}{Si}}-O-\underset{\underset{R}{|}}{\overset{\overset{O\boxed{H}}{|}}{Si}}-O-$$

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

$\xrightarrow[\text{(}-x\text{H}_2\text{O)}]{\text{Condensation}}$

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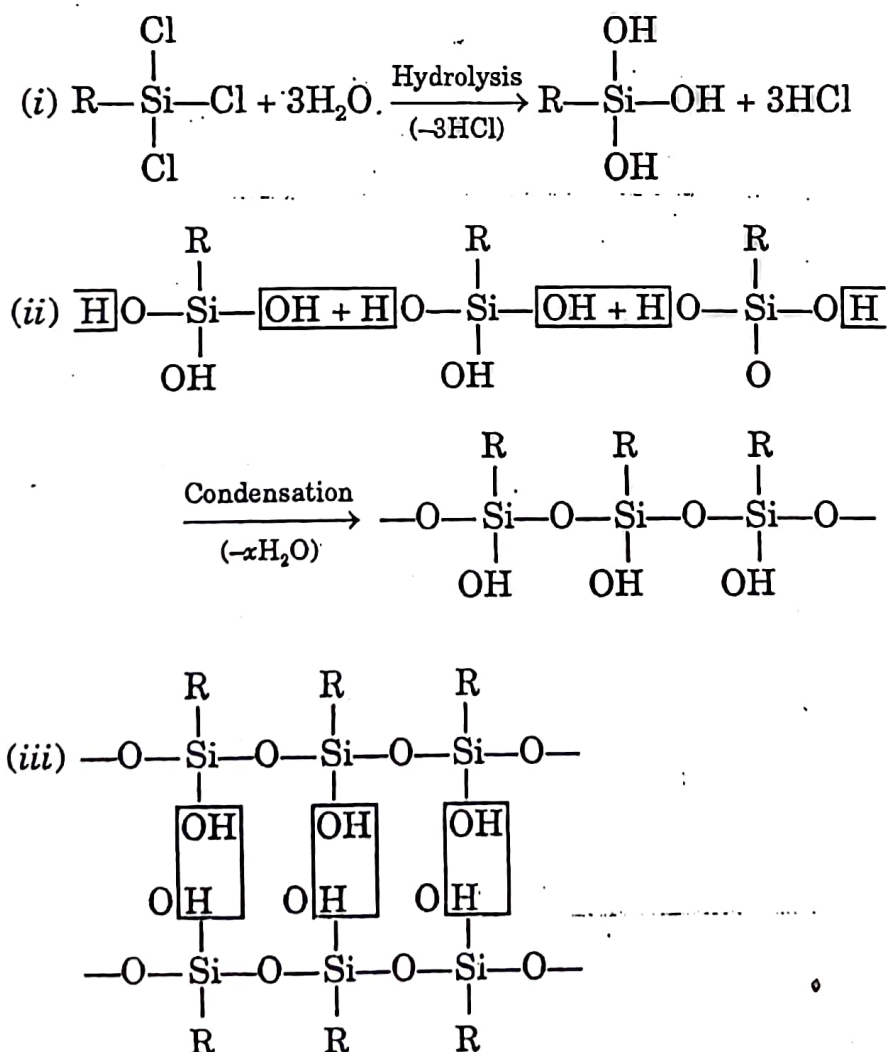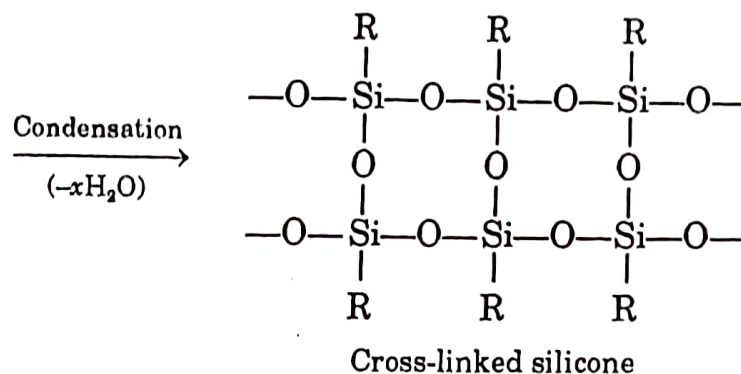
It may be noted that R_2SiCl on hydrolysis produces only a *dimer*, $R_3Si-O-SiR_3$ as shown below :

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

$$
\begin{array}{c}
R \\
| \\
R-Si-\boxed{OH + H}O-Si-R \\
| \\
R
\end{array}
\begin{array}{c}
R \\
| \\
\\
| \\
R
\end{array}
\xrightarrow[\text{(-H}_2\text{O)}]{\text{Condensation}}
\begin{array}{cc}
R & R \\
| & | \\
R-Si-O-Si-R \\
| & | \\
R & R
\end{array}
$$
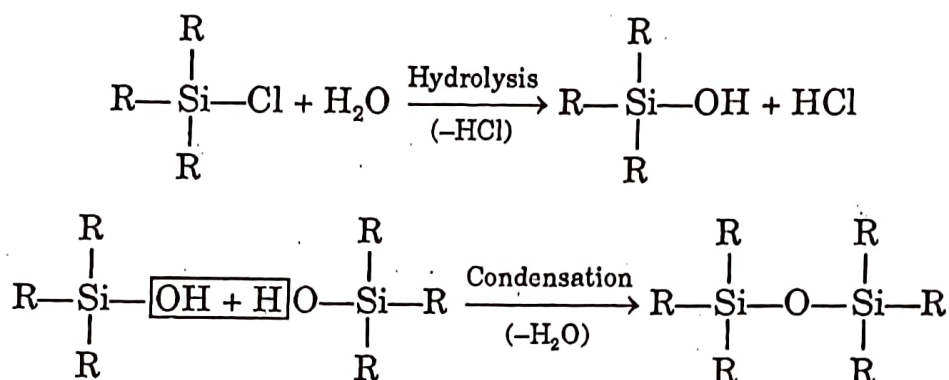
Properties. The lower silicones are oily liquids, but the higher members containing long chains or ring structures are waxy and rubbery solids. Silicones are remarkably stable towards heat and chemical reagents. These are not wetted by water. They are non-toxic and chemically inert. The viscosity of 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.