CHAPTER 22

THE HALOGENS AND THE MANGANESE GROUP

(The Elements of Group VII)

The elements of Group VII are divided into two sub-groups VIIA and VIIB. The elements of sub-group VIIA are non-metals and are commonly known as *Halogens*. The sub-group IIB consists of transition metals of which Mn is important. Technetium is radioactive and prepared artificially as it does not occur in nature. Rhenium is rather unfamiliar.

Sub-group VIIA

Halogens

F — Fluorine
Cl — Chlorine
Br — Bromine
I — Iodine
At — Astatine

Sub-group VIIB

Mn — Manganese
Tc — Technetium
Re — Rhenium

THE HALOGENS

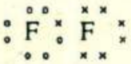
Comparison of the Properties of Halogens

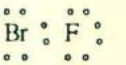
The name halogen was given to the elements of sub-group VIIA because the salts of these elements are common in nature (halogen means salt-former). All these elements combine with alkali metals to produce salt like sodium chloride. The electronic structures of the halogens are given in Table 22.1.

Table 22.1 Electronic structures of the halogens.

At. No.	*Elements*	*Electronic structures*	*Valence electrons*
9	F	(He core) $2s^2$ $2p^5$	$2s^2$ $2p^5$
17	Cl	(Ne core) $2s^2$ $3p^5$	$3s^2$ $3p^5$
35	Br	(Ar core) $3d^{10}$ $4s^2$ $4p^5$	$4s^2$ $4p^5$
53	I	(Kr core) $4d^{10}$ $5s^2$ $5p^5$	$5s^2$ $5p^5$
85	At	(Xe core) $4f^{14}$ $5d^{10}$ $6s^2$ $6p^5$	$6s^2$ $6p^5$

Thus the outermost electron orbitals of F. Cl, Br, I and At consist of s^2p^5 electrons in each case whereas the inert gas outer orbitals contain s^2p^6 electrons. The chemical behaviours of halogens, therefore, show a tendency to achieve the inert gas configuration by accepting an electron from other atoms either by transfer or by sharing. At the ordinary temperatures the halogens exist as diatomic molecules, F_2, Cl_2, Br_2 and I_2 for the same reason, because diatomic halogens have achieved stability by sharing an electron from each atom in an electron pair bond (covalent molecules) :





A list of some of the physical properties are given in Table 22.2 It may be pointed out that these figures are not to be committed to memory but have been included to facilitate the study on the basis of the electronic structures.

The relative sizes of the halogens are particularly useful in explaining many of their physical and chemical properties. The increase in the sizes of the atomic and ionic radii with the increasing atomic number appears to be more well-marked from F to Cl than from Cl to the succeeding halogens. This is an indication that F has a sharp difference in properties as compared to other halogens. The screening electrons in F atom are only two (ls^2) followed by the 7 outermost electrons ($2s^2$ $2p^5$). But the other halogens have at least one complete shell of 8 shielding electrons in addition to other shielding levels. Thus the reactivity of F_2, by and large, is the greatest of all halogens. Chlorine and bromine have more chemical similarity because their atomic and ionic radii have nearly similar values with only slight difference. The incomplete nuclear shielding of 3d electrons in bromine is responsible for this characteristic.

The colours of the halogens (or as a matter of fact any other substance) arise due to absorption of visible light which excites one or more electrons of the outer levels to higher energy levels. The values of the ionization potentials of halogens as given in Table 22.2 indicate this trend. F_2 requires high energy for excitation and hence is pale yellow and the excitation of electrons from I_2 molecule requires lower energy and appears dark violet. From F_2 to I_2 the colour deepens for the same reason.

The melting and boiling points of halogens regularly increase with the increase in their atomic number or molecular weights. As the size of the atoms increases, the electron clouds of the halogen molecules become larger and more readily distorted or polarized.

The greater the size of the electron clouds, the greater is the deformation and elements show greater increase in the van der Waals' forces. Thus at room temperature F_2 is a pale yellow gas, Cl_2 is a greenish yellow gas, Br_2 is a reddish-brown liquid and I_2 is a dark violet solid. Astatine is also a solid having somewhat metallic character. These physical states may be explained on the basis of the relative strengths of the attractive forces acting between the halogen molecules. The diatomic I_2 molecules form the crystal lattice linked together by strong van der Waals' forces among the outermost electrons and hence it is solid. Br_2 is liquid; Cl_2 and F_2 are gases due to decrease in the attractive forces between the molecules (weaker van der Waals' forces) and this trend is indicated by the values of the heats of vaporization of the halogens in Table 22.2

The dissociation energy of halogens indicate that the halogen molecules are quite stable because of the inert gas configuration. Cl_2 molecule is more stable than Br_2 which is more stable than I_2 indicating decrease in the stability of covalent bond with the increase in the size of the atoms.

$$F_2 \rightarrow F + F + 37.8\ \text{Kcal}$$

$$Cl_2 \rightarrow Cl + Cl + 58.0\ \text{Kcal}$$

$$Br_2 \rightarrow Br + Br + 53.4\ \text{Kcal}$$

$$I_2 \rightarrow I + I + 51.0\ \text{Kcal}$$

Table 22.2. Properties of the halogens.

Properties	*F*	*Cl*	*Br*	*I*	*At*
Atomic No.	9	17	35	53	85
Atomic Wt.	19.00	35.46	79.92	126.92	210
Physical state	Pale Yellow gas	Greenish-yellow gas	Reddish-brown liquid	Violet black solid	Solid almost metallic
Outer electron Orbitals	$2s^2\ 2p^5$	$3s^2\ 3p^5$	$3d^{10}\,4s^2\,4p^5$	$4d^{10}5s^2$ $5p^5$	$4f^{14}\ 5d^{10}$ $6s^2\ 6p^5$
Covalent radius (Å)	0.72	1.00	1.14	1.35	—
Ionic radius (Å)	1.36	1.81	1.16	2.16	—
Ionization potential (ev)	17.42	13.01	11.84	10.45	9.50
Melting point (°C)	− 223	−102	− 7	114	—
Boiling point (°C)	−188	− 34	59	185	—
Electronegativity	4.00	3.00	2.80	2.50	2.20
Electrode potential X/X	− 2.87	− 2.36	− 1.10	− 0.54	− 0.30
Oxidation states	−1,0	−1,0,1,3 5,7	−1,0,1,3,5	−1,0,1, 5,7	—
Dissociation energy $X_2 \rightleftharpoons 2X$ (Kcal)	37.80	58.00	53.40	51.00	27.70
Electron affinity (ev)	3.70	4.00	3.80	3.40	3.20
Heats of vaporization (Kcal/mole)	1.60	4.40	7.40	10.40	—

In general, the strengths of the covalent bond increase with the decrease in the atomic size. But F_2 is an exception to this rule. The small value of F—F bond energy is possibly due to the repulsion of non-bonding electrons in the small F atom.

The very great oxidizing power of F molecule is associated with the low heat of dissociation and high heat of hydration of the fluoride (F^-) ion and not with the electron affinity of F having about the same value as that of Br_2.

Halogens with high atomic numbers show greater tendency to increase their oxidation numbe as compared to that of F. This trend is best exemplified by the following interhalogen compounds. F combines with only one F, whereas other halogens can combine with 3, 5 and 7 fluorines :

F—F ClF_3 BrF_5 IF_7

In the above compounds F has, 7, Cl has 7+3 (=10), Br has 7+5 (=12) and I has 7+7 (=14) total number of valence electrons.

Halides of the same metals, such as SnF_4, $SnCl_4$, $SnBr_4$ and SnI_4 or AgF, AgCl, AgBr and AgI etc. exhibit different bond character. The fluorides are almost ionic whereas the iodides are almost covalent. This is attributed to the electronegativity and the extent of polarization of the halide ions. The crystal structures of the halides also depend upon the electronegativity difference of the metals and the halogens and their polarization besides the radius ratios of the cation and polarization of the halide anion as mentioned in the case of Ag-halides. Similarly, TiX_6^{-2} ions have different colours as in K_2TiX_6 :

K_2TiF_6	Colourless
K_2TiCl_6	Yellow
K_2TiBr_6	Red
K_2TiI_6	Deep red

These colours (spectra) are due to the excitation of electrons in the large halide ion to the metal orbitals. The energy of excitation in iodides is the least and hence the longest wavelengths of absorption for which these are deeply coloured.

Summary of the comparison of properties of the halogens

(1) The valence levels of halogens contains s^2p^5 electrons.

(2) Many of the physical and chemical properties of the halogens can be explained on the basis of their relative sizes.

(3) The colours of the halogens are due to the absorption of visible light leading to the excitation of outer electrons. This trend is indicated by their ionization potential.

(4) The melting and boiling points of halogens can be explained on the basis of intermolecular van der Waals' forces between the halogen molecules.

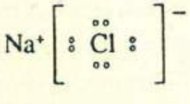
(5) The stability of the halogen molecules is dependent upon the dissociation energy. F_2 has the lowest heat of dissociation and Cl_2 has the highest value which decreases in the case of Br_2 and I_2.

(6) Halogens with high atomic numbers have greater tendency to use outer d-orbitals to form multiple bonds.

(7) Halides of the same metals exhibit different bonding character. Fluorides are more ionic whereas iodides are more covalent.

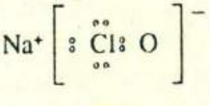
(8) The halides of large ionic radii are deeply coloured whereas the lower halides are colourless.

Oxidation states : The range of the oxidation states of halogens varies from −1 to +7, although −1 state is predominant. But compounds having +1, +5 and +7 states are also formed. Other oxidation states are known in some cases but +2 state is non-existent. F does not show positive oxidation states and Br is never +7. In water solutions the valence states are −1, +1, +3, +5 and +7 (i. e., difference in 2 units). This is mainly due to (i) covalent halogen-to-oxygen bonds and (ii) coordination of an additional oxygen atom to a lone pair of electrons of halogen thus,



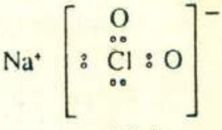
$\mathrm{Na^+}\left[\,:\underset{\circ\circ}{\overset{\circ\circ}{\mathrm{Cl}}}:\,\right]^-$

$(\mathrm{Cl^-})$



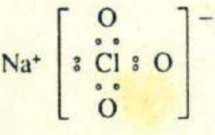
$\mathrm{Na^+}\left[\,:\underset{\circ\circ}{\overset{\circ\circ}{\mathrm{Cl}}}:\mathrm{O}\,\right]^-$

$(\mathrm{Cl^{+1}})$



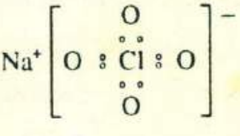
$\mathrm{Na^+}\left[\,:\underset{\circ\circ}{\overset{\overset{\mathrm{O}}{\circ\circ}}{\mathrm{Cl}}}:\mathrm{O}\,\right]^-$

$(\mathrm{Cl^{+3}})$



$\mathrm{Na^+}\left[\,:\underset{\underset{\mathrm{O}}{\circ\circ}}{\overset{\overset{\mathrm{O}}{\circ\circ}}{\mathrm{Cl}}}:\mathrm{O}\,\right]^-$

$(\mathrm{Cl^{+5}})$



$\mathrm{Na^+}\left[\,\mathrm{O}:\underset{\underset{\mathrm{O}}{\circ\circ}}{\overset{\overset{\mathrm{O}}{\circ\circ}}{\mathrm{Cl}}}:\mathrm{O}\,\right]^-$

$(\mathrm{Cl^{+7}})$

Not many compounds are known which have even oxidation states of halogen. ClO_2 has +4 state of Cl. F_2O_2 is ill-defined as +2 for F and Cl_2O_6 has +6 oxidation state for Cl. These may be regarded as peroxides.

The odd oxidation states arise due to the stability of electronic structures involving pairs of electrons either shared or unshared. The odd oxidation states are generally exhibited by odd groups. ClO_2, BrO_2 and IO_2 having oxidation number +4 for the halogens have odd number of electrons in their molecules. Table 22.3 shows the various oxidation states of halogens in well-known compounds.

Table 22.3. Oxidation states of halogens.

Oxidation states	*F*	*Cl*	*Br*	*I*
−1	NaF	NaCl	NaBr	NaI
0	F_2	Cl_2	Br_2	I_2
+1	—	HClO	HBrO	HIO
		Cl_2O	Br_2O	—
+2	—	—	—	—
+3	—	$HClO_2$	—	
+4	—	ClO_2	BrO_2	IO_2
+5	—	$HClO_3$	$HBrO_3$	HIO_3
				I_2O_5
+7	—	$HClO_4$	—	H_5IO_6
		Cl_2O_7		

Anomalies of fluorine : Fluorine differs in many ways from other halogens. For instance, F does not form oxyacids and oxysalts. It can not be prepared by the general method of formation of other halogens. There are numerous insoluble fluorides, such as those of Ca, Mg, Ba, Sr, lanthanides and actinides. F is the only halogen which exhibits hydrogen bonding and forms only one covalent bond. These anomalies may be attributed to the following reasons :—

(1) The highest electronegativity of F (4.0) is greater than that of oxygen (3.5). Other halogens are less electronegative than oxygen.

(2) Small size of the F atom.

(3) F_2 molecule has low bond energy.

(4) F has no d orbitals available.

(5) The reaction of F with other element is highly exothermic (high bond energy).

(6) Insolubility of most fluorides is due to high lattice energies of their three-dimensional network structures. The higher halides have either chain or layer structures.

Chemical properties of the halogens : The chemical properties of the halogens may be summarized in some of the important reactions which take place with other substances. All the reactions of halogens are normally oxidizing actions.

(a) Reaction with hydrogen : All halogens react with hydrogen, although under different conditions giving hydrogen halides :

$$X_2 + H_2 = 2HX \qquad (X = \text{halogens})$$

The reaction of F_2 is very vigorous ; Cl_2 reacts in presence of light. Br_2 reacts readily but I_2 is not very reactive because HI formed is unstable.

(b) Reaction with oxygen : Halogens form a number of oxides by indirect reactions and are discussed under the oxides of halogens.

(c) Reaction with water : All the halogens give HX and HOX with water except F_2:

$$Cl_2 + H_2O = HCl + HOCl$$

But F_2 reacts violently with water to give oxygen flouride, OF_2 :

$$F_2 + H_2O = OF_2 + H_2$$

(d) Reactions with acids : No significant reaction.

(e) Reactions with alkalies : Different salts of oxyacids of halogens are formed under different conditions.

(f) Reactions with metals : Almost all metals react with halogens at various conditions and with different rates. Some react very vigorously and others

slowly under heated conditions. They normally form halides of the metals with high oxidations state :

$$2Fe + 3Cl_2 = 2FeCl_3$$

or generally, $$2M + nX_2 = 2MX_n \qquad (M = \text{metal})$$

(g) Reactions with non-metals : S is converted to S_2Cl_2 and P is changed to PCl_3 or PCl_5 by the reaction with Cl_2. All halogens show this behaviour.

(h) Reactions with organic compounds : Hydrocarbons burn in Cl_2 gas to form HX and free carbon. Unsaturated organic compounds give important reactions with halogens.

(i) Reactions between halogens : The halogens react among themselves giving a large number of compounds. These are known as interhalogen compounds.

(j) Solubility in organic solvents : Cl_2, Br_2, and I_2 dissolve in many organic solvents. I_2 gives different colour in different solvents. Thus in alcohol it is brown but in CCl_4 or CS_2 it is violet due to molecular I_2. The colour is due to excitation of electrons and breaking of I—I bonds. In aqueous alkali, complete breaking of I—I bonds leads to a colourless solution.

The oxidation reactions of halogens *:* As pointed out before, oxidations by the halogens are the important and familiar reactions. These may be termed as *fluorination, chlorination, bromination and iodination* for the reactions with F_2, Cl_2, Br_2, and I_2 respectively. Fluorination is the most vigorous and iodination is the least vigorous, but this depends on the materials with which the halogen reacts. Generally the reactions are termed as *halogination*.

When halogens react with covalent compounds giving products which are only halides, the reactions are known as *halogenolysis*. Thus F_2 oxidizes organic compounds, such as C_2H_6, to produce HF and CF_4 by *fluorinolysis* and Cl_2 oxidizes CS_2 to CCl_4 and S_2Cl_2 :

$$H_3C—CH_3 + 7F_2 = 6HF + 2CF_4$$

$$CS_2 + 3Cl_2 = S_2Cl_2 + CCl_4$$

Iodine oxidizes many reducing agents in aqueous solutions, such as the active metals and metal ions of lower valence states, e. g, Cr^{+2}, Sn^{+2} and also negative ions, like SO_3^{-2}, $S_2O_3^{-2}$ etc., e. g.,

$$2Na_2S_2O_3 + I_2 \;=\; Na_2S_4O_6 + 2NaI$$

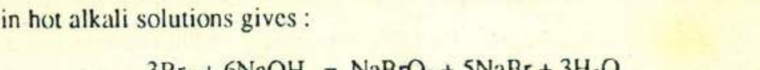
Br_2 being more powerful oxidizing agent oxidizes many reducing agents and also oxidizes an iodide to free I_2. Chlorine oxidizes bromides to free Br_2. Fluorine in aqueous solution, not only oxidizes the reducing substances but also H_2O to produce free oxygen gas.

Hydrolysis of the halogens : Halogens react with water in two ways :

$$X_2 + H_2O \;=\; HX + HOX$$

$$X_2 + H_2O \;=\; 2HX + \tfrac{1}{2}O_2$$

In dilute aqueous alkali solutions, halogens undergo auto-oxidation or, more precisely, a disproportionation reactions in which the halogens are converted to −1 and +1 oxidation states. F_2 does not show this behaviour. The colours of Cl_2, Br_2 and I_2 disappear by hydrolysis in aqueous alkaline solutions :



$$Na^+ \, \overset{\circ\circ}{\underset{\circ\circ}{:O:}} \, H^- + \overset{\circ\circ\;\circ\circ}{\underset{\circ\circ\;\circ\circ}{:X:X:}} \longrightarrow H\overset{\circ\circ}{\underset{\circ\circ}{:O:}}X + Na^+ + \overset{\circ\circ}{\underset{\circ\circ}{:X:}}^{-}$$

The elementary halogens again reappear on acidification of the alkali solution indicating reversible process. In hot solutions HOX (hypohalites) are further oxidised (auto-oxidation) to XO_2^- and XO_3^- together with X^- ions. Thus Br_2 in hot alkali solutions gives :

$$3Br_2 + 6NaOH \;=\; NaBrO_3 + 5NaBr + 3H_2O$$

With F_2 the hydrolysis results in the formation of oxygen gas.

Sources of Halogens and their Preparations

Occurrence : The occurrence of the elements in nature gives an idea about the chemical properties and reactivities. Halogens do not occur in nature in the free state but always in the most stable ionic state of −1. Halogens are, therefore, the most electronegative elements and do not occur free in nature.

Fluorine, the most reactive of all elements, is found as fluorspar, CaF_2, fluorapatite, $CaF_2 . 3Ca_3(PO_4)_2$. and cryolite, Na_3AlF_6. Chlorine is always found as chloride in various compounds, such as NaCl, $MgCl_2$, AgCl etc. Bromine is far less abundant and is found as NaBr, KBr and MgBr in sea water and salt deposits. Iodine in sea water is selectively absorbed by sea-weed (Kelp) but the most important source is Chile saltpeter, $NaNO_3$, in which it is found as sodium iodate, $NaIO_3$, and sodium periodate, $NaIO_4$, and it also occurs in brine wells.

Preparation of halogens : All halogens are obtained from their compounds containing negative halides, X^- ions, by oxidation to free halogen, X_2. The oxidation can be carried out by (i) chemical and (ii) electrolytic methods.

Fluorine

Sources : Fluorspar—CaF_2
Cryolite—Na_3AlF_6

Fluorine is prepared both commercially and in the laboratory by the electrolytic method. Since it is highly reactive, it caused the death of several scientists who attempted to prepare fluorine in the early stages.

Commercially F_2 is obtained by the electrolysis of fused KHF_2 or by the electrolysis of anhydrous liquid HF to which KHF_2 is added to conduct electricity through liquid HF which is a nonconductor. HF is obtained from CaF_2 by the reaction of conc H_2SO_4 and KHF_2 is made from HF and KF. A sketch of an electrolytic cell for the production of F_2 is given in Fig. 22—1.

The highly reactive nature of fluorine and the explosive situation created when H_2 and F_2 become mixed during electrolysis are the main drawbacks. The electrodes are separated by means of copper gauze which surrounds the cathode.

All traces of moisture must be excluded because of the vigorous reaction of F_2 with H_2O. The electrolytes, KHF_2 or HF + KHF_2 are electrolysed in the liquid condition (100-200°C). The cell material, such as copper, becomes coated with a layer of CuF_2 and protects the vessel from the reaction of F_2.

Fluorine is produced at the anode and hydrogen is liberated at the cathode :

$$\underset{\text{(fused)}}{2KHF_2} \xrightarrow{\text{electrolysed}} \underset{\text{at the anode}}{F_2} + \underset{\text{at the cathode}}{H_2} + 2KF$$

$$2HF \xrightarrow[+KHF_2]{\text{electrolysed}} \underset{\text{at the anode}}{F_2} + \underset{\text{at the cathode}}{H_2}$$

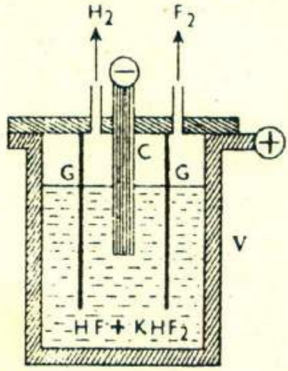


Fig. 22—1. A sketch of the electrolytic cell for the production of fluorine.

V—Electrolytic vessel made of copper which is the anode.

C—Carbon cathode.

G—Copper gauze.

It is to be noted that the electrolysis of an aqueous solution of KHF_2 or NaF does not produce H_2 and F_2 but H_2 and O_2 gas. This is because H_2O is oxidized to O_2. at a much lower voltage (−1.23 volts) than F^- ion which requires a higher voltage to be oxidized to F_2 (− 2.85) volts).

Chlorine

Sources : Rock-salt and common salt in sea water.

Chlorine can be prepared by the chemical and electrolytic methods of oxidation of Cl^- ions from NaCl, other metal chlorides or HCl in aqueous solutions. Cl_2 also be made by the electrolysis of fused NaCl or other chlorides. The electrolysis of brine may be represented by the equation :

$$Na^+ + Cl^- + H_2O \xrightarrow{\text{electrolysis}} Na^+ + OH^- + Cl_2 + H_2$$

Cl_2 is liberated at the anode, usually a carbon rod, and H_2 is evolved at the cathode which is the iron cell itself or mercury. Various designs of cells, such as Nelson, Hooker and Vorce cells are used. Br_2 and I_2 can be prepared by similar electrolytic method as in the case of Cl_2, but these are generally made by chemical methods. The preparation of chlorine or other halogens (except F_2) by the chemical oxidation depends upon the oxidation potentials of the halogen halide ion couples :

$$2X \longrightarrow X_2 + e^-$$

The standard oxidation potential of the various oxidation-reduction reactions are given in Table 7.2 (page ....). But the oxidation potentials of some oxidation-reduction reactions of ionic systems are given in Table 22.4 in order to understand which oxidizing agent will be more suitable to bring about the oxidation of halide ions into halogens.

The oxidized form of the above reaction systems can oxidize the reduced form of any other system provided the potential is lower or more positive. F_2 is the strongest oxidizing agent with highly negative value of oxidation potential. Cl^- can be oxidized to Cl_2 by $KMnO_4$ and PbO_2 but not by $K_2Cr_2O_7$. The oxidation potential of MnO_2 is lower than Cl^-/Cl_2 system but the increase of H^+ in the form of HCl and reducing the pressure of Cl_2 gas by heating the reaction mixture, the oxidation of Cl^- to Cl_2 by MnO_2 is brought to completion. This is an example of concentration effect on electrode potential. The oxidation potentials also indicate that F_2 will oxidize Cl^- to Cl_2 which, in turn will oxidize Br^- to Br_2 which will oxidize I^- to I_2. Thus the oxidation potentials

Table 22.4 Oxidation potentials of some oxidizing systems compared for the preparation of halogens.

Electrode reaction			*Standard oxidation potential* *E° (Volts)*
$2I$	=	$I_2 + 2e$	− 0.53
Fe^{+2}	=	$Fe^{+3} + e$	− 0.77
$2Br^-$	=	$Br_2 + 2e$	− 1.06
$Mn^{+2} + 2H_2O$	+	$MnO_2 + 4H^- + 2e$	− 1.23
$2Cl^-$	=	$Cl_2 + 2e$	− 1.36
$2Cr^{+3} + 7H_2O$	=	$Cr_2O_7^{-2} + 14H + 6e$	− 1.36
$Pb^{+2} + 2H_2O$	=	$PbO_2 + 4H^+ + 2e$	− 1.46
$Mn^{+2} + 4H_2O$	=	$MnO_4^- + 8H^+ + 5e$	− 1.51
$2F^-$	=	$F_2 + 2e$	− 2.80

of halide/halogen systems give informations regarding the gradation in the chemical properties of halogens also.

The oxidation of HCl for the preparation of chlorine may be carried out by the following reactions :

1. $4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$
2. $16HCl + 2KMnO_4 = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
3. $4HCl + PbO_2 = PbCl_2 + 2H_2O + Cl_2$
4. $2HCl + NaOCl = NaCl + H_2O + Cl_2$

The starting material may be chloride, such as NaCl, which on oxidation with an oxidizing agent in presence of H_2SO_4 gives the reactions represented by the general equations :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl$$

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$$

The industrial production of Cl_2 by the *Deacon's Process* involving oxidation of HCl by the atmospheric oxygen in presence of $CuCl_2$ as a catalyst has been replaced by the electrolytic methods. The overall reaction in Deacon's Process in said to involve the equilibrium :

$$4HCl + O_2 \overset{CuCl_2}{\rightleftharpoons} 2H_2O + Cl_2$$

The catalyst, $CuCl_2$, functions as shown by the equations :

$$2CuCl_2 = Cu_2Cl_2 + Cl_2$$

$$Cu_2Cl_2 + O = CuO.CuCl_2$$

$$CuO.CuCl_2 + 2HCl = 2CuCl_2 + H_2O$$

Bromine

Sources : Magnesium bromide, $MgBr_2$ (in sea water).

Brom-carnallite, $MgBr_2.\ 6H_2O$ (in carnallite).

The commercial preparation of bromine form bromides from sea-water or carnallite is done by oxidizing action of chlorine. The pH value is adjusted between 1—4 with H_2SO_4, and then treated with chlorine. A stream of air is blown to free the liberated bromine which is absorbed in Na_2CO_3 solution. The solution is distilled after acidification :

$$Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$$

$$3Br_2 + 3CO_3^{-2} \rightarrow 5Br^- + 5BrO_3^- + 3CO_2$$

$$5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

Chlorine present is removed from the bromine by reaction with a bromide, such as $FeBr_3$. Further purification from chlorine and iodine is carried out by distilling it with KBr and ZnO which removes chlorine and iodine respectively.

Iodine

Sources : Sea-weed (Kelp)

Chile saltpeter ($NaNO_3$ contains $NaIO_3$)

Burnt sea-weed contains alkali iodide, such as NaI, from which iodine is obtained by heating with an excess of H_2SO_4 and MnO_2. The iodine vapours are condensed in receiver known as *eludels*.

Iodine is mostly obtained by the sulphite reduction of iodates in aqueous solution :

$$2NaIO_3 + 5NaHSO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$$

Iodine is purified by sublimation over KI.

Astatine

It occurs in very small amount in nature due to the disintegration of ^{215}Po and ^{218}Po. But astatine has not been isolated from natural sources. It has been prepared from bismuth by bombardment with α-particles.

$$Bi^{209} + He^4 = At^{211} + 2n^1$$

Astatine is radioactive with half-life of 8.3 hours. As would be expected, astatine is a solid element more metallic than iodine.

The solid is volatile and is soluble in carbon disulphide and tetrachloride. Elementary astatine is the weakest oxidizing agent of all the halogens.

Uses of Halogens

Fluorine : F_2 is used in—(i) The productions of fluorocarbon compounds used as lubricants, insecticides etc. Thus Freon, CCl_2F_2, is used as a refrigerant, CCl_3F is an insecticide. Teflon is a plastic having C_2F_4 units in the polymer. (ii) The production of UF_6, SF_6 etc. (iii) The production of ClF_3, a liquid incendiary for war purposes.

Chlorine : Cl_2 used for —(i) bleaching wood pulp and cotton cloth; (ii) chlorinating agents for water; (iii) chlorinating agents for producing organic compounds, such as CCl_4, $CHCl_3$ etc.

Bromine : Br_2 is used in —(i) the manufacture of ethylene dibromide, an antiknock gasoline along with lead tetra-ethyl, Pb $(C_2H_5)_4$; (ii) the production of organic dyes; (iii) the production of AgBr for photography.

Iodine : I_2 is used in—(i) the production of iodoform, CHI_3 ; (ii) the preparation of *tincture of iodine* and (iii) a vast number of medicinal compounds.

Some Important Compounds of Halogens

Hydrogen halide, HX : Both HF and HCl are obtained by the action of concentrated H_2SO_4 on their readily available salts, NaCl and CaF_2. But HBr and HI can not be prepared by the analogous methods since HBr and HI are oxidized to Br_2 and I_2 in concentrated H_2SO_4. Although H_2 and F_2 will react vigorously to form HF, the reaction is too violent to be adopted as a method of preparation of HF.

General Methods of Preparation of HX

1. By direct union of the the elements : The general equation for the reaction of hydrogen and halogen is :

$$H_2 + X_2 = 2HX$$

The heat of formation of HX rapidly decreases with increasing atomic number of halogens. As mentioned above, HF is not prepared by this method. But HCl is commercially produced by combustion of hydrogen, H_2, with chlorine in burners specially designed for this purpose. Both H_2 and Cl_2 are obtained by the electrolysis of brine.

The reaction $H_2 + Br_2 \rightleftharpoons 2HBr$ is much less vigorous and the production of HBr involves heating the mixture of H_2 and Br_2 to 200°C is contact with catalyst, such as Pt or C, and using excess of H_2 to force the equilibrium reaction towards HBr.

HI is not prepared by this method because of the slow reaction and decomposition at equilibrium :

$$H_2 + I_2 \rightleftharpoons 2HI$$

2. By the action of conc H_2SO_4 or conc H_3PO_4 on metallic halide : This is the most convenient method of preparation of HF and HCl.

HF is prepared by heating a mixture of the mineral fluorite, CaF_2, and conc H_2SO_4 in a lead or platinum retort :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

HF evolved is absorbed in water forming hydrofluoric acid. This is stored in bottle made of lead, wax, plastic or polythene, because HF acts upon glass and other metals. Pure anhydrous HF can be obtained by heating KHF_2 :

$$KHF_2 = KF + HF$$

HCl is also made in the laboratory and commercially by the reaction of NaCl with conc H_2SO_4 :

$$NaCl + H_2SO_4 = HCl + NaHSO_4$$
$$NaCl + NaHSO_4 = HCl + Na_2SO_4$$

HCl is distilled off because it is more volatile than H_2SO_4 .

HBr and HI cannot be prepared by the action of conc H_2SO_4 on a bromide or iodide because HBr and HI are reducing agents. Some HBr and HI produced react with hot H_2SO_4 as follows :

$$NaBr + H_2SO_4 = NaHSO_4 + HBr$$
$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2$$
$$NaI + H_2SO_4 = NaHSO_4 + HI$$
$$8HI + H_2SO_4 = H_2S + 4I_2 + 4H_2O$$

HI is a stronger reducing agent than HBr. Hence the reduction of H_2SO_4 to H_2S in the case of HI and to SO_2 by HBr. But HI also produces some SO_2 and elementary S.

HBr and HI are commonly prepared by the action of a soluble metal bromide or iodide with H_3PO_4 which is non-volatile and non-oxidizing acid :

$$NaBr + H_3PO_4 = HBr + NaH_2PO_4$$

$$NaI + H_3PO_4 = HI + NaH_2PO_4$$

3. By the hydrolysis of non-metallic halides : Some covalent halides of non-metals are hydrolysed to give HX. Thus hydrolysis of PCl_3, PBr_3, PI_3, SCl_4 etc. gives the respective HX. This method is particularly useful for the preparation of HBr and HI :

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr$$

$$PI_3 + 3H_2O = H_3PO_3 + 3HI$$

4. By the halogenation of hydrocarbons : Except HI, other hydrogen halides are obtained as by-products when F_2, Cl_2 and Br_2 react with saturated hydrocarbons in presence of a catalyst for the formation of halogenated hydrocarbons. When ethyl chloride is manufactured, HCl is obtained as a by-product in large quantity :

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl$$

5. By reduction with H_2S or H_2SO_3 : This method is suitable for producing HBr and HI in aqueous solution. The reactions involved are :

$$Br_2 + H_2S = 2\ HBr + S$$

$$Br_2 + H_2SO_3 + H_2O = 2\ HBr + H_2SO_4$$

$$I_2 + H_2S = 2\ HI + S$$

$$I_2 + H_2SO_3 + H_2O = 2\ HI + H_2SO_4$$

The elementary S produced is filtered off and the solution is concentrated or distilled.

General Properties of Hydrogen Halides

Anhydrous HF, HCl, HBr, HI are colourless gases, having penetrating odour and fume in moist air. Pure HX are non-conductors of electricity and extremely soluble in water. The solubility in H_2O is due to the reaction :

$$HX + H_2O = H_3O^+ + X^-$$

because H_2O is more basic and O is more electronegative than Cl, Br. and I. Hydrofluoric acid, HF, behaves differently and H—F bond has some unique properties. Hydrogen halides in aqueous solutions are generally known as *hydrohalic acids.*

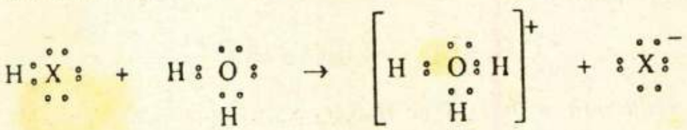
HX in aqueous solutions reacts with metals above H in the E. M. F. series giving oxidation-reduction reaction of the type :

$$2\overset{+1}{HX} + \overset{0}{Zn} = \overset{+2}{ZnX_2} + \overset{0}{H_2}$$

They react with bases to form salt and water. HF in aqueous solution reacts with SiO_2 and also with constituent of glass, $CaSiO_3$, evolving SiF_4 (a volatile gas) :

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

The ionization of HX in water as shown by the equation :



depends upon H—X bond strengths as compared to H—O bond strength in H_3O^+ ion. HF bond is as strong as H—O and HF is not completely ionized. This is due to greater electronegativity of F than that of O. HF molecule is strongly bonded to H_2O by hydrogen bonding :

The bond strength in HCl, HBr and HI are gradually much weaker as compared to H—O. The interatomic distance in HF is also much smaller than that of HI.

Apart form the above considerations the high electronegativity of F is responsible for the association in liquid HF discussed earlier. Therefore, it is liquid at ordinary temperature with higher boiling point than any other HX. The hydrogen bonding in HF is responsible for the formation of many metal fluorides to form hydrogen difluorides, such as $NaHF_2$, KHF_2 etc. HF_2^- ion is represented as :

$$\left[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\ H\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\right]^- \quad \text{or} \quad [F^- H^+ F^-]^-$$

The Cl, Br and I atoms in HCl, HBr and HI are much less electronegative and their sizes increase to a great extent as compared to that of F. Hydrogen bonding, therefore, is not significant in these cases.

Some of the properties of hydrogen halides are given in Table 22.5 for the sake of comparison.

Table 22.5 Some properties of hydrogen halides.

Properties	*HF*	*HCl*	*HBr*	*HI*
Molecular weights	20.008	36.465	80.924	127.92
Boiling point (°C)	20	− 85	− 67	− 35
Melting point (°C)	− 83	−114	− 87	− 51
Solubility in H_2O (g/100g. of H_2O)	98(−10°)	93(−15°)	221(0°)	425(10°)
Heat of formation Kcal/mole	64.00	22.00	8.70	− 5.90
Dielectric constant of liquid	66	9	6	3
% dissociation at 1000°C	—	3×10^{-7}	0.003	19

Metal halides : All metals form halides and there are great variations in their properties. For instance, alkali metals, alkaline earth metals of higher atomic weights, all metal fluorides and some of the transition metal halides are ionic compounds.

These halides have electrical conductivities in the fused state and have high melting and boiling points and those soluble in water are not hydrolysed. Thus Na-halides are good examples of Fajan's rule as given by the melting points : NaF—993°C, NaCl—801°C, NaBr—775°C, NaI—651°C. But halides of metals with high charge-to-size ratios are covalent in character. These are $AlCl_3$, $SnCl_4$, $TiCl_4$ etc. and are volatile, soluble in organic solvents, have no electrical conductivity and are extensively hydrolysed in water. Some halides are in-between the above two types. Thus $FeCl_3$ is volatile, hydrolysed in water, soluble in organic solvents, but conduct electricity in the fused state. Solubility of halides in water differs to a great extent and even halides of the same metal have different solubility. Thus AgF is soluble in water but AgCl, AgBr and AgI are insoluble. CaF_2 is insoluble but $CaCl_2$, $CaBr_2$ and CaI_2 are soluble. Similarly, Hg_2Cl_2 and $PbCl_2$ are insoluble.

The properties of metal halides are convincing examples of the application of Fajan's rules.

Uses of hydrohalic acids and halides

Hydrofluoric acid : HF is used—(i) in etching and writing on glass; (ii) in analysis of rocks and minerals ; (iii) in the production of fluorides, such as BF_3, UF_6 etc. (iv) CaF_2, NaF etc. are used as fluxes. (iv) consumption of blast furnace slag $CaSiO_3$ to SiF_4 (v) Producing freons such as CF_2Cl_2.

Hydrochloric acid : HCl is the most important acid in industry. It is used—(i) in the formation of metal chlorides ; (ii) in the manufacture of dyes, glucose etc.

Hydrobromic acid : HBr is used—(i) in analytical chemistry and (ii) in the synthesis of organic compounds.

Hydroiodide acid : HI is also used for the same purpose as HBr.

Interhalogen compounds :

The compounds formed by the combination of different halogens are called *Interhalogen Compounds*. Examples of interhalogen compounds are given below :

ICl
IBr
ICl_3
IF_5
IF_7
$BrCl$
BrF
BrF_3
BrF_5
ClF
ClF_3

Interhalogen compounds are classified as follows :

Interhalogen compounds

AB type	**AB_3 type**	**AB_5 type**	**AB_7 type**
ClF	ClF_3		IF_7
BrF	BrF_3	BrF_5	
$BrCl$		IF_5	
ICl	ICl_3		

It is interesting to note that interhalogen compounds consist of one atom of heavier halogen bonded to a number of the lighter halogen. The larger-sized I atom has greater number of interhalogen compounds and also greater number of halogen atoms around it. The great difference in electronegativity between halogens gives rise to these compounds. The larger-sized halogens are positive and form compounds with more negative ones. Thus we have IF_7, BrF_5 and ClF_3. Most of these compounds are unstable and extremely reactive like halogens. Hydrolysis in basic reactions give halide of the smaller halogen and oxy-halide from the larger halogens :

$$ICl + NaOH = NaCl + HOI$$

ICl, ICl_3 are formed by the oxidation of I_2 or I^- ion in conc HCl. This may be made by the reaction, $I_2 + Cl_2 = 2ICl$. Iodine chloride, ICl, is a liquid at room temperature. Iodine trichloride is obtained by the reaction $I_2 + 3Cl_2$ (excess) = $2ICl_3$. Iodine trichloride, ICl_3 is a yellow solid and can also be obtained by the reaction :

$$I_2O_5 + 10HCl = 2ICl_3 + 5H_2O + 2Cl_2$$

IBr is obtained by the direct reaction of $I^- + Br_2 = 2IBr$. Chlorine fluoride, ClF, is obtained by reaction of HF and Cl_2 at the temperature of liquid air. Similarly, Br or HBr on reaction with F_2 gives BrF_3 as a colourless liquid. BrF_5 is made from BrF_3 and fluorine. IF_5 and IF_7 are obtained from I_2O_5 and F_2.

The bonding in the interhalogen compounds do not follow normal valence or bonding rules. ClF_3 is supposed to use **sp^3d** orbitals of Cl.

Similarly, BrF_5 uses **sp^3d^2** octahedral bonding of Br and IF_7 has **sp^3d^3** hybrid orbitals of I.

Polyhalides :

Compounds in which halogens or interhalogens become associated together are called *Polyhalides*. Thus KI_3 is a K-polyiodide (tri-iodide). Compounds containing I_5^-, I_7^- and I_9^-, Br_3^-, Cl_3^- etc. have also been prepared. The larger polyhalides are generally found in compounds having large cations, such as Cs^+I_7, $Rb^+ I_9$, $(C_2H_5)_4N^+I_7^-$ etc. Br_3^- and Cl_3^- are unstable ions ; F_3^- does not exist. The well-known examples of polyhalides of two different halogens are $KICl_2$, $CsIBr_2$, $CsClBr_2$, CsIBrCl, $KICl_4$ etc. These are known as mixed polyhalides.

It is well-known that the solubility of iodine in water is greatly increased by adding KI. It has been shown that the deep-brown solution contains I_3^- anion (tri-iodide ion). Here iodine and iodide ion combine giving the reversible reaction :

$$I^- + I_2 \rightleftharpoons I_3^-$$

The combination is due to induced dipole action of I^- ion on I_2. The negative I^- ion when close to a large I_2 molecule, disturbs the electronic arrangements forming the induced dipole leading to the attraction between the negative end of the iodide ion and the positive end of the polar iodine molecule.

The Oxides and Oxyacids of Halogens

The oxides and oxyacids of halogens and their salts are formed by sharing of electrons with oxygen. These compound are important oxidizing agents.

Oxides of Halogens : A number of binary compounds of halogens and oxygen have been made by indirect methods since the two elements do not combine directly. These are :

OF_2
O_2F_2

Cl_2O
ClO_2
Cl_2O_6
Cl_2O_7

Br_2O
Br_3O_8
BrO_2

I_2O_4
I_4O_9
I_2O_5

Because oxygen is more electronegative than Cl, Br and I, their oxygen compounds are halogen oxides. But F compounds are oxygen fluorides because F is more electronegative than oxygen.

Oxygen fluorides : Oxygen difluoride, OF_2, is a colourless gas and oxygen monofluoride, O_2F_2, is a red liquid. OF_2 is a covalent compound having O and F in + 2 and −1 oxidation states respectively. OF_2 is formed when F_2 reacts with NaOH solution :

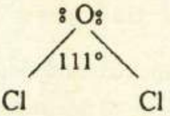
$$2F_2 + 2NaOH = 2NaF + OF_2 + H_2O$$

OF_2 is immediately separated. It is a powerful oxidizing agent. The aqueous solution of OF_2 is not acidic indicating that it is not the anhydride of an acid.

Oxides of chlorine : *Chlorine monoxide* Cl_2O, is a yellowish red gas which explodes violently on heating. This is prepared by passing Cl_2 gas over HgO (300 — 400°C)

$$2Cl_2 + 2HgO = HgCl_2. + Cl_2O$$

Cl_2O is the anhydride of HClO (Hypochlorous acid) and reacts readily with water to form HOCl. The structure of Cl_2O is based on the use of sp^3 hybrid bonds of O. The angle ClOCl is 111° greater than tetrahedral angle due to electronegativity difference in O and Cl atoms.



Chlorine dioxide : ClO_2, is a reddish-yellow gas and explodes violently when pure. It is handled in diluted form with air or CO_2. It is formed along with $HClO_4$, when $KClO_3$ is treated with conc H_2SO_4. This method is dangerous and oxalic acid is conveniently used in the reactions :

$$4KClO_3 + 4H_2SO_4 = 4KHSO_4 + 4ClO_2 + O_2 + 2H_2O$$

$$2KClO_3 + 3H_2C_2O_4 = 2ClO_2 + 2CO_2 + 2H_2O + 2KHC_2O_4.$$

A convenient commercial method involves the reaction of sodium chlorite with Cl_2 diluted with air :

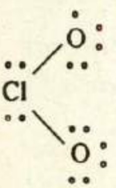
$$2NaClO_2 + Cl_2 = 2NaCl + 2ClO_2$$

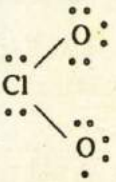
Pure ClO_2 is obtained by the reaction :

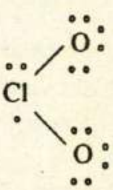
$$Cl_2\,(dry) + 2AgClO_3 \longrightarrow 2AgCl + 2ClO_2 + O_2$$

ClO_2 is now an important commercial product and is used as an antiseptic, in water purification and bleaching of cellulose materials and high grade paper pulp. Also in making unshrinkable woolen fabrics.

ClO_2 is an odd molecule, but it is not dimerized. It contains a three-electron bond and has one unpaired electron. The formula can be written in several forms. It is the only compound in which Cl has +4 oxidation state :







The single electron floats between the two O atoms and the Cl atom. Cl atom in ClO_2 uses possible sp^3d hybrid bonds.

When ClO_2 is dissolved in alkaline solution, alkali chlorate and chlorites are formed.

Chlorine heptoxidi Cl_2O_7 : This is obtained as an oily liquid by dehydrating $HClO_4$ over P_2O_5 at –10°C and distilling :

$$4HClO_4 + P_4O_{10} = 2Cl_2O_7 + 4HPO_3$$

Cl_2O_7 slowly reacts with water giving $HClO_4$.Cl_2O_7 is composed of two ClO_4 tetrahedra joined by an O atom. $O_3Cl—O—ClO_3$

The oxides of bromine are not well established.

Iodine Pentoxide : I_2O_5 is the most stable of all the halogen oxides. It is made by evaporating HIO_3 (dehydrating) :

$$2HIO_3 = I_2O_5 + H_2O$$

I_2O_4, I_2O_5 and I_4O_9 are stable solids.

Basic Iodine : Oxides of iodine are unreactive and it has been suggested that these are ionic compounds. Thus I_4O_9 has been formulated as $I\,(IO_3)_3$. Iodine is the most metallic of the halogens (except At). Since the oxides of iodine are ionic compounds these are most stable. There are other compounds in which iodine behaves as cation. Both +1 and +3 oxidation states are found but +3 oxidation state is the most stable. Thus the acetate, phosphate, nitrate and perchlorate etc. of I^{+3} have been isolated :

$$I\,(CH_3COO)_3,\ IPO_4,\ I(NO_3)_3,\ I\,(ClO_4)_3.2H_2O$$

These are analogous to trivalent Al^{+3} and are hydrolysed easily disproportionating into iodate and I_2. Chloride, pyridine and olefine compounds of I^{+1} are formed and resemble those of Ag^{+1} compounds :

$$[I\,(Py)]^+\,Cl^- \qquad I\,(C_2H_4)\,Cl$$

Oxyacids of the Halogens and their Salts

Oxyacids of fluorine or their salts are unknown. Chlorine has greater tendency to form oxyacids than Br_2 and I_2. The series of oxyacids formed by Cl_2 Br_2 and I_2 are given in Table 22.6

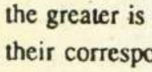
Table 22.6. Oxyacids of halogens.

Oxidation states	Cl_2	Br_2	I_2
+ 1	$HClO$	$HBrO$	HIO
+ 3	$HClO_2$	$HBrO_2$	—
+ 5	$HClO_3$	$HBrO_3$	HIO_3
+ 7	$HClO_4$	—	HIO_4 H_5IO_6

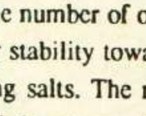
The greater the number of oxygen in the oxyacid of halogens or their salts, the greater is their stability towards heat. But the acids are more unstable than their corresponding salts. The reactivity also is dependent on the number of oxygen atoms and decreases with increasing number of oxygen atoms. Thus HXO is more reactive than HXO_4. But the strength of acids in terms of ionization is greater, the larger the number of oxygen atoms in the molecule. Thus HXO_4 is a stronger acid than HXO_3 which is a stronger acid than HXO_2 or HXO. The sequence of strength of acid is as follows :

$$HXO_4 > HXO_3 > HXO_2 > HXO$$

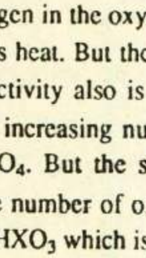
The acid molecules contain H linked to the halogen through an oxygen atom. Thus in the case of chlorine, we have,


$H-O-\ddot{Cl}:$

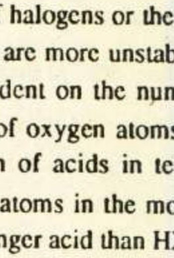
Hypochlorous acid


$H-O-\underset{\cdot\cdot}{\overset{O}{\overset{|}{Cl}}}:$

Chlorous acid

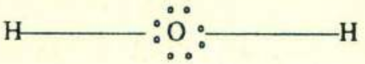

$H-O-\underset{\underset{O}{|}}{\overset{O}{\overset{|}{Cl}}}:$

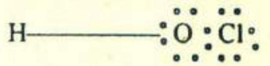
Chloric acid


$H-O-\underset{\underset{O}{|}}{\overset{O}{\overset{|}{Cl}}}-O$

Perchloric acid

The bonds between H and O are polar in nature and all the oxygen atoms are linked to the halogen by covalent bonding. The oxidation states of the halogen are dependent on the number of electrons shared with oxygen. Thus in HClO, $HClO_2$, $HClO_3$ and $HClO_4$, chlorine shares 1, 3, 5 and 7 electrons respectively with oxygen atoms. Hence the corresponding oxidation states of Cl are +1, +3, +5 and +7 in these acids or their salts. The positive oxidation state of halogen lead to the shifting of the bonding electrons from hydrogen and the tendency to lose a proton to water in aqueous solution is greatly increased. The electron density is shifted away from H and becomes concentrated around Cl and O:

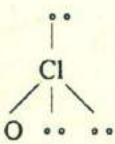




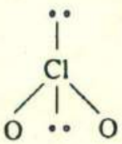
The greater the number of oxygen atoms around the halogen, the greater is the shift of electron density around it. Hence the acid strength increases in the case of, say, perchloric acid, $HClO_4$ as mentioned above.

It has also been observed that large size of the halogen and small values of electronegativity give rise to weaker acids and lower stability for the corresponding ions. Thus HClO is a stronger acid than HBrO which is stronger than HIO. Similarly, hypoiodite ion is much less stable than hypobromite and hypochlorite ions and are hydrolysed and decomposed readily.

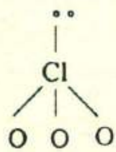
The structure of ClO^-, ClO_2^-, ClO_3^- and ClO_4^- ions are tetrahedral with O atom occupying 1, 2, 3, 4 corners respectively. Thus the configurations may be represented as



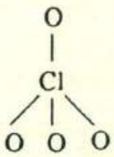
Hypochlorite ion
(ClO^-)



Chlorite ion
(ClO_2^-)



Chlorate ion
(ClO_3^-)



Perchlorate ion
(ClO_4^-)

But with iodine, more than four oxygen atoms can be accommodated. IO_4^- ion is tetrahedral like ClO_4^- ion. But IO_6^- ion is octahedral with the oxygen at the corners of an octahedron.

All the oxyghalogen anions are good oxidizing agents.

Hypohalous Acids and Hypohalites

Hypohalous acid, HXO, has not been obtained in the pure state but can be made in aqueous solutions. The aqueous solutions of HXO are prepared by hydrolysis of the free halogens. Cl_2 has greater tendency to undergo the hydrolysis than other halogens :

$$X_2 + H_2O \rightleftharpoons HX + HXO$$

Addition of cold and dilute alkali shifts the equilibrium towards the right :

$$X_2 + 2NaOH = NaX + NaXO + H_2O$$

At higher temperatures NaXO are unstable and undergo disproportionation :

$$\underset{\text{hypohalite}}{3XO^-} = \underset{\text{halide}}{2X^-} + \underset{\text{halate}}{XO_3^-}$$

Solutions of HClO is prepared by several methods as given by the equation :

$$HgO + 2Cl_2 + H_2O = HgCl_2 + 2HClO$$

This is a general method and all HXO may be prepared by the action of halogens on moist HgO. $CaCO_3$ is also used :

$$CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + 2HClO + CO_2$$

Sodium Hypochlorite, NaClO, is produced on a large-scale by the electrolysis of aqueous NaCl under the condition that NaOH and Cl_2 formed are mixed at low temperature. The solution of sodium hypochlorite contains NaCl and is sold as such for the purpose of bleaching agent and antiseptic.

NaOCl is used as an oxidizing agent for converting Cr^{+3} to chromate, Pb-salts to PbO_2, arsenites to arsenates, bleaching paper pulp and cellulose etc.

Bleaching powder, $CaOCl_2$ or CaCl(OCl) : It is a salt which contains both Cl^- and OCl^- ions, It is manufactured by the reaction of Cl_2 with slaked lime. Several designs of the manufacturing plants have been used. The principle of the process is to push slaked lime, $Ca(OH)_2$ from one direction while Cl_2 gas is passed from the other direction based on counter current principle. Thus in Bachmann plant slaked lime is introduced from the top of a tower containing shelves and rotating blades and Cl_2 with hot air is passed from the bottom of the tower upwards. The intimate mixing of Cl_2 with $Ca(OH)_2$ is thus achieved :

$$Ca(OH)_2 + Cl_2 = CaCl(OCl) + H_2O$$

Bleaching powder is a yellow powder, has the smelling of chlorine and has been used for a long time as a bleaching agent and a source of chlorine and hypochlorous acid. Also used for sterilization of water and for manufacture of chloroform.

The average percentage of *available chlorine* in bleaching powder is about 40% (theoretical 49%). The available chlorine is determined by mixing a known volume of bleaching powder suspension with excess of KI and titrating the liberated iodine with $Na_2S_2O_3$ solution.

$$CaOCl_2 + 2KI + CH_3COOH = (CH_3COO)_2Ca + 2KCl + I_2$$

Calcium hypochlorite, $Ca(ClO)_2$: This is also known as high test hypochlorite (H. T. H.). This is obtained from $CaCl_2$ and NaClO.

$$CaCl_2 + 2NaClO = Ca(ClO)_2 + 2NaCl$$

$Ca(ClO)_2$ is more soluble, more stable and more effective as a bleaching agent than bleaching powder.

Halous Acids and Halites

Halous acids, **HXO_2** : cannot be isolated in the free form. Only the chlorites give well-defined salts. The reaction of ClO_2 on caustic alkalis gives the products chlorite, ClO_2^- ion and chlorate, ClO_3^- ion :

$$2ClO_2 + 2KOH = KClO_3 + H_2O$$

Thus ClO_2 is not a true anhydride since its Cl atom has an oxidation state different from that exhibited by either chlorite or chlorate ions.

An aqueous solution of $HClO_2$ is obtained by the action of $Ba(ClO_2)_2$ with H_2SO_4 and filtering off $BaSO_4$ precipitate :

$$Ba(ClO_2)_2 + H_2SO_4 = BaSO_4 + 2HClO_2$$

$HClO_2$ is decomposed to HClO and $HClO_3$ at ordinary temperatures indicating disproportionation. The chlorites are prepared by the action of ClO_2 on peroxides:

$$2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2$$

$$2ClO_2 + BaO_2 = Ba(ClO_2)_2 + O_2$$

Bromous acid. $HBrO_2$, is obtained by the action of $AgNO_3$ with excess of Br_2-water :

$$2Br_2 + 2AgNO_3 + 2H_2O = HBrO_2 + 3AgBr + 3HNO_3$$

Halic Acids and Halates

Both *Chloric acid, $HClO_3$, and bromic acid, $HBrO_3$,* are obtained in solution and are decomposed readily. But *iodic acid,* HIO_3, is obtained in the form of colourless crystals soluble in water.

Solutions of $HClO_3$ is readily obtained from barium chlorate by the reaction with H_2SO_4 and filtering. The method is applied to $HBrO_3$ and HIO_3 also :

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3$$

HIO_3 is obtained by oxidizing I_2 with conc HNO_3 :

$$I_2 + 10HNO_3 = 2HIO_3 + 10NO_2 + 4H_2O$$

Chlorine gas oxidizes both Br_2 and I_2 in aqueous solutions to give $HBrO_3$ and HIO_3 solutions :

$$5Cl_2 + Br_2 + 6H_2O = 2HBrO_3 + 10HCl$$

$$5Cl_2 + I_2 + 6H_2O = 2HIO_3 + 10HCl$$

All halic acids are strong acids and active oxidizing agents. $HClO_3$ is decomposed according to the equation :

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O$$

The halogens react with hot solutions of alkalis producing *halates* and *halides* :

$$2X_2 + 6NaOH = NaXO_3 + 5NaX + 3H_2O$$

$NaXO_3$ may be separated from NaX by fractional crystallisation. Among the alkali halates $KClO_3$ is one of the most important compound.

Potassium chlorate, $KClO_3$: This is obtained when Cl_2 is passed into hot milk of lime and the solution of $Ca(ClO_3)_2$ so formed gives $KClO_3$ on treatment with KCl. $KClO_3$ is less soluble than the Ca-salt :

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O$$

$$Ca(CO_3)_2 + 2KCl = 2KClO_3 + CaCl_2$$

The modern method of the production of $KClO_3$ (or other halates as well) is based on the electrolysis of hot halide solutions.

When a solution of KCl is electrolysed at 60—70°C in a cell with a number of electrodes which are close to each other the products of electrolysis, KOH and Cl_2, get mixed with each other giving $MClO_3$. The reaction in the cell is given by the equation :

$KCl + 3H_2O$ + electrical energy = $KClO_3 + 3H_2$ The general equation is, therefore :

$$X^- + 3H_2O \xrightarrow{\text{electrolysis}} XO_3^- + 3H_2$$

Chlorates are normally water soluble, bromates are less soluble and many iodates are insoluble. All halates decompose on heating. $MClO_3$ on strong heating gives O_2 :

$$2KClO_3 = 2KCl + 3O_2$$

On moderate heating $4KClO_3 = 3KClO_4 + KCl$. Bromates and iodates are decomposed in numerous ways. $KClO_3$ is used in the manufacture of matches etc. Bromates and iodates are used as oxidizing agents in analysis.

Perhalic Acids and Perhalates

Perchloric acid, $HClO_4$, and *periodic acid*, HIO_4, are well-defined compounds, but perbromic acid is unknown.

$HClO_4$ and HIO_4 also form well-defined salts which are not formed by bromine.

$HClO_4$ is obtained by adding H_2SO_4 to $KClO_4$:

$$KClO_4 + H_2SO_4 = KHSO_4 + HClO_4$$

$HClO_4$ is distilled under reduced pressure below 92°C. Above 92°C it explodes violently. It is a powerful oxidizing agent in the concentrated and hot condition but the action in dilute and cold solution is slow. $HClO_3$ is turned to $HClO_4$ on slight heating or exposure to light :

$$3HClO_3 = HClO_4 + Cl_2 + 2O_2 + H_2O$$

$KClO_3$ on moderate heating gives $KClO_4$ + KCl from which sparingly soluble $KClO_4$ is separated by leaching out KCl with water.

The perchlorates of Na^+ and K^+ are produced commercially by prolonged electrolysis of hot solutions of NaCl or KCl. The ClO_3^- ion first formed is converted to ClO_4^- ion.

$$ClO_3^- + H_2O \xrightarrow{\text{electrolysis}} ClO_4^- + 2H^+$$

The perchlorates are strong oxidizing agents but less so than the chlorates. $KClO_4$ is used in match industry and explosives. Anhydrous $Mg(ClO_4)_2$ is used as an excellent drying agent.

A number of periodic acids and their salts are known; among these *metaperiodic acids*, HIO_4, and *Paraperiodic acid*, H_5IO_6, are the most important. The larger iodine atom can accommodate more oxygen atoms.

$NaIO_4$ is prepared by oxidation of $NaIO_3$ in hot alkali solutions with Cl_2. Electrolytic method is also used.

It is rather puzzling that so far perbromic acid and perbromates have not been prepared.

MANGANESE

Manganese (Mn), Technetium (Tc) and Rhenium (Re) are the metals of group VIIB. Rhenium has been discovered recently and Technetium is a synthetic

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element existing as radioactive isotopes. The electron arrangement in the outer orbitals are the same in the three elements :

Mn (25)—Ar core, ... $3d^5\ 4s^2$
Tc (43)—Kr core, ... $4d^5\ 5s^2$
Re (75)—Xe core, ... $4f^{14}\ 5d^5\ 6s^2$

Comparison of Mn group with halogens

(1) The Mn group elements also have 7 electrons (d^5s^2) in the outermost orbitals as in the case of halogens but the outermost electron groupings in the latter are s^2p^5. (2) The halogens are active non-metals whereas the manganese group are transition metals in which **d**-levels are being involved. (3) But in the higher oxidation states group VIIA and VIIB have some similarities. Thus Mn_2O_7 and Cl_2O_7 are volatile compounds and explosive. $KClO_4$ and $KMnO_4$ are strong oxidizing agents and form isomorphous crystals.

Extraction of Manganese (Metallurgy)

Sources : (1) Pyrolusite—MnO_2
(2) Braunite—Mn_2O_3
(3) Manganite—$MnO(OH)$ or $Mn_2O_3.H_2O$
(4) Hausmanite—Mn_3O_4

Metallic manganese is obtained by carbon reduction process of MnO_2 which is the chief ore of Mn. Very high temperature is required because MnO first formed is not readily reduced by C :

$$MnO_2 + 2C = Mn + 2CO$$

Nearly pure Mn is obtained by the reduction of MnO_2 by Al (aluminothermic process) :

$$3MnO_2 + 4Al = 3Mn + 2Al_2O_3$$

Pure metal is obtained by the electrolysis of $MnCl_2$ solution with a Hg-cathod. Mn—Hg (amalgam) formed is distilled in vacuum to remove Hg.

Uses of Mn : (1) Production of ferromanganese in steel industry; (2) Production of pure MnO_2 for dry cells.

Alloys of Mn : Since alloys of Mn and Fe are extensively used in the production of steel, such alloys are usually produced instend of the pure metal. These are made by reducing the mixed oxide of MnO_2 and Fe_2O_3 with coke in a blast furnace. The alloy formed is rich in manganese (70—80% Mn) and called *Ferromanganese*. Those products having low percentages of Mn (20—30%) are known as *spiegeleisen* used in steel industry. *Manganin* (Cu—83%, Mn—13%, Ni—4%) is used for making resistance coils. Manganese steel (13% Mn). is very hard and is used for making rails, armour plates etc.

General properties of Mn : It is a grey-white metal and brittle. It is readily oxidized by moist air and decomposes water slowly giving $Mn(OH)_2$ and H_2. It is easily dissolved in dilute acids forming salts of Mn^{+2} ion. Mn forms five oxides and five corresponding series of compounds having oxidation states of +2, +3, +4, +6 and +7. The compounds of Mn, therefore, can be grouped as shown in Table 22.7.

Table 22.7. Different oxides and salts of Mn.

Oxidation states	*Oxides*	*Hydroxide*	*Properties*	*Derivaties*	*Colour*
+2	MnO	$Mn(OH)_2$	Basic	$MnCl_2$ (manganous)	Faint Pink
+3	Mn_2O_3	$Mn(OH)_3$	Weak base	$MnCl_3$ (manganic)	Violet
+4	MnO_2	H_2MnO_3	Weak acid	$CaMnO_3$ (manganite)	Brown
+6	MnO_3	M_2MnO_4	Acidic	K_2MnO_4 (Manganate)	Green
+7	Mn_2O_7	$HMnO_4$	Strong acid	$KMnO_4$ (Permanganate)	Purple

Some Important Compounds of Mn

Manganous Salts : These contain Mn in the +2 state. ***Manganous halide***, MnX_2, form beautiful pink crystals. In the anhydrous state these are prepared by the general reactions :

$$Mn + 2HX \xrightarrow{heat} MnX_2 + H_2$$

$$MnO + 2HX \xrightarrow{heat} MnX_2 + H_2O$$

In solution manganous halides are formed by dissolving manganese compounds in halogen acid. These are hydrated compounds :

$$MnO + HCl\,(aq) \rightarrow MnCl_2$$

When an alkali solution is added to Mn^{+2} salts in solution, the pink $Mn(OH)_2$ is precipitated but on exposure to air it is converted to dark brown Mn^{+3} compound of the composition $MnO(OH)$.

Manganous nitrate, $Mn(NO_3)_2$: This is prepared by adding $Ba(NO_3)_2$ to manganous sulphate and filtering off $BaSO_4$:

$$MnSO_4 + Ba(NO_3)_2 \rightarrow Mn(NO_3)_2 + BaSO_4$$

$Mn(NO_3)_2, 6H_2O$ is the common manganous nitrate and is decomposed to MnO_2 when heated.

Manganous sulphate $MnSO_4$: This is prepared by the action of dilute H_2SO_4 on manganese and separated by crystallisation. At room temperature $MnSO_4.\ 4H_2O$ is obtained. Water is removed easily on heating but $MnSO_4$ decomposes only after heating above 800°C.

Manganese trichloride, $MnCl_3$: Only MnF_3 and $MnCl_3$ are known containing Mn in the +3 state. Bromide and iodide are easily oxidized by Mn^{+3} ion. Even $MnCl_3$ exists as a dark coloured solution which is obtained by the action of HCl on MnO_2 in the cold :

$$MnO_2 + 4HCl \rightarrow MnCl_4 + 2H_2O$$

$$2MnCl_4 \rightarrow 2MnCl_3 + Cl_2$$

$$2MnCl_3 \rightarrow 2MnCl_2 + Cl_2$$

On warming, $MnCl_3$ is decomposed to stable $MnCl_2$ and Cl_2 is evolved. Solutions of complex chlorides are obtained on adding alkali metal chlorides to $MnCl_3$ solutions.

Manganese dioxide (Peroxide), MnO_2 : This occurs naturally as pyrolusite known as *Black oxide*. It is almost pure MnO_2 and the purity of pyrolusite is determined by the reaction with HCl when Cl_2 is evolved and liberates I_2 from KI to be titrated iodometrically. Alternatively pyrolusite may be reacted with oxalic acid in presence of H_2SO_4 and the excess oxalic is determined by titration with $KMnO_4$ solution.

MnO_2 may be prepared by heating $Mn(NO_2)_2$ to 200°C :

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2$$

Reduction of $KMnO_4$ in neutral medium also gives MnO_2 :

$$MnO_4^- + SO_3^{-2} \xrightarrow{H_2O} SO_4^{-2} + MnO_2$$

MnO_2 is a black solid which conducts electricity.

It reacts with H_2 or CO to give MnO which is a green solid :

$$MnO_2 + H_2 \xrightarrow{heat} MnO$$

When MnO_2 is heated to 600°C it gives Mn_2O_3 which on further heating to 900°C is converted to Mn_3O_4 with evolution of oxygen :

$$MnO_2 \xrightarrow{600°C} Mn_2O_3 \xrightarrow{900°C} Mn_3O_4$$

Mn_3O_4 behaves as a mixture of MnO and Mn_2O_3. When MnO_2 reacts with alkaline oxide or hydroxide manganites containing MnO_3^{-2} ions are formed :

$$MnO_2 + 2\,OH^- \rightleftharpoons MnO_3^{-2} + H_2O$$

$$MnO_2 + CaO \xrightarrow{heat} CaMnO_3$$

MnO_2 also gives green manganate with alkali when heated in presence of a little oxidizing agent such as KNO_3 :

$$MnO_2 + K_2O + O_2 \xrightarrow{heat} 2K_2MnO_4$$

MnO_2 is converted to permanganate MnO_4^- by oxidizing agents such as Cl_2, PbO_2 etc. :

Uses of MnO_2 : It is used in (1) dry cells, (2) for producing chlorine gas, (3) for producing manganese steel, (4) as a catalyst, (5) in explosives etc.

Potassium manganate, K_2MnO_4 : This is obtained when MnO_2 is fused with alkali hydroxide or carbonate in presence of air or $KClO_3$:

$$2MnO_2 + 4KOH + O_2 = 2K_2MnO_4 + 2H_2O$$

Manganates are green in colour and stable in presence of alkali. Na_2MnO_4. $10H_3O$ is isomorphous with Na_2SO_4. $10H_2O$.

Potassium Permanganate, $KMnO_4$: This is an important compound of Mn. It is prepared from pyrolusite, MnO_2, by first converting it to K_2MnO_4 with K_2CO_3 and air :

$$MnO_2 + K_2CO_3 + O_2 \rightarrow K_2MnO_4 + CO_2$$

When K_2MnO_4 solution is neutralized by adding H_2SO_4 or by passing CO_2 the manganate is converted to permanganate :

$$3\,K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$$

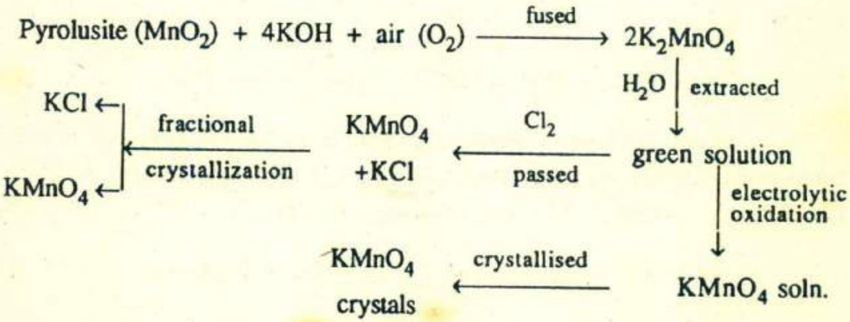
In order to avoid precipitation of MnO_2, permanganate is made by oxidation with Cl_2.

$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl$$

K_2MnO_4 is also converted to $KMnO_4$ by electrolytic oxidation between iron electrodes. The oxygen evolved at the anode oxidizes K_2MnO_4 to $KMnO_4$:

$$2K_2MnO_4 + H_2O + O \xrightarrow{\text{electrolysis}} 2KMnO_4 + 2KOH$$

The production of $KMnO_4$ is schematically represented as follows :



***Properties of $KMnO_4$*:** It is a powerful oxidizing agent and is used for oxidation in acidic, neutral or alkaline medium. It is used as a valuable laboratory reagent.

In acid medium, $KMnO_4$ is reduced to Mn^{+2} compounds. The change of oxidation state from Mn^{+7} to Mn^{+2} involves acceptance of 5 electrons by $KMnO_4$. The equivalent weight of $KMnO_4$ in acid medium is $\frac{1}{5}$ of the molecular weight.

In acid medium some of the oxidation reactions are :

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO + 8H_2O$$

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 5Na_2SO_4 + 8H_2O$$

$$5H_2SO_3 + 2KMnO_4 = 2H_2SO_4 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

It is to be noted that in acid medium HCl and HNO_3 cannot be used since HCl is oxidized to Cl_2 by $KMnO_4$ and HNO_3 itself is an oxidizing agent. Hence H_2SO_4 is generally used for reactions in acid medium.

In neutral medium, $KMnO_4$ changes to MnO_2, i.e., from Mn^{+7} to Mn^{+4} and the solution turns alkaline due to liberation of KOH. The equivalent weight for such reaction is $\frac{1}{3}$ of the molecular weight of $KMnO_4$. The oxidation of NH_3 to N_2 is an example:

$$2KMnO_4 + 2NH_3 = 2KOH + 2MnO_2 + N_2 + 2H_2O$$

In alkaline medium, $KMnO_4$ is mostly used for oxidation of organic compounds. Alkali converts $KMnO_4$ to K_2MnO_4, i. e., change of Mn^{+7} to Mn^{+6}. But K_2MnO_4 is unstable and is further changed to MnO_2 :

$$KMnO_4 + KOH + H_2O_2 = K_2MnO_4 + H_2O + O_2$$

$$6KMnO_4 + KI + 6KOH = 6K_2MnO_4 + 3H_2O + KIO_3$$

$$2K_2MnO_4 + 2H_2O = 2MnO_2 + 4KOH + O_2$$

It is to be noted that the electrode potentials

$$Mn^{+2}/MnO_4^- = 1.52 \text{ Volts}$$

$$MnO_2/MnO_4^- = 1.67 \text{ volts}$$

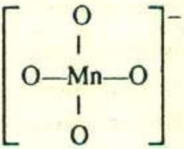
$$MnO_4^{-2}/MnO_4^- = 0.50 \text{ volts}$$

govern the reduction of Mn^{+7} to either Mn^{+4} or Mn^{+2} (K_2MnO_4 being unstable is changed to MnO_2 from Mn^{+6} to Mn^{+4}). The change depend upon the pH of the solution.

Free $HMnO_4$ in solution is obtained by the reaction of $Ba(MnO_4)_2$ with H_2SO_4 :

$$Ba(MnO_4)_2 + H_2SO_4 = BaSO_4 + 2HMnO_4$$

The structure of MnO_4^- ion is tetrahedral



$$\left[\begin{array}{c} O \\ | \\ O—Mn—O \\ | \\ O \end{array}\right]^-$$

Uses of $KMnO_4$: (1) As a reagent in quantitative analysis, (2) In organic reactions. (3) Dilute solution used in skin diseases (4) As an antibacterial reagent in water purification etc.

QUESTIONS AND PROBLEMS

1. (a) Write down the electronic formula of the oxy-ions of chlorine.
   (b) Discuss the reactions of Fluorine with (i) Alkalis, (ii) Carbon, (iii) Sulphur.
2. Write a note on Interhalogen compounds.
3. Discuss the properties of the members of group VIIA (The halogens). Give an account of the oxides and oxyacids of chlorine.
4. How would you prepare the following compounds? Give their reactions and tests :-
   Potassium chlorate and Potassium perchlorate.
5. How will you identify chloride, bromide and iodide in presence of each other?

6. Describe the preparation, properties and uses of bleaching powder. What chemical formula is assigned to it and why?

7. How is fluorine prepared? Compare its properties with those of other halogens.

8. Write a note on the commercial preparation of iodine. What reactions take place when iodine is treated with the following compounds :—

   (a) Caustic potash solution. (b) Chlorine, (c) Potassium chlorate

   (d) Hydrogen sulphide, (e) Sulphur dioxide.

9. Describe a method for preparing anhydrous hydrofluoric acid. How can you obtain fluorine from it? Discuss reactions to show that hydrofluoric acid and fluorides behave differently from other halides.

10. Explain, with examples, the behaviour of potassium permanganate as an oxidizing agent in acidic and alkaline medium.

11. How would you explain the highly reactive nature of alkali metals and halogens on the basis of their electronic structures?

12. Describe the preparation and uses of sodium hypochlorite.

13. Describe what happens when—(i) iodine reacts with a solution of $Na_2S_2O_3$, (ii) dry chlorine is passed over heated mixture of silica and charcoal.

14. Write a concise account of oxyacids of halogens.

15. Discuss the uses of $KMnO_4$ as a reagent in volumetric analysis.

16. Compare the chemistry of halogens and their important compounds.

17. Starting with pyrolusite how would you prepare $KMnO_4$? Discuss with examples, the oxidizing behaviour of $KMnO_4$ in acid, alkaline and neutral solutions.

18. Describe the preparation, properties and uses of :—

    (a) Potassium permanganate.

    (b) Hydroiodic acid.

    (c) Potassium chlorate,

    (d) Fluorine.

19. When a metal exhibits more than one oxidation states the halides of the lower states are the more ionic. Comment.

20. The ionic radii of F^- and O^{-2} are almost the same. What is the relationship between the two?

21. Fluorine is very reactive but HF is a weak acid. Discuss.

22. What is the reaction of glass with HF?

23. Discuss: Halogens are reactive elements.

24. On electrolysing a solution of NaCl, hydrogen gas is evolved at one electrode and Cl_2 at the other. Explain how NaOH is formed in the process.

25. Hydrogen fluoride attacks glass but hydrogen chloride does not. Does it prove that HF is a stronger acid than HCl?

26. Why is it necessary to prepare fluorine by electrolysis?

27. What is the difference between hydrochloric acid and hydrogen chloride?

28. HF is a liquid and has higher boiling point where other halogen acids are gases or liquids. Explain.

29. HF cannot be concentrated in aqueous solution. Explain

30. F shows only -1 oxidation states whereas other halogens show -1, $+3$, $+4$, $+5$ and $+7$ oxidation states. Explain with examples..

31. Explain why the compounds of fluorine with oxygen are fluorides of oxygen whereas those of other halogens are called oxides of halogen.

32. What are "freons" and "teflons"?

33. Write an account of the oxides and oxyacids of chlorine

34. Why is iodine more soluble in KI solution than in water

35. Describe the chemistry of interhalogen compounds.

36. Write a short note on basic iodine

37. Give the structures of oxyacids of chlorine.

38. What is bleaching powder? How does it react with KI in H_2SO_4? What is meant by "available chlorine" of bleaching powder ? How is this determined?

39. What is HTH? How is it prepared? Mention some uses of HTH.

40. Explain why interhalogen compounds are more reactive than halogen and are always diamagnetic

41. Discuss the structures of BrF_3 as IF_5

42. Discuss the structures of the following

(a) ClO_2, ICl_2^-, ICl_4^-, Cl_2O

CHAPTER 23

IRON, COBALT AND NICKEL

(The Elements of Group VIII)

The elements of group VIII occupy the central positions of the Periodic Table and consists of three sets of triads. They belong to the first, second and third series of transition metals in which **d**-orbitals are being filled up. The atomic numbers, the outer electron orbitals and the oxidation states of group VIII metals are given in Table 23.1. This group has not been divided into sub-groups because of the proximity and electronic relationships.

Table 23.1. Group VIII metals

Elements	*At. No.*	*At. Wt.*	*Outer electron orbitals*	*Oxidation states Unstable ( )*
Fe	26	55.85	$3d^6 4s^2$	2, 3, (4), 6
Co	27	58.95	$3d^7 4s^2$	2, 3, 4
Ni	28	58.71	$3d^8 4s^2$	(1), 2, (3), 4
Ru	44	101.10	$4d^7 5s^1$	2, 3, 4, 6, 7, 8
Rh	45	102.91	$4d^8 5s^1$	(1), (2), 3, 4, (6)
Pd	46	106.40	$4d^{10} 5s^0$	(1), 2, —, 4, (6)
Os	76	190.20	$5d^6 7s^2$	(2), 3, 4, 6, (7), 8
Ir	77	192.20	$5d^9 7s^0$	(1), (2), 3, 4, 6
Pt	78	195.10	$5d^9 7s^1$	(1), 2, (3), 4, (6)

It is seen that the three sets of triads of group VIII elements have almost similar atomic weights. Similarity in many of the physical and chemical properties are also observed. But the increase in atomic numbers produces some alterations in the electron arrangements of the outer orbitals and consequently this affects the variable oxidation states. Among the triads the first series are more reactive and the reactivity decreases with the increase of atomic number to a marked extent until the last triads, particularly Ir and Pt, are inert and noble metals. The six elements of the second and the third series of triads have similar properties and they occur in nature together in the form of alloys or in the free state. These six elements (Ru to Pt) are generally known as *Platinum group* of metals.

General Properties of Iron Group

1. The first series of triads—Fe, Co and Ni—show similar properties since the outer electron orbitals in each case consists of two 4s electrons outside a partially filled 3d orbital.

Fe (26)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Co (27)—$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$

Ni (28)—$1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^6\ 3d^8\ 4s^2$

The three metals—Fe, Co and Ni are readily oxidized to +2 state by the removal of $4s^2$ electrons. Removal of a third electron from 3d orbital is easy for Fe because d^5 arrangement is more stable, and Fe readily forms the +3 state. But +3 state for cobalt is less stable and for Ni it is the least stable which occurs in some complexes only. Powerful oxidizing agents in alkaline solutions give +4 state for all the three elements and +6 state in the case of Fe as in ferrates, having FeO_4^{-2} ions. In each of the horizontal series of group VIII the tendency to lose electrons decreases as the nuclear charge increases

2. Trivalent cobalt is a powerful oxidizing agent and trivalent iron is less strong than cobalt. Co^{+3} is quite stable in the form of complexes, such as in $[Co(NH_3)_6]^{+3}$, $[Co(CN)_6]^{-3}$ etc. Ni^{+4} occurs in NiO_2.

3. Fe, Co and Ni have great tendency to form complex compounds which is due to the partially filled **d** electron orbitals. Fe and Co complexes are mostly octahedral having coordination number 6. Ni forms in addition to square planar and tetrahedral compounds having coordination number 4, a large number of octahedral complexes as well.

Physical properties : The metals Fe, Co and Ni have similar appearance in the free state. It is remarkable that not only they have similar atomic weights but also similar melting points, density and other physical properties. Fe exists in four solid forms and Co and Ni have two modifications. The high oxidation states (6) in Fe, Co, Ni causes the bonds in the metals to be very strong and imparts valuable physical properties which are almost similar. They have also magnetic properties. The closeness of melting and boiling points of these metals indicate similarity in metallic bonding. Some of their physical properties are given in Table 23.2 for comparison.

Table 23.2 Physical properties of Fe, Co and Ni.

Properties	*Fe* *26*	*Co* *27*	*Ni* *28*
Melting point (°C)	1540	1480	1450
Boiling point (°(C)	3000	2900	2900
Density (g/cm^3)	7.86	8.93	8.89
Ionization potential (ev)	7.83	7.70	7.69
Metallic radius (Å)	1.26$_1$	1.25	1.24
Ionic radius M^{+2} (Å)	0.75	0.72	0.70
Oxidation potential M/M^{+2} (v)	0.44	0.28	0.25
Magnetic properties	Highly magnetic	Feebly magnetic	Feebly magnetic
Electronegativity	1.64	1.70	1.75

These metals have special technological importance due to the special properties which they possess. Apart from these the general reactions of Fe, Co and Ni have been summarized in Table 23.3 for comparison indicating the similarities in many of their properties.

IRON

Metallurgy of Iron

Occurrence : Iron is one of the most abundant elements found in the earth's crusts, meteors, rocks, minerals, soils, plants and animals. The haemoglobin of the blood contains iron which functions as oxygen carrier.

Table 23.3. Reactions of Fe, Co and Ni.

Reagents	*Fe*	*Co*	*Ni*	*Conditions of reactions*
Air (O_2)	Fe_3O_4, Fe_2O_3	Co_3O_4	NiO	500°C and above
Water (steam)	$Fe_3O_4 + H_2$	$CoO + H_2$	$NiO + H_2$	Red heat
Halogens	FeX_3, FeI_2	CoF_3, CoX_2	NiX_2	Generally at elevated temperature
Carbon	Fe_3C	Co_3C	Ni_3C	Above 1200°C
Sulphur	FeS	CoS	NiS	Heated
Carbon monoxide	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$	Below 100°C
NH_3	$Fe_2N + H_2$	$Co_4N_2 + H_2$	$Ni_4N_2 + H_2$	400—600°C (No direct reaction with N_2)
Conc. HNO_3	Passive	Passive	Passive	In other strong oxidizing agents also

Sources : The following are the important iron bearing ores :

Hematite—Fe_2O_3

Magnetite—Fe_3O_4

Limonite—$2Fe_2O_3 . 3H_2O$

Siderite—$FeCO_3$

The sulphide ore, *pyrites*, FeS_2, occurs as pale yellow crystals and looks like gold ; hence the name *fool's gold.* Pyrites is a quite abundant mineral of iron but only used for production of SO_2. The impure iron oxide residue is not generally used for the metallurgy of iron.

Metallurgical process for pig iron : The main operation for production of iron is based on the principle of the reduction of the iron oxide with carbon monoxide. The reduction is carried out in a furnace called *blast furnace.*

The iron ore used for the purpose is first washed, concentrated and then roasted in order to removes as much sulphur and phosphorus as possible. The roasting process removes water, decomposes carbonates to oxides and oxidizes sulphides. The prepared oxide ore is mixed with sufficient limestone and coke and this mixture is fed into the blast furnace from the top with double cup and cone arrangements.

The blast furnace is made of steel and lined with fire bricks in the shape of a large cylindrical shaft about 100 feet high and 25 feet in diameter. Dry air under pressure preheated to about 500°C is blown in through the nozzles or *tuyeres* at the bottom part of the furnace. The bottom part also contains the outlet for the molten iron and an outlet to drain out the molten slag from the top of the molten metal. The illustration in Fig. 23—1 gives an outline of a diagrammatic sketch of a blast furnace. The blast furnace has arrangements for continuous operations and produces pig iron in tons quantities.

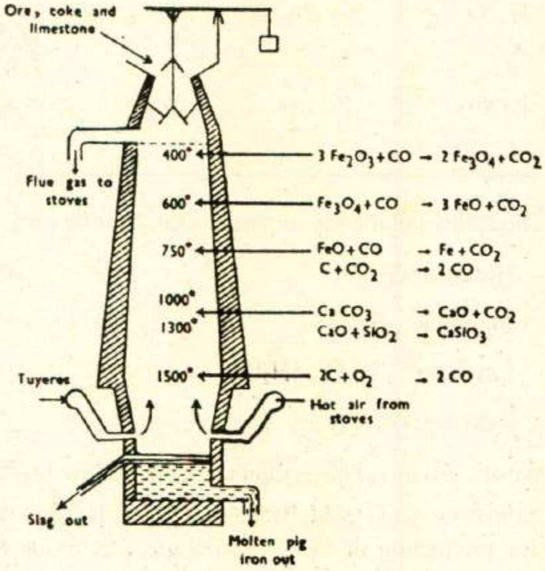


Fig. 23—1. Blast furnace for pig iron.

The reactions taking place in the various regions of the blast furnace have been given in Fig. 23—1. The coke is first oxidized by the hot blast of air at the bottom to produce CO and CO_2 with the liberation of much heat upto 1500°C. The intense heat at this region liquefies the iron and the slag is formed at the central region of the furnace due to the reduction by CO and decomposition of $CaCO_3$ to CaO and CO_2. The reduction of Fe_2O_3 by CO is a reversible process :

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$$

The excess of CO formed in the furnace shifts the equilibrium to the right. The flux used depends upon the impurities present in the ore. Limestone is used when sand is present and sand is added when limestone is the impurity. CaO forms the slag with SiO_2, i.e., $CaSiO_3$.

At the bottom the molten iron and the slag collect in two layers. The molten slag floats on top of the molten iron. The molten iron is withdrawn through the bottom tap hole and may be cast in the form of pigs known ads *Pig Iron*. The slag is often used in the manufacture of *Portland cement*.

The exhaust or flue gases which come out from the top of the blast furnace contain considerable amount of CO. This is mixed with air and burnt to preheat the air blast.

Pig iron and cast iron : The iron metal obtained from the blast furnace is called *Pig Iron*. It contains a number of impurities, such as 3—4% C together with Si, P, Mn and small amount of S. It is brittle and converted to cast iron and steel.

Cast Iron is obtained when pig iron is remelted and cooled. Rapid cooling of molten pig iron produces *White Cast Iron*. The white appearance is due to the chemical combination of C with Fe to form Fe_3C, known as *Cementite*, which is of light colour. It is brittle and hard. When pig iron is slowly cooled, the carbon separates as graphite and gives the iron a grey appearance. This is called *Grey Cast Iron* and is soft but tough.

Wrought iron : Wrought iron is a pure form of iron and is manufactured by melting pig iron with an excess of iron oxide which oxidizes out most of the impurities. Carbon and sulphur are expelled as CO_2 and SO_2. Si-and P-oxides react with Fe and Mn-oxides or with limestone which is sometimes added as flux to form slag. As the iron becomes pure its melting point rises and the metal collects in lumps which are removed. The operation is carried out in a reverberatory furnace.

Wrought iron is soft, malleable and ductile. It contains only 0.2% carbon. It has fibrous structure which is mainly due to thin films of slag between layers of pure iron.

It is used in the manufacture of articles which are subject to sudden stresses such as chains, anchors, bolts, frame-work etc. But now-a-days wrought iron has been displaced by *mild steel*.

Manufacture of Steel

The term *steel* is used for many different types of iron alloys with carbon. Iron which contains from 0.05 to 2% carbon and which is capable of being hardened by quenching is called *steel*. Other metals, such as Mn, Cr, Ni, W, Mo, V are added to produce different types of *alloy steels* for specific uses. Steel is made by various methods; the important methods are —(1) Bessemer Process and (2) Open-hearth Process.

(1) Bessemer Process : In this process a blast of air is blown through molten pig iron in a large oval-shaped vessel called ***Bessemer converter***. The air blast enters through perforations at the bottom and oxidizes most of the impurities in the pig iron. Only a part of the carbon is oxidized. When Bessemer converter is lined with silica bricks, it is called the ***Acid Bessemer Process***. This is applicable in the case of pig iron containing low percentages of S and P. The *acid* lining acts as a flux toward basic oxides produced during oxidation. A Basic Bessemer Process uses a ***basic lining*** of magnesia or lime for pig iron containing higher proportions of P and some amount of S. These impurities burn up to their oxides:

$$P_4 + 5O_2 = P_4O_{10}$$

$$S + O_2 = SO_2$$

After the first blast for about 15 minutes (during which period CO along with other impurities burns at the mouth of the converter) the desired composition of steel is adjusted by adding calculated quantities of carbon, manganese in the form of ***spiegeleisen***, or other metals.

Bessemer steel is a low-grade steel and is used for steel frameworks for buildings, bridges and other constructional purposes.

(2) Open-hearth Process : In this process the pig iron is generally mixed with scrap iron, iron oxide and some limestone in a shallow hearth open at the top. The heat is supplied by a gas flame directly over the top surface. The iron ore and the rust on scrap iron which are parts of the charge help in the oxidation of the impurities. CO escapes, while the oxides of S and P combine with Fe_2O_3 and the basic oxides of the lining to form a slag which adds to the lining.

About 8-12 hours are required for the oxidation of the impurities :

$$3P_4 + 10\,Fe_2O_3 = 3P_4O_{10} + 20Fe$$

$$3S + 2Fe_2O_3 = 3SO_2 + 4Fe$$

When the desired carbon content is reached, the molten steel is run out into ladles. The capacity of a large furnace is about 500 tons of steel per charge. Some iron, low in sulphur and phosphorus, are made by open-hearth containing acid lining of silica. Desired quantities of other metals are added as in the case of Bessemer Process for special steel.

Open-hearth steel is high grade steel and uniform in quality. It is used for making girders, heavy rails, guns, armour plates, ship industries etc.

(3) Duplex Process : High-grade steel is manufactured by combining operations of acid Bessemer converter and basic open hearth process. Pig iron is first processed in acid bessemer converter and then transferred to basic Open-Hearth. Steel of very low phosphorus content is obtained.

(4) Other Processes: Other high-grade steels are made in small quantity for specific purposes. These are: (a) *Crucible Steel* produced by heating wrought iron with graphite in small crucibles. (b) *Electrothermal steels* are high-grade steel and alloy steel made in a furnace heated electrically at rigidly controlled temperatures. Both crucible steel and electrical steel are used as tool-steel. (c) *Case-hardened steel* is made by heating low-carbon steel in closed containers with powdered carbon followed by quenching in oil. The carbon reacts on the surface and forms cementite, Fe_3C. Such steel is very hard on the surface and tough in the interior. This is used for making axles, auto-parts, machine parts, anvil etc. (d) *Nitriding steel* is surface-coated by case-hardening process with ammonia or nitrogen compounds. A very hard surface of nitride of Fe or alloy metal is formed.

Heat treatment of steel : Various methods of heat-treating produce steel of different qualities. Such processes are : *Annealing*, steel heated to redness and allowed to cool slowly. *Quenching*, steel heated to redness and rapidly cooled in water or oil. *Tempering*, steel held at a fixed temperature for sometime before cooling. These treatments produce different sizes of interlacing crystals.

Alloy steel : Many important special steels are manufactured by adding metals other than carbon. Steel of widely varying properties are made by appropriate choice of the number and percentages of these elements. Some of these are given in Table 23.4.

Table 23.4 Comparison of some alloy steels.

Alloy	*Composition*	*Properties*	*Use*
Mn-steel	10—18% Mn	Hard, tough, resistant to wear	Rails, armour plates, ball crushers
Si-steel	1—5% Si	Hard, strong, highly magnetic	Magnets
Duriron	12—15% Si	Corrosion resistant	Pipes, sheets
Invar	36% Ni	Low co-efficient of expansion	Pendulum rods, meter scale, measuring instruments
Stainless steel	14—18% Cr 7—9% Ni	Corrosion resistant	Cutlery, machine parts and in industry
High-speed steel	14—20% W or 6—12% Mo	Retain temper at high temperature	High speed cutting tools

Rusting of Iron : Pure iron is silvery white but when left in moist air it is covered with reddish deposit commonly known as *rusting of iron*. It undergoes the process of *corrosion* (rusting) which is favoured by (i) impurities in water, (ii) impurities in iron, (iii) presence of moist air, (iv) presence of dissolved oxygen and CO_2 in water, (v) higher temperature than the normal.

Thus pure iron will not rust in pure water and pure air. Rusting has been explained on the basis of setting up of small galvanic or electrical cells in which iron acts as anode and an impurity, particularly of less active metals, e.g., Cu, Pb, Sn etc., acts as cathode and the impure water serves as the electrolyte. Dissolved oxygen removes the hydrogen formed during the process and accelerates corrosion. Presence of more active metal, such as Zn, retards corrosion. Ferrous iron combines with hydroxide ion of the electrolytic solution forming $Fe(OH)_2$ which is readily oxidized in presence of air to $Fe_2O_3.H_2O$ which is the composition of *iron rust*.

Several methods have been devised to prevent or retard iron rust. Some of these are—(i) coating the surface with paint, grease, asphalt etc., (ii) coating with other metals such as Zn, Ni, Al etc., (iii) coating with enamels, (iv) coating with an adherent oxide such as Pb_3O_4, (v) alloying to produce non-rusting materials, (vi) cathodic protection.

Passivity of Iron : Iron dissolves in HCl and dilute H_2SO_4 to form Fe^{+2} ions and H_2. Cold concentrated HNO_3 renders the iron inactive. Such treated iron does not react with dilute acids and does not displace Cu from $CuSO_4$ solution. This state of iron is called *passivity* and the iron itself is called *passive iron*. Passivity can be produced by means of compounds, such as $K_2Cr_2O_7$, H_2O_2, $HClO_3$ and HIO_3 and other oxidizing agents in solutions. Passivity has been explained from various points of views. One view is the formation of Fe_3O_4 film on the surface. Passivity of iron can be removed by scratching and polishing the surface, by treating with halogens, by heating in presence of H_2 and by anodic electrolysis in salt solutions.

Compounds of Iron

Oxides and hydroxides of Fe : Iron forms three oxides having composition FeO, Fe_2O_3 and Fe_3O_4. FeO is obtained by thermal decomposition of ferrous oxalate, FeC_2O_4, or by reduction of Fe_2O_3 in hydrogen at 300°C:

$$FeC_2O_4 = FeO + CO + CO_2$$

$$Fe_2O_3 + H_2 = 2FeO + H_2O$$

FeO is unstable and has the structure like that of NaCl. On standing it is converted to a mixture of Fe and Fe_3O_4 (disproportionation):

$$4FeO = Fe + Fe_3O_4$$

FeO is also a non-stoichiometric compound in which the composition does not exactly correspond to FeO.

$Fe(OH)_2$ is formed when a ferrous salts solution is treated with alkali hydroxide. It is a white precipitate when freshly formed, but quickly turns green and reddish brown due to oxidation of Fe^{+2} to Fe^{+3}:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

Fe_2O_3 is obtained by igniting $Fe(OH)_3$ or by roasting pyrites, FeS_2 in the air. It is a red powder and is used as paints under the name of red oxide of iron, *rouge* and also *Venetian red.* Fe^{+3} salt solutions give precipitate of $Fe(OH)_3$ or hydrated iron oxide, $FeO.xH_2O$, on treatment with alkali solution. Fe_3O_4 or magnetic oxide of iron is actually a mixed oxide containing $FeO.Fe_2O_3$. The magnetic oxide of iron Fe_3O_4, is obtained when Fe is heated strongly in air. This is the most stable form of iron oxide at high temperature. Fe_3O_4 is also $FeFe_2O_4$ possessing the spinel structure.

Ferrous compounds : The two most familiar ferrous salts are sulphates, $FeSO_4.7H_2O$ and $FeSO_4.(NH_4)_2SO_4.6H_2O$ (*Mohr's salt*). These are used as laboratory reagents. Mohr's salt is a double salt and is prepared by crystallising from an equimolar solution of $(NH_4)_2SO_4$ and $FeSO_4$. Unlike $FeSO_4$ which is readily hydrolysed in aqueous solutions and oxidized in air, Mohr's salt does not undergo quick hydrolysis and oxidation in air.

Fenton's Reagent : A solution of $FeSO_4$ and H_2O_2 (mixture) is called Fenton's Reagent and is used to catalyse the conversion of acrylonitrile $CH_2 = CH_2 - CN$ to its polymer. The reaction is

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\circ} + OH^{-}\cdot$$

The OH° radical functions for polymerisation.

Complex compounds of iron (II)

Fe^{+2} salts form complexes, such as with KCN, to form potassium hexacyanoferrate i.e, potassium ferrocyanide, $K_4Fe(CN)_6$. This is the most stable complex of ferrous iron. This is obtained by adding excess of KCN to a ferrous salt solution and recrystallising. $K_4Fe(CN)_6$. is used as a reagent for ferric iron forming *Prussian blue* :

$$Fe^{+2} + 6CN^{-} = [Fe(CN)_6]^{-4}$$

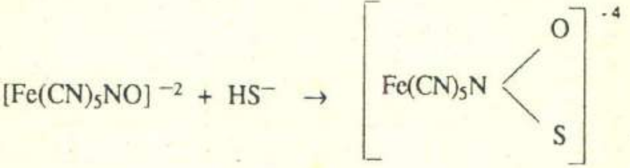
$$FeCl_3 + K_4[Fe(CN)_6] = KFeFe(CN)_6 + 3KCl$$

$$4FeCl_3 + 3K_4[Fe(CN)_6 = Fe_4[Fe(CN)_6]_3 + 12KCl$$

$K_4Fe(CN)_6$ is used as a reagent for other metals, e. g., Cu, Zn etc. $K_4Fe(CN)_6$ forms the nitroderivative with NO_2^- ion. This on treatment with acid gives the *nitroprusside* ion :

$$Na_4[Fe(CN)_5NO_2] + 2HCl = \underset{\text{Na-nitroprusside}}{Na_2[Fe(CN)_5NO]} + H_2O + 2NaCl$$

Na-nitroprusside forms a thionitro-complex with sulphide forming an intense blue-violet solution used as a delicate test for sulphides. The reaction takes place with HS^- ion :



NO may be present as NO^+ and Fe as Fe^{+2} or NO is neutral and Fe is present as Fe^{+3}. The composition is, therefore, uncertain.

Ferric compounds : $FeCl_3$, $Fe_2(SO_4)_3$, $Fe(NO_3)_3$, $Fe(OH)_3$ and $FePO_4$ etc. are quite familiar compounds. The colours of these compounds differ mainly due to hydrated or dehydrated state. Fe^{+3} ion is smaller in size and has greater charge than Fe^{+2} and, therefore, the compounds of Fe^{+3} are more acidic. Ferric salts are, therefore, greatly hydrolysed in aqueous solution and resemble Al^{+3} in many respects.

Anhydrous $FeCl_3$ is obtained by heating Fe in Cl_2 gas. The composition corresponds to Fe_2Cl_6. Hydrated $FeCl_3.6H_2O$ solutions contain undefined $FeCl_3$ complexes because its solution is more intensely coloured than $Fe(NO_3)_3$ or $Fe_2(SO_4)_3$ solutions :

Complex Compounds of iron (III)

Excess KCN forms $K_3Fe(CN)_6$ with ferric salt solutions. $K_3Fe(CN)_6$, i.e., potassium hexacyanoferrate (III) or potassium ferricyanide gives blue-coloured precipitate or solution with Fe^{+2} salt solution. The blue compound in this case having $Fe_3[Fe(CN)_6]_2.\ H_2O$ is known as *Turnbull's blue* and is used as pigment. Acid insoluble Turnbull's blue was considered to be formed by the reaction :

$$3FeSO_4 + 2K_3Fe(CN)_6 \rightarrow Fe_3[Fe(CN)_6]_2 + 3K_2SO_4$$

The other compound known as *Prussian blue* soluble in acids is considered to be formed by the reaction :

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4[Fe(CN_6]_3 + 12KCl$$

The commercial Prussian blue as well as Turnbull's blue do not exactly correspond in their compositions to the above formula. Both the compounds contain combined water. Both the compounds are decomposed by alkali. The colour of these compounds depends on the conditions of their formation. It is now generally believed that Turnbull's blue (ferrous ferricyanide) and Prussian blue (ferric ferrocyanide) having blue colours are potassium ferric ferrocyanide $KFe[Fe(CN)_6]. H_2O$.

Ferric Ammonium Alum : $Fe_2(SO_4)_3.(NH_4)_2SO_4.$ 24 H_2O is obtained by oxidation of Mohr's salt, $FeSO_4.(NH_4)_2SO_4.$ $6H_2O$, with HNO_3 with additional $FeSO_4.7H_2O$ and H_2SO_4. The solution after complete oxidation and evaporation gives crystalline product. The iron alum forms large reddish octahedral crystals.

SCN^- ions produce blood-red coloured solution of $[Fe(SCN)_6]^{-3}$ ions with Fe^{+3} ion. This is used to detect the presence of Fe^{+3} in solution.

Cl_2 in alkaline solution converts $Fe(OH)_3$ to ferrate, FeO_4^{-2} ion containing Fe^{+6}. Potassium ferrate is formed by the reactions :

$$3Cl_2 + 2Fe(OH)_3 + 10KOH = 2K_2FeO_4 + 6KCl + 8H_2O$$

Ferrate ion, FeO_4^{-2}, is an extremely powerful oxidizing agent in acid solution and like SO_4^{-2}, CrO_4^{-2},MnO_4^{-2} ions form insoluble barium ferrate, $BaFeO_4$.

COBALT

Sources: The following are the important cobalt bearing ores :

Cobaltite—CoAsS (cobalt glance)

Smaltite—$CoAs_2$

Extraction : The metallurgy of cobalt involves separation from Cu, Ni, Fe etc. and then the conversion of the ore to CoO to Co_3O_4. These oxides on reduction with Al gives metallic Co by alumino thermit process :

$$3Co_3O_4 + 8Al = 9Co + 4Al_2O_3$$

Purification of cobalt is made by electrolytic process. Co is used as a catalyst in the Fischer–Tropsch Process for the hydrogenation of CO to various hydrocarbons and for oxidation of NH_3. When heated in air Co_3O_4 is formed.

Compounds of cobalt (II) : Soluble salts of Co^{+2}, such as chloride, nitrate, sulphate, acetate etc. are of pink colour in the hydrated condition formulated as $Co(H_2O)_6^{+2}$. When dehydrated the deep blue colour of the anhydrous salts appears. The hydration or the dehydration follows the equilibrium:

$$\underset{\text{pink}}{2[Co(H_2O)_6]\,Cl_2} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} \underset{\text{blue}}{Co[CoCl_4]} + 12H_2O$$

Co on both sides of the equation has Co^{+2} oxidation states.

$Co(OH)_2$ is first precipitated by adding caustic alkali to a Co^{+2}-salt solution but soon becomes black due to the formation of hydrated cobaltic oxide, Co_2O_3 :

$$4Co(OH)_2 + 2H_2O + O_2 \rightarrow 4Co(OH)_3$$

In concentrated NH_4OH, the precipitate of $Co(OH)_2$ dissolves forming hexaminocobalt(II) hydroxide, $[Co(NH_3)_6](OH)_2$. The complex ion, $[Co(NH_3)_6]^{+2}$, is readily oxidized in air to form $[Co(NH_3)_6]^{+3}$ complexes :

$$4[Co(NH_3)_6]^{+2} + O_2 + 2H_2O \rightarrow 4[Co(NH_3)_6]^{+3} + 4OH^-$$

$Co(NH_3)_6\,Cl_3$ is prepared by adding NH_4Cl and NH_4OH to a solution of $CoCl_2$ and passing a current of air through the dark red solution. The rose coloured precipitate of $[Co(NH_3)_5\,H_2O]Cl_3$ with HCl gives $[Co(NH_3)_6]Cl_3$ as orange coloured crystals.

Cobalt nitrate, $Co(NO_3)_2.6H_2O$, is obtained by dissolving CoO or $CoCO_3$ in HNO_3. The anhydrous salt is made by the action of NO_2 on heated salts of Co^{+2}. Cobalt nitrate solution is used in the analytical tests for Zn, Al, PO_4^{-3} etc. by heating to incandescence with a drop or two of cobalt nitrate solution on a piece of charcoal.

Al	—	$CoO.\,Al_2O_3$	Blue	Thenard's blue
Zn	—	CoO. ZnO	Green	Rinman's green
PO_4^{-3}	—	$CoPO_4$	Blue	—

Sodium cobaltinitrite, $Na_3[Co(NO_2)_6]$, is prepared from Co^{+2} salt solutions by adding $NaNO_2$ in presence of acetic acid (aerial oxidation) :

$$2CoCl_2 + 14NaNO_2 + 4CH_3COOH = 2Na_3[Co(NO_2)_6]$$
$$+ 4CH_3COONa + 4NaCl + 2H_2O + 2NO$$

This is used as a reagent for K^+ ion, the insoluble yellow $K_3[Co(NO_2)_6]$ being precipitated out.

It will be seen that the cyanide complexes of Co^{+2} and Co^{+3} ions formed by adding excess of KCN to a solution of Co^{+2} ions might have the compositions $K_4Co(CN)_6$ and $K_3Co(CN)_6$ respectively. But $K_4Co(CN)_6$ has one electron in an unstable position beyond the inert gas core or one extra electron at a higher energy level than that required for d^2sp^3 hybrid bond formation. Hence this acts as a powerful reducing agent by easily giving up the single electron. But it is now known that the complex is $K_3[Co(CN)_5 H_2O]$ and not $K_4[Co(CN)_6]$.

Cobalt forms quite a large number of complexes with many types of ligands (coordinating groups).

NICKEL

Occurrence : Nickel occurs with iron meteorites in the form of an alloy. Metallic Ni and Fe constitute most of the core of the earth. Ores of nickel always contain Co and other metals. The commercial sources of nickel ores are :

Sources : Nickelite—NiAs (Kupfer nickel)
Linnacite—$(Fe, Co, Ni)_3S$
Nickel glance—NiAsS
Pentalandite—(FeNi)S

Pentalandite, (FeNi)S, is abundantly found is Sudbury of Canada, which is the world's chief supplier of nickel.

Metallurgy of Nickel

Large amount of impurities and the presence of Fe, Co, Cu etc. make it difficult for the production of pure Ni. The following steps are involved in the metallurgical operations of Ni.

(1) Concentration of the ore : This is usually done by selective froth floatation by which means NiS, CoS and FeS are separated.

(2) Roasting : The separated NiS is roasted to produce NiO which is generally mixed with some FeO and CuO together with unconverted FeS, CoS, NiS etc.

(3) Smelting : The roasted ore is smelted with coke, sand and some limestone to remove some Fe as the slag, $FeSiO_3$. The product is called *Matte*.

(4) Bessemerization : The matte is bessemerized in a Bessemer converter with silica as flux and iron is almost completely removed. The product consists of NiS, CoS and some NiO. The bessemerized matte is further roasted to convert the sulphides to oxides. Any CuO left is removed by leaching out with H_2SO_4.

(5) Production of Nickel : (a) Mond's Process and (b) Orford Process.

(a) Mond's Process : Nickel forms a volatile compound with CO giving nickel carbonyl, $Ni(CO)_4$. When $Ni(CO)_4$, which is a volatile liquid, is heated to 180°C in the vapour state, it is decomposed to give pure Ni and CO.

The impure nickel oxide is heated to 300°C in a current of water gas (H_2 + CO). NiO is reduced to Ni but impurities remain as oxides. The reduced product is treated with carbon monoxide, CO, in a volatilizer at about 60°C. Volatile $Ni(CO)_4$ is formed which is passed through the decomposer at 180°C by means of sweeping with water gas. $Ni(CO)_4$ is decomposed to give nickel :

$$Ni(CO)_4 = Ni + 4CO$$

CO released is used over again.

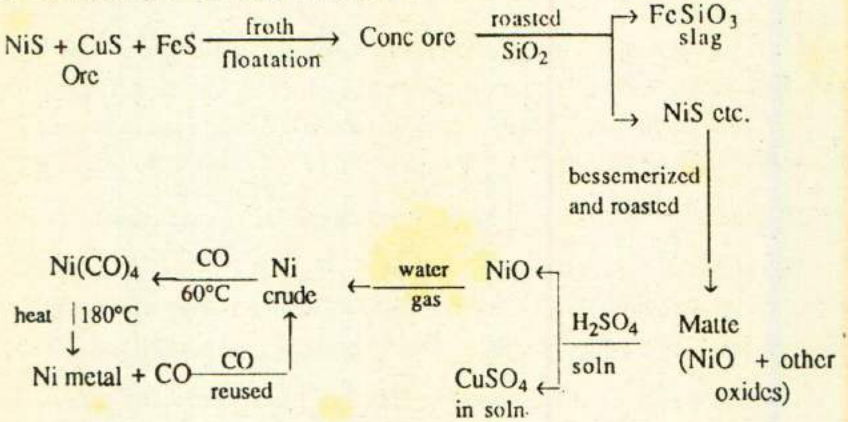
This process may be described by the flow-sheet. (see page 672)

(b) Orford Process : The Bessemer matte consisting mainly of NiS and CuS is fused with carbon and sodium sulphate. Na_2S is formed which in the molten condition dissolves both CuS and NiS. But the solution of NiS in molten Na_2S has greater specific gravity than that of CuS in molten Na_2S and they separate in two layers. The bottom layer consisting of NiS in Na_2S which is separated, cooled and Na_2S is leached out by washing with water.

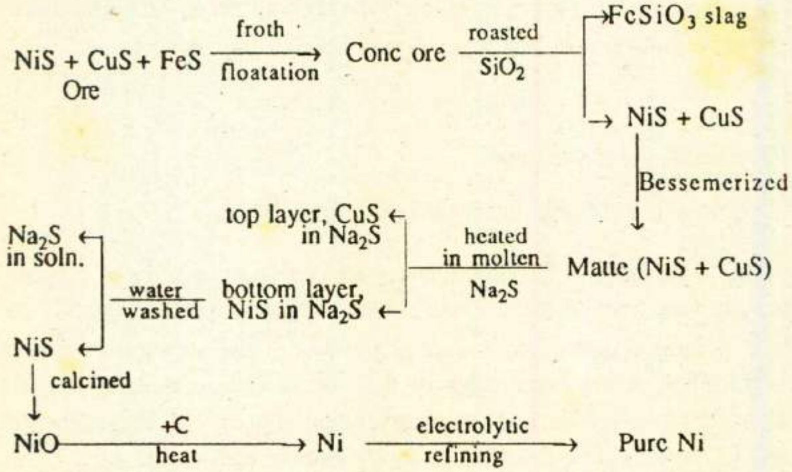
$(CuS + NiS)$ matte $+ 2NaHSO_4 + 8C = CuS + NiS + Na_2S + H_2S + 8CO$. The NiS produced may contain small quantity of CuS. This is removed by chloridizing the copper when heated with NaCl. $CuCl_2$ formed is removed by washing with water. NiS is then calcined to form NiO which on heating with carbon gives Ni:

$$NiO + C = Ni + CO$$

Flow-sheet for Mond's Process :



Flow-sheet for Orford Process :



Refining of nickel : Curde nickel is cast into anodes and refined electrolytically in a $NiSO_4$ or $NiSO_4.(NH_4)_2SO_4$ bath having strips of pure nickel as cathodes on which, pure nickel is deposited during electrolysis. Noble metals, specially platinum, are recovered from the anode mud which collect in the anode region at the bottom of the cell.

Uses of Nickel : (1) In a finely divided form (known as Raney nickel) it is used as a catalyst in the hydrogenation of oils and fats. (2) For making crucibles and laboratory apparatus. (3) Nickel used for electroplating. (4) For making special alloys, such as the following :—

(a) Nichrome—Ni(60%), Fe(25%), Cr(15%), used for resistance heaters.

(b) German silver—Cu (55%), Ni (20%), Zn (15%), used for cutlery and household utensils.

(c) Monel metal—Cu (60%), Ni(40%), used for both industrial and household wares.

(d) Invar—Ni (35%), steel, used for pendulums of clocks.

(e) Alnico, (Al-Ni-Co-Fe alloy) and other alloys of special use.

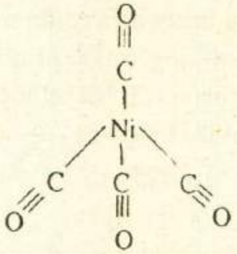
Nickel plating : Because of its hardness, resistance to corrosion and high reflectivity when polished, nickel is widely used in plating of iron, steel, copper etc. The article to be plated is first given a coat of thin film of copper. The electrolytic bath is a mixture of $NiSO_4$ or $NiSO_4.(NH_4)_2SO_4$ containing only small concentration of Ni. At the cathode Ni is deposited while an equivalent amount goes into solution from the Ni anode. The pH of the electrolyte is controlled at about 6.5 with the help of H_3BO_3. Bright deposits are obtained by adding some glucose or cadmium salt in the bath which is operated at about 50°C with a current density of 2.5 amp/decimeter^2.

Compounds of Nickel

The divalent form of Ni is the most important oxidation state. Most of the anhydrous Ni salts are yellow but in aqueous solution they are all green due to the formation of $[Ni\ (H_2O)_6]^{+2}$ ions.

NiO is obtained by heating $NiCO_3$ and the other divalent salts are prepared by the reactions of NiO, $Ni(OH)_2$ or $NiCO_3$ with the appropriate acids and crystallisation.

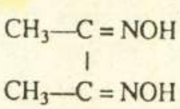
It is formed as a colourless volatile liquid when CO is passed over finely divided Ni. It readily decomposes at higher temperatures depositing pure Ni (basis of Mond's Process). The oxidation state of Ni in $Ni(CO)_4$ is zero. $Ni(CO)_4$ has the tetrahedral structure having Ni at the centre and the four CO at the corners of the tetrahedron. Ni uses sp^3 bonds in $Ni(CO)_4$.



Tetrahedral structure of $Ni(CO)_4$

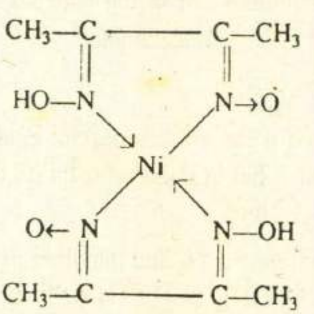
Ni-salts in presence of NH_4Cl and excess NH_4OH produce complex hexamine nickel(II) compounds. $Ni(OH)_2$ first formed goes into solution in excess giving deep blue solutions.

Complexes of $[Ni(CN)_4]^{-2}$ and chelates of organic ligands are square planar. Ni-chelates of 1,2-dioximes are of deep red colour and used for both specific identification and quantitative determination of nickel. Thus dimethyl glyoxime,



$$\begin{array}{c} CH_3-C=NOH \\ | \\ CH_3-C=NOH \end{array}$$

gives a red coloured precipitate with Ni^{+2} salt solutions, soluble in acid but insoluble in ammonia solution and is a specific test for Ni :



Ni-dimethyl glyoxime complex

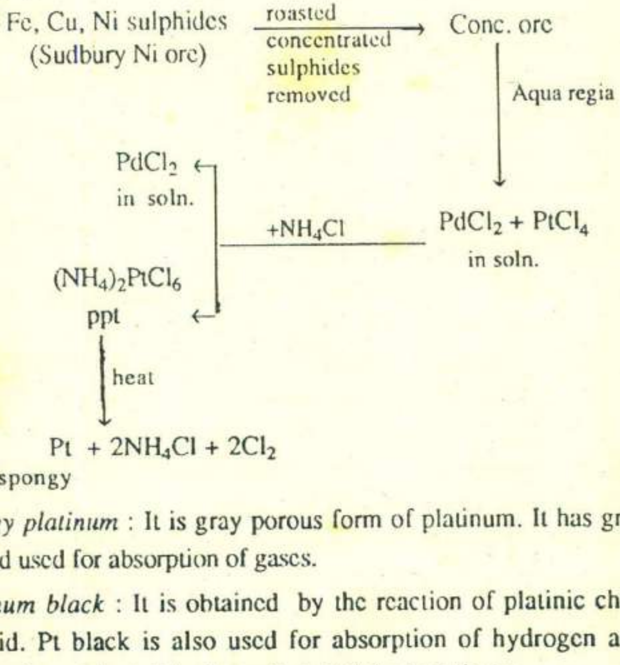
Such complexes are known as chelates or inner complex salts, because they are electrically neutral and do not conduct electricity in solution. Cobalt does not form such complexes with dimethyl glyoxime. Hence the formation of red precipitate with dimethyl glyoxime is a means to identify Ni in presence of Co. This is also used in quantitative method for the determination of nickel.

The other triads of Group VIII elements are Ru, Rh, Pd and Os, Ir, Pt. A brief chemistry of Pt is described.

Platinum

Occurrence : Pt occurs in native form with gold and also along with Cu, Fe, Ni and other Pt-metals. Ural mountains in Russia is the main source. Pt is generally extracted from Sudbury Ni-ore also.

Extraction :



Spongy platinum : It is gray porous form of platinum. It has great surface activity and used for absorption of gases.

Platinum black : It is obtained by the reaction of platinic chloride with formic acid. Pt black is also used for absorption of hydrogen and used in reduction and a catalyst. It is also called platinized platinum.

Platinized asbestos : Asbestos soaked in platinic chloride in presence of HCl and NH_4Cl when heated gives the Pt metal in reduced from and deposited on the asbestos. This is used as a catalyst.

Platinum and Platinum compounds are used in (a) making scientific instruments, (b) as catalyst in contact process for H_2SO_4 and manufacture of HNO_3, (c) for formaldehyde, (d) hydrogenation industries, (e) in jewellery, (f) in dentistry and (g) in printing and toning photography.

QUESTIONS AND PROBLEMS

1. Describe the metallurgy of nickel from its ores. Describe its properties and its alloys. Explain the method of separating nickel from cobalt.
2. Write a note with the reactions involved on the Passivity and the Rusting of iron.
3. Describe any two important methods of preparing high-grade steel from pig iron. Mention a few special steels and their chief uses.
4. Give an account of the metallurgy of iron. Briefly explain the difference between cast iron, wrought iron and steel.
5. What are the important uses of iron? Discuss the chemical reactions occurring in the blast furnace. How is cast iron converted into steel?
6. What are the chief sources of nickel? How is pure nickel obtained from its ores? Describe the important uses of nickel.
7. (a) Describe the process of conversion of pig iron into steel by the Open-hearth Process. Discuss the chemistry of the reactions involved.

   (b) How will you compare Open-hearth Process with that of Bessemer Process.

   (c) What part do Ni and Cr play in the preparation of steel alloys?
8. Give a brief account of the metallurgy of nickel by Mond's Process. Mention some of the important alloys of nickel and mention their uses. Describe a method for the determination of nickel in a sample.
9. Describe the preparation, properties and the uses of following :—

   (a) Mohr's salt ;

   (b) Ferrochrome;

   (c) Nickel carbonyl.
10. What are iron, steel and pig iron? Discuss the principal process of production of pig iron and its subsequent conversion to steel by the Bessemer Process.
11. Compare the physical and chemical properties of the metals Fe, Co, and Ni and their simple compounds.

12. (a) Describe briefly the two compounds whose anions contain a metal.

    (b) Explain why $[Co(H_2O)_6]^{-2}$ is pink whilst $[CoCl_4]^{-2}$ is blue.

    (b) Name two alloys of nickel and mention their special properties.

    (c) How would you detect nickel in solutions containing cobalt and manganese?

13. Discuss the chemistry underlying the process of production of pig iron and its subsequent conversion to steel by the Bessemer Process.

14. How is nickel extracted from its sulphide ores? Mention two uses of nickel. How would you detect nickel in presence of cobalt in a mixture of their salts?

15. Give brief descriptions of metallurgical process for the production of pig iron.

16. Discuss briefly how pig iron can be converted into steel.

17. (a) Describe briefly the metallurgy of iron. (b) What is stainless steel? (c) Discuss the oxidation states of iron. (d) What is the difference between wrought iron and steel?

18. What is the difference between pig iron, white cast iron, gray cast iron, wrought iron and mild steel.

19. What are the raw materials for the production of steel by the Open-Hearth Process? Indicate the chemical reactions. How would you analyse the purity of iron in a sample of mild steel rod?

20. Explain passivity and rusting of iron.

21. What happen when NH_4OH and NH_4Cl is added to a solution of $CoCl_2$ in water?

22. Explain why Co^{+2} is stable in presence of water but is oxidized to Co^{+3} in presence of NH_4OH.

23. Discuss the relative facilities of plating with nickel and chromium.

24. Fe^{+3} gives blood-red colouration with NH_4CNS solution. What is the reaction?

25. How would you test for Fe^{+3} in a sample of Mohr's salt?

26. Write the geometrical figures of $[FeCl_5H_2O]^{-2}$, $[Co(CN)_5H_2O]^{-2}$ and $[Ni(CN)_4]^{-2}$

27. Why a piece of iron is attracted by magnet but zinc is not?

28. Describe the extraction of platinum.

CHAPTER 24

COMPLEX COMPOUNDS

(Coordination Chemistry)

A very large number of chemical compounds exist which appear to be composed of two or more compounds which are capable of independent existence and are themselves well-defined compounds. It was rather difficult to explain on the basis of classical theory of valency as to why such complex compounds are formed. For instance, compounds having the compositions $CuSO_4.5H_2O$; $K_2SO_4.Al_2(SO_4)_3.24H_2O$; $CoCl_3.6NH_3$; K_2PtCl_4 ; $K_4Fe(CN)_6$ etc. have real existence but could not be represented structurally on the basis of the classical concept of valency. For this reason, such compound used to be called as *molecular compounds* in which it was supposed that the component molecules were held together by some unknown forces. The molecular compounds were also referred to as *addition compounds*. Such compounds differ widely in their stability and their properties.

Let us consider the following compounds as regards stability :—

1. In $Na_2CO_3.10H_2O$ the water molecules are very loosely held and 9 molecules are lost on exposure to air. From $CuSO_4.5H_2O$ the water molecules are not so easily lost but only on strong heating. $CuSO_4$ is colourless whereas $CuSO_4.5H_2O$ is blue. These are generally classified as *hydrated compounds or hydrates*. The smaller the size of the cation, the lesser is the number of H_2O molecules in the hydrates. Thus $BeCl_2$ contains $4H_2O$ and $AlCl_3$ contains $6H_2O$. In hydrates some H_2O are combined with the cations and some with anions. Thus in $CuSO_4.5H_2O$ we have $4H_2O$ combined to Cu^{+2} and one H_2O to SO_4^{-2} ions. Similarly, in $MgSO_4.7H_2O$ we have $6H_2O$ combined to Mg^{+2} and one H_2O to SO_4^{-2} ions.

2. $K_2SO_4.Al_2(SO_4)_3$ $.24H_2O$ (alum) exists in the solid state as a single compound but on dissolution in water, all the ions (K^+, Al^{+3} and SO_4^{-2}) can be detected due to complete dissociation. Complex compounds of this type are generally called *double salts*.

3. There are compounds such as $K_2[Cd(CN)_4]$ which are reversibly dissociated into all the ions present in the molecule :

$$\begin{array}{rl} K_2[Cd(CN)_4] \rightleftharpoons 2K^+ + & [Cd(CN)_4]^{-2} \\ & \quad\downarrow\uparrow \\ & Cd^{+2} + CN^- \end{array}$$

But the copper complex, $K_2[Cu(CN)_4]$, is not dissociated as in the case of $K_2[Cd(CN)_4]$, but only to the following ionic species :

$$K_2[Cu(CN)_4] \rightleftharpoons 2K^+ + [Cu(CN)_4]^{-2}$$

It is for this reason that Cd can be precipitated from $K_2[Cd(CN)_4]$ solution by H_2S as CdS but not copper from $K_2[Cu(CN)_4]$ solution.

Again, $K_3[Fe(CN)_6]$ in aqueous solution does not give tests for either Fe^{+3} or for CN^-. Similarly, in the compound $Co(NH_3)_6Cl_3$, heating with H_2SO_4 does not remove ammonia but 3 molecules of HCl are lost per molecule of $Co(NH_3)_6Cl_3$ and also cobalt does not respond to ordinary tests. But from $Co(NH_3)_6Cl_2$ ammonia is removed quite easily.

$$2[Co(NH_3)_6]\,Cl_3 + 3H_2SO_4 \longrightarrow [Co(NH_3)_6]_2(SO_4)_3 + 6HCl$$

$$[Co(NH_3)_6]Cl_2 \longrightarrow CoCl_2 + 6NH_3$$

Thus $K_3Fe(CN)_6$ and $Co(NH_3)_6Cl_3$ belong to the group known as *True Penetration Complexes*. Those complex compounds which are reversibly dissociated in solution into their components are known as Normal Complexes, such as $K_2Cd(CN)_4$ and $Co(NH_3)_6Cl_2$. Thus we can classify complex compounds according to their stability into four groups :—

1. Hydrates and related compounds ;

2. Double Salts ;

3. Normal Complexes ;
4. True Complexes.

It is evident that actually there is no fundamental difference between these complex compounds. Only the degrees of complexity and stability either depending on temperature or hydrolytic decompositions indicate different modes of combinations.

Complex compounds are chemical substances formed by the combination of components which are capable of independent existence.

Complex compounds are also known as coordination compounds.

The nomenclature of coordination compounds is derived from the electronic theory of the formation of coordination bond in which donation of a lone pair of electrons occur from one molecule or ion to another but are coshared between the donor and acceptor.

$$H_3N\!: + H^+ \longrightarrow H_3N : H^+ \longrightarrow NH_4^+$$

$$H_3N\!: + BF_3 \longrightarrow H_3N : BF_3 \longrightarrow NH_3BF_3$$

When a simple ion combines with one or more other ions or with one or more neutral molecules to form a new ion it is called a Complex Ion. Thus,

$[Co(NH_3)_6]^{+3}$, $[Cu(CN)_4]^{-2}$, $[Fe(CN)_6]^{-3}$
$[Cu(H_2O)_4]^{+2}$ etc. are complex ions.

Thus complex compounds contain complex ions which differ in their stabilities. The stability of complex ions is determined by their *dissociation* in solution at the equilibrium conditions. Thus :

$$Cu(CN)_4^{-2} \overset{Ki}{\rightleftharpoons} Cu^{+2} + 4CN^-$$

$$Cd(CN)_4^{-2} \overset{Ki}{\rightleftharpoons} Cd^{+2} + 4CN^-$$

The equilibrium constants also known as the instability constants of the complexes are give by the equation :

$$Ki = \frac{[Cu^{+2}][CN^-]^4}{[Cu(CN)_4^{-2}]} \qquad Ki = \frac{[Cd^{+2}][CN^-]^4}{[Cu(CN)_4^{-2}]}$$

Conversely, the *stability constants* K*s* indicate the *formation* of the complex compounds :

$$Ks = \frac{[Cu(CN)_4^{-2}]}{[Cu^{+2}][CN^-]^4}$$

N.B. The terms in square brackets refer to the concentrations of the ionic species raised to the appropriate power. The concentration of water being taken as constant.

If the concentration of CN^- ions is large, naturally the complex ions is unstable and instability constant K*i* will be very large. Actually this happens in the case of $K_2[Cd(CN)_4]$ complex whereas in the case of $K_2[Cu(CN)_4]$ low value of $[CN^-]$ ion gives low result for the instability constant and, therefore, copper complex is more stable than the cadmium complex. In other words, the stability constant of the copper complex has a much higher value than that of cadmium complex. This principle is applicable to all complex ions. The overall stability constant of a complex is expressed by $\log\beta$ where β = sum of successive or stepwise equilibrium constant given by $\beta = \frac{[MLn]}{[M][L]^n}$. The factors governing the stability of a complex ion or species is obviously related to the metal M and Ligand L.

Metal factors are : (i) Charge and size (ii) Variation in d-orbitals (iii) Number of electrons in the d-orbitals (iv) Electronegativity of M. The ligand factors of stability are : (i) Electron donating capacity of the donor atom in the ligand, (ii) Basicity of the ligand, (iii) Chelate effect (iv) Ring size (v) Steric effect of the large ligands (vi) Entropy effect (vii) π-bonding effect of ligand.

Transition metals are particularly involved in complex formation. It is therefore essential to understand the electronic characteristics of the transition metals.

The Characteristics of the Transition Metals

The tendency of the elements to form complexes with various ligands or groups is very much dependent on the electronic structure of the particular atom. In most cases this appears to be a special characteristics of the transition elements. Although other non-transition elements also form complexes. The remarkable characteristics of the transition metals to form complexes, in most cases coloured, having variable oxidation states and magnetic properties are mainly due to the presence of incomplete **d** orbitals. The intervening elements between group IIA and group IIIA in the Periodic Table are collectively referred to as Transition Elements. The transition elements may, therefore, be defined as those which have incomplete or partly filled **d** or **f** orbitals. Strictly speaking, the elements involving the incomplete **3d**, **4d** and **5d** orbitals are the transition elements and those involving incomplete **4f** orbitals are the inner transition elements or lanthanides or rare earths.

The transition elements in which **d** orbitals are generally being filled up with electrons are divided into three series. The first series involve **3d** orbitals from Sc (21) to Zn (30), the second series involve **4d** orbitals from Y (39) to Cd (48) and the third series involve **5d** orbitals from Hf (72) to Hg (80). Sometimes Zn, Cd and Hg are excluded from this group.

The filling up of **d** orbitals in transition metals is rather anomalous mainly on the consideration that the tendency is to attain stability by half-filled or completely filled **d** electron arrangements. The electronic configurations and the oxidation states of the first series of transition metals containing **3d** electrons are given in Table 24.1

Table 24.1. Electronic structures and oxidation states of the first series of the transition metals.

Metals	*At. No.*	*Electronic Structures*			*Oxidation states (+)*
Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6$	$3d^1$	$4s^2$	3.
Ti	22	"	$3d^2$	$4s^2$	2, 3, 4
V	23	"	$3d^3$	$4s^2$	2, 3, 4, 5
Cr	24	"	$3d^5$	$4s^1$	2, 3, 4, 5, 6
Mn	25	"	$3d^5$	$4s^2$	2, 3, 4, 5, 6, 7
Fe	26	"	$3d^6$	$4s^2$	2, 3, 4, 5.
Co	27	"	$3d^7$	$4s^2$	2, 3, 4
Ni	28	"	$3d^8$	$4s^2$	2, 3
Cu	29	"	$3d^{10}$	$4s^1$	1, 2
Zn	30	"	$3d^{10}$	$4s^2$	2

The formation of coloured ions and magnetic properties of transition metals are related to the presence of unpaired electrons in the system. A substance is called paramagnetic when it is attracted into a magnetic field. A diamagnetic substance is repelled by a magnetic field due to induced magnetism in the substance. Magnetic moments of substances are measured in terms of *Bohr magnetons* (BM). The values of Bohr magnetons indicate the number of unpaired electrons in a molecule of the substance and give informations regarding the structures. The relationship between the magnetic moment and unpaired electrons and also the colour of some transition metal ions in aqueous solutions are given in Table 24.2.

Table 24.2 Magnetic moments and colours of some transition metal ions as related to the number of unpaired electrons.

No. of unpaired electrons	*Magnetic Moment (BM)*	*Ionic species*	*Colour*
0,	—	Ti^{+4}, Zn^{+2}	Colourless
1	1.7	Ti^{+3} V^{+4}, Cu^{+2}	Purple Blue
2	2.8	V^{+3}, Ni^{+2}	Green
3	3.9	V^{+2}, Cr^{+3}	Violet
4	4.9	Cr^{+2} Mn^{+3}	Blue Violet
5.	5.9	Mn^{+2}	Rose

Colour is not only due to the presence of unpaired electrons but also due to other factors as well as electron transitions in presence of lights.

The **d**-orbitals play very important role in the formation of coordination compounds and the modern theories of the structures of inorganic complexes are based on the orientations of **d**-orbitals in space.

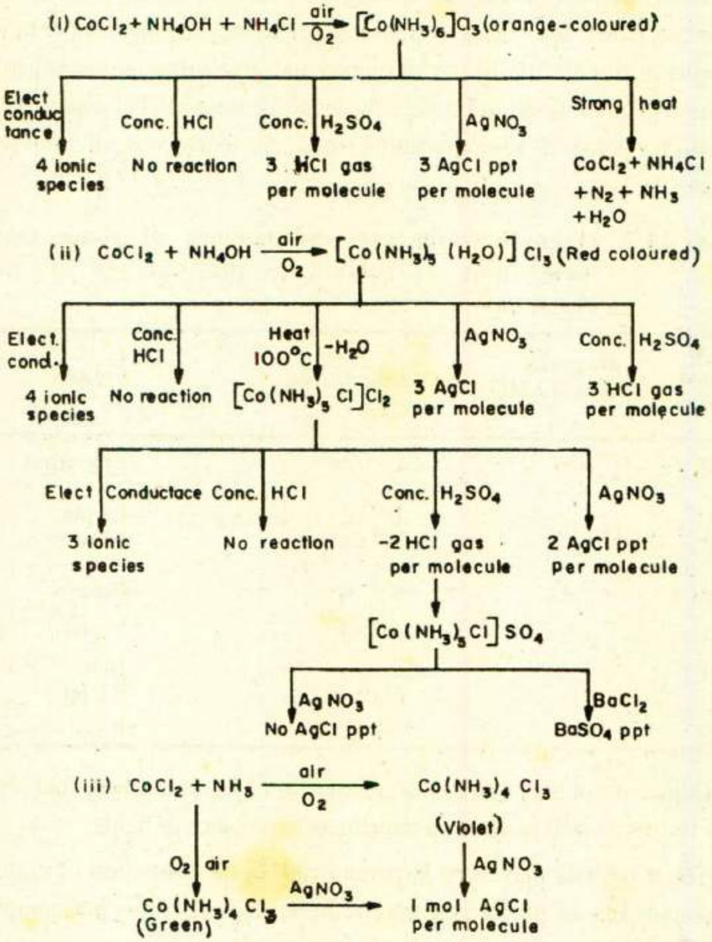
Synthesis and reactions of some Cobaltammine Complexes :

The orange-coloured $[Co(NH_3)_6]Cl_3$ is obtained by the reaction of aqueous pink $CoCl_2$ solution with NH_4OH and NH_4Cl by aerial axidation.

(i) $CoCl_2 + NH_4OH + NH_4Cl \xrightarrow[O_2]{air} [Co(NH_3)_6]Cl_3$ (orange-coloured)

(ii) $CoCl_2 + NH_4OH \xrightarrow[O_2]{air} [Co(NH_3)_5(H_2O)]Cl_3$ (red coloured).

The reactions are shown in the following scheme :



The reactions indicate the stability of the complex compounds in course of the various chemical reactions. These complex compounds require the need of interpretation of their structures and mode of combinations.

Structures of the Complex Compounds

Complex compounds created a great difficulty regarding the nature of bonding present in such species. Many attempts were made in this direction but the most remarkable advancement for the interpretation of the structures of complexes according to the classical concept goes to the credit of Alfred Werner. He advanced a brilliant theory to explain the characteristics of complex compounds and also predicted future developments in the field of structural chemistry. For his pioneer contributions Werner was awarded the Nobel Prize in chemistry in 1913.

Werner's Theory : The theory is known as the Coordination Theory of Complex Compounds and is based upon certain assumptions using the classical concept of valency which are summarized below :—

1. Metals possess two types of valencies :

   (a) Primary valency and (b) Secondary valency.

2. Primary valency combines the acidic and basic radicals or ions and hence the components united by this valency are ionizable. Simple covalent compounds are also formed by primary valency. Thus NaCl, CCl_4, NH_3, $FeCl_3$ are compounds formed by primary valency. These are both ionic and covalent compounds.

3. Secondary valency combines simple molecules or groups which are capable of independent existence, as well as the negative radicals to the metal atoms or ions. The components united by this valency are not capable of ionization. Thus $AgCl.2NH_3$; $CuSO_4.5H_2O$; $K_4[Fe(CN)_6]$ etc.

4. Every complex compound has a metal atom situated at the *centre* of a coordination sphere. The neutral molecules or ions united to the central atom by secondary valency are within the coordination sphere. The number of groups or ions so combined to the central atom is called the coordination number of the central metal atom.

Thus in $[Cu(NH_3)_4]SO_4$ copper is the central metal atom. $4NH_3$ are united to Cu by secondary valency and exist within the coordination sphere and 4 is the coordination number of copper. The attached groups or molecules are called coordinated, groups or Ligands. SO_4^{-2} ion is combined to copper by means of primary valency and neutralizes the +2 charge of Cu.

5. The fulfillment of coordination number appears to be an essential criterion in complex compound formation.

6. The secondary valencies are directed in space about the central metal ion. The coordinated groups are arranged in symmetrical manner at the corners of geometrical figures in space. Thus, 6 groups are situated at the corners of a regular octahedron, shown in Fig. 24—1.

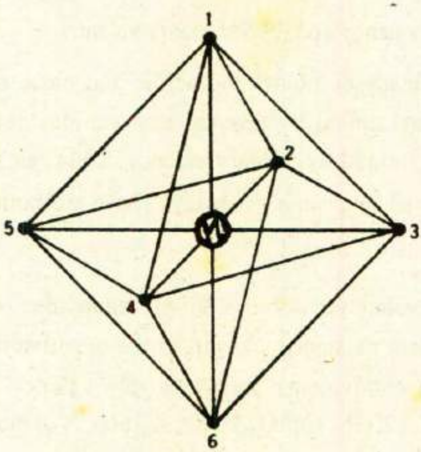
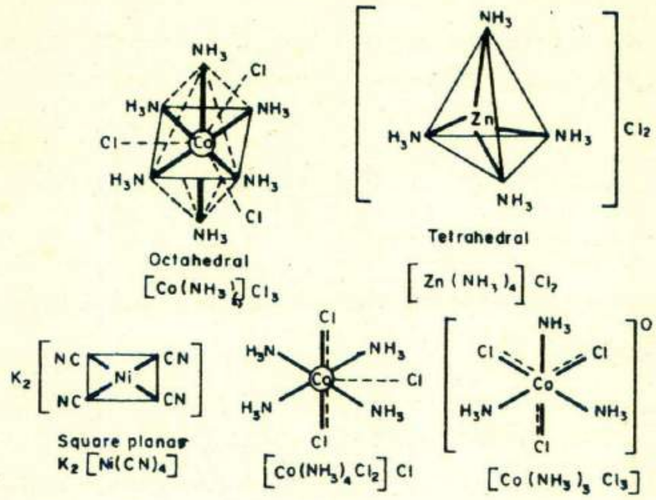


Fig. 24—1. Octahedral configuration. M is the central metal atom.

Werner's Theory predicts the existence of isomerism which has been experimentally proved. The examples of the structures of some complex compounds according to Werner's theory are illustrated in Fig. 24—2.



Octahedral

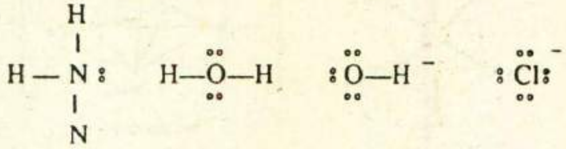
Fig. 24—2. The structure of complex compounds, $[Co(NH_3)_6]Cl_3$, $K_2[Ni(CN)_4]$, $Zn(NH_3)_4Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$ according to Werner.

Werner's theory had some serious drawbacks. No theoretical reasons for assuming the two types of valency and the space configurations of the coordinated groups were given. Formulations of complexes, such as $K_4[Fe(CN)_6]$, $Na_3[Co(NO_2)_6,]$ are not satisfactory. No explanation as regards the particular coordination number of metal was given.

Electronic Interpretation of the Structure of Complex Compounds

Sidgwick's Theory : An electronic theory of the structure of complex compounds was put forward by Sidgwick in 1923. According to this theory the formation of a complex compound involves the donation of an electron pair by each coordinating group or ligand to the metal atom. Each coordinating group has at least one lone pair of electrons which are used for the formation of coordination bonds with the metal atom by sharing. In the formation of NH_4^+ ion a proton accepts and shares the lone pair of electrons from the nitrogen of NH_3 (Lewis acid-base reaction) :

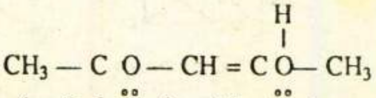
Thus NH_3 has one lone pair, H_2O has two lone pairs OH^- has three lone pairs and Cl^- has four lone pairs.



Some groups or ions have two or more than two atoms with lone pair for donation to metal atoms.

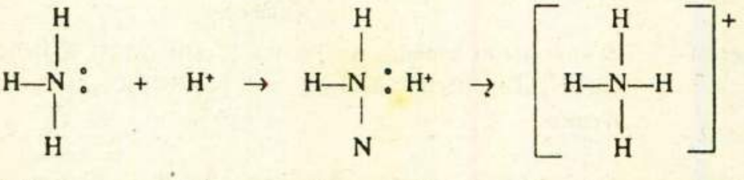
$:NH_2-CH_2-CH_2-H_2N:$

(ethylene diamine)

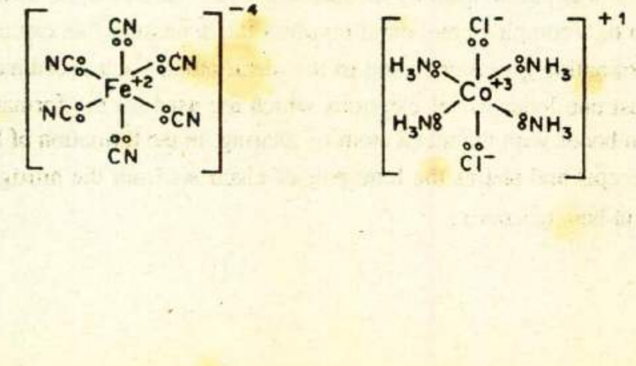


$$CH_3-C\,\ddot{O}-CH=C\overset{H}{\underset{}{\ddot{O}}}-CH_3$$

(enolic form of acetylacetone)



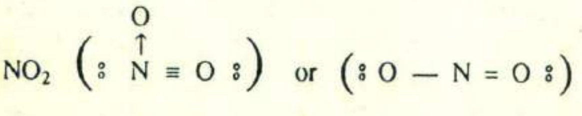
Similarly, a metal ion coordinates with a number of groups or ions containing at least one lone pair electrons. Thus $6NH_3$ or $6H_2O$ become coordinated to Co^{+3} ion and $6CN^-$ coordinated to Fe^{+2} ion to give complex ions :



In the above examples, it is seen that the net charge of the complex ion is the algebraic sum of the oxidation number of the central atom and the oxidation numbers of the coordinating group. The question as to why the metal ion coordinates with a large number of groups or ions by means of coordination bonds was explained from the point of view of the effective atomic number of the metal atoms.

Some groups may have possibilities of coordinating with metals by donation from any site as in

$$CO\ \left(:C \equiv O:\right),\qquad CN^-\ \left(:C \equiv N:\right)^-,$$



$$NO_2\ \left(:\overset{\overset{O}{\uparrow}}{N} \equiv O:\right)\ \text{or}\ \left(:O - N = O:\right)$$

Effective Atomic Number (E. A. N.)

The effective atomic number of a metal atom in a complex is obtained by subtracting from the atomic number of the metal, the number of electrons lost in ion formation and adding the total number of electrons gained in coordination (two electrons from each coordinating group). Thus,

$$E.\ A.\ N. = A - El + Eg$$

where A is the atomic number of the metal atom;

El, number of electrons lost in ion formation ;

Eg, Total number of electrons gained in coordination, each ligand donating two electrons.

Sidgwick pointed out that the formation of the complex compounds is caused by a *tendency of the central metal atom to attain the electronic configuration of an inert gas*. That is the effective atomic number of the metal atom after complex formation becomes equal to the atomic number of an inert gas.

Thus in $K_4[Fe(CN)_6]$ the atomic number of Fe is 26 and number of electrons lost to form Fe^{+2} ion is 2. The 6 coordinated groups donate a total of $2 \times 6 = 12$ electrons which are gained by Fe^{+2} ion in coordination. Thus E.A.N.

of Fe in $K_4[Fe(CN)_6]$ is 26 −2 + 12 = 36 which is the atomic number of krypton. This was considered to be the reason for the stability of $[Fe(CN)_6]^{-4}$ ion. The effective atomic number of some of the metal atoms forming complex compounds are given in Table 24·3.

Table 24.3. The effective atomic number of some metal ions in complexes.

Metal ions	*Atomic number*	*Coordination number*	*Electrons lost in ion formation*	*Electrons gained in coordination*	*E.A.N.*
Fe^{+2}	26	6	2	12	36(Kr)
Co^{+3}	27	6	3	12	36(Kr)
Zn^{+2}	30	4	2	8	36(Kr)
Pd^{+4}	46	6	4	12	54(Xe)
Pt^{+4}	78	6	4	12	86(Rn)
Hg^{+2}	80	4	2	8	86 (Rn)

In a nutshell Sidqwick's theory of coordination compounds may be summarised in the following points :

1. Groups coordinating with metal atom or ions contain lone pairs of electrons.
2. The lone pairs are donated to the metal atom or ions forming coordination bonds.
3. The number of groups or ligands are coordinated to the metal atom or ions according to Effective Atomic Number rule.
4. Effective Atomic Number of the metal atom or ion corresponds to that of an inert gas thereby imparting stability to the complex compounds.

Limitations of Sidgwick's Theory : (1) There are quite a large number of complex ions in which the effective atomic numbers of metal atoms are not those of the inert gases. It may have either less or more electrons than an inert gas. Yet the complexes formed are quite stable. This point is illustrated by some examples in Table 24.4.

Table 24.4. E.A.N. of metal atoms of some complexes (Non-inert gas).

Metal ions	*Atomic number*	*Coordination number*	*Electrons lost in ion formation*	*Electrons gained in coordination*	*E.A.N.*
Cr^{+3}	24	6	3	12	33
Fe^{+3}	26	6	3	12	35
Ni^{+2}	28	6	2	12	38
Pd^{+2}	46	4	2	8	52
Ag^{+}	47	2	1	4	50

(2) Sidgwick attempted to explain this drawback in the electronic theory on the basis that the tendency of the metal atom is not only to attain the inert gas configurations but also to produce symmetrical structures (planar, tetrahedral, octahedral etc.), irrespective of the actual numbers of electrons involved. But the bonding character of the lone pair of electrons from the ligands to the metal could not be satisfactorily explained since the lone pair electrons ordinarily have opposed spins (anti-bonding property).

(3) The theory does not explain the geometry of the molecules.

(4) Metals with odd atomic numbers in many cases do not obey the E. A. N rule

(5) Magnetic properties of some complexes and isomerism could not be explained.

The electronic theory of complex compounds has been developed to a very great extent and is one of the most advanced field of chemistry. Salient points from the modern theories are given.

Pauling's Theory (Valence Bond Theory)

According to the Valence Bond Theory the donation of an electron pair by each coordinating group for the creation of coordination bonds involves the orbitals of the central metal atom into which the donated electrons enter. The important features of Valence Bond Theory (VBT) are : –

(1) The electron pairs of the groups acquire bonding characteristics because of hybridization, such as sp^3 in NH_3, PH_3, H_2O etc. and may also be pure p or s orbital electrons as in the cases of Cl^-, F^- and H^- ions etc.

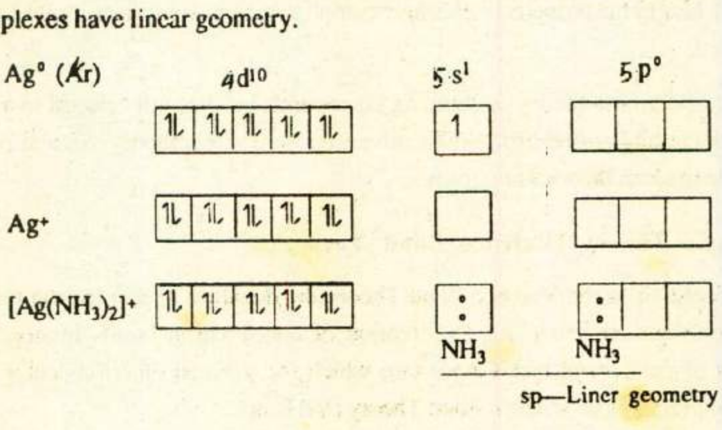
(2) The electron pairs from the coordinating groups enter into the vacant, vacated and available orbitals of the metal atom with or without rearrangements of electrons present in the metal orbitals.

(3) The electrons from the coordinating groups enter into the vacated, vacant and available orbitals of the metal, two electrons in each, forming hybrid orbitals directed in space. The electronic arrangements determine which of the possible geometrical structures the complex will assume. Thus,

sp—linear sp^3—tetrahedral dsp^2—square planar
sp^2 — trigonal dsp^3 — trigonal bipyramidal
dsp^3 — square pyramidal
d^2sp^3 or sp^3d^2—octahedral.

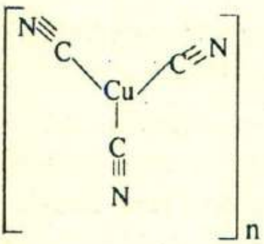
The formation of hybrid bonds in some complex compounds are illustrated to show space arrangement of the coordinated groups about the central metal atom through the concept of hybridization of orbitals according to VBT.

1. Coordination Number (C. N.) = 2 : Only a few complexes have C. N. = 2. These are $[N \equiv C—Ag—C \equiv N]^-$, $[Cl\text{-}Au\text{-}Cl]^-$, $[H_3N\text{-}Ag\text{-}NH_3]^+$, $[Cl—Cu^+—Cl]^-$ etc. The metals use **sp** hybrid orbitals and the complexes have linear geometry.

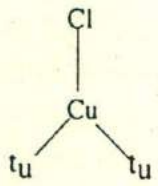


sp—Liner geometry

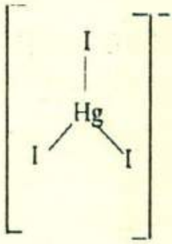
*2. **Coordination Number (C. N.) =3*** : Complexes having C. N. = 3 are uncommon. Some examples are given. These have metals using **sp^2** hybrids $[Cu^+ Cl(tu)_2]^o$, $[Cu(CN)_2]^-$, KH_gI_3 $Cu[S_3(PR_3)_3]$ etc.



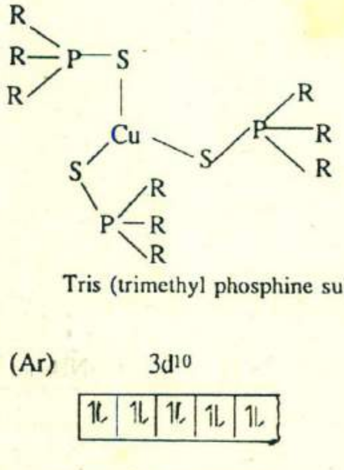
$[Cu(CN)_2]_n$ Polymer



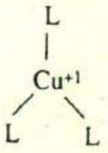
bis (thiourea) Cu(I)

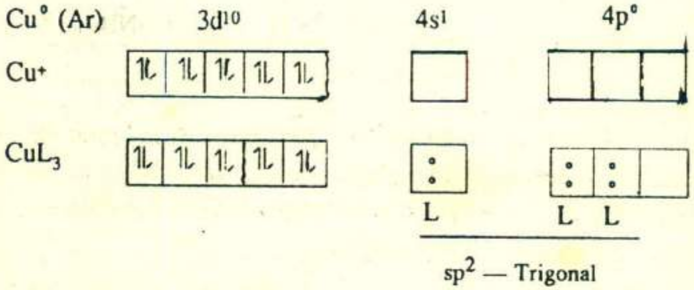


K HgI_3



Tris (trimethyl phosphine sulphide) Cu (I)





*3. **Coordination Number (C. N.) = 4*** : The Complexes having C. N.=4 may assume two types of geometries: (i) Tetrahedral (ii) Square Planar.

Tetrahedral Complexes :

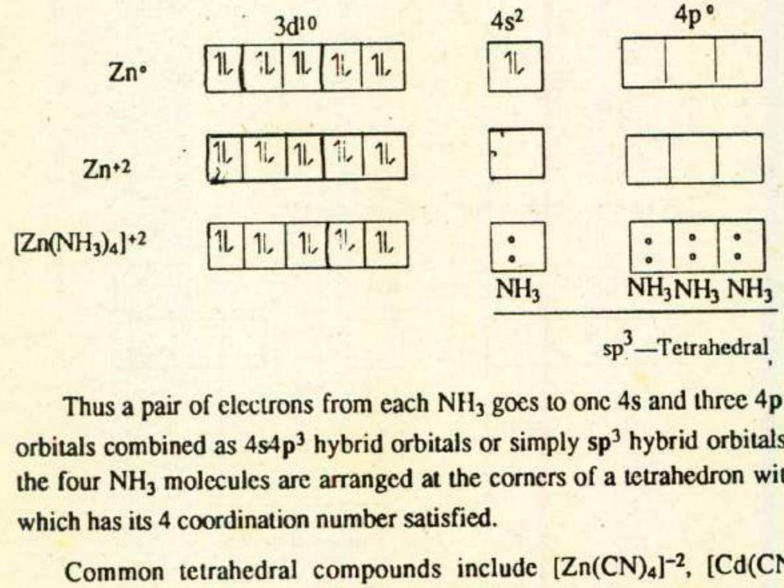
Tetrahedral complexes are most numerous such as :

$[BH_4]^-$, $[AlH_4]^-$, $[BeF_4]^{-2}$, $[Zn(NH_3)_4]^{+2}$, $[Cd(CN)_4]^{-2}$

$[Ni(CO)_4]^0$ and also MnO_4^-, CrO_4^{-2} etc are some examples of tetrahedral structures. They have metals using sp^3 hybrid orbitals for complex formation.

$[Zn(NH_3)_4]^{+2}$: When the orbitals of Zn^{+2} ion coordinate with four NH_3 molecules to form the complex ion $[Zn(NH_3)_4]^{+2}$, each nitrogen atom of NH_3 molecules donates its lone pair of electrons to Zn^{+2}. These donated electrons occupy the vacant 4s and 4p orbitals of Zn^{+2} ion as shown below. The vacant orbitals are shown by empty boxes.

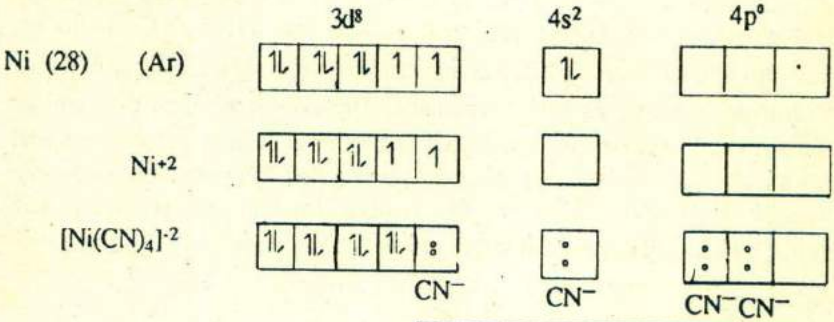
$Zn(30)—1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3s^{10}\ 4s^2$



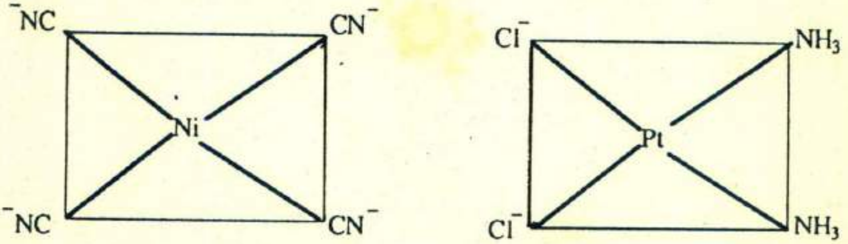
Thus a pair of electrons from each NH_3 goes to one 4s and three 4p vacant orbitals combined as $4s4p^3$ hybrid orbitals or simply sp^3 hybrid orbitals. Thus the four NH_3 molecules are arranged at the corners of a tetrahedron with Zn^{+2} which has its 4 coordination number satisfied.

Common tetrahedral compounds include $[Zn(CN)_4]^{-2}$, $[Cd(CN)_4]^{-2}$, $[Hg(CN)_4]^{-2}$, $[Cu(CN)_4]^{-3}$, $[BeF_4]^{-2}$, $Ni(CO)_4$, $[CuCl_4]^{-2}$ and even anions such as MnO_4^-, CrO_4^{-2} etc.

Square planar geometry :



dsp^2 hybrid bonds of Ni^{+2}
square planar geometry



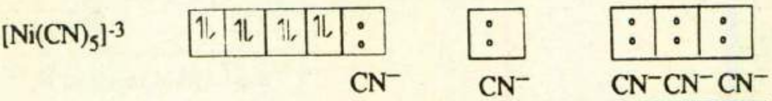
Square plar geometries of $[Ni(CN)_4]^{-2}$ and $[Pt(NH_3)_2Cl_2]$

Square planar Complexes :

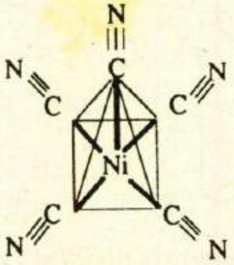
Square planar are not very common because of sterical factors. Some metal ions form square planar complexes particularly those having **d⁸** ions such as Ni^{+2}, Pd^{+2}, Pt^{+2} and Au^{+3}. Co^{+2} (d^7) may form square planar compounds. In the cases of chlorophyll and other biocomplexes the square planar forms of the metal complexes are forced by the rigid structures of large ligands such as porphyrine groups etc.

The bond hybridization in square planar complexes is **dsp²**. $[Ni(CN)_4]^{-2}$, $[Pt(NH_3)_2Cl_2]$, $[NiDmg_2]^{\circ}$, (Dmg = dimethylglyoxime) are some of the examples.

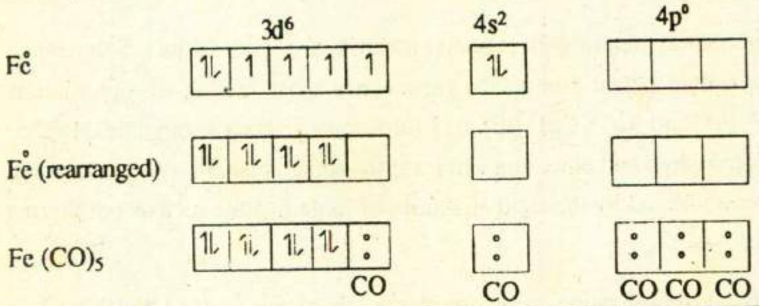
4. Coordination number (C. N.) = 5 : 5-coordinated complexes are much less common as compared to C. N. 4 or 6. Complexes apparently considered to have C. N. = 5 such as Cs_3CoCl_5 and $(NH_4)_3ZnCl_5$ actually contain discrete tetrahedral MCl_4^{-2} anions and free chloride ions. Recently some 5-coordinated complexes have been made. These have trigonal bipyramidal geometry which may be regular and distorted forms as well as square pyramidal forms having both regular and distorted geometries. Thus pentachlorocuprate (II) anion in $[Cr(NH_3)_6][CuCl_5]$ has regular bipyramidal geometry and $[Cr(en)_3]$ $[Ni(CN)_5]$ has distorted square planar configuration.



$d_{x^2-y^2}$ sp^3 square pyramidal geometry

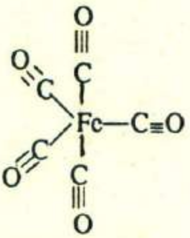


dsp^3 i.e. **$(d_{x^2-y^2})$ sp^3** hybrid orbitals of Ni leads to square pyramidal geometry of $[NiCl_5]^{-3}$ ion. $Fe(CO)_5$ has regular trigonal bipyramidal geometry



d_{z^2} sp^3 hybrid orbitals of Fe^0 (dsp^3) in Fe $(CO)_5$

involving **dsp^3 ($d_{z^2}sp^3$)** hybrid orbital of Fe° give trigonal bipyramidal geometry



Trigonal bipyramidal geometry of $Fe(CO)_5$

5. Coordination Number (C. N.) = 6 :

Of all the coordination complexes known, those containing 6-coordinated bonds having octahedral geometry are most numerous. Transition metals as well as non-transition elements form large number of species. Examples like $[Al(H_2O)_6]^{+3}$, $[Ti(H_2O)_6]^{+3}$, $[Pt(Cl)_6]^{-2}$, $[Fe(CN)_6]^{-3}$ and the most discussed case of $[Co(NH_3)_6]^{+3}$ are familiar. Examples.

$[Co(NH_3)_6]^{+3}$ complex ion :

Co (27) — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$

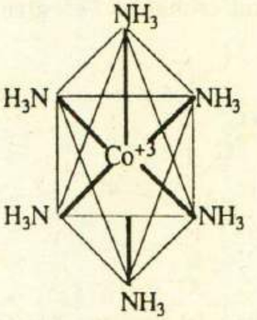
	$3d^7$					$4s^2$	$4p^0$		
Co(Ar)	⇅	⇅	↑	↑	↑	⇅			
Co^{+3}	⇅	⇅	↑	↑					
$[Co^{+3}$ (rearranged)	⇅	⇅	⇅						
$[Co(NH_3)_6)]^{+3}$	⇅	⇅	⇅	:	:	:	:	:	:
				NH_3	NH_3	NH_3	NH_3	NH_3	NH_3

d^2sp^3 hybrid orbitals of Co^{+3}

d^2sp^3 is actually **$(dx^2\text{-}y^2\ dz^2)sp^3$** hybrid orbitals giving octahedral geometry.

Thus 12 electrons from $6NH_3$ molecules enter into two **3d**, one **4s** and three **4p** orbitals, two electrons from each. Since all the 6 bonds in the $[Co(NH_3)_6]^{+3}$ complex ions are completely equivalent, the formation of six **d^2sp^3** hybrid bonds take place which are directed in space with octahedral geometry.

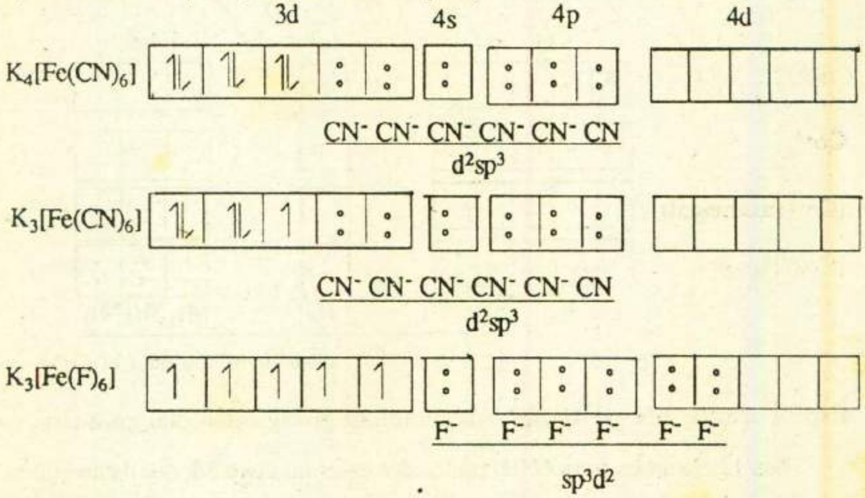
d^2sp^3 ($d_{x^2-y^2}, d_{z^2}$) sp^3 hybrid orbitals having octahedral geometry :



Octahedral geometry of $[Co(NH_3)_6]^{+3}$ ion

The oxidation of Co^{+2} in presence of some ligands has been considered as an achievement of VBT. Thus $[Co(H_2O)_6]Cl_2$ in presence of NH_3 as ligands oxidizes Co^{+2} to Co^{+3} forming $[Co(NH_3)_6]^{+3}$.

$K_3[Fe(CN)_6]^{-3}$ like $[Co(NH_3)_6]^{+3}$ has the octahedral geometry since Fe^{+3} uses d^2sp^3 hybrid orbitals but has one unpaired electron in the **d**-orbital thereby acquiring the magnetic property. However, $[Fe(F)_6]^{-3}$ although has the same octahedral geometry but possesses five unpaired electrons. In the latter case the hybridization is sp^3d^2 (outer orbital complex).



The most important noticeable effect of the rearrangement of electrons during complex formation is the appearance of paired and unpaired electrons.

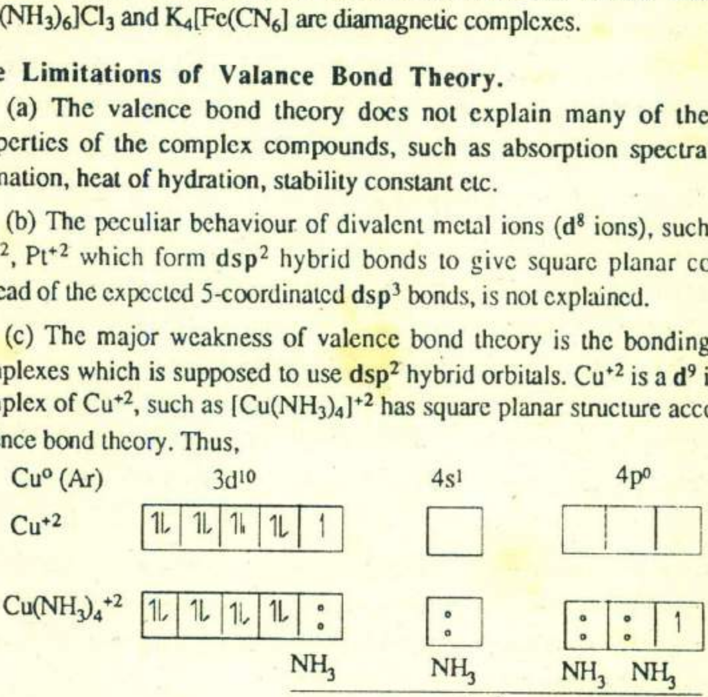
This manifests itself in the magnetic properties of the compounds before and after complex formation. Compounds with unpaired electrons are attracted into magnetic fields and are called paramagnetic. Thus $K_3Fe(CN)_6$ and K_3FeF_6 are paramagnetic complexes having 1 and 5 unpaired electrons respectively. Compounds containing paired-up electrons are not attracted into the magnetic field but tend to move out. Such substances are called diamagnetic. $[Co(NH_3)_6]Cl_3$ and $K_4[Fe(CN_6]$ are diamagnetic complexes.

The Limitations of Valance Bond Theory.

(a) The valence bond theory does not explain many of the physical properties of the complex compounds, such as absorption spectra, heats of formation, heat of hydration, stability constant etc.

(b) The peculiar behaviour of divalent metal ions (d^8 ions), such as Ni^{+2}, Pd^{+2}, Pt^{+2} which form **dsp^2** hybrid bonds to give square planar complexes instead of the expected 5-coordinated **dsp^3** bonds, is not explained.

(c) The major weakness of valence bond theory is the bonding in Cu^{+2} complexes which is supposed to use **dsp^2** hybrid orbitals. Cu^{+2} is a **d^9** ion and a complex of Cu^{+2}, such as $[Cu(NH_3)_4]^{+2}$ has square planar structure according to valence bond theory. Thus,



In order that **dsp^2** bonds are formed, the unpaired electron in 3d must be promoted to a high energy level, such as in 4p as shown above. This gives instability to the complex and the unpaired electron should be easily lost producing a Cu^{+3} state. But this does not happen. Cu^{+2} complexes are stable compounds.

(d) The magnetic moments of some complexes of the same transition metal are widely different. Thus the Fe^{+3} complexes. $K_3Fe(CN)_6$ and $K_3Fe(F)_6$ have magnetic moments 1·7 and 6·0 B.M. (Bohr Magneton) corresponding to one unpaired electron and five unpaired electrons in their respective molecular structure.

(e) The distortions in molecular structures have not been explained.

These and other limitations have been successfully explained from the point of view of the Crystal Field Theory (CFT) or Ligand Field Theory (LFT) which provides a simple explanations regarding the structures o. complexes.

The structures of complexes have also been explained on the basis of valence shell electron pair repulsions as discussed in Chapter 5 mainly for compounds of non-transition elements but the presence of **d** electrons produce a great deal of deviations as expected.

Isomerism in Complex Compounds

Since the groups coordinated to metal atoms in complexes are situated in space, there can be various modes of their arrangements. This situation gives rise to the phenomenon of isomerism in complex compounds. Isomers are defined as compounds having the same formula but different structures. Again, because of the different types of bonding system and the various ways of arranging the co-ordinated groups, a large number of different types of isomerism are exhibited by the inorganic complex compounds. Some of these types of isomerism are discussed. :

1. Ionization isomerism, 2. Hydrate isomerism, 3. Linkage isomerism, 4. Geometrical isomerism, 5. Optical isomerism, 6. Polymerisation isomerism. 7. Coordination isomerism 8. Ligand isomerism 9. Ring size isomerism. 10. Electronic isomerism etc.

A brief description of some important types of isomerism is given with reference to the 6-coordination complexes (complexes containing 6-coordinated groups).

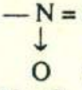
1. Ionization isomerism : Complexes containing the same chemical composition but giving different ions in solution are called ionization isomers. Thus $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ are ionization isomers. In solution these compounds give tests of SO_4^{-2} and Br^{-1} ions respectively. Similarly, $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ are differently ionized in solution. The acidic groups within the coordination sphere are not ionizable.

2. Hydrate isomerism: Water molecules coordinate with metal ions through the electron pair of oxygen. It can also combine with a complex as water of crystallisation. Isomerism exhibited by complex compounds due to the different mode of combination of water molecules is called hydrate isomerism. Thus $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$ are hydrate isomers.

Similarly, $[Co(NH_3)_4H_2O.Cl]Br_2$ and $[Co(NH_3)_4\,Br_2]Cl.H_2O$ are hydrate isomers.

These hydrate isomers show difference in physical and chemical properties and also in colour.

3. Linkage isomerism : Linkage isomerism or structural isomerism occurs when a coordinated group has two or more atoms which can function as electron donor. Thus in the nitro group, NO_2^- the donor atom may be either N or O. Similarly, in the thiocyanate group, SCN^-, the donor atom may be S or N. Isomerism exhibited by complexes due to different modes of coordination of the same group with metal ion is known as linkage or structural isomerism. This arises due to the electronic arrangement in the molecular structures of the coordinated group. Thus NO_2^- group has structures (I) and (II) :

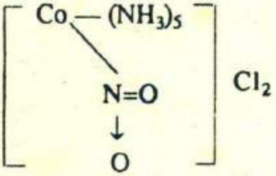


$-\underset{\substack{\downarrow \\ O}}{N}=O$ (I)

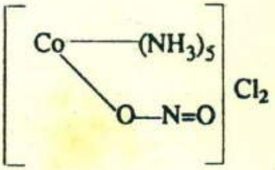
$-O-N=O$ (II)

$\colon S-C\equiv N$ and $\colon N\equiv C-S$ also produce linkage isomerism.

The cobalt complex, therefore, has two forms :



or



4. Coordination isomerism : Complexes containing both cations and anions as coordinated compounds exhibit coordination isomerism.

$[Co(NH_3)_6]\,[Cr(SCN)_6]$ and $[Co(SCN)_6]\,[Cr(NH_3)_6]$,

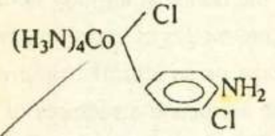
$[Cr(NH_3)_4(CN)_2][Co(NH_3)_2(CN)_4]$ and $[Co(CN)_2(NH_3)_4][Co(CN)_4(NH_3)_2]$ are isomers

5. ***Polymerisation isomerism*** : The units of the polymers are of different complexity. Thus in $[Co(NH_3)_3(NO_2)_3]_n$, 9 isomers occur. Similarly $[Co(OH)_3\ CoX_3.\ 6NH_3]_2$ units are present in the following complexes which exhibit polymerisation isomerism.

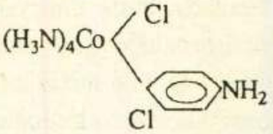
$[(H_3N)_3Co(OH)_3\ Co(NH_3)_3]_2\ X_6$ and
$[Co\{(OH)_2\ Co(NH_3)_4\}_3]X_6$

6. ***Ligand isomerism*** : Ligands having different structures and different chemical species produce ligand isomerism.

$[H_3N)_4CoSO_3SCN]$ and $[(H_3N)_4\ CoS_2O_3CN]$ and also the following are ligand isomers :



and



7. ***Electronic isomerism*** : Isomerism arises due to different electron distributions between metal and ligands.

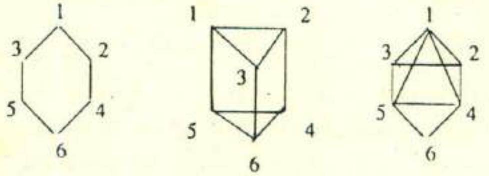
$[(H_3N)_5CoNO]^{+2}$ and $[(H_3N)_5\ CoNO]^{+3}$

These may have Co^{+2}, Co^{+3}, NO, NO^- and NO^+ species in the molecular structures.

8 ***Geometrical isomerism*** : This is also known as stereoisomerism or cis-trans isomerism . This is the most important type of isomerism in the co-ordination compounds and is a direct outcome of the arrangement of the co-ordinated groups in space. The geometrical isomerisom is based on the geometry of the coordination complexes and is exhibited by compounds of 6-coordination numbers and also by other coordination numbers.

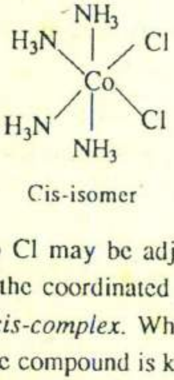
It may be noted that when the coordinated groups are the same, no geometrical isomerism is possible. Geometrical isomerisom is possible only when there are at least two groups different from the rest as in (MA_4B_2) in the octahedral and (MA_2B_2) in square planar complexes, where M is the metal atom and A and B are the different groups.

In fact the two isomers in MA_4B_2 was the convincing proof of the octahedral geometry since other hexa-coordinated or substituted forms of MA_4B_2 have different configurations

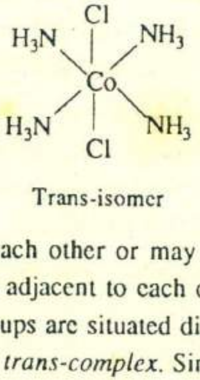


	plane hexagon	trigonal prism	octahedron	Experimental
MA_5B	1 Isomer	1 isomer	1 isomer	1 isomer
MA_4B_2	3 Isomers	3 isomers	2 isomers.	2 isomers.
MA_3B_3	3 isomers	3 isomers	2 isomers	2 isomers

For example, $[Co(NH_3)_4Cl_2]Cl$ will have two isomers due to different arrangement of the 2Cl within the complex ion; the ionic Cl^- is not shown in the diagrams below :

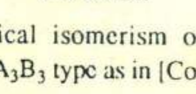


Cis-isomer

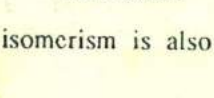


Trans-isomer

The two Cl may be adjacent to each other or may be apart. When the positions of the coordinated group are adjacent to each other the complex is known as a *cis-complex*. When the groups are situated diagonally opposite to each other the compound is known as a *trans-complex*. Similar is the case with $[Pt(NH_3)_2Cl_2]$, a 4-coordination complex :

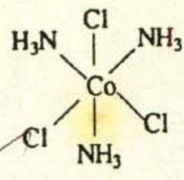


Cis-isomer

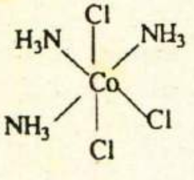


Trans-isomer

Geometrical isomerism or cis-trans isomerism is also exhibited by compound MA_3B_3 type as in $[Co(NH_3)_3\,Cl_3]$.



Cis, cis, cis



Cis, cis, trans

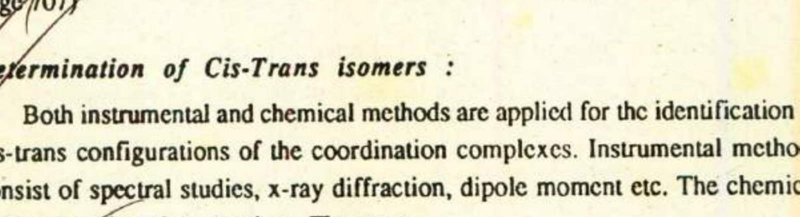
9. ***Optical isomerism*** : This is also known as mirror-image isomerism. In most cases when chelates (groups or ligands or species such as $NH_2—CH_2—CH_2—NH_2$ form two N—M bonds) enter into 6-coordinated complexes forming compounds of the type $Co(en)_2AB$ where (en) stands for $NH_2CH_2CH_2NH_2$ and A and B are the different groups coordinated to cobalt, both cis-and trans-forms are possible. The cis forms show optical isomerism. (See page 707)

Determination of Cis-Trans isomers :

Both instrumental and chemical methods are applied for the identification of cis-trans configurations of the coordination complexes. Instrumental methods consist of spectral studies, x-ray diffraction, dipole moment etc. The chemical methods are based on reactions. These are :

(i) Introduction of a bifunctional group : A bifunctional group is also known as *bidentate* group. The process of introducing a bifunctional group in a complex structure is known as *chelation*. A bifunctional group "bites" the metal ion at two positions. These groups are :

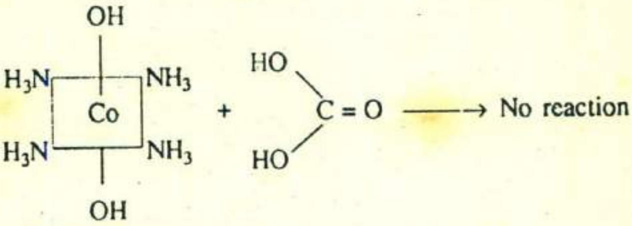
$NH_2—CH_2—CH_2—NH_2$, NH_2CH_2COOH, CO_3^{-2}, $C_2O_4^{-2}$ etc.



Cis-compound

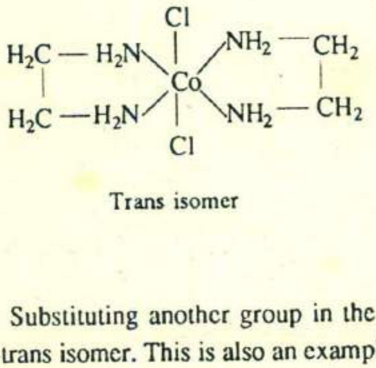
H_2CO_3
CO_3^{-2} (bifunctional group)

Reaction occurs

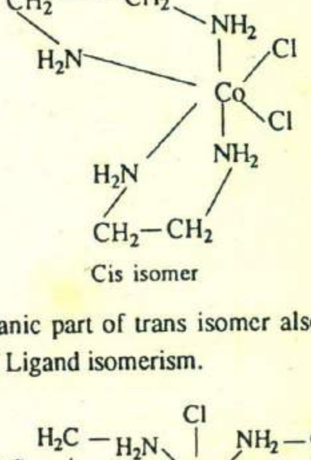


Trans-compound

A more common group is ethylenediamine $NH_2CH_2CH_2H_2N$ (en) in which the two N atoms coordinate in two, four or all the 6 positions of 6-coordinated complexes i.e. one (en), two (en) or three (en). Cis-trans isomers identified through coordination of two (en) quite clearly.

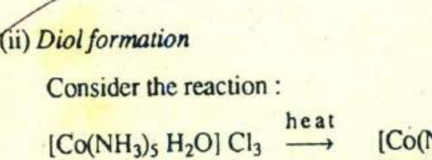


Trans isomer



Cis isomer

Substituting another group in the organic part of trans isomer also gives cis-trans isomer. This is also an example of Ligand isomerism.



Cis-isomer

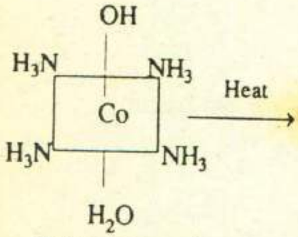
Trans-isomer

(ii) *Diol formation*

Consider the reaction :

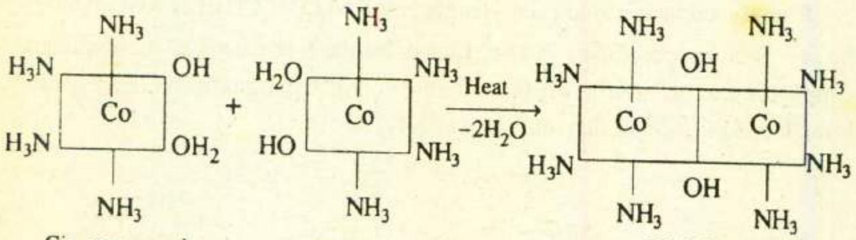
$$[Co(NH_3)_5\ H_2O]\ Cl_3 \xrightarrow{\text{heat}} [Co(NH_3)_5Cl]Cl_2$$

No diol formation



No diol formation since OH and H_2O are in trans positions.

Trans-compound

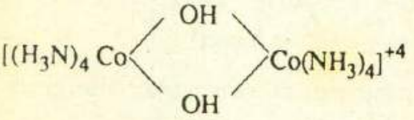


Cis-compound

Diol formation

Simply the reaction may be represented as :

$$[Co(NH_3)_4(H_2O)OH]^{+2} + [Co(NH_3)_4(H_2O)OH]^{+2} \xrightarrow{-2H_2O}$$



$$[(H_3N)_4Co\begin{matrix}OH\\ \\ OH\end{matrix}Co(NH_3)_4]^{+4}$$

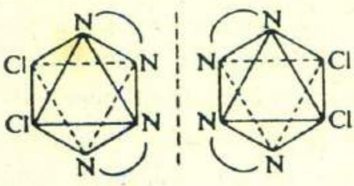
which is a diol (*polynuclear complex*)

Only the cis-compounds with appropriate ligands formed the dinuclear (containing two metal atoms) or a diol (complexes containing two OH groups). OH group acts as a bridge group between the two Co atoms. Other bridge groups are : —NH—, —SH—, —O— etc. and may combine two or more metal complexes forming polynuclear species with one, two or three bridge groups.

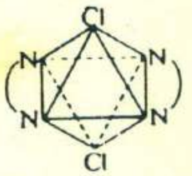
Optical Activity in complexes :

(iii) Obviously, the trans-form is symmetrical and, therefore, has a plane of symmetry. But the cis-form has a mirror-image which is not superimposable and thus does not possess any plane of symmetry. Such molecular structures are found to be optically active, i. e., they rotate the plane of a polarized light. A large number of inorganic optically active complex compounds have been found to exist. The cis-form $[Co(en)_2NH_3Cl]Br_2$ has been found to be optically active because the mirror-image form is not superimposable :

$NH_2\ CH_2\ CH_2\ H_2N$ represented as N⌒N or en



cis

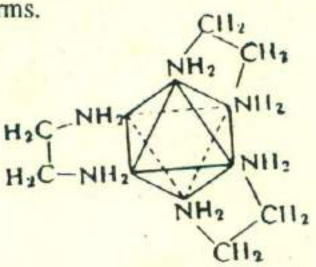


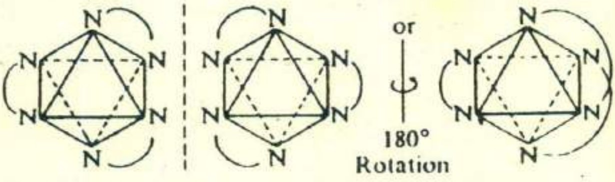
trans

Cis-forms are optically active
(Non-symmetrical)

trans-form not optically active
(symmetical)

Optical activity is retained even when A=B (both are NH_3 or Cl). Compounds of the compositions $[Co(en)_3]^{+3}$ are also optically active and are enantiomorphs. Some need resolutions into *d*- and *l*-forms.





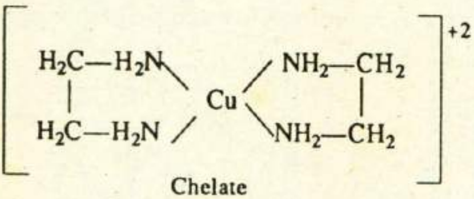
Optical isomers (en = $NH_2\ CH_2\ CH_2\ NH_2$)

Chelate complexes : In the following examples the coordinated group has only one atom which donates a pair of electrons to form a coordinated bond with the central metal ion and, each group occupies only one position :

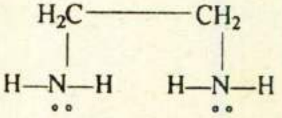
$[Cr(H_2O)_6]^{+3}$ $[Co(NH_3)_6]^{+3}$ $[Ag(NH_3)_2]^{+}$ $[Ni(CN)_4]^{-2}$

Such groups or ligands are called *monodentate* ligands. But there are groups which may have two or more atoms which coordinate with the metal atom simultaneously and occupy two or more positions in the molecular structure. The ligands are known as bidentate, tridentate or polydentate.

A coordinating group or ligand that occupies two or more coordination positions in a complex and contributes more than a single pair of electrons is known as a *chelate group*, and the complex is known as *Chelate*. The process by which chelates are formed is called *Chelation*. Thus $C_2O_4^{-2}$ ion, ethylenediamine, $NH_2CH_2CH_2NH_2$, glycine, etc donate electrons to the metal atom at the same time occupy two positions in the complexes. Thus $NH_2CH_2CH_2NH_2$ has two nitrogen atoms and each has a pair of electrons for coordination with, say, Cu^{+2} ion. Hence only two molecules of $NH_2CH_2CH_2NH_2$ will satisfy the coordination number 4 of Cu^{+2} ion forming $[Cu(NH_2—CH_2—CH_2—NH_2)_2]^{+2}$ having the following configuration in the molecular structure :

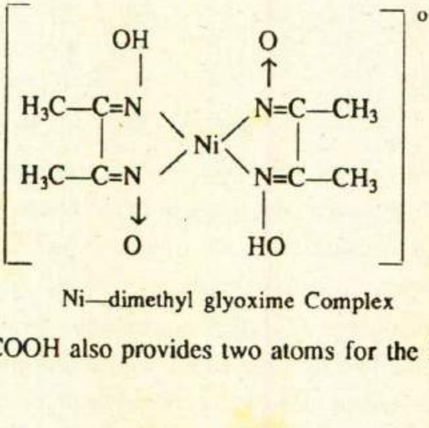


Chelate
Cu—ethylenediamine



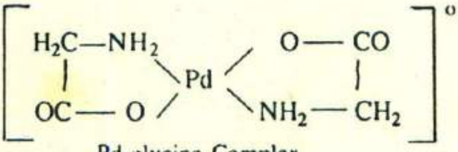
Chelate group
(ethylenediamine)

Dimethyl glyoxime which is generally used for identification and quantitative determination of nickel also occupies two positions in the complex having the structure :

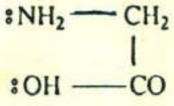


Ni—dimethyl glyoxime Complex

Similarly, NH_2CH_2COOH also provides two atoms for the formation of chelate. Thus with Pd^{+2} :

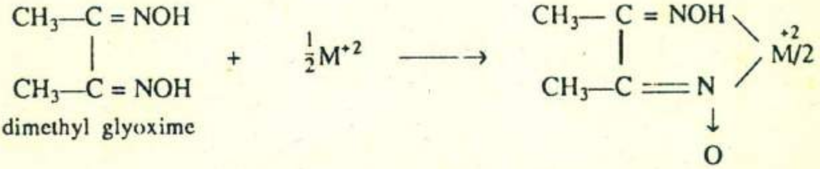


Pd-glycine Complex



Glycine

Notice that there is difference between the charges of the complex ions formed by ethylenediamine, dimethyl glyoxime and glycine. Ethylenediamine has two nitrogen atoms which provides the two pairs of electrons to Cu^{+2} ion and, therefore, satisfies the coordination member 4 of Cu^{+2} ion by two molecules of $NH_2CH_2CH_2NH_2$ The dimethyl glyoxime and glycine not only satisfy the coordination number but also neutralize the charges on the metal ion, that is, satisfy the oxidation number of the metal ion at the same time, because the molecules of dimethyl glyoxime and glycine have H atoms which can be replaced by metals. It means that the acidic part of these groups also acts simultaneously. These produce electrically neutral complexes. The lone pairs of electrons on O in OH provide the coordinating electrons :

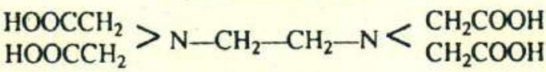


dimethyl glyoxime

These ligands which "bite" at two positions in the metal ion are known as bidentate ligands. $\underset{\cdot\cdot}{N}H_2CH_2CH_2\underset{\cdot\cdot}{N}HCH_2CH_2\underset{\cdot\cdot}{N}H_2$ is a terdentate a ligand,

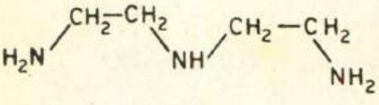
$$\underset{\cdot\cdot}{N}H_2CH_2CH_2\underset{\cdot\cdot}{N}HCH_2CH_2\underset{\cdot\cdot}{N}HCH_2CH_2\underset{\cdot\cdot}{N}H_2$$

a quadridentate ligand

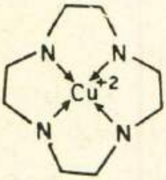


$$\begin{matrix}HOOCCH_2\\HOOCCH_2\end{matrix}>N-CH_2-CH_2-N<\begin{matrix}CH_2COOH\\CH_2COOH\end{matrix}$$

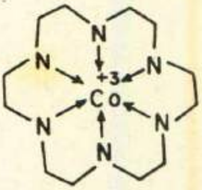
a hexadentate ligand (EDTA). The configuration of such chelate complexes are :



Tridentate Ligand



Tetradentate



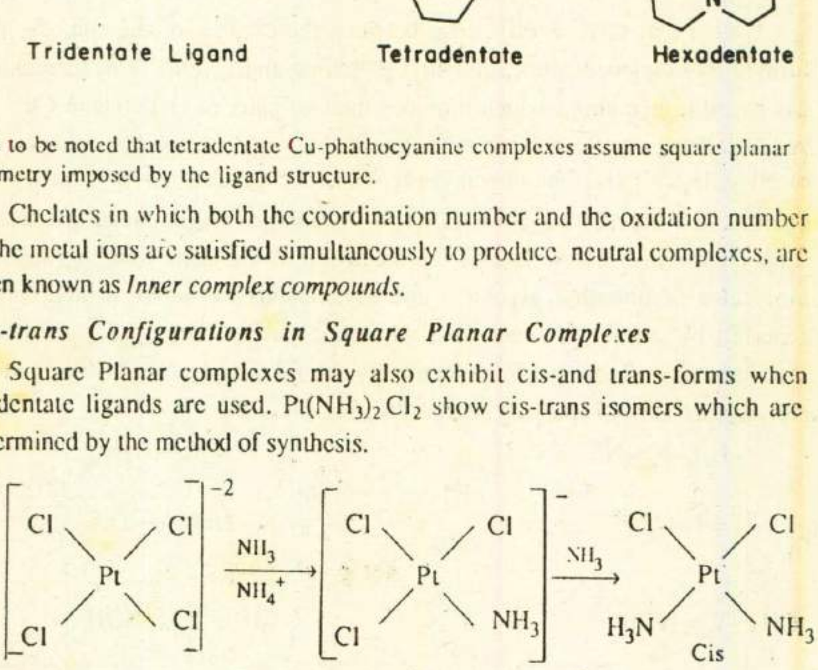
Hexadentate

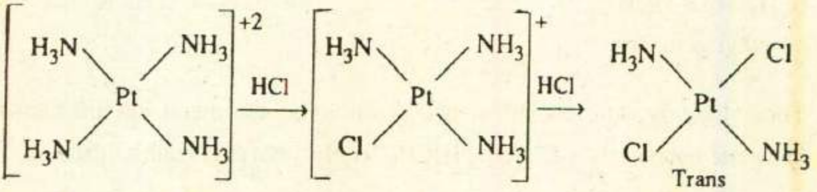
It is to be noted that tetradentate Cu-phathocyanine complexes assume square planar geometry imposed by the ligand structure.

Chelates in which both the coordination number and the oxidation number of the metal ions are satisfied simultaneously to produce neutral complexes, are often known as *Inner complex compounds.*

Cis-trans Configurations in Square Planar Complexes

Square Planar complexes may also exhibit cis-and trans-forms when unidentate ligands are used. $Pt(NH_3)_2Cl_2$ show cis-trans isomers which are determined by the method of synthesis.

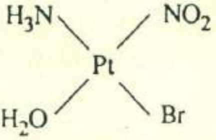




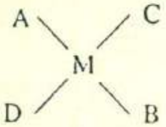
The synthesis is based on the principle known as *Trans Effect*. The trans effect is defined as the property of a ligand to direct an incoming ligand during the replacement reaction to take a position in the complex trans (opposite) to itself. Some of the ligands arranged in the decreasing order of the ability to function as trans eliminating group is as follows:

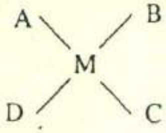
$CO \approx CN^- > NO_2^- > I^- > Br^- > Cl^- > NH_3 > OH^- > H_2O$

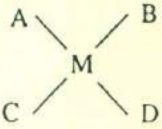
Application of the trans effect principle has made it possible to make complex species. Such as



This species is not optically active although there are four different ligands but it has three geometrical isomers.





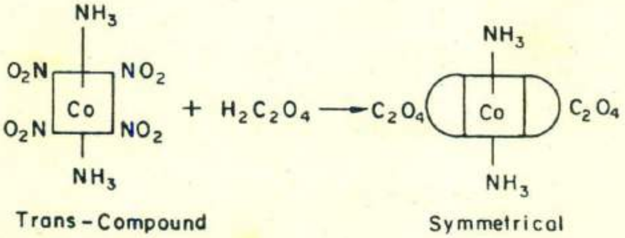


$A = NH_3$, $B = NO_2$, $C = Br$ and $D = H_2O$.

Cis-Trans isomers in simple complexes through chelation

Optical activity in chelated complexes may also be used in connection with the determination of cis-trans isomers. The classical example of the cis-trans form of Erdmann's salt $NH_4[Co(NO_2)_4(NH_3)_2]$ which has both the cis-and trans-form configurations may be cited.

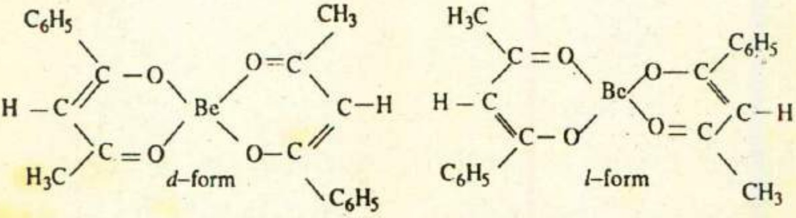
The conversion to oxalate complexes of the two forms leads to the introduction of metal oxlate complex ions.



The trans form has mirror-images which are superimpossable and has no optical activity. But the cis-forms is optically active.

The mirror-image of cis-form is not supremipossable and therefore Erdmann's salt was proved to be a Cis-Compound. More examples have been given under chelate complexes.

Normally the tetrahedral arrangements of ligand give rise to the formation of optically active isomers. A unique case of optical isomerism occurs when 1-phenylbutan-1, 3-dione forms a complex with Be^{+2}.



In square planar complexes, no optical isomerism arises but an optically active ligand may impart optical activity in special cases.

METAL CARBONYLS

The transition metals having **d**-orbitals possess the ability to form compounds with various neutral molecules such as CO. These compounds of metals and CO are known as metal carbonyls. There are two groups of metal carbonyls namely (i) monometallic carbonyls such as $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ etc and (ii) polymetallic carbonlys such as $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $Mn_2(CO)_{10}$ etc.

Preparation : These metal carbonyls are formed by various direct and indirect methods.

$$Ni + 4CO \xrightarrow[1\ atmos]{30\text{—}50°C} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow[100\ atmos]{50°C} Fe(CO)_5$$

$$Co + 6CO \xrightarrow[200\ atmos]{100°C} Co(CO)_6$$

$$CoS + 8CO \xrightarrow[\text{300 atmos}]{\text{Cu or Ag}} Co_2(CO)_8$$

X = halide

$$\begin{tikzcd}
MX_n + yCO \arrow[r, "\text{Tempr.}", "\text{Pressure}"'] & Mx(CO)y\,Xn \arrow[d, "\begin{array}{l}\text{(unstable)}\\ \text{+ reducing agents}\\ \text{Ag, Na, Al, Mg etc.}\end{array}"] \\
\text{THF} & Mx(CO)y
\end{tikzcd}$$

M = metal

THF (tetra-hydrofurane) solvent

x = No. of metal atoms

y = No. of CO groups

$$Fe(CO)_5 \xrightarrow[\text{photosynthesis}]{\text{uv-light}} Fe_2(CO)_9 \longrightarrow Fe(CO)_5 + Fe_3(CO)_{12}$$

$$H_2Fe(CO)_4 \xrightarrow{MnO_2} Fe_3(CO)_{12}$$

$$HCo(CO)_4 \xrightarrow{\text{heat}} Co_2(CO)_8$$

Properties :

(a) Decomposed by heating giving very pure metals :

$$Ni(CO)_4 \xrightarrow{150^\circ} Ni + 4CO$$

$$Fe(CO)_5 \xrightarrow{\text{heat}} Fe + 5CO$$

(b) Act as reducing agent and react violently with O_2 or H_2O

$$Fe(CO)_5 + H_2O \xrightarrow{O_2} Fe_2O_3 + CO_2 + H_2$$

(c) No action of acids

(d) Reacts with NO and CO is replaced according to $3CO = 2NO$

$$Cr(CO)_6 + 2NO \longrightarrow Cr(CO)_3(NO)_2 + 3CO$$

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

$$Co_2(CO)_8 + 2NO \longrightarrow 2Co(CO)_3\,NO + 2CO$$

(e) $Fe(CO)_5 + \underset{\text{aq. soln.}}{Ba(OH)_2} \longrightarrow H_2Fe(CO)_4 + BaCO_3$

(f) $Mn_2(CO)_{10} + 2Na \longrightarrow 2NaMn(CO)_5$

Structures of Metal carbonyls :

Lewis structure of CO is : C : : : O : and E. A. N. Rule is obeyed.

(i) E. A. N. for Metal Carbonyls:

Coordination with metals takes place through the lone pair of C. In many cases Effective Atomic Number Rule is obeyed in the cases of monometallic, polymetallic carbonyls, carbonyl hydrides and also carbonylate ions.

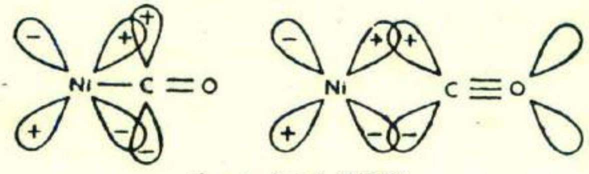
$Ni(CO)_4$ Ni = 28e + 4CO = 8e Total 28+8 = 36e (Kr)
$Fe(CO)_5$ Fe = 26e + 5CO = 10e Total 26+10 = 36e (Kr)
$Cr(CO)_6$ Cr = 24e + 6CO = 12e Total 24+12 = 36e (Kr)
$Mo(CO)_6$ Mo = 42e + 6CO = 12e Total 42+12 = 54e (Xe)
$W(CO)_6$ W = 74e + 6CO = 12e Total 74+12 = 86e (Rn)

It is to be noted that metal carbonyls contain metals in the zero oxidation states.

Odd atomic number metals carbonyls obey E. A. N. Rule in the ionic forms and in polymeric metal carbonyls, the metal-metal bonds satisfy the inert gas formalism :

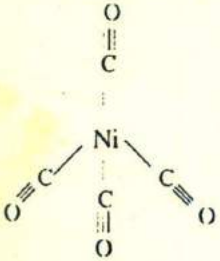
$Mn(CO)_5Cl$ Mn = 25e 5CO = 10e Cl^- = 1e Total = 36e
$Na[Mn(CO)_5]$ Mn = 25e 5CO = 10e + 1e Total = 36e
$H[Co(CO)_4]$ Co = 27e 4CO = 8e + 1e Total = 36e
$Fe_2(CO)_9$ 2Fe = 52e 9CO = 18e Fe—Fe = 2e Total 72/2 = 36e
$Co_2(CO)_8$ 2Co = 54e 8CO = 16e Co_2 = 2e Total 72/2 = 36e
$Fe_3(CO)_{12}$ 3Fe = 78e 12CO = 24e Fe_3 = 6e Total = 108/3 = 36e
$Co_4(CO)_{12}$ 4Co = 108e 12CO = 24e Co_4 = 12e Total 144/4 = 36e

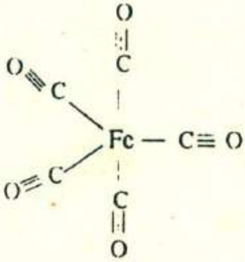
(ii) *VBT and hybridization for Metal Carbonyls* : The metal-carbonyl bonds are linear and in monometallic carbonyls the formation of bonds occur due to hybridization of metal orbitals through overlap of d_π metal orbitals with p_π orbitals of CO and M—CO-bond. In $Ni(CO)_4$ metal uses sp^3 hybrid bonds giving tetrahedral geometry to the molecule. Similarly in $Cr(CO)_6$, chromium uses d^2sp^3 hybrid orbitals forming octahedral geometry of the

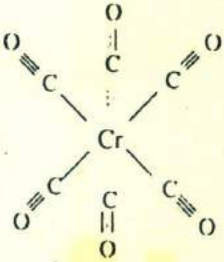


d_π - p_π bond. (VBT)

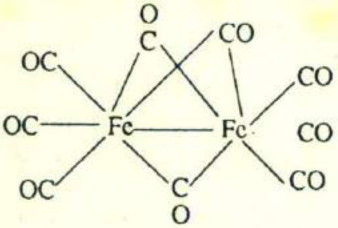
molecular structure. $Fe(CO)_5$ obviously is formed by the use of **dsp^3** hybrid orbital of Fe (**dz^2sp^3**)



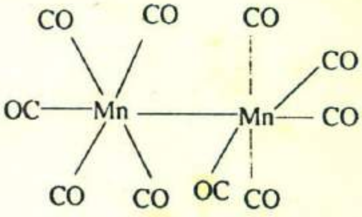




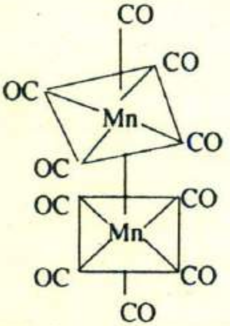
The polynuclear metal carbonyls contain metal-metal bonds which are not adequately explained according to Valence Bond Theory.



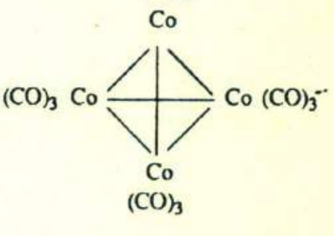
$Fe_2(CO)_9$



$Mn_2(CO)_{10}$

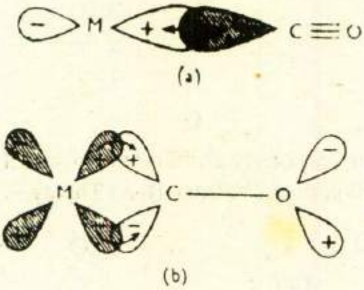


Tilted structure of $Mn_2(CO)_{10}$



$Co_4(CO)_{12}$

(iii) Structure of metal carbonyls according to Molecular Orbital Theory (MOT) : This is an elaborate treatment for bonding in metal carbonyls. The following points are taken into considerations: (i) C—O bond in CO (ii) metal-carbon bonds (iii) metal-metal bonds and (iv) bridging groups in polynuclear metal carbonyls. Firstly, there are triple bonds in CO having 1σ and 2π bonds. The carbon lone pair is actually hybrid sp bond. Secondly, the overlap of lone pair of carbon with **d**, s, **p** vacant metal orbital form metal-carbon bond. Thirdly, the C—M σ bond is further stabilized by back donation of π electrons from metal to C. This process takes place by the overlapping of filled non-bonding **d** orbitals of metal with the π^* antibonding orbitals of CO forming metal- ligand π-bonds.



(a) Overlap of metal orbital with filled σ–orbital of C giving M–C σ–bond. (b) Overlap of filled metal d_π or hybrid dp_π orbital with empty p_{π^*} antibonding orbital of CO.

Thus according to VBT, M—CO bonds in metal carbonyls are distinguished as C—M σ and M—C as d_π—p_π bonds, whereas MOT indicates C—M $_\sigma$ bond and M—C bonds are d_π—p_{π^*} (anitbonding orbitals of CO).

METAL NITROSYLS

Nitric oxide NO exists in three forms : NO, NO^+ and NO^-. Metal nitrosyls are the compounds of metals with the neutral NO which is coordinated to metal through N. The odd electron in NO in the antibonding orbitals is first transferred to the metal thereby reducing its oxidation number by one unit. NO^+ is isoelectronic with CO but coordinates with metals by donating 3 electron in the neutral form. Thus NO coordinates with metals to satisfy the need for an odd number of electrons for the E. A. N. rule. Therefore generally metal nitrosyls occur in complexes with mixed ligands.

$$Fe(CO)_5 + 2NO \longrightarrow Fe(CO)_2(NO)_2 + 3CO$$
$$Co_2(CO)_8 + 2NO \longrightarrow 2Co(CO)_3NO + 2CO$$
$$Ni(C_5H_5)_2 + NO \longrightarrow C_5H_5NiNO$$
$$Cr(CO)_6 + NO \longrightarrow Cr(CO)_3(NO)_2$$

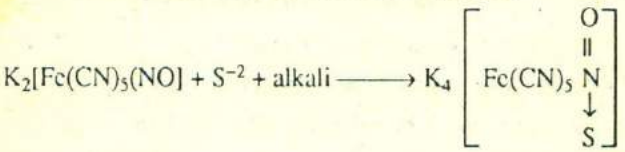
NO^+ is isoelectronic with CO and CN^- and therefore mixed ligand complexes are formed as :

$K_2[Fe(CN)_5NO]$

$K_3[Fe(CN)_5CO]$

$K_4[Fe(CN)_5CN]$ i.e. $K_4[Fe(CN)_6]$

Nitroprusside ion $[Fe(CN)_5NO]^{-2}$ reacts with S^{-2} ion in alkaline medium to give violet colour used for identification of sulphides.

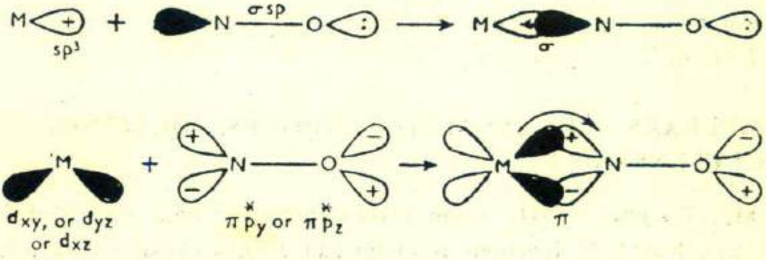


$$K_2[Fe(CN)_5(NO)] + S^{-2} + \text{alkali} \longrightarrow K_4\left[Fe(CN)_5\,\underset{\underset{S}{\downarrow}}{\overset{\overset{O}{\|}}{N}}\right]$$

Structure of metal nitrosyls : (i) NO transfers the odd electron to metal and the ligand NO^+ isoelectronic to CO coordinates with the metal. Hence NO is a 3 electron donor. Metal nitrosyls obey the E. A. N. rule as in the case of $Ni(CO)_4$, $Co(CO)_3(NO)$, $Fe(CO)_2(NO)_2$, $MnCO(NO)_3$ etc.

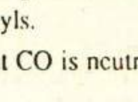
$$M + NO \longrightarrow M^- + NO^+ \longrightarrow M^{-2}-\overset{+}{N}\equiv\overset{+}{O} \longleftrightarrow M^{-}=\overset{+}{N}=O$$

According to MOT, NO^+ is a σ– donor and back donation form metal to NO also occur. But π^*p_y and π^*p_z antibonding orbitals of NO^+ are empty and accept electrons from the metal d-orbitals. In the case of octahedral structure back



donation occurs from d_{xy}, d_{yz} and d_{xz} and in the case of tetrahedral the back donation occurs from $d_{x^2-y^2}$ and d_{z^2} metal orbitals.

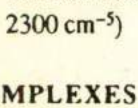
(ii) The alternative assumption that NO first accepts an electron to form NO^- and then coordinates with an electron pair to the metal also holds good. Since apart from linear M—N=O bond system there are examples in which NO is bent.

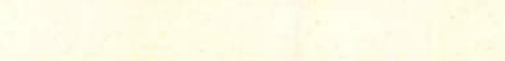

(N using sp^2 hybrid bonds)

Thus NO indicates anomalous behaviour.

Comparison of Metal Nitrosyls and Metal Carbonyls

1. NO is a 3 electron donor. CO is a 2 electron donor.
2. 3 CO are replaced by 2 NO in a molecular structure
3. Both NO and CO give σ and π bonds with metals to form metal nitrosyls and metal carbonyls.
4. NO^+ is acidic but CO is neutral. Bonding of the two with metals appear to be complex.
5. CO always gives linear M—C ≡ O bonds. But M—N = O is also bent as well as linear



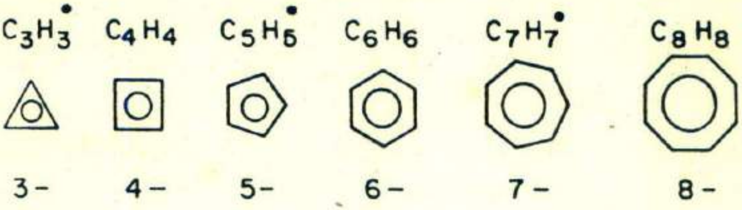


$$\underset{sp}{M^{2-}\text{——}N^+ \equiv O^+} \longleftrightarrow \underset{sp}{M^- = N^+ = O}$$

6. Substitution reactions occur in metal carbonyls but not in metal nitrosyls.
7. M—N bond is 1.57 – 1.67 Å whereas M—C bond is 1.7—1.9Å
8. Infrared absorption regions are different. (CO—1600 cm^{-1}, NO—1800 to 2300 cm^{-5})

COMPLEXES OF AROMATIC GROUPS. OLEFINES AND ACETYLENES

Metallocenes : C_5H_5 anion (cyclopentadienyl anion) derived from cyclopentadiene C_5H_6 functions as a uninegative ligand. Besides C_5H_6 a large number of carbocyclic systems and their derivatives give π-complexes with metals. The following are common π-complexes ligands.



π – ELECTRONS

The π-complexes of metals with C_5H_5 ion is generally called *Metallocenes*. The general formula is :

$$[(C_5H_5)_2 M^{n+}] X_{n-2}$$

where n = oxidation state of metal M and X is a uninegative ion such as Cl^-

Thus Fe^{+2} complex $Fe(C_5H_5)_2$ is known as Ferrocene

Ni^{+2} complex $Ni(C_5H_5)_2$ is known as nickelocene

Co^{+3} complex $Co(C_5H_5)_2Cl$ is known as dicyclopentadienyl cobalt(III) chloride. and so on.

Preparation : *1.* General method is the reaction of sodium cyclopentadienide with a metal halide or complex halide in suitable solvents such as tetrahydrofurane, ethylene glycol, dimethylformamide etc.

$$\begin{tikzcd} 2C_5H_6 + 2Na \arrow[r, "\text{THF or}", "\text{Ether}"'] & 2C_5H_5Na + H_2 \arrow[d, "\text{THF}"', "MX_2"] \\ & M(C_5H_5)_2 + 2NaX \end{tikzcd}$$

2. Direct reaction : When vapour of cyclopentadiene is passed over heated Fe at 300°C, ferrocene is produced.

$$2C_5H_6 + Fe \xrightarrow{300°C} (C_5H_5)_2 Fe$$

3. Grignard's reaction using cyclopentadienyl magnesium halide.

$$2C_5H_5MgBr + MX_2 \longrightarrow M(C_5H_5)_2 + MgX_2 + MgBr_2$$

$$C_5H_5MgI + FeCl_3 \longrightarrow Fe(C_5H_5)_2$$

Properties : (i) Complexes of first transition series Sc—Zn have all m. p. about 173°C. (ii) Vibrational spectra of the complexes resemble closely (iii)

M^{+3} complexes are strong electrolytes. (iv) These complexes are intensely coloured compounds.

Aromaticity : This is the property of a cyclic, conjugatively unsaturated molecule to undergo substitution reaction rather than addition reaction. Such substances are benzene and other such organic molecules, carboranes, phosphazines, carbocyclic ring metal π—complexes. etc.

Structures of Ferrocene

The peculiar structures were noted by the following reactions:

(i) $Fe(C_5H_5)_2$ could not be reduced by H_2 + a catalyst

(ii) $Fe(C_5H_5)_2 + KMNO_4 \longrightarrow$ No evidence of unsatruation

(iii) $Fe(C_5H_5)_2 + Br_2$ or $HNO_3 \longrightarrow [Fe^{+3}(C_5H_5)_2]^+$ Ferricinium cation.

(iv) Only one C—H stretching frequency in infrared spectra indicating all H are structurally similar and equivalent.

(v) Fe—C bond not localized to one C atom.

(vi) Multiple bonding occur between C rings and Fe due to donation of π-electrons to the vacant metal orbitals. But such donation is unlikely because of aromatic nature of the ring.

(vii) Donation of 6 electrons from each C_5H_5 - rings leads to $\mathbf{d^2sp^3}$ hybrid bonds of Fe. This could not be proved by x-ray diffraction.

(viii) Significant Electron Number Rule (S. E. N.) indicated assumption of inert gas configuration by the metal atom in neutral condition for outer electron configuration such as :

$(C_5H_5)_2Fe$ Fe = 8e $2C_5H_5$ = 10e   Total 18e (Ar)

$(C_5H_5)_2Co$ Co = 9 − 1 = 8e $2C_5H_5$ = 10e   Total 18e (Ar)

C_5H_5NiNO Ni = 10e C_5H_5 = 5e   NO=3e   Total 18e (Ar)

But not all fitted into the SEN rule.

$(C_5H_5)_2Ni$ Ni = 10e $2C_2H_5$ = 10e   Total 20e

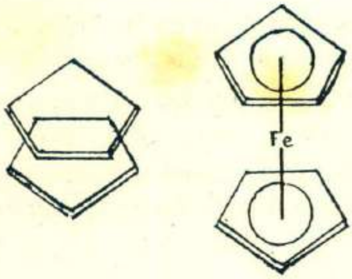
$(C_5H_5)_2Cr$ $Cr = 6e$ $2C_5H_5 = 10e$ Total 16e

$[(C_5H_5)_2Fe]^+$ $Fe = 8 - 1 = 7e$ $2C_5H_5 = 10e$ Total 17e

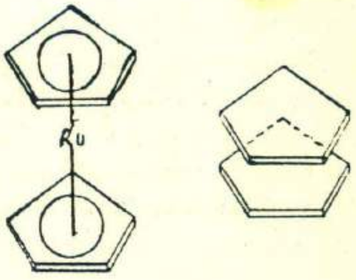
E. A. N. Rule is not obeyed by these types of compounds.

(ix) Overlap may occur between two hybrid orbitals of metal atom with π orbitals of C_5H_5 rings. There are 5 M. O. for each ring with 6 electrons: 3 molecular orbitals are occupied by 3 pairs. The overlap of 3 filled M. O. of C_5H_5 rings with the vacant orbitals of Fe gives the bonding leading to Sandwich Bond.

Fe electrons are distributed as $d_{x^2-y^2}(2)$ $d_{z^2}(2)$ $d_{xy}(2)$, $d_{yz}(1)$ and $d_{xz}(1)$. The hybridization of d_{yz} and d_{xz} give cup-shaped molecular orbitals along z-axis. Sandwich bond is essentially one electron pair bond with $2C_5H_5^-$ rings with Fe^{+2}. The orientation of C_5H_5 rings may be staggrad or eclipsed :



staggard
$Fe(C_5H_5)_2$



eclipsed
$Ru(C_5H_5)_2$

It is to be noted that metal with d^{10} electrons do not give π- complexes but give σ complexes as in $Pb(C_5H_5)_2$.

$Mn(C_5H_5)_2$ does not give π complex but σ complex due to d^5 electrons according to Hunds' Rule.

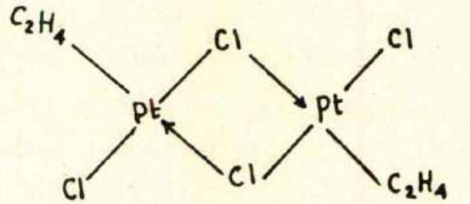
Complexes of Olefins and Acetylenes.

Ethylene, propylene etc complexes are easily formed by absorption of the hydrocarbon in the metal halide solutions. Pd^{+2}, Pt^{+2}, Cu^+, Ag^+, Hg^{+2} absorb a variety of olefines and acetylenes. The general reaction :

$$\begin{array}{lcl} PtCl_4 + RCH = CH_2 & \longrightarrow & [PtCl_2.RCH = CH_2]_2 \\ & & \downarrow \\ & & [PtCl_3\ RCH = CH_2]^- \end{array}$$

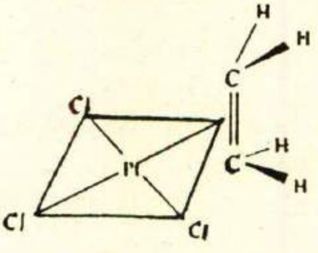
$$PtCl_4^{-2} + RCH = CH_2 \longrightarrow [PtCl_3\ RCH = CH_2]^- + Cl^-$$

$Pt\ Cl_2.C_2H_4$ is represented as a dimer.



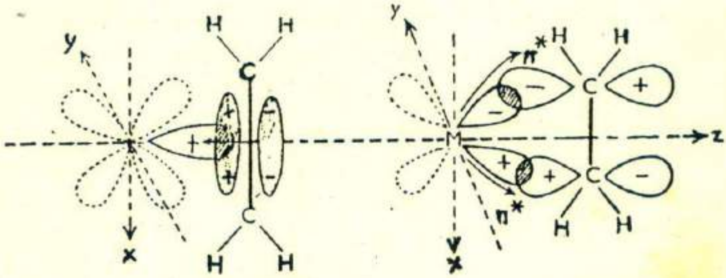
Dimer of $Pt\ Cl_2\ C_2\ H_4$

This instability of $[PtCl_2(C_2H_4)]_2$ is due to strong *trans effect* in substitution reaction. The type of bonds between the metal and the ligand appear to be quite complicated but it is clear that there is no localized σ bond between M and the ligand C (M—C bond). The bonding arises because of interaction of π electrons in the unsaturated molecule and hybrid orbitals of the metal. The double bond acts as a monodentate ligand and forms π bond with metals. Thus $K[PtCl_3C_2H_4]$ known as Zeise's salt has coordinated double bond perpendicular to coordination plane.



Anion $[C_2\ H_4\ Pt\ Cl_3]^-$ of Zeise's salt

Orbital overlap of C_2H_4 $2p_z$ orbital and **s**, **p** and **d** orbitals of metal is suggested involving no σ bonding.



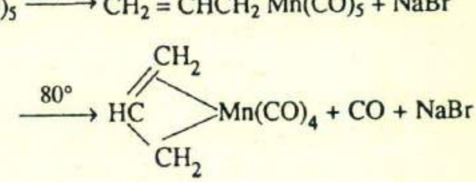
(a) Donation from filled π-orbital to vacant metal dsp^2 orbital. (b) Back donation from filled metal dπ-pπ orbital to acceptor antibonding π^* orbital (π^*_z 2p) MO of C_2H_4.

Acetylene complexes are similar to those of ethylene and are formed with metals such as Pt, Cu etc. C_2H_2 has 2 π bonds at right angles to each other. In acetylide ion $[RC{\equiv}C]^-$ the complex formation is through the lone pair of electron. The acetylene complexes have complicated structure. The possibility of π bonding between metal and carbon in C_2H_2-complexes has been realized from the reactions with metal carbonyls.

$Co_2(CO)_8 + RC{\equiv}CR \longrightarrow Co_2(CO)_6\,(RC{\equiv}CR) + 2CO$

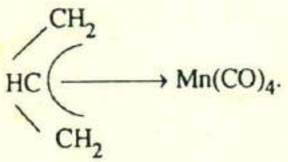
Reaction of allylbromide with $NaMn(CO)_5$ also shows the π bonding

$$CH_2{=}CH{-}CH_2Br + 2NaMn(CO)_5 \xrightarrow{20°} CH_2 = CHCH_2\,Mn(CO)_5 + NaBr$$



$$\xrightarrow{80°} HC\begin{matrix} \overset{CH_2}{//} \\ \\ \underset{CH_2}{\diagdown} \end{matrix} {>} Mn(CO)_4 + CO + NaBr$$

The allyl group in this compound is symmetrical therefore, the actual molecular structure is represented as :



$$HC\begin{pmatrix} CH_2 \\ \\ CH_2 \end{pmatrix} \longrightarrow Mn(CO)_4.$$

THE CRYSTAL FIELD THEORY (CFT) AND THE LIGAND FIELD THEORY (LFT) OF COORDINATION COMPOUNDS.

The basic principle of the crystal field theory is rather simple and depends on the factors : (1) shapes of the **d** orbitals, (2) the simple law of electrostatics that electrons or like charges repel each other. (3) The groups or ligands are considered as point charge of electricity.

It is necessary here to illustrate the potential energy diagram for the formation of a stable molecule through hybridized or excited state involving lowering of energy as given symbolically in Fig. 2—5 (Page 73). Similar situations arise during the formation of complex compounds when coordinating groups or *ligands* approach the **d** orbitals of the central metal ion. The influence of the charge clouds of the surrounding groups on the charge clouds of the metal ion (**d** orbitals) produces an electrostatic field known as the *crystal field.* The theory deals with this environmental electrostatic influence and is known as the *Crystal Field Theory.* The ***Ligand Field Theory*** is an extension of the Crystal Field Theory incorporating some aspects of the molecular orbital theory involving overlapping of orbitals.

The Octahedral symmetry

The five **d** orbitals which are degenerate (having the same energy) in the free metals ions have the shapes (boundary surfaces) with respect to x, y and z directions of Cartesian coordinates as given in Fig. 1—23 (page 54). Of the five **d** orbitals the $d_{x^2-y^2}$ and d_{z^2} are directed along the axes x, y, and z whereas d_{xy}, d_{yz}, d_{xz} are directed in between (i.e., 45°) to the axes x, y and z. In an octahedral complex (6-coordinated complex) the ligands approach the metal ion along $d_{x^2-y^2}$ and d_{z^2} orbitals as shown in Fig. 24-3. which are directed towards the ligands. The electrostatic repulsion raises the energy of these two **d** orbitals ($d_{x^2-y^2}$ and d_{z^2}) more than d_{xy}, d_{yz} and d_{xz}. Thus the **d** orbitals are split into two groups one of higher energy level comprising $d_{x^2-y^2}$ and d_{z^2} (also represented as e_g) and the other of lower energy level d_{xy}, d_{yz} and d_{xz} (also represented as t_{2g}). The stronger the field, the greater is the separation $10Dq$ between the energy levels.

This splitting ($10Dq$) of **d** orbitals lowers the total energy of the system thereby imparting stability to the new system as are illustrated in Fig. 24—4 The **d** orbitals of the ion in the field of spherical symmetry are split in an octahedral field. The decrease in energy E caused by the splitting of **d** orbitals in presence of ligands is known as the *Crystal Field Stabilization Energy* (CFSE). or Ligand field Stabilization Energy (LFSE)

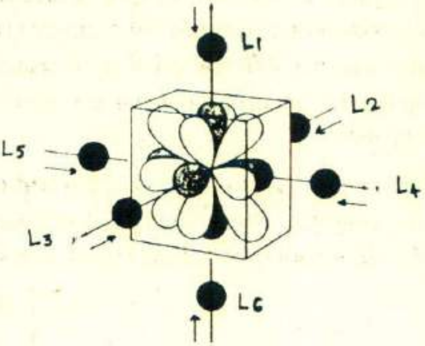


Fig. 24-3. 6 ligands approaching metal ion along dx^2-y^2 and dz^2 orbitals in octahedral complexes.

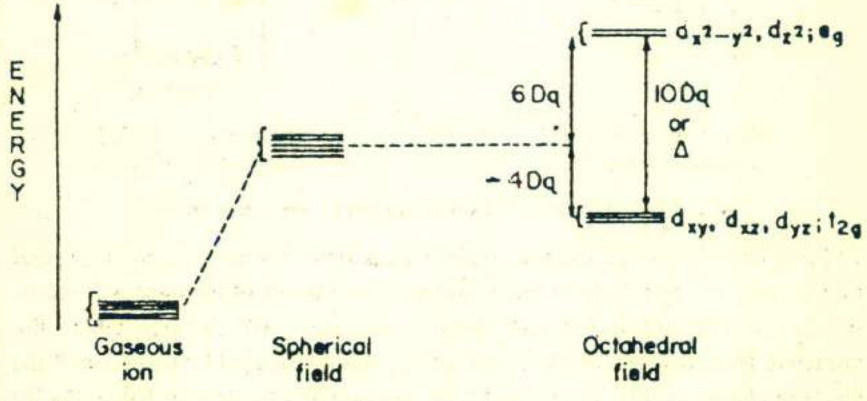
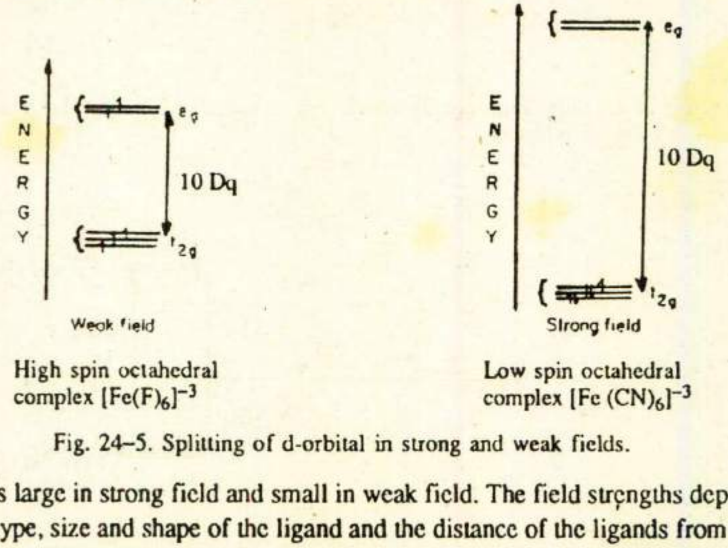


Fig. 24—4. Energy relationship of the formation of stable octahedral system by lowering of energy due to splitting of d orbitals.

Thus the splitting of **d** orbitals occurs because **d**-orbitals have different orientation in space and are subjected to different interactions by the approaching ligands. The splitting of the **d**-orbitals under the influence of ligand field apparently depend on (i) charge or dipole of the ligand (ii) size and shape of the ligand (iii) number of the ligand (iv) polarisability (v) oxidation state of the metal (vi) variation in the **d**-orbitals (vii) ultimate geometry of the molecule.

The approaching ligands avoid areas of greater electron density and seek more comfortable positions with respect to the **d** orbitals of the metal ion. For this reason the complexes assume different geometrical shapes which thus depend on (1) the electrons in the **d** orbitals of the metal ion and (2) the strength of the field produced by the ligands.

Strong field produces pairing of electrons at lower **d** orbitals (t_{2g}) to give ***Low Spin*** form of the complex. Weak field produces more of unpairing of electrons and gives the ***High Spin*** forms of the complex as shown in Fig. 24-5.



High spin octahedral complex $[Fe(F)_6]^{-3}$

Low spin octahedral complex $[Fe(CN)_6]^{-3}$

Fig. 24–5. Splitting of d-orbital in strong and weak fields.

CFSE is large in strong field and small in weak field. The field strengths depend on the type, size and shape of the ligand and the distance of the ligands from the metal ion. The equilibrium internuclear distance is the position where the attractive force between the metal ion and ligand is balanced by repulsion of the electron-charge clouds. The crystal field splitting and electron distributions for octahedral $[Ni(NH_3)_6]^{+2}$, square planar $[Ni(CN)_4]^{-2}$ and tetrahedral $[NiCl_4]^{-2}$ complex ions are given in Fig. 24–6.

The Tetrahedral symmetry : This is closely related to the octahedral symmetry and contains four ligands arranged at the corners of a tetrahedron with the metal atom at the centre. The tetrahedral coordination is also closely related to the cubic system. The four ligands are situated at the alternate corners of the

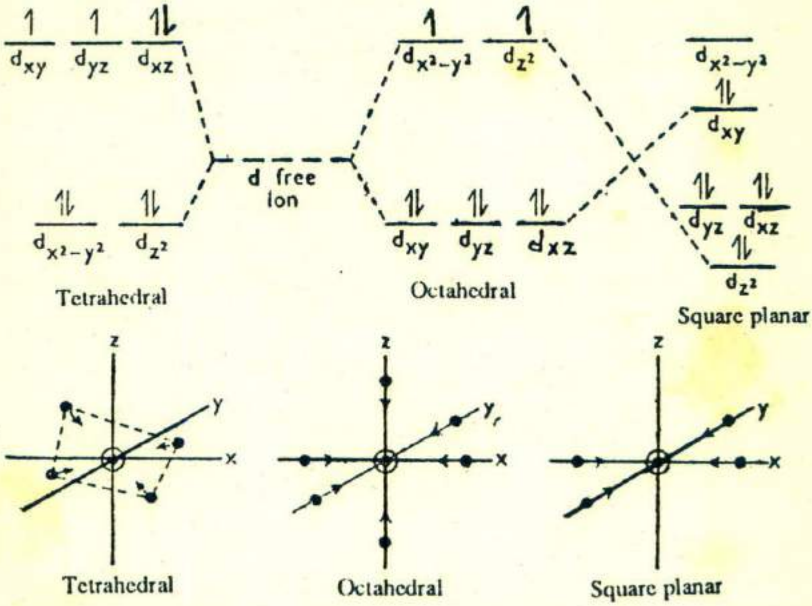


Fig. 24—6. Crystal field splitting in a tetrahedral $[Ni(Cl)_4)^{-2}$, octahedral $[Ni(NH_3)_6]^{+2}$ and square planar $[Ni(CN)_4]^{-2}$ complexes showing also the electron distribution (above).

cube. The orbitals which are directly affected on the approach of the 4 ligands are $\mathbf{d}_{xy}$, $\mathbf{d}_{xz}$ and $\mathbf{d}_{yz}$. Hence these orbitals are raised to higher energy level giving the splitting opposite to that of the octahedral symmetry as shown in Fig 24–7.

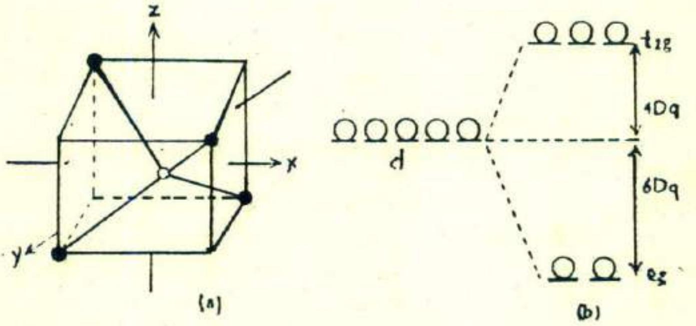


Fig 24–7. (a) Tetrahedral complex with ligands at alternate corners of a cube. (b) Splitting of the d- orbitals in tetrahedral field.

In this case the e_g orbitals are at lower energy and t_{2g} at higher energy. But the splitting in this case is less marked since the orientation of the d-orbitals produces smaller value of $10\,D_q$ so that

$$10\,Dq_{\text{tetrahedral}} = \frac{4}{9}\,10\,Dq_{\text{octahedral}}.$$

Tetrahedral Complexes are more common in the case of non-transition elements and for d°, d^5 (high spin) and d^{10} ions. Due to smaller splitting of d-orbitals the tetrahedral complexes are always high spin form and no low spin form are observed in this geometry.

The Merits of the Ligand Field Theory :

(1) It gives clear understanding regarding the distortions in the geometry of the complex molecule.

(2) It explains the variations in the magnetic properties of the same metal ion in different compounds.

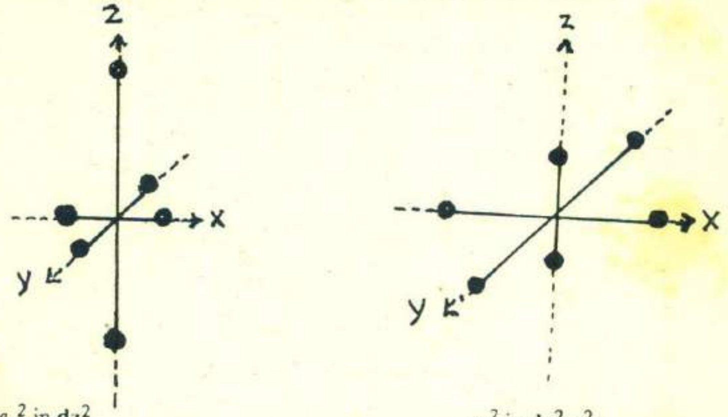
(3) It gives satisfactory explanations of the twin peaks observed when many physical properties of transition metal complexes of similar nature and compositions are plotted against the atomic numbers of the metals.

(4) It gives clear and quantitative understanding of the spectra of complexes.

(5) It gives general understanding of the structures of metal complexes in all states and forms, such as oxide systems.

The Jahn-Teller Effect : The distortion in symmetrical structures due to partially filled energy levels is known as Jahn-Teller distortion. According to this concept the following points may be noted. (i) Any non-linear molecule having degenerate electronic system will be unstable. (ii) Such system becomes distorted to remove the degeneracy and lower the symmetry. (iii) The distortion splits the degenrate state and increases the stability of the molecule. (iv) The removal of degeneracy results in additional stabilization by lowering the energy.

The distortions (generally known as Jahn-Teller distortions) in complex compounds, such as those of Cu^{+2} ion having d^9 ion explain the defect of the valence bond approach. Cu^{+2} complexes have generally distorted octahedral structure. The splitting of the d orbitals of Cu^{+2} ion with 9 electrons gives two different distributions in the higher energy level (e_g) as shown in Fig 24—8. Cu^{+2} complexes have 4 short and 2 long bonds obviously due to the comfortable approach of the ligands along x and y directions because of less electron density in $d_{x^2-y^2}$ orbital (one unpaired electron) as compared to two electrons (paired) in d_{z^2} orbitals which exerts greater repulsion to approaching ligands.

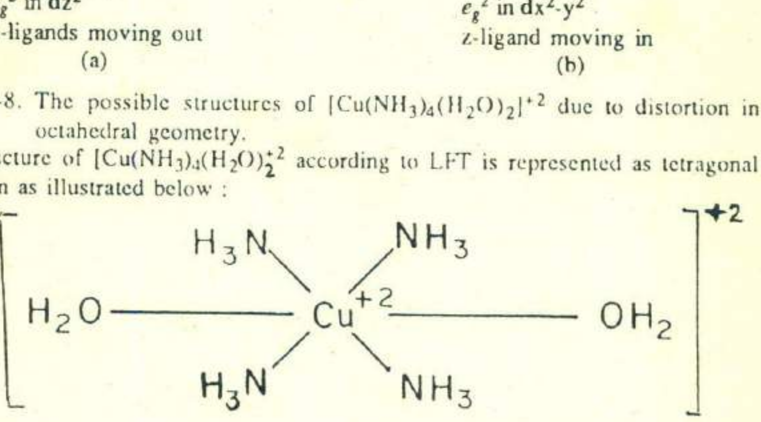


e_g^2 in dz^2
z-ligands moving out
(a)

e_g^2 in dx^2-y^2
z-ligand moving in
(b)

Fig. 24-8. The possible structures of $[Cu(NH_3)_4(H_2O)_2]^{+2}$ due to distortion in octahedral geometry.

The structure of $[Cu(NH_3)_4(H_2O)_2^{+2}$ according to LFT is represented as tetragonal distortion as illustrated below :



In Fig. 24—8 two possible arrangements of d^9 complex ion give distorted octahedral structures. $[Cu(NH_3)_4(H_2O)_2]^{+2}$ has the structure (a) in which four bonds are closer to Cu atom and two bonds are far removed indicating the splitting having unpaired electron in $d_{x^2-y^2}$ orbital and not the structure (b) having the unpaired electron in d_{z^2}. The extent of olistortions in octahedral and tetrahedral geometries are given in Table 24.5.

The explanation of the twin peaks observed when a physical property of a similar series of the complex compounds is plotted against the respective atomic numbers is one of the important achievements of the Ligand Field Theory. Thus

Table 24.5 Jahn-Teller distortion due to d-electrons in octahedral and Tetrahedral system

Systems.	*Electron Configuration*		*Predicted distortions*
Octahedral	d^1, d^6	High spin	Tetragonal distortion (slight)
	d^2, d^7	"	Tetragonal distortion
	d^3, d^8	"	No distortion (ligand field effect only)
	d^4, d^9	"	Large distortion
	d^5, d^{10}	"	No distortion
	d^6	Low spin	No distortion
	d^8	"	Large distortion (square planar)
Tetrahedral	d^1 d^2 d^6 d^7	High spin	No distortion
	d^3 d^4 d^8 d^9	High spin	Large distortion

when the heats of hydration and stability constants of a series of complexes with the same ligand are plotted against atomic number from Ca (20) to Zn (30), as for $[ML_6]^{+2}$ complexes the curves obtained are given in Fig. 24–9.

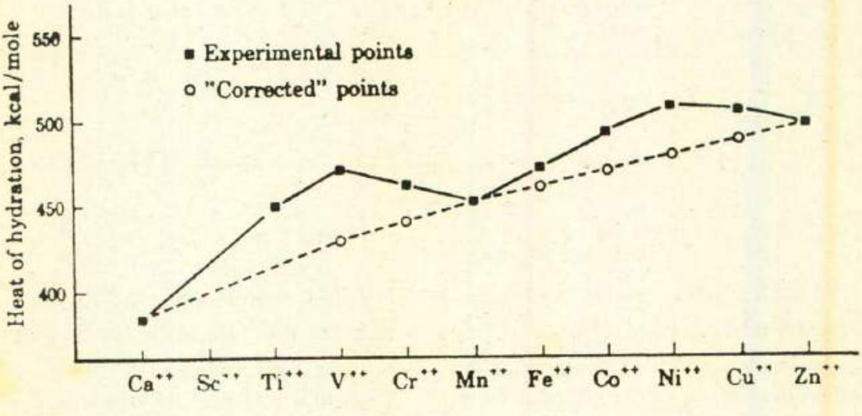


Fig. 24—9. Twin peaks in the case of heats of hydration or stability constant of complexes of M^{+2} transition metal ion such as $[M(H_2O)_6]^{+2}$ plotted against atomic number. In the absence of crystal field, the values would be expected to follow a regular increase as indicated by the broken lines.

For the divalent M^{+2} ions surrounded by $6H_2O$ molecules in solution the double peaks of the curve are due to the extra stability by the **d** electrons in the octahedral field. Notice that **d°**, **d^5** **d^{10}** ions do not show extra stabilization due to the symmetrical distribution. Similarly, the stability constant K of the complex equilibrium :

$$M^{+2} + 6L \rightleftharpoons [ML_6]^{+2}$$

is given by $K = \frac{[ML_6]^{+2}}{[M^{+2}][L]^6}$ where M^{+2} is a divalent metal ion and L is the ligand molecule, such as NH_3. When log K or log β is plotted against atomic number of M^{+2}, the curve obtained gives similar double peaks (Fig. 24–9). Without the concept of crystal field theory the values would be expected to increase regularly along a straight line.

Fig. 24–5 (page 726) gives an idea as to why the strong field of CN^- ion gives $K_3[Fe(CN)_6]$ in which the magnetic moment indicates the presence of a single unpaired electron whereas the weak field of F^- ion gives $K_3[Fe(F)_6]$ producing 5 unpaired electrons showing large value of magnetic moment.

In the complex of $[Ti(H_2O)_6]^{+3}$ there is only one d electron (d^1 ion). In the ground state this single electron occupies t_{2g} orbital. However, excitation of the electron to an e_g orbital is possible when energy required for the transition corresponding to the separation ($10Dq$) is supplied. The absorption of visible light brings about this transition. $[Ti(H_2O)_6]^{+3}$ absorbs most strongly at the wavelength of approximately 5000 Å (yellow region) or 20300 cm^{-1}. Due to a single unpaired electron, a single absorption band of the solution of $[Ti(H_2O)_6]^{+3}$ is obtained which spreads to a considerable portion of the visible spectrum. Thus the solution of $[Ti(H_2O)_6]^{+3}$ is violet-red because it absorbs yellow light (app. 5000 Å or 20300 cm^{-1}) but transmits the red and violet which are not absorbed as shown in Fig. 24—10.

The Spectrochemical Series : On the basis of the experimental studies on the spectral measurements of a large number of metal complexes with various ligands, it has been possible to arrange the ligands in the increasering or decreasing order of their ability to produce the ligand field splitting.

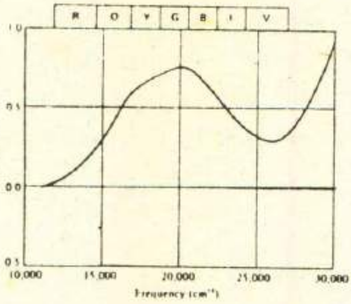


Fig. 24—10. The **d—d** transition (d^1 electron) in aqueous solutions of $[Ti(H_2O)_6]^{+3}$ ion giving violet-red colour of the solution. The curve on the right shows absorbance of yellow and transmission in the region of violet and red wavelength.

The arrangement of the ligands in the decreasing order or *vice versa* of the wave lengths corresponding to the splitting of the **d**-orbitals is generally known as the *Spectrochemical Series* of the ligands.

The series gives an idea of the splitting of the **d**-orbital under the normal conditions. The seriese in decreasing order gives some of the ligands of the series:

$CO > CN^- > NO_2^- > en > NH_3 > Py > NSC^- > H_2O > OH^- > F^- > NO_3^- > Cl^- > Br^- > I^-$

Thus the 10*Dq* values of some Ni–complexes are shown below :

Ligand	*10Dq in* cm^{-1}
Br^-	7000
Cl^-	7300
H_2O	8500
NH_3	10600
en	11200
O-Phen	12,700
CO	23000

It may be noted that both anhydrous $CuSO_4$ and $K_2[Cu(CN)_4]$ are colourless. SO_4^{-2} provides a very weak field and the d-d transition bands move into the infrared region. CN^- provides a very strong ligand field and d-d absorption bands occur in the ultraviolet region.

THE MOLECULAR ORBITAL THEORY (MOT) OF INORGANIC COMPLEXES

Molecular orbital theory provides an elaborate method for explaining the structures of inorganic complexes. The composite orbitals of the ligands are combined with the atomic orbitals of metal ions according to symmetry. Both bonding and antibonding orbitals are formed according to LCAO—MO. The MO treatment is highly mathematical and the building up of MO diagrammes for complexes are rather difficult. Only a simple pictorial representation are given here.

When a molecular orbital is formed in complexes the electrons from the metal ions and ligands first occupy the lowest energy molecular orbitals of the molecule and then progressively higher energy orbitals are filled up until the supply of electrons is exhausted.

Molecular orbital picture of complexes consists of both σ and π bonded groups. Examples of octahedral symmetry have the metal σ orbitals classified as:

p_x, p_y, p_z designated as t_{1u}
s designated as a_{1g}
dx^2-y^2 and d_{z^2} designated as e_g
The π orbitals involved are :
d_{xy} d_{yz} d_{xz} designated as t_{2g}
p_x, p_y, p_z designated as t_{1u}

The combination of atomic orbitals of metal ion with the Ligand Group Orbitals (LGO) may be represented pictorially as follows :

(1) The six LGO combine with s orbitals of metal to give 6 M—L σ bonds (Fig. 24–11).

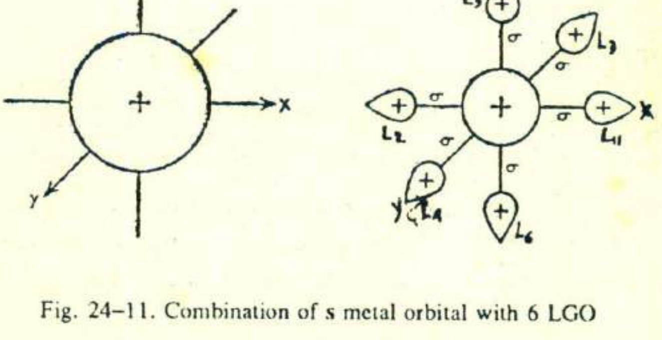
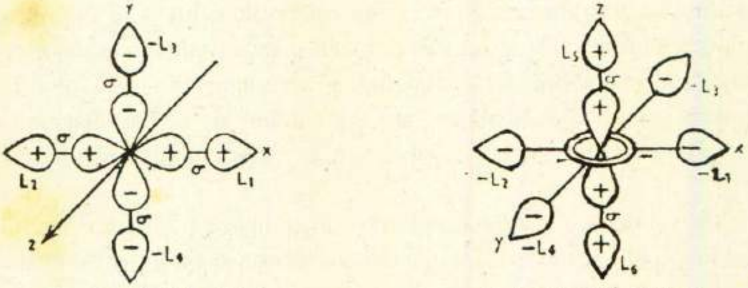


Fig. 24–11. Combination of s metal orbital with 6 LGO

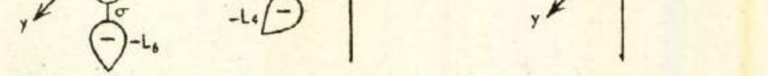
(2) The $\mathbf{d}_{x^2-y^2}$ and $\mathbf{d}_{z^2}$ orbitals combine with 4 LGO and 6 LGO respectively of the same symmetry (e_g) as in Fig 24–12)



σ – bonds with dx^2-y^2 (eg) σ bonds with dz^2 (eg)

Fig. 24–12. Combination of dx^2-y^2 and dz^2 with ligands

(3) The $\mathbf{p}_x$, $\mathbf{p}_y$, $\mathbf{p}_z$ orbitals (t_{1u}) of metal overlap with the 6 LGO two for each p orbital (Fig 24-13)



σ - bonds with p_z (t_{1u}) p_y (t_{1u}) p_x (t_{1u})

Fig. 24-13. Three **p** orbitals overlap with 6 LGO (two for each p)

The $\mathbf{d}_{xy}$, $\mathbf{d}_{xz}$ and $\mathbf{d}_{yz}$ (t_{2g}) orbitals do not form σ- bonded complex.

The MO diagramme on the basis of calculation of energies based on Wolfberg-Helmholtz (WH) method gives the following picture of $[Ni(NH_3)_6]^{+2}$ complexes with σ bonds only as shown in Fig 24–14.

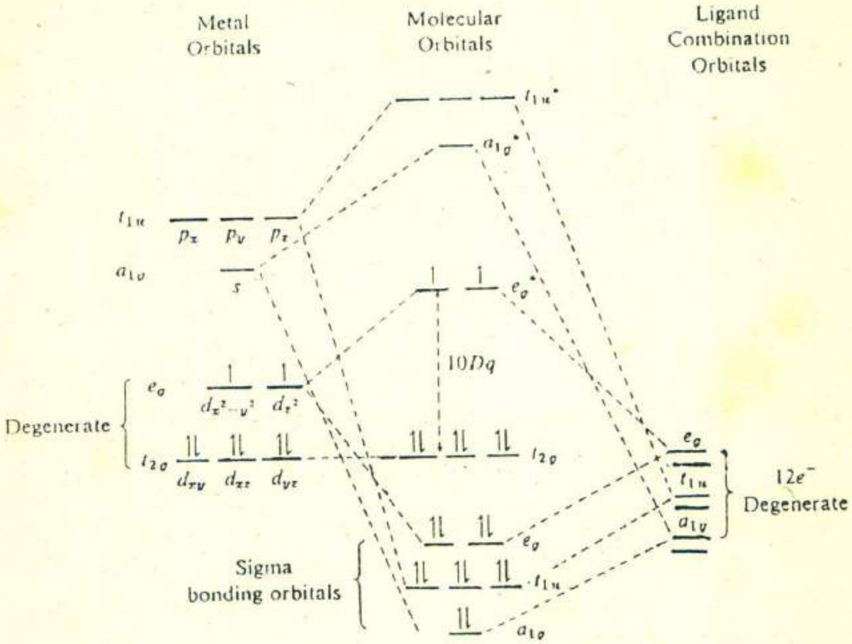


Fig. 24-14. MO diagram of $[Ni(NH_3)_6]^{+2}$ complex with σ bonds only.

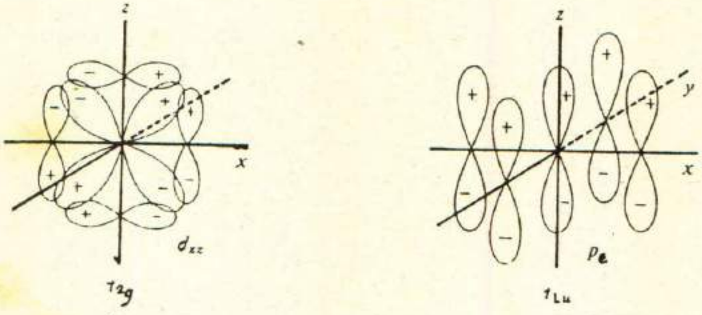
Notice that the values of 10 Dq in terms of LFT and MOT are different.

LFT 10 $Dq = t_{2g} - e_g$, MOT 10 $Dq = t_{2g} - e_g^*$ (eg^*—antibonding molecular orbitals).

MOT and π Bonding Complexes

The t_{2g} metal orbitals are not always non-bonding but as in CN^- the π-orbitals has filled π bonding and also π^* orbitals. The ligand π orbitals may be simple $\mathbf{p_\pi}$ orbital as in Cl^- ion or simple $\mathbf{d_\pi}$ orbitals as in PH_3 or MO as in CO and CN^- ligands.

The metal $\mathbf{d_{xy}}, \mathbf{d_{xz}}, \mathbf{d_{yz}}$ may interact with $\mathbf{p_x}, \mathbf{p_y}, \mathbf{p_z}$ orbitals according to symmetry giving π_{xz}, π_{xy} and π_{yz}, orbitals. Similarly **p—p** interactions shall produce $\mathbf{p_{\pi x}}, \mathbf{p_{\pi y}}$ and $\mathbf{p_{\pi z}}$ molecular orbitals as shown in Fig. 24–15.



(a) (b)

Fig. 24-15. (a) Interaction of d_{xz} with p_x and p_z orbitals of ligand giving π_{xz}. Similar interaction gives π_{xy} and π_{yz} (not shown). (b) Interaction of metal p_z orbital with ligand p_z orbitals. In all, $p\pi_z$, $p\pi_x$ and $p\pi_y$ are formed.

The resultant effect of π bonding shall be to increase the shifting of 10*Dq* or decrease it according to the ligand energies. π bonding effect of ligands of high energy shall increase the value of 10*Dq* from purely σ-bonded complex to have π-bonded effect as it happens in the cases of CO and CN^-.

But π orbitals of lower energy ligands than t_{2g} leads to the decrease of the splitting of 10*Dq* from σ bonded complexes having some π bonding effects as in the case of I^-, Br^- etc. shown in Fig 24–16.

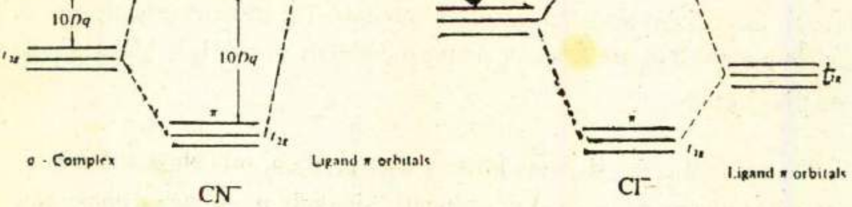


Fig. 2-16 Effects of π-bonding on the splitting of d-orbitals

Applications of Complex Compounds

Apart from the theoretical interests, the complex compounds have great importance not only in the field of chemistry but also in arts, industry and commerce. These have also great functional values in nature and biological functions. A few examples of the application of the complex compounds are given below.

In analytical chemistry, complex compounds are used more conveniently both for identification and quantitative determinations. Fehling solution, a tartrate complex of copper, is used to test for sugars, glucore and aldedydes in general. Dimethyl glyoxime provides a specific test for nickel and also gives an accurate method for its quantitative determination. Complexometric titrations using the complex disodium-EDTA (ethylenediamine tetra-acetic acid) have been largely used for the determination of calcium, magnesium etc.

Gold and silver are extracted from their ores by processes involving the formation of complex ions $Au(CN)_4^-$ and $Ag(CN)_2^-$. The complexes are also used in electroplating.

Complex compounds are used for dyeing fabrics which produces beautiful and fast colour due to the formation of complexes known as *lakes* with mordant dyes.

Beautiful paints and pigments used by the artists, consist of complex compound. In fact, the ink with which we write also consists of iron complexes.

From the point of view of a large number of application of complex compounds, these are substances of great commercial value.

Complex compounds occur in nature such as in blood (haemoglobin) which is an iron-complex and functions as the oxygen carrier of the blood stream. Similarly, the green colour of the leaves are due to magnesium complex of chlorophyll. Some vitamins such as B_{12} and enzymes consist of metal complexes.

Chelates are also used in medicines, drugs and treatment of diseases.

There are numerous applications of coordination complexes in industrial productions such as polymers, biochemical catalysis etc.

QUESTIONS AND PROBLEMS

1. Explain the bonding in $Co(NH_3)_6Cl_3$.
2. Write a short note on "Isomerism in 6-coordinated complexes".
3. Write note on the actions of ammonia on salts of mercury and silver.
4. Describe the reaction which occur when an aqueous solution of mercuric chloride is treated with an aqueous solution of potassium iodide.
5. Discuss the use of sodium cobaltinitrite in analytical chemistry.
6. Explain "Coordination compounds."
7. Cite some examples of the complex salts of chromium.
8. Explain the formation of coordination complexes according to VBT.
9. Describe what happens when ammonia is gradually added to an aqueous solution of $CuCl_2$.
10. Name a few complex compounds in which chromium shows σ-coordination number and give their structures.
11. Write a concise account of the Werner's theory of complex compounds.
12. Explain "Effective Atomic Number" and show how this idea explains the stability of some complex compounds.
13. Discuss Pauling's Valence Bond Theory to explain the structures of some complexes.
14. Make drawings to represent the structures of the following complex ions:—
    (a) $[Zn(NH_3)_4Cl_2]^{+2}$, (b) $[Cr(H_2O)_6]^{+3}$, (c) $[Ni(H_2O)_6]^{+2}$.
15. Discuss, with four examples, the uses of coordination compounds in analytical chemistry.
16. Write a note on Double salts and Complex salts.
17. What are coordination compounds ? Give the salient features of Ligand Field Theory.
18. Write brief accounts on :
    (a) Structure of metal carbonyls.
    (b) Inner complex salts.
    (c) Trans effect in 4-coordinated complexes.
19. Write a note on co-ordination bond.
20. (a) What is meant by "Coordination complexes"? Give three examples of such complexes.

    (b) Explain "Effective Atomic Number" and show how this principle explain the structure and stability of some complex compounds.

21. AgCl is soluble is soluble in ammonia but not in HCl. Explain.
22. Account for the existence of 2 and 3 forms of the following respectively : $Pt(NH_3)_2Cl_2$ and $[Pt(NO_2)(NH_3)BrCl]$
23. Write notes on :
    (a) Mond's process
    (b) Comparison of metal carbonyls and metal nitrosyls
    (c) Spectrochemical series of ligands.
24. H_2O coordinates with H^+ ion forming H_3O^+. Do you expect coordination of another H^+ ion forming H_4O^{+2}?
25. Discuss methods of identification of cis-trans isomers of inorganic complexes.
26. Draw sketches of 2 tetrahedral, 2 planar and 2 octahedral, coordination complexes.
27. Discuss the limitations of VBT involved in coordination compounds.
28. Discuss the structures of metal carbonyls.
29. Explain high spin and low spin inorganic complexes.
30. Explain the distortions of the geometry of metal complexes.
31. Write a note on Jahn-Teller Effect.
32. What are the effects of π-bonding on the splitting of d-orbitals during the formation of coordination complexes.-